# Chiral Recognition Properties in Complexation of Two Asymmetric Hemicarcerands[1]

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**Abstract:** The synthesis, characterizations and binding properties of new chiral hemicarcerands (*S*)-**1** and (*SS*)-**2** are described. From diol **5** and enantiomerically pure (*S*)-(−)-**3** in $Me_2NCOMe-Cs_2CO_3$, (*S*)-**1**⊙$CHCl_3$ was obtained (79%, guest exchanged during isolation). Treatment of **5** with (*SS*)-**4** in $Me_2NCOMe-Cs_2CO_3$ produced (*SS*)-**2**⊙$Me_2$-NCOMe (58%). When the chiral bridge of **1** was introduced into **5** in $(Me_2N)_3PO$, a solvent too large to enter **5** but which contained large excesses of PhC*HOHMe, PhS*OMe or $MeCH_2C$*$HMeCH_2OH$, the respective diastereomeric ratios of **1**⊙guest produced were 1:1.5, 1:1.5, and 1:1. When (*S*)-**1**⊙$CHCl_3$ was heated (115−160 °C) in the presence of eight different racemic potential guests (neat or in $Ph_2O$), the $CHCl_3$ was replaced as guest to give diastereomeric equilibrated ratios for **1**⊙guest that ranged from a high of 2.7:1 for $BrCH_2CH_2C$*HBrMe to a low of 1:1 for $ClCH_2C$*$HClCH_3$ and $Me_2CHCH_2CH_2C$*HOHMe. The guests that replace $CHCl_3$ are entering and departing through the chiral portals, which are larger than those which are non-chiral. The diastereomers of **1**⊙PhS*OMe gave widely differing $R_f$ values (0.41 and 0.27) on thin layer chromatographic plates. Similar introductions of six enantiomeric pairs of guests into the inner phase of **2** gave diastereomeric ratios that ranged between 1.4:1 for **2**⊙MeC*$HOHCH_2$-Me to 1:1 for **2**⊙PhS*OMe, **2**⊙1,2-propanediol, and **2**⊙2-methyl-1-butanol. The two nonchiral 26-membered ring portals are less encumbering than the two chiral 26-membered ring portals of **2**. When a mixture of (*S*)-**1** and $Ph_2O$ was heated (25 °C, 1 d) with racemic 4-$MeC_6H_4S$(O)Me, only (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S$(O)Me was isolated. When (*S*)-4-$MeC_6H_4S$(O)Me was substituted for the racemic sulfoxide, no sulfoxide complex was isolated. The $^1$H NMR spectra of the guests in diastereomerically related complexes are substantially different from one another.

The cycloveratrylene-based cyclophane **6** (Figure 1), which is chiral, was especially designed by Collet *et al*. to complex stereoselectively C*HFClBr. At 53 °C a difference in thermodynamic stability of $\Delta\Delta G° = 260$ cal mol$^{-1}$ was observed between the two diastereomeric complexes.[2] In later work we prepared ($S_4$)-**7**⊙(*S*)-$MeCH_2C$*H(Me)$CH_2Br$ and ($R_4$)-**7**⊙(*S*)-$MeCH_2C$*H(Me)$CH_2Br$ and determined the relative rate of decomplexation in $CDCl_3$ at 23 °C to be $k_{(R_4)-7\odot(S)}/k_{(S_4)-7\odot(S)} = 7$.[3] Recently, we reported that when (*SS*)-**8** was heated at 95 °C in 4:1 MeCHOHCH$_2$Me (racemic)−$Ph_2O$, a 2/1 ratio of diastereomeric complexes was formed.[4]

In this paper we report the synthesis and characterization of hemicarceplexes (*S*)-**1** and (*SS*)-**2**, each of which contains only one chiral bridge. The two identical chiral portals of (*S*)-**1** are composed of 28-membered rings whose diameters and shapes vary with the conformations of one $O(CH_2)_4O$ and one 2,2′-bisoxymethylene-1,1′-binaphthyl bridge. The two nonchiral portals of (*S*)-**1** are composed of 26-membered rings containing two $O(CH_2)_4O$ bridges. Scale molecular models (CPK) of (*S*)-**1** clearly indicate the two chiral entryways to the inner phase are much less encumbering than the smaller nonchiral passages. In contrast, all four portals of (*SS*)-**2** are 26-membered rings, but the two that are chiral are rigidified by the presence of the fused five-membered acetonide ring. Molecular model examination of (*SS*)-**2** suggests the nonchiral entrances to the inner phase are more likely to be used than those that are chiral. We report here a survey of the chiral recognition properties of (*S*)-**1** and (*SS*)-**2** in complexing the enantiomers of simple guest compounds containing a single chiral center to test these preconceptions.

A second object of this research was to determine the extent of communication between incarcerated guests through the host's shell to external physical probes. Specifically, we wondered how large were the differences in $^1$H NMR spectra and thin-layer chromatographic retention times of diastereomerically related hemicarceplexes.

The complexes of (*S*)-**1** and (*SS*)-**2** were chosen for this study for several reasons. (1) Earlier studies established that of the many hemicarcerands examined, **9** formed the widest variety of hemicarceplexes stabilized by constrictive binding.[5,6] (2) The key starting material for the synthesis of **1** and **2** was diol **5** which was easily prepared.[7] (3) The chiral units of **1** and **2** contain $C_2$ axes with limited conformational mobility and a high degree of preorganization, which we hoped would provide the greatest chance for observing chiral recognition in complexation.

## Results

**Syntheses.** Treatment of readily available diol **5**[7] with excess (*S*)-(−)-2,2′-bis(bromomethyl)-1,1-binaphthyl[8] (**3**) in $Cs_2CO_3-Me_2NCOMe$ at 40 °C followed by chromatographic purification

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Host−Guest Complexation. 69.

(2) (a) Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1985**, *107*, 6993−6996. (b) Costante-Crassons, J.; Marrone, T. J.; Briggs, J. M.; McCammon, J. A.; Collet, A. *J. Am. Chem. Soc.* **1997**, *119*, 3818−3823.

(3) Judice, J. K.; Cram, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 2790−2791.

(4) Park, B. S.; Knobler, C. B.; Eid, C. N., Jr.; Warmuth, R.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1997**, in press.

(5) Robbins, T. A.; Knobler, C. B.; Bellew, D. R.; Cram, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 111−122.

(6) Cram, D. J.; Cram, J. M. Container Molecules and Their Guests. *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Thomas Graham House, Science Park, Cambridge, U.K., 1994; pp 131−216.

(7) Yoon, J.; Sheu, C.; Houk, K. N.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1996**, *61*, 9323−9339.

(8) (a) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242−1251. (b) Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747−2751.

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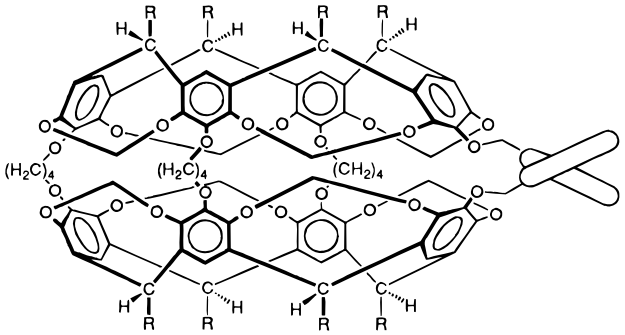
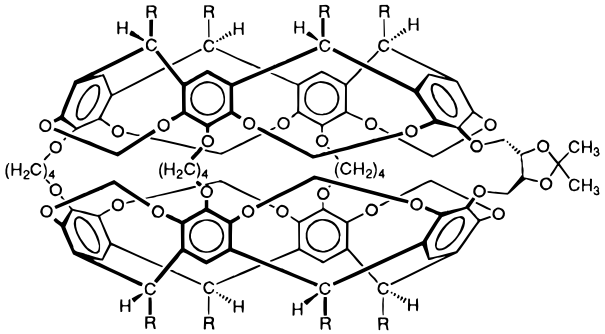


(S) - 1, R = $PhCH_2CH_2$



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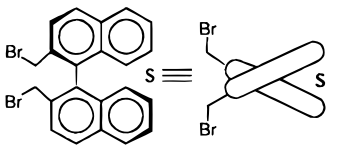

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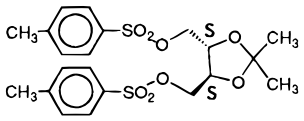

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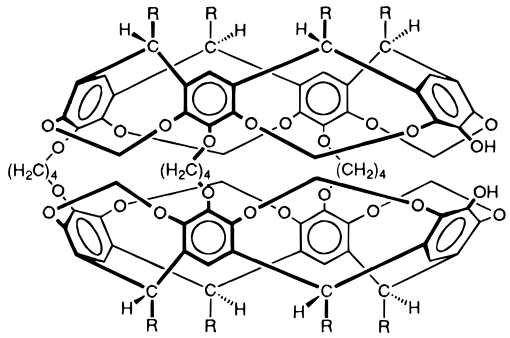
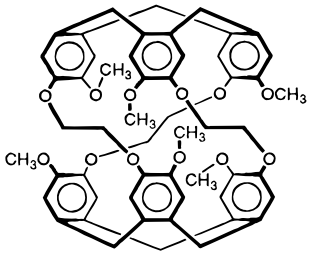
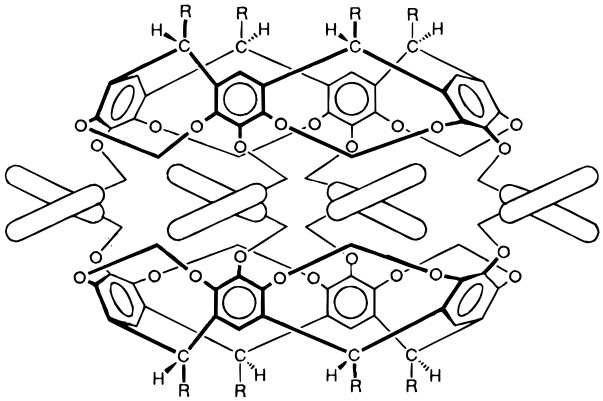


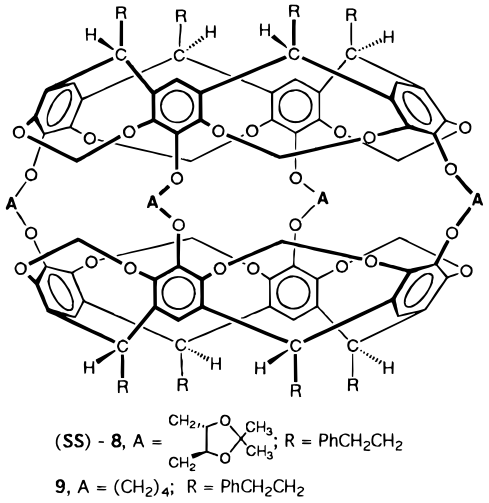
5, R = $PhCH_2CH_2$



6



($S_4$) - 7, R = $PhCH_2CH_2$



(SS) - 8, A = ; R = $PhCH_2CH_2$

9, A = $(CH_2)_4$; R = $PhCH_2CH_2$

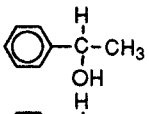
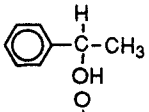
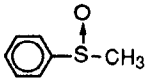
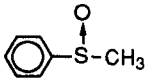
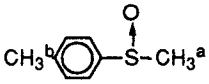
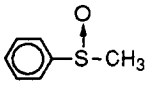
**Figure 1.**

of the product with $CHCl_3$ as the mobile phase gave (*S*)-**1**⊙-$CHCl_3$ (79%). The $^1H$ NMR spectrum of this complex was interpreted through use of the $^1H$ COSY method. Very likely (*S*)-**1**⊙$Me_2NCOMe$ was formed initially but underwent guest exchange driven by mass law during purification. Molecular model (CPK) examination of **5**, $(Me_2N)_3PO$, and $Ph_2O$ indicated the two solvents to be too large to enter the inner phase of the former. Some shell closures were carried out in the aprotic dipolar solvent $(Me_2N)_3PO$, containing at least a 100-fold excess of racemic potential guests, by a "sealing in" of these guests during formation of the last bridges to form mixtures of diastereomeric hemicarceplexes. Alternatively hemicarceplexes were prepared by heating **1**⊙$CHCl_3$ dissolved in racemic potential guests directly or in guests diluted with $Ph_2O$. At 115−160 °C, bulk solvent or solute molecules replaced the $CHCl_3$ in the inner phase of the host, a process driven by mass law. The $^1H$ NMR spectral (360 MHz) chemical shifts of the guests' methyl protons were different enough to allow diastereomeric ratios to be detemined. Table 1 records the reaction conditions, yields, diastereomeric ratios, $\delta$ values for the guests' methyl signals, and $\Delta\delta$ values for diastereomeric guests.

When diol **5** was treated with (*SS*)-1,4-di-*O*-tosyl-2,3-*O*-isopropylidene-L-threitol (**4**)[9] -$Cs_2CO_3$−$Me_2NCHO$ at 70 °C for 48 h, guest-free **2** (56%) was isolated after evaporation of the solvent, precipitation of the product with MeOH, and its purification by silica gel−$CHCl_3$ chromatography. If $Me_2NCHO$ occupied the inner phase of **2** during shell closure, as is probable, it must have departed during isolation. When $Me_2NCOMe$, $Me_2SO$, or *N*-methylpyrrolidinone were employed as

(9) Mash, E. A.; Nelson, K. A.; Van Deusen, S.; Hemperly, S. B. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. VIII, pp 155−159.

**Table 1.** Complexes of Chiral Hosts and Guests and the $^1$H NMR Spectral Signals in $CDCl_3$ at 25 °C of Guest Methyl Protons

| | | | | diastereomeric complexes | | |
|---|---|---|---|---|---|---|
| host | racemic guest | reaction conditions | % yld | ratio† | δ (ppm)‡ | Δδ (ppm)§ |
| (S)-1 |  | sealed in | 35 | 1.5(S)/1(R) | -2.51(-):-2.40(+) | 0.11 |
| (S)-1 |  | guest/$Ph_2O$, 160 °C, 2 d | 97 | 2.5(S)/1(R) | -2.51(-):-2.40(+) | 0.11 |
| (S)-1 |  | sealed in | 33 | 1.5(R)/1(S) | -1.30(+):-1.24(-) | 0.06 |
| (S)-1 |  | guest/$Ph_2O$, 125 °C, 1.5 d | 96 | 1.6(R)/1(S) | -1.30(+):-1.24(-) | 0.06 |
| (S)-1 |  | guest/$Ph_2O$, 125 °C, 1.5 d | 30 | >20(R)/1(S) | $H^a$,-1.39(R); $H^b$,-1.71(R) | |
| (S)-1 | $ClCH_2CHClCH_3$ | neat, reflux, 1 d | 97 | 1/1 | -1.82:-1.54 | 0.28 |
| (S)-1 | $BrCH_2CHBrCH_3$ | neat,115-120 °C, 2d | 95 | 1.1/1 | 0.01:0.25 | 0.24 |
| (S)-1 | $CH_3{}^aCHBrCH_2CH_3{}^b$ | neat, reflux, 2 d | 95 | 1.4/1 | $H^a$,-1.19:-1.02 | 0.17 |
| | | | | | $H^b$,-2.50:-2.68 | 0.18 |
| (S)-1 | $BrCH_2CHBrCH_2CH_3$ | neat,115-120 °C, 2d | 95 | 2.3/1 | -2.83:-2.75 | 0.08 |
| (S)-1 | $BrCH_2CH_2CHBrCH_3$ | neat,115-120 °C, 2d | 95 | 2.7/1 | -1.21:-0.97 | 0.24 |
| (S)-1 | $HOCH_2CH(CH_3{}^a)CH_2CH_3{}^b$ | sealed in | 30 | 1/1 | $H^a$,-1.62:-1.50 | 0.12 |
| | | | | | $H^b$,-2.84:-2.66 | 0.18 |
| (S)-1 | $CH_3{}^aCH(OH)CH_2CH_2CH(CH_3{}^b)CH_3{}^c$ | guest/$Ph_2O$, 150 °C, 2 d | 89 | 1/1 | $H^a$,-3.05(overlap) | |
| | | | | | $H^b$,-1.62(overlap) | |
| | | | | | $H^c$,-1.69(overlap) | |
| (SS)-2 |  | sealed in | 33 | 1/1 | -1.15:-1.14 | 0.01 |
| (SS)-2 | $CH_3CHOHCH_2OH$ | guest/$Ph_2O$, reflux, 2 d | 93 | 1/1 | -2.14:-2.06 | 0.08 |
| (SS)-2 | $CH_3{}^aCHOHCH_2CH_3{}^b$ | sealed in | 39 | 1.1(R)/1(S) | $H^a$,-2.55(-):-2.45(+) | 0.10 |
| (SS)-2 | $CH_3{}^aCHOHCH_2CH_3{}^b$ | guest/$Ph_2O$, 160 °C, 2 d | 93 | 1.4(R)/1(S) | $H^b$,-2.83(-):-2.90(+) | 0.07 |
| (SS)-2 | $HOCH_2CH(CH_3{}^a)CH_2CH_3{}^b$ | sealed in | 33 | 1/1 | $H^a$,-1.61:-1.56 | 0.05 |
| | | | | | $H^b$,-2.77:-2.90 | 0.13 |
| (SS)-2 | $CH_3{}^aCH(OH)CH_2CH_2CH_3{}^b$ | sealed in | 40 | 1.2/1 | $H^a$+$H^b$,-2.72 (overlap) | |
| (SS)-2 | $CH_3{}^aCH(OH)CH_2CH_2CH(CH_3{}^b)CH_3{}^c$ | sealed in | 39 | 1.2/1 | $H^a$,-3.11(overlap) | |
| | | | | | $H^b$,-1.25:-0.96 | 0.29 |
| | | | | | $H^c$,-2.03:-2.39 | 0.36 |

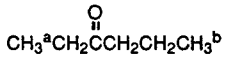
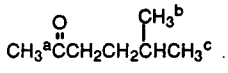
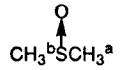
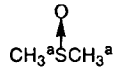
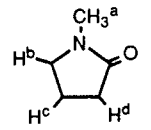
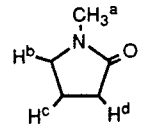
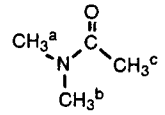
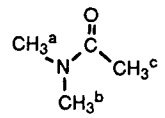
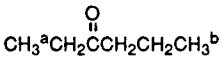
† Configurations of the diastereomers are given in the ratios only when known and material to the discussion.

‡ The (+) or (-) following the δ values refer to the signs of optical rotations of the guest enantiomers involved in the complex.

§ Differences in magnitude between diastereomers, irrespective of signs.

solvents, (*SS*)-**2**⊙$Me_2NCOMe$, (*SS*)-**2**⊙$Me_2SO$, and (*SS*)-**2**⊙*N*-methylpyrrolidinone were produced (55−60%), respectively. When (*SS*)-**2** was heated to reflux in MeCOEt, EtOAc, or $EtCOCH_2Et$, (*SS*)-**2**⊙MeCOEt, (*SS*)-**2**⊙EtOAc, and (*SS*)-**2**⊙-

**Table 2.** Complexes of Chiral Hosts and Non-chiral Guests (Thermally Complexed or 'Sealed In'), and $^1$H NMR Spectral Change Comparisons in $CDCl_3$ at 25 °C of Guests' Methyl Protons Upon Complexation

| host | guest | reaction conditions | % yld | proton | δ (ppm) free | δ (ppm) complexed | Δδ† (ppm) |
|---|---|---|---|---|---|---|---|
| (S)-**1** |  | neat, 130 °C, 2 d | 82 | $H^a$ | 1.05 | -3.15 | 4.20 |
| | | | | $H^b$ | 0.91 | -3.15 | 4.06 |
| (S)-**1** |  | neat, 130 °C, 2 d | 95 | $H^a$ | 2.13 | -2.14 | 4.27 |
| | | | | $H^b$ | 0.88 | -1.49 | 2.37 |
| | | | | $H^c$ | 0.88 | -2.28 | 3.16 |
| (SS)-**2** |  | sealed in | 55 | $H^a$ | 2.46 | -0.54 | 3.00 |
| | | | | $H^b$ | 2.46 | -0.68 | 3.14 |
| **9**‡ |  | sealed in | 20 | $H^a$ | 2.46 | -0.49 | 2.95 |
| (SS)-**2** |  | sealed in | 55 | $H^a$ | 2.70 | -1.01 | 3.71 |
| | | | | $H^b$ | 2.23 | -0.77 | 3.00 |
| | | | | $H^c$ | 1.90 | -1.04 | 2.94 |
| | | | | $H^d$ | 3.26 | hidden | |
| **9**§ |  | sealed in | 55 | $H^a$ | 2.70 | -0.89 | 3.59 |
| | | | | $H^b$ | 2.23 | -0.59 | 2.82 |
| | | | | $H^c$ | 1.90 | -0.78 | 2.68 |
| | | | | $H^d$ | 3.26 | hidden | |
| (SS)-**2** |  | sealed in | 58 | $H^a$ | 3.02 | -0.67 | 3.69 |
| | | | | $H^b$ | 2.94 | 1.54 | 1.40 |
| | | | | $H^c$ | 2.08 | -1.78 | 3.86 |
| **9**‡ |  | sealed in | 30 | $H^a$ | 3.02 | -0.42 | 3.44 |
| | | | | $H^b$ | 2.94 | 1.61 | 1.33 |
| | | | | $H^c$ | 2.08 | -1.64 | 3.72 |
| (SS)-**2** |  | neat, 130 °C, 2 d | 94 | $H^a$ | 1.05 | -3.10 | 4.15 |
| | | | | $H^b$ | 0.95 | -3.10 | 4.05 |

† δ of free guest minus δ of complexed guest. ‡ Reference 5. § Reference 7.

$EtCOCH_2Et$ were produced, respectively (93−95%). Table 2 lists the reaction conditions, yields, and $^1$H NMR chemical shift values for the methyl signals of nonchiral guests in (*S*)-**1**⊙guest and (*SS*)-**2**⊙guest and also for hemicarceplexes **9**⊙guest when comparable values are available. Also listed are Δδ values which equal δ values for free guests in $CDCl_3$ minus δ values of complexed guest. Chiral guests were also introduced into (*SS*)-**2** by either "sealing in" or thermal means. The guests, conditions, yields, diastereomeric ratios, and $^1$H NMR signals for each diastereomeric methyl signal with the differences in δ values (independent of sign) are given in Table 1.

**Configurations of Diastereomeric Complexes.** Configurational assignments were made for the two diastereomers produced from racemic guests and enantiomerically pure hosts in the following cases: (*S*)-**1**⊙(*R*)-PhS(O)Me; (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$; (*S*)-**1**⊙(*R*)-PhCH(OH)Me; (*S*)-**1**⊙(*S*)-PhCH(OH)Me; (*SS*)-**2**⊙(*R*)-$MeCHOHCH_2Me$; and (*SS*)-**2**⊙(*S*)-$MeCHOHCH_2Me$. This was done by complexing enantiomerically pure guests of known absolute configuration[10] to give diastereomerically pure complexes, whose signals in their $^1$H NMR spectra differed from those of the corresponding complexes containing guests of the opposite configuration. Subjection of (*S*)-**1** and (−)-(*S*)-4-$MeC_6H_4S(O)Me$ to the conditions for successfully making (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$ from (+)-(*R*)-guest gave only recovered starting material. This result confirmed the high stereospecificity observed when under these conditions (*S*)-**1** and racemic 4-$MeC_6H_4S(O)Me$ gave only (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$ to provide a > 20/1 ratio of [(*S*)-**1**⊙(*R*)-guest]/[(*S*)-**1**⊙(*S*)-guest]. We estimate we could have detected by $^1$H NMR spectral means at least 5% of the minor diastereomer had it been formed. The configurations of the two diastereomers of **1**⊙PhS(O)Me were established by complexing thermally, enantiomerically pure (+)-(*R*)-PhS(O)Me[11] with (*S*)-**1** to give (*S*)-**1**⊙(*R*)-PhS(O)Me, whose guest methyl gave a signal at −1.30 ppm. From commercially available (+)-(*R*)-PhCHOHMe[10] and (−)-(*S*)-PhCHOHMe[10] were prepared (thermally) (*S*)-**1**⊙(*R*)-PhCHOHMe (Me-δ = −2.40 ppm) and (*S*)-**1**⊙(*S*)-PhCHOHMe[10] (Me-δ = −2.51 ppm), respectively.

(10) Klyne, W.; Buckingham, J. *Atlas of Stereochemistry*; Oxford University Press: New York, 1978; Vol. 1.

(11) We warmly thank Professor Fumio Toda of Ehime University (Matsuyama, Ehime 790, Japan) for a sample of optically pure PhS(O)Me.

**Table 3.** Half-Lives, Relative Rates, and Activation Free Energies for Diastereomeric Complexes of (*S*)-**1**⊙Guests (Racemic) in $CDCl_3$ at 25 °C

| | $BrCH_2CHBrCH_3$ | $ClCH_2CHClCH_3$ |
|---|---|---|
| $t_{1/2}$ slow (h) | 3100 | 64 |
| $t_{1/2}$ fast (h) | 1100 | 41 |
| $k_{relative}$ | 3 | 1.6 |
| $\Delta\Delta G_{298}^{\ddagger}$ [a] | 0.6 | 0.3 |

[a] Calculated from $\Delta\Delta G_{298}^{\ddagger} = -RT \ln k_{relative}$ at 298 K.

Likewise, by thermal complexation, enantiomerically pure (+)-(*S*)-$Me^aCHOHCH_2Me^b$ with (*SS*)-**2** gave (*SS*)-**2**⊙(*S*)-$Me^aCHOHCH_2Me^b$ ($Me^a$-$\delta = -2.45$, $Me^b$-$\delta = -2.90$ ppm) and (−)-(*R*)-$Me^aCHOHCH_2Me^b$ gave (*SS*)-**2**⊙(*R*)-$Me^aCHOHCH_2Me^b$ ($Me^a$-$\delta = -2.55$, $Me^b$-$\delta = -2.83$ ppm).[10] The configurations of the guests in the other diastereomeric complexes were not identified.

**Chromatographic Behavior of Diastereomers.** When racemic PhS(O)Me was complexed with (*S*)-**1**, the diastereomeric products were easily separated on thin layer silica gel plates with 2% EtOAc in $CH_2Cl_2$ (v). The (*S*)-**1**⊙(*R*)-PhS(O)Me had a retention time $R_f$ of 0.41, and the $CH_3$ of its guest gave $\delta = -1.30$ ppm. The (*S*)-**1**⊙(*S*)-PhS(O)Me gave $R_f = 0.27$ and $\delta = -1.24$ ppm. When subjected to the same chromatographic treatment, the one-to-one mixture of diastereomers obtained by the sealing of racemic PhS(O)Me into (*SS*)-**2** to give (*SS*)-**2**⊙(*R*)(*S*)-PhS(O)Me (ratio one-to-one) gave no separation of diastereomers.

**Kinetics of Decomplexation.** Decomplexation half-lives and free energies of activation were calculated from the rates of decomplexation in $CDCl_3$ at 25 °C of a few of the diastereomeric complexes. The first-order decomplexations[12] were followed by $^1$H NMR spectral Me-$\delta$ changes of the guests with time, and the results are listed in Table 3. Besides those listed, the half-life for decomplexation of (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$ (the only diastereomer obtained) gave $t_{1/2} \cong 12$ h under the same conditions. Under the same conditions, (*S*)-**1**⊙guest (racemic) with guest $MeCHBrCH_2Me$, less than 5% decomplexation was observed after 30 days, whereas no decomplexation was observed after 30 days with guest $BrCH_2CH_2CHBrMe$. In comparison, in $CDCl_3$ at 23 °C, ($S_4$)-**7**⊙$BrCH_2CH_2CHBrMe$ gave $t_{1/2} = 12$ and 2 h for the respective slow and fast rates of decomplexation.[3]

## Discussion

**Chiral Recognition in Complexation.** The most dramatic example in this study of chiral recognition in complexation involves (*S*)-**1** as host distinguishing between (*R*)- and (*S*)-enantiomers of 4-$MeC_6H_4S(O)Me$ as guest at 398 K in a mixture of racemic guest (100 equiv) and $Ph_2O$ as solvent. The ratio, [(*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$]/[(*S*)-**1**⊙(*S*)-4-$MeC_6H_4S(O)Me$] produced was conservatively estimated as >20, since none of the complexed guest of the (*S*)-configuration could be detected by $^1$H NMR spectral analysis, even in a similar experiment in which only (−)-(*S*)-4-$MeC_6H_4S(O)Me$, (*S*)-**1**, and $Ph_2O$ were present. The fact that in $CDCl_3$ at 25 °C, 100 °C less than the complexation temperature, (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$ decomplexes with $t_{1/2} = 12$ h indicates this chiral recognition factor involves a diastereomeric equilibration rather than a rate factor. Application of the equation

$$\Delta\Delta G_T^\circ = -RT \ln(\text{ratio})$$

provides a value of >2.4 kcal mol$^{-1}$ difference in free energy for the two diastereomeric complexes at 398 K. When the 4-Me group of the guest was omitted as in racemic $C_6H_5S(O)Me$, a similar experiment resulted in [(*S*)-**1**⊙(*R*)-$C_6H_5S(O)Me$]/[(*S*)-**1**⊙(*S*)-$C_6H_5S(O)Me$] = 1.6, or $\Delta\Delta G_{398}^\circ = 0.37$ kcal mol$^{-1}$.

Examination of CPK molecular models (assembled with new connectors) of the four complexes provides a probable explanation of these results. In models, all four guests easily enter and depart the inner phase of (*S*)-**1** through either of the two larger 28-membered chiral rings in a conformation in which one of the oxygens attached to a methylene naphthyl turns its unshared electron pairs outward, which widens the other 28-membered ring and makes it accommodating to entry of 1,4-disubstituted benzenes. The resulting complexes have structures in which the tablet-shaped guests lie roughly in the equatorial plane of the host. Such orientations provide minimum host−guest contacts. Rotations of the enclosed guests about 90° around an equatorial axis of the host nearly aligns the two long axes of host and guest which allows the methyl groups of the guest to occupy the polar regions of the host, greatly increasing the number of close contacts between host and guest. Such rotations are sterically easy for both diastereomers involving $C_6H_5S(O)Me$, more difficult for (*R*)-4-$MeC_6H_4S(O)Me$ which "clicks into place", while (*S*)-4-$MeC_6H_4S(O)Me$ sterically resists rotation to give a stable complex with the model of (*S*)-**1**.

Support for host−guest long axis alignment in (*S*)-**1**⊙(*R*)-4-$MeC_6H_4S(O)Me$ is found in the high values of $\Delta\delta = 4.13$ for *Me*Ar and 4.09 ppm for *Me*S(O), where $\Delta\delta$ is $\delta$ for the $^1$H NMR signal for protons of guest dissolved in $CDCl_3$ minus $\delta$ for the guest in the complex dissolved in $CDCl_3$ at 25 °C. The four aryl faces of each hemisphere of **1** are highly shielding, and when occupied by Me groups provide upfield shifts of these magnitudes (e.g., see values in Table 2).

Of the nine guests of Table 1 that complex (*S*)-**1** thermally, 4-$MeC_6H_4S(O)Me$ is both the largest (10 non-hydrogen atoms) and most rigid guest (8 coplanar atoms). Examination of CPK models of both diastereomeric complexes of all of the other (*S*)-**1**⊙guest combinations indicates relatively easy passage of guests in and out of (*S*)-**1**. There is no doubt that equilibration between diastereomers occurred at the temperatures involved in their preparations by thermal means. In other words, the observed chiral recognition factors are thermodynamic rather than kinetic. The arrangement of the remaining guests in decreasing order of their chiral recognition factors (given parenthetically) in complexing (*S*)-**1** is as follows: $BrCH_2CH_2CHBrMe$ (2.7), PhCHOHMe (2.5), $BrCH_2CHBrCH_2Me$ (2.3), PhS(O)Me (1.6), $MeCHBrCH_2Me$ (1.4), $BrCH_2CHBrMe$ (1.1), $ClCH_2CHClMe$ (1.0), and $MeCHOHCH_2CH_2CH(Me)_2$ (1.0).

As might be expected, when the mixtures of diastereomers were sealed in by the reactions needed to acquire the fourth bridge, the diastereomeric ratios were smaller, but showed the same chiral bias as the thermal equilibrations. Thus the sealing in of PhCHOHMe and PhS(O)Me provided diastereomeric ratios of 1.5, whereas $HOCH_2CHMeCH_2Me$ gave a value of unity.

The chiral recognition factors in both the thermal and sealing in methods of introducing diastereomeric guests into (*SS*)-**2** ranged from a high of 1.4 for (*SS*)-**2**⊙$MeCHOHCH_2Me$ in thermal formation (sealing in gave the same preferred isomer by a factor of 1.1) to a low of 1 for PhS(O)Me, $MeCHOHCH_2OH$, and $HOCH_2CH(Me)CH_2Me$. The factors are undoubtedly kinetic in the low temperature (40 °C) sealing in method, but thermodynamic in the high temperature (160 °C) thermally-caused complexations. In the thermal complex formations, all four portals are 26-membered rings, only two of which are chiral. The greater conformational flexibility of the nonchiral rings suggests these are the more used portals.

The differences in magnitudes of the chemical shifts ($\Delta\delta$) for the methyl protons in the diastereomeric pairs of guests listed

(12) Cram, D. J.; Blanda, M. T.; Paek, K.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7765−7773.

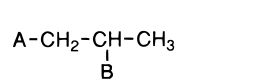
in Table 1 vary from a high of 0.36 ppm for (*SS*)-**2**⊙MeCH(OH)$CH_2CH_2CH(Me)_2$ to a low of 0.01 ppm for (*SS*)-**2**⊙PhS(O)Me. Generally, the more conformationally flexible guests provided the larger $\Delta\delta$ values.

**Through Shell Recognition of Host−Guest Configurational Relationships.** Diastereomerically related compounds usually exhibit retention times different enough to allow them to be separated chromatographically. However, the interesting question arises: do the shells of chiral hemicarceplexes shield guest configurations so much from polar chromatographic surfaces that the same retention times will be found for complexes that differ only in the configuration of the guest? In earlier work we demonstrated that carceplexes with the same host but with different guests were easily separable by chromatography.[13] In the present work (*S*)-**1**⊙(*R*)-PhS(O)Me was found to give an $R_f = 0.41$ value compared to a 0.27 value for (*S*)-**1**⊙(*S*)-PhS(O)Me on thin layer silica gel plates—$CH_2Cl_2$, 2% EtOAc (v), yet (*SS*)-**2**⊙-(*R*)-PhS(O)Me and (*SS*)-**2**⊙-(*S*)-PhS(O)Me gave the same retention times. We believe the marked difference in behavior of the two sets of diastereomeric complexes reflects the difference in rigidity of their chiral bridges. The chiral threitol acetonide bridge of the (*SS*)-**2** host is relatively rigid and adapts its shape very little to the configuration of the guest. In contrast, the bismethylenebinaphthyl bridge of (*S*)-**1** can readily change its naphthyl-to-naphthyl dihedral angle in response to the differing degrees of complementarity between host and guest in the diastereomeric complexes. Furthermore, small differences in dihedral angles leverage into large changes in the shape of the diastereomeric complexes because the two naphthalene rings' axis of rotation is close to the guest but distant from the outer ends of the aromatic rings.

**Differences in $^1$H NMR Chemical Shifts of Free and Incarcerated Nonchiral Guests.** Table 2 lists $^1$H NMR spectral signal differences for Me groups of non-chiral guests dissolved in $CDCl_3$ and for the same guests incarcerated in the inner phases of (*S*)-**1**, (*SS*)-**2**, and **9** (all four bridges of which are $O(CH_2)_4O$) that are dissolved in $CDCl_3$ at 25 °C. Included in the table are the thermal conditions for preparing and the yields of the hemicarceplexes. The values of $\Delta\delta$ at 4.20 and 4.06 respectively for (*S*)-**1**⊙$Me^aCH_2COCH_2CH_2Me^b$ indicate that the two methyl groups occupy the two polar bowls whose strong shielding properties move these signals far upfield. Very similar $\Delta\delta$ values of 4.15 and 4.05 due to $H^a$ and $H^b$, respectively, are found for (*SS*)-**2**⊙$Me^aCH_2COCH_2CH_2Me^b$ which suggests (*S*)-**1** and (*SS*)-**2** in their relaxed state possess similar cavity lengths in their axial dimensions. For (*S*)-**1**⊙$Me^aCOCH_2CH_2CH(Me^b)$-$Me^c$, $Me^a$ provides $\Delta\delta = 4.27$, even further upfield, which places its attached carbonyl group deep in one polar bowl. An attempt to reduce this carbonyl group in the complex with $BH_3$−$O(CH_2)_4$ at 25 °C failed because the C═O is surrounded on all sides with shielding aryl groups. (When the reaction medium was heated, decomplexation occurred.) The $\Delta\delta$ values for $Me^b$ and $Me^c$ are 2.37 and 3.16 ppm, respectively, and reflect the prochiral character of their attached CH in an asymmetric environment. The same situation is encountered in (*SS*)-**2**⊙$Me^aS(O)Me^b$, whose two $\Delta\delta$ values are 3.00 and 3.14 ppm (the sulfur is prochiral in a chiral environment). In **9**⊙$Me^aS(O)Me^a$, whose nonchiral host has four $O(CH_2)_4O$ bridges, only one Me signal is observed and $\Delta\delta = 2.95$ ppm, which also shows the two Me groups in this host are rapidly exchanging their positions in the latter complex at 25 °C. Although the patterns of $\Delta\delta$ values for the guest protons of *N*-methylpyrrolidinone and of $Me_2NCOMe$ complexed with (*SS*)-**2** and **9** are similar, without exception these values are somewhat larger for (*SS*)-**2** than for **9**. This fact indicates the guests are more closely held in (*SS*)-**2** than in **9**, which we attribute to the somewhat shorter and less flexible unique bridge in (*SS*)-**2** compared to the fourth $O(CH_2)_4O$ bridge in **9**.

**Decomplexation Rate Comparisons.** Decomplexation rate factor changes with changes in host and guest structures provide one kind of measure of structural recognition. For example, in $CDCl_3$ at 25 °C the ($t_{1/2}$ slow)/($t_{1/2}$ fast) for decomplexation of the diastereomers of (*S*)-**1**⊙$BrCH_2CHBrMe$ and of (*S*)-**1**⊙$ClCH_2CHClMe$ were respectively 2.8 and 1.6 (Table 3). However, [($t_{1/2}$ for $BrCH_2CHBrMe$)/($t_{1/2}$ for $ClCH_2CHClMe$)]$^{(S)-\mathbf{1}}_{slow} = 49$ whereas [($t_{1/2}$ for $BrCH_2CHBrMe$)/($t_{1/2}$ for $ClCH_2CHClMe$)]$^{(S)-\mathbf{1}}_{fast} = 26$; the corresponding $\Delta\Delta G^{\ddagger}$ values are 2.31 and 1.93 kcal mol$^{-1}$, respectively. Under the same conditions, the decomplexation half-life for (*S*)-**1**⊙$MeCH_2CHBrMe$ is estimated to be >10000 h, or >0.6 kcal mol$^{-1}$ greater activation free energy than that for (*S*)-**1**⊙$BrCH_2CHBrMe$.

Notice that all of the guests compared in this section possess the general formula **10** which contains: five non-hydrogen atoms at least three of which are carbons; one branch which defines a stereogenic center; an A group which is Me, Br or Cl; and a B group which is either Br or Cl but not Me. The bulks and shapes of Me, Br, and Cl are similar but their bond moments and polarizabilities are different. The total range in free energies of activation for decomplexation for these complexes is only a few kcal mol$^{-1}$. Insertion of an additional $CH_2$ group into the chain of **10** as in $BrCH_2CH_2CHBrMe$ slows the decomplexation rate to being immeasurable at 25 °C in $CDCl_3$. In contrast to (*S*)-**1**⊙$BrCH_2CH_2CHBrMe$, decomplexations of the slow and fast diastereomers of ($S_4$)-**7**⊙$BrCH_2CH_2CHBrMe$ gave $t_{1/2} = 12$ and 2 h, respectively. The four portals of ($S_4$)-**7** consist of 30-membered rings compared to the two 28-membered ring portals in (*S*)-**1**.



**10**, A = Me, Br or Cl; B = Br or Cl

## Conclusions

Two new chiral systems (*S*)-**1** and (*SS*)-**2** have been synthesized which form stable hemicarceplexes with guests that range from 4 to 10 non-hydrogen atoms in size. Guests have been introduced into their inner phases either by thermal means in which guests driven by mass law pass through 26 or 28-membered ring portals, or by a sealing-in process during introduction of the fourth bridge into the host. Equilibrium chiral recognition factors for complexation achieved by (*S*)-**1** of chiral guests ranged from unity for two branched alcohols and 1,2-dichloropropane to > 20 favoring (*R*)-4-$MeC_6H_4S(O)$-Me. Higher chiral recognition was observed with (*S*)-**1** than with (*SS*)-**2** as host and with thermal rather than sealing methods of diastereomeric complex formation. The differences in $^1$H NMR guest $\delta$ values for diastereomeric complexes varied from a low of 0.01 ppm to a high of 0.36 ppm, but did not correlate with chiral recognition factors. The $\Delta\delta$ values for nonchiral guests' methyl protons in $CDCl_3$ and in the inner phases of the two hosts dissolved in $CDCl_3$ varied from a low of 1.33 to a high of 4.27 ppm, according to where the guest moieties were located in the inner phases of the hosts.

## Experimental Section

**General.** All chemicals were reagent grade and used directly unless otherwise noted. Dimethylacetamide (DMA), *N*-methylpyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) were degassed under high vacuum just before use. A Bruker 360-MHz spectrometer was used

(13) Sherman, J. C.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 2194−2204.

to record $^1$H NMR spectra. Spectra were taken in $CDCl_3$ and unless otherwise noted were referenced to residual $CHCl_3$ at 7.26 ppm. For convenience in proton counting, the data for mixtures are treated as if the diastereomeric ratios were one-to-one. FAB MS were determined on a ZAB SE instrument with 3-nitrobenzyl alcohol (NOBA) as a matrix and Xe as carrier gas. Gravity chromotography was performed on E. Merck silica gel 60 (70−230 mesh). Thin-layer chromotography involved glass-backed plates (silica gel 60, $F_{245}$, 0.25 mm).

**11,39,40,41,42,70-Hexahydro-18,26,28,53,55,63,82,90-octaphenethyl-34,47-(epoxybutanoxy)-20,24:57,61-dimethano-17,29:52,64-dimetheno-16,30,51,65-(methynoxybutanoxymethyno)-18*H*,26*H*,28*H*,53*H*,55*H*,63*H*-bis[1,3]benzodioxocino[9,8-*d*:9′,8′-*d*′]bis[1,3]benzodioxocino[9′,10′:17,18;10″,9″:27,28]dinaphtho[2′,1′:21,22;1″,2″:23,24][1,3,6,11,14,16,19,26]octaoxacyclooctacosino[4,5-*j*:13,12-*j*′]bis[1,3]benzodioxocin (1⊙CHCl$_3$).** A mixture of diol **5** (100 mg, 0.045 mmol), 30 mL of DMA, 1 g of $Cs_2CO_3$, and 40 mg (0.09 mmol) of (*S*)-(−)-2,2′-bis(bromomethyl)-1,1′-binaphthyl (**3**) was stirred at 40 °C for 24 h under argon, and an additional 40 mg (0.09 mmol) of **3** was added. The mixture was stirred at 40 °C for another 24 h, the solvent was removed in vacuo, and the residue was dissolved in $CHCl_3$. The remaining solids were filtered through a 1 cm pad of Celite, and the solvent was rotary evaporated, concentrated to ∼3 mL, and poured into 100 mL of MeOH. The precipitate that formed was filtered and chromatographed on a preparatory TLC plate with $CHCl_3$ to give 92.2 mg (79% yield) of **1**⊙CHCl$_3$: $^1$H NMR $\delta$ 1.88 (6 H, br s, bridge $OCH_2CH_2$), 2.12 (6 H, m, bridge $OCH_2CH_2$), 2.36 (4 H, m, $CH_2CH_2$Ph), 2.48 (8 H, m, $CH_2CH_2$Ph), 2.48 (4 H, m, $CH_2CH_2$Ph), 2.54 (4 H, m, $CH_2CH_2$Ph), 2.67 (12 H, br s, $CH_2CH_2$Ph), 3.62 (6 H, m, bridge $OCH_2CH_2$), 3.89 (2 H, d, $J$ = 7.2 Hz, inner $OCH_2O$), 4.20 (6 H, m, bridge $OCH_2CH_2$), 4.20 (6 H, m, inner $OCH_2O$), 4.32 (2 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 4.48 (2 H, t, $J$ = 7.9 Hz, methine), 4.81 (4 H, m, methine), 4.89 (2 H, t, $J$ = 7.9 Hz, methine), 4.98 (2 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 5.12 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 5.86 (4 H, t, $J$ = 5.4 Hz, outer $OCH_2O$), 5.99 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.72 (2 H, s, ArH on bowl), 6.78 (2 H, s, ArH on bowl), 6.80 (2 H, s, ArH on bowl), 6.82 (2 H, s, ArH on bowl), 7.03 (2 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.14 (16 H, m, ArH on feet), 7.21 (24 H, m, ArH on feet); 7.52 (2 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge); 8.05 (2 H, d, $J$ = 8.3 Hz, H$^f$ of binaphthyl bridge), 8.19 (4 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2591, M$^+$), 2594 (20), 2472 (100). Anal. Calcd for $C_{163}H_{145}Cl_3O_{24}$·2H$_2$O (2630): C, 74.43; H, 5.71. Found: C, 74.22; H, 5.60.

**1⊙(±)-1,3-Dibromobutane. Procedure A.** Into a Pyrex test tube capped with a rubber septum were placed 20 mg (7.7 $\mu$mol) of **1**⊙$CHCl_3$ and 3 mL of 1,3-dibromobutane. This test tube was then shrouded in aluminum foil, flushed with argon, and heated at 115−120 °C for 48 h. This mixture was poured into 30 mL of MeOH. The precipitate that formed was filtered and chromatographed on a preparatory TLC plate with $CHCl_3$ to give 21 mg (95% yield) of **1**⊙(±)-1,3-dibromobutane as an approximately 2.7:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ −1.21 (3 H, d, $J$ = 7.0 Hz, guest $CH_3$), −0.97 (3 H, d, $J$ = 6.6 Hz, guest $CH_3$), 1.84 (12 H, br s, bridge $OCH_2CH_2$), 2.06 (12 H, m, bridge $OCH_2CH_2$), 2.37 (8 H, m, $CH_2CH_2$Ph), 2.48 (16 H, m, $CH_2CH_2$Ph), 2.48 (8 H, m, $CH_2CH_2$Ph), 2.53 (8 H, m, $CH_2CH_2$Ph), 2.67 (24 H, br s, $CH_2CH_2$Ph), 3.64 (12 H, m, bridge $OCH_2CH_2$), 4.09 (4 H, dd, $J$ = 7.0 Hz, inner $OCH_2O$), 4.22 (12 H, m, bridge $OCH_2CH_2$), 4.22 (12 H, m, inner $OCH_2O$), 4.42 (4 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 4.49 (4 H, t, $J$ = 7.8 Hz, methine), 4.79 (8 H, m, methine), 4.92 (4H, partially hidden, naphthyl $CH_2$), 4.92 (4 H, partially hidden, methine), 5.01 (4 H, d, $J$ = 7.1 Hz, outer $OCH_2O$), 5.77 (8 H, m, outer $OCH_2O$), 5.95 (4 H, d, $J$ = 7.1 Hz, outer $OCH_2O$), 6.71 (4 H, s, ArH on bowl), 6.76 (4 H, s, ArH on bowl), 6.78 (4 H, s, ArH on bowl), 6.82 (4 H, s, ArH on bowl), 7.03 (4 H, d, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.51 (4 H, t, $J$ = 7.5 Hz, H$^e$ of binaphthyl bridge), 8.04 (4 H, d, $J$ = 8.3 Hz, H$^f$ of binaphthyl bridge), 8.18 (4 H, d, $J$ = 8.6 Hz, H$^a$ of binaphthyl bridge), 8.32 (4 H, m, H$^b$ of binaphthyl bridge); FAB MS *m/e* (2687, M$^+$), 2687 (10), 2472 (100). Anal. Calcd for $C_{166}H_{152}Br_2O_{24}$·H$_2$O (2709): C, 73.60; H, 5.73. Found: C, 73.67; H, 5.83.

**1⊙(±)-1,2-Dibromobutane.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol) and 3 mL of 1,2-dibromobutane provided 21 mg (95% yield) of **1**⊙(±)-1,2-dibromobutane as a 2.3:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ −2.83 (3 H, t, $J$ = 7.0 Hz, guest $CH_3$), −2.75 (3 H, t, $J$ = 7.0 Hz, guest $CH_3$), 1.87 (12 H, br s, bridge $OCH_2CH_2$), 2.07 (12 H, m, bridge $OCH_2CH_2$), 2.36 (8 H, m, $CH_2CH_2$Ph), 2.48 (16 H, m, $CH_2CH_2$Ph), 2.48 (8 H, m, $CH_2CH_2$Ph), 2.55 (8 H, m, $CH_2CH_2$Ph), 2.69 (24 H, br s, $CH_2CH_2$Ph), 3.49−3.74 (12 H, m, bridge $OCH_2CH_2$), 4.09 (4 H, d, $J$ = 7.0 Hz, inner $OCH_2O$), 4.10−4.32 (12 H, m, bridge $OCH_2CH_2$), 4.10−4.32 (12 H, m, inner $OCH_2O$), 4.32 (4 H, partially hidden, naphthyl $CH_2$), 4.53 (4 H, m, methine), 4.79 (8 H, m, methine), 4.82 (4H, partially hidden, naphthyl $CH_2$), 4.92 (4 H, m, methine), 5.01 (4 H, m, outer $OCH_2O$), 5.77−6.01 (12 H, m, outer $OCH_2O$), 6.65−6.85 (16 H, s, ArH on bowl), 7.04 (4 H, m, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.52 (4 H, t, $J$ = 7.1 Hz, H$^e$ of binaphthyl bridge), 8.04 (4 H, m, H$^f$ of binaphthyl bridge), 8.19 (4 H, m, H$^a$ of binaphthyl bridge), 8.27 (4 H, m, H$^b$ of binaphthyl bridge); FAB MS *m/e* (2687, M$^+$), 2687 (10), 2472 (100). Anal. Calcd for $C_{166}H_{152}Br_2O_{24}$·2H$_2$O (2727): C, 73.12; H, 5.77. Found: C, 72.92; H, 5.81.

**1⊙(±)-1,2-Dibromopropane.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol) and 3 mL of 1,2-dibromopropane provided 21 mg (95% yield) of **1**⊙(±)1,2-dibromopropane as an approximately 1.1:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ 0.01 (3 H, d, $J$ = 6.4 Hz, guest $CH_3$), 0.25 (3 H, d $J$ = 6.4 Hz, guest $CH_3$), 1.87 (12 H, br s, bridge $OCH_2CH_2$), 2.09 (12 H, m, bridge $OCH_2CH_2$), 2.36 (8 H, m, $CH_2CH_2$Ph), 2.47 (16 H, m, $CH_2CH_2$Ph), 2.47 (8 H, m, $CH_2CH_2$Ph), 2.56 (8 H, m, $CH_2CH_2$Ph), 2.68 (24 H, br s, $CH_2CH_2$Ph), 3.59 (4 H, t, bridge $OCH_2CH_2$), 3.68 (8 H, m, bridge $OCH_2CH_2$), 3.97 (4 H, d, $J$ = 6.7 Hz, inner $OCH_2O$), 4.20 (12 H, m, bridge $OCH_2CH_2$), 4.20 (12 H, m, inner $OCH_2O$), 4.36 (4 H, d, $J$ = 11.8 Hz, naphthyl $CH_2$), 4.49 (4 H, m, methine), 4.81 (8 H, m, methine), 4.90 (4 H, t, methine), 4.96 (4 H, d, $J$ = 11.8 Hz, naphthyl $CH_2$), 4.99 (4 H, hidden, outer $OCH_2O$), 5.80 (8 H, d, $J$ = 6.8 Hz, outer $OCH_2O$), 5.95 (4 H, m, outer $OCH_2O$), 6.71 (4 H, s, ArH on bowl), 6.76 (8 H, s, ArH on bowl), 6.81 (4 H, s, ArH on bowl), 7.04 (4 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.51 (4 H, t, $J$ = 7.4 Hz, H$^e$ of binaphthyl bridge), 8.04 (4 H, d, $J$ = 8.1 Hz, H$^f$ of binaphthyl bridge), 8.18 (4 H, d, $J$ = 8.2 Hz, H$^a$ of binaphthyl bridge), 8.27 (4 H, d, $J$ = 8.2 Hz, H$^b$ of binaphthyl bridge); FAB MS *m/e* (2673, M$^+$), 2677 (20), 2475 (100). Anal. Calcd for $C_{165}H_{150}Br_2O_{24}$ (2677): C, 74.04; H, 5.65. Found: C, 73.71 ; H, 5.50.

**1⊙(±)-1,2-Dichloropropane. Procedure B.** A flask equipped with a reflux condenser was charged with 20 mL of (±)-1,2-dichloropropane and 20 mg of **1**⊙$CHCl_3$. The resulting solution was heated at reflux under argon for 24 h and then concentrated to a volume of *ca*. 3 mL on a rotovap. This solution was poured into 30 mL of MeOH. The precipitate was filtered and chromatographed on a preparatory TLC plate with $CHCl_3$ to give 19 mg (97% yield) of **1**⊙(±)-1,2-dichloropropane as a 1:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ −1.82 (3 H, d, $J$ = 6.8 Hz, guest $CH_3$), −1.54 (3 H, d $J$ = 6.8 Hz, guest $CH_3$), 1.88 (12 H, br s, bridge $OCH_2CH_2$), 2.09 (12 H, m, bridge $OCH_2CH_2$), 2.37 (8 H, m, $CH_2CH_2$Ph), 2.48 (16 H, m, $CH_2CH_2$Ph), 2.48 (8 H, m, $CH_2CH_2$Ph), 2.53 (8 H, m, $CH_2CH_2$Ph), 2.68 (24 H, br s, $CH_2CH_2$Ph), 3.61 (12 H, m, bridge $OCH_2CH_2$), 3.89 (4 H, dd, $J$ = 6.8 Hz, inner $OCH_2O$), 4.17 (12 H, m, bridge $OCH_2CH_2$), 4.17 (12 H, m, inner $OCH_2O$), 4.32 (4 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 4.49 (4 H, t, $J$ = 7.9 Hz, methine), 4.81 (8 H, m, methine), 4.90 (4 H, t, $J$ = 7.9 Hz, methine), 4.97 (4 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 5.01 (4 H, d, $J$ = 5.7 Hz, outer $OCH_2O$), 5.82 (8 H, m, outer $OCH_2O$), 5.96 (4 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.73 (4 H, s, ArH on bowl), 6.79 (4 H, s, ArH on bowl), 6.80 (4 H, s, ArH on bowl), 6.83 (4 H, s, ArH on bowl), 7.04 (4 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.51 (4 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge), 8.04 (4 H, d, $J$ = 8.3 Hz, H$^f$ of binaphthyl bridge), 8.20 (8 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2585, M$^+$), 2586 (20), 2475 (100). Anal. Calcd for $C_{165}H_{150}Cl_2O_{24}$·H$_2$O (2606): C, 76.05; H, 5.88. Found: C, 75.67; H, 5.50.

**1⊙(+)-Methyl Phenyl Sulfoxide and 1⊙(−)-Methyl Phenyl Sulfoxide.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol), 250 mg of (±)-PhS(O)Me (1.8 mmol), and 0.5 mL of $Ph_2O$ at 125 °C for 36 h provided 19 mg (96% yield) of **1**⊙(±)-PhS(O)Me as a 1.6:1 mixture of diastereomeric complexes. **1**⊙(+)-PhS(O)Me and **1**⊙(−)-PhS(O)Me were separated by preparatory TLC using $CH_2Cl_2$ as the mobile phase.

**Procedure C.** Into a flask equipped with a magnetic stirrer and blanketed with argon were placed 100 mg (0.045 mmol) of diol **5**, 10

mL of $(Me_2N)_3PO$ (HMPA), 1 g of $Cs_2CO_3$, 1 g (7.2 mmol) of (±)-PhS(O)Me, and 40 mg (0.09 mmol) of dibromide **3**. The reaction mixture was stirred at 40 °C for 24 h under argon, and 40 mg (0.09 mmol) of **3** was added. After being stirred at 40 °C for another 24 h, the reaction mixture was poured into 200 mL of 5% NaCl(aq). The precipitate that formed was filtered, washed with MeOH, and chromatographed on a preparatory TLC plate with $CH_2Cl_2$. The combined yield of product was 33% (39 mg), and the ratio of **1**⊙(+)-PhS(O)Me/**1**⊙(−)-PhS(O)Me was 1.5:1.

**1⊙(+)-methyl phenyl sulfoxide:** $^1$H NMR $\delta$ −1.30 (3 H, s, guest $CH_3$), 1.80 (6 H, br s, bridge $OCH_2CH_2$), 1.93 (6 H, m, bridge $OCH_2CH_2$), 2.50 (16 H, m, $CH_2CH_2Ph$), 2.67 (16 H, m, $CH_2CH_2Ph$), 3.65 (4 H, br s, bridge $OCH_2CH_2$), 3.94 (1 H, m, guest), 3.94 (4 H, br s, bridge $OCH_2CH_2$), 4.03 (4 H, br s, bridge $OCH_2CH_2$), 4.03 (4 H, br s, inner $OCH_2O$), 4.43 (2H, partially hidden, naphthyl $CH_2$), 4.43 (4 H, t, $J$ = 7.7 Hz, inner $OCH_2O$), 4.73 (4 H, t, $J$ = 7.7 Hz, methine), 4.89 (4 H, t, $J$ = 7.7 Hz, methine), 5.02 (2H, partially hidden, naphthyl $CH_2$), 5.02 (2 H, t, $J$ = 7.7 Hz, outer $OCH_2O$), 5.60 (2 H, t, $J$ = 7.7 Hz, outer $OCH_2O$), 5.81 (1 H, br s, guest), 6.05 (2 H, d, $J$ = 7.5 Hz, outer $OCH_2O$), 6.52 (2 H, d, $J$ = 7.5 Hz, outer $OCH_2O$), 6.78 (2 H, s, ArH on bowl), 6.88 (6 H, s, ArH on bowl), 7.03 (2 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.15 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet), 7.50 (2 H, t, $J$ = 7.8 Hz, H$^e$ of binaphthyl bridge), 8.02 (2 H, d, $J$ = 8.1 Hz, H$^f$ of binaphthyl bridge), 8.19 (4 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2613, M$^+$), 2613 (20), 2475 (100). Anal. Calcd for $C_{169}H_{152}O_{25}S$ (2615): C, 77.62; H, 5.86. Found: C, 77.26; H, 5.70.

**1⊙(−)-methyl phenyl sulfoxide:** $^1$H NMR $\delta$ −1.24 (3 H, s, guest $CH_3$), 1.74 (6 H, br s, bridge $OCH_2CH_2$), 1.94 (6 H, m, bridge $OCH_2CH_2$), 2.52 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.60 (4 H, br s, bridge $OCH_2CH_2$), 3.71 (1 H, m, guest), 4.06 (4 H, br s, bridge $OCH_2CH_2$), 4.16 (4 H, br s, bridge $OCH_2CH_2$), 4.16 (4 H, br s, inner $OCH_2O$), 4.44 (2H, partially hidden, naphthyl $CH_2$), 4.45 (4 H, t, $J$ = 7.7 Hz, inner $OCH_2O$), 4.74 (1 H, br s, guest), 4.88 (4 H, t, $J$ = 8.1 Hz, methine), 5.00 (2 H, partially hidden, naphthyl $CH_2$), 5.00 (4 H, m, overlap, methine), 5.44 (4 H, t, $J$ = 7.7 Hz, outer $OCH_2O$), 5.51 (1 H, br s, guest), 5.79 (1 H, br s, guest), 5.99 (2 H, d, $J$ = 7.6 Hz, outer $OCH_2O$), 6.53 (2 H, d, $J$ = 7.6 Hz, outer $OCH_2O$), 6.80 (2 H, s, ArH on bowl), 6.90 (6 H, s, ArH on bowl), 7.03 (2 H, d, $J$ = 7.9 Hz, H$^c$ of binaphthyl bridge), 7.15 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet), 7.51 (2 H, t, $J$ = 8.3 Hz, H$^e$ of binaphthyl bridge), 8.03 (2 H, d, $J$ = 7.9 Hz, H$^f$ of binaphthyl bridge), 8.19 (2 H, d, $J$ = 8.2 Hz, H$^a$ of binaphthyl bridge), 8.20 (4 H, m, H$^b$ of binaphthyl bridge); FAB MS *m/e* (2613, M$^+$), 2613 (20), 2475 (100). Anal. Calcd for $C_{169}H_{152}O_{25}S$ (2615): C, 77.62; H, 5.86. Found: C, 77.26; H, 6.09.

**1⊙(±)-1-Phenylethanol.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol), 262 mg of [(±)-PhCHOHMe or (+)-PhCHOHMe or (−)-PhCHOHMe (1.8 mmol)] and 1 mL of $Ph_2O$ at 160 °C for 48 h provided [19 mg (97% yield) of **1**⊙(±)-PhCHOHMe as a 2.5:1 mixture of diastereomeric complexes or 18 mg (90%) of **1**⊙(+)-PhCHOHMe or 19 mg (97%) of **1**⊙(−)-PhCHOHMe] after purification by preparatory TLC with $CH_2Cl_2$.

Application of procedure C to 100 mg (0.045 mmol) of diol **5**, 10 mL of HMPA, 1 g of $Cs_2CO_3$, 657 mg (4.5 mmol) of (±)-PhCHOHMe, and 80 mg (0.18 mmol) of dibromide **3** provided 40 mg (35% yield) of **1**⊙(±)-PhCHOHMe as a 1.5:1 mixture of diastereomeric complexes after the purification by preparatory TLC ($CH_2Cl_2$).

**1⊙(+)-1-phenylethanol:** $^1$H NMR $\delta$ −2.40 (3 H, d, $J$ = 6.2 Hz, guest $CH_3$), 1.85 (6 H, br s, bridge $OCH_2CH_2$), 1.96 (6 H, m, bridge $OCH_2CH_2$), 2.51 (16 H, m, $CH_2CH_2Ph$), 2.68 (16 H, m, $CH_2CH_2Ph$), 3.63 (1 H, m, guest), 3.94−4.05 (8 H, m, bridge $OCH_2CH_2$), 4.32 (2H, d, partially hidden, naphthyl $CH_2$), 4.17−4.49 (8 H, m, inner $OCH_2O$), 4.89 (2H, partially hidden, naphthyl $CH_2$), 4.89 (4 H, m, methine), 5.03 (2 H, t, $J$ = 7.5 Hz, methine), 5.13 (2 H, t, $J$ = 7.5 Hz, methine), 5.61 (4H, d, $J$ = 8.0 Hz, outer $OCH_2O$), 5.81 (2 H, br s, guest); 6.03 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.12 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.80 (2 H, s, ArH on bowl), 6.89 (6 H, s, ArH on bowl), 7.05 (2 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.17 (16 H, m, ArH on feet), 7.24 (24 H, m, ArH on feet), 7.52 (2 H, t, $J$ = 7.8 Hz, H$^e$ of binaphthyl bridge), 8.07 (2 H, d, $J$ = 8.1 Hz, H$^f$ of binaphthyl bridge), 8.28 (2 H, d, $J$ = 8.2 Hz, H$^a$ of binaphthyl bridge), 8.40 (4 H, m, H$^b$ of binaphthyl bridge); FAB MS *m/e* (2595, M$^+$), 2595 (20), 2475 (100). Anal. Calcd for $C_{170}H_{154}O_{25}$ (2597): C, 78.62; H, 5.98. Found: C, 78.59; H, 5.79.

**1⊙(−)-1-phenylethanol:** $^1$H NMR $\delta$ −2.51 (3 H, d, $J$ = 6.3 Hz, guest $CH_3$), 1.83 (6 H, br s, bridge $OCH_2CH_2$), 1.96 (6 H, m, bridge $OCH_2CH_2$), 2.51 (16 H, m, $CH_2CH_2Ph$), 2.68 (16 H, m, $CH_2CH_2Ph$), 3.62 (1 H, m, guest), 3.84−4.05 (8 H, m, bridge $OCH_2CH_2$), 4.34 (2H, hidden, naphthyl $CH_2$), 4.18−4.39 (8 H, m, inner $OCH_2O$), 4.72−4.91 (4 H, m, methine), 5.02 (2H, d, $J$ = 7.5 Hz, naphthyl $CH_2$), 5.02 (2 H, t, hidden, methine), 5.13 (2 H, t, $J$ = 7.3 Hz, methine), 5.60 (4H, d, $J$ = 8.0 Hz, outer $OCH_2O$), 5.83 (2 H, br s, guest), 5.99 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.11 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.80 (2 H, s, ArH on bowl), 6.89 (6 H, s, ArH on bowl), 7.05 (2 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.17 (16 H, m, ArH on feet), 7.24 (24 H, m, ArH on feet), 7.51 (2 H, t, $J$ = 7.8 Hz, H$^e$ of binaphthyl bridge), 8.05 (2 H, d, $J$ = 8.1 Hz, H$^f$ of binaphthyl bridge), 8.21 (4 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2595, M$^+$), 2595 (20), 2475 (100). Anal. Calcd for $C_{170}H_{154}O_{25}$ (2597): C, 78.62; H, 5.98. Found: C, 78.77; H, 5.72.

**1⊙(+)-*p*-Tolyl Methyl Sulfoxide.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol), 277 mg of (±)-4-$MeC_6H_4S(O)Me$ (1.8 mmol), and 0.5 mL of $Ph_2O$ at 125 °C for 36 h provided about 30% of **1**⊙(+)-4-$MeC_6H_4S(O)Me$. No further purification was attempted: $^1$H NMR $\delta$ −1.71 (3 H, s, guest $CH_3$), −1.39 (3 H, s, guest $CH_3$), 1.82 (6 H, br s, bridge $OCH_2CH_2$), 1.94 (6 H, m, bridge $OCH_2CH_2$), 2.54 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.66 (4 H, br s, bridge $OCH_2CH_2$), 3.94 (4 H, br s, bridge $OCH_2CH_2$), 4.02 (4 H, br s, bridge $OCH_2CH_2$), 4.06 (4 H, br s, inner $OCH_2O$), 4.43 (4 H, partially hidden, inner $OCH_2O$), 4.71 (2 H, partially hidden, methine), 4.88 (4 H, partially hidden, methine), 4.98 (2H, partially hidden, naphthyl $CH_2$), 5.12 (2 H, hidden, methine), 5.30 (1H, guest), 5.68 (1H, guest), 5.81 (4 H, hidden, outer $OCH_2O$), 6.01 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.50 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.75 (2 H, s, ArH on bowl), 6.86 (6 H, s, ArH on bowl), 7.03 (2 H, partially hidden, H$^c$ of binaphthyl bridge), 7.15 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet), 7.50 (2 H, partially hidden, H$^e$ of binaphthyl bridge), 8.05 (2 H, d, $J$ = 8.1 Hz, H$^f$ of binaphthyl bridge), 8.38 (4 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS ($C_{170}H_{154}O_{25}S$) *m/e* (2627, M$^+$), 2628 (20), 2475 (100).

**1⊙(±)-5-Methyl-2-hexanol.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol), 0.2 mL of (±)-5-methyl-2-hexanol, and 1 mL $Ph_2O$ at 150 °C for 48 h provided 18 mg (89% yield) of **1**⊙(±)-5-methyl-2-hexanol as a 1:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ −3.05 (6 H, m, guest $CH_3$), −1.69 (3 H, d, guest $CH_3$), −1.62 (3 H, d, guest $CH_3$), 1.88 (24 H, br s, bridge $OCH_2CH_2$), 2.37 (8 H, m, $CH_2CH_2Ph$), 2.48 (16 H, m, $CH_2CH_2Ph$), 2.48 (8 H, m, $CH_2CH_2Ph$), 2.53 (8 H, m, $CH_2CH_2Ph$), 2.68 (24 H, br s, $CH_2CH_2Ph$), 4.06 (12 H, m, bridge $OCH_2CH_2$), 4.12 (4 H, m, inner $OCH_2O$), 4.24 (12 H, m, bridge $OCH_2CH_2$), 4.52 (4 H, hidden, naphthyl $CH_2$), 4.52 (8 H, partial overlap, inner $OCH_2O$), 4.80 (4H, hidden, inner $OCH_2O$), 4.82 (12 H, m, methine), 4.99 (4 H, m, methine), 5.74 (4 H, m outer $OCH_2O$), 5.76 (8 H, m, outer $OCH_2O$), 6.01 (4 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 6.75 (4 H, s, ArH on bowl), 6.78 (12 H, s, ArH on bowl), 7.05 (4 H, d, $J$ = 6.8 Hz, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.51 (4 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge), 8.04 (4 H, d, $J$ = 8.3 Hz, H$^f$ of binaphthyl bridge), 8.19 (8 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2589, M$^+$), 2593 (20), 2475 (100). Anal. Calcd for $C_{169}H_{160}O_{25}\cdot 2H_2O$ (2627): C, 77.26; H, 6.29. Found: C, 77.24; H, 5.96.

**1⊙(±)-2-Methyl-1-butanol.** Application of procedure C to 100 mg (0.045 mmol) of diol **5**, 10 mL of HMPA, 1 g of $Cs_2CO_3$, 657 mg (4.5 mmol) of (±)2-methyl-1-butanol and 80 mg (0.18 mmol) of dibromide **3** provided 35 mg (30% yield) of **1**⊙(±)-2-methyl-1-butanol as a 1:1 mixture of diastereomeric complexes after the purification by preparatory TLC with $CH_2Cl_2$: $^1$H NMR $\delta$ −2.84 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −2.66 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −1.62 (3 H, d, $J$ = 6.3 Hz, guest $CH_3$), −1.50 (3 H, d, $J$ = 6.3 Hz, guest $CH_3$), 1.90−2.11 (24 H, br s, bridge $OCH_2CH_2$), 2.38 (8 H, m, $CH_2CH_2Ph$), 2.49 (16 H, m, $CH_2CH_2Ph$), 2.56 (8 H, m, $CH_2CH_2Ph$), 2.64 (8 H, m, $CH_2CH_2Ph$), 2.67 (24 H, br s, $CH_2CH_2Ph$), 3.59−3.80 (12 H, m, bridge $OCH_2CH_2$), 4.12 (4 H, m, inner $OCH_2O$), 4.27 (12 H, m, bridge $OCH_2CH_2$), 4.33 (4H, hidden, naphthyl $CH_2$), 4.38 (12 H, m, inner $OCH_2O$), 4.51 (4 H, t, $J$ = 7.2 Hz, methine), 4.88 (16 H, m, methine), 4.98 (4 H, hidden, naphthyl $CH_2$), 5.02 (4 H, hidden, outer $OCH_2O$), 5.83 (8 H, d, $J$ = 7.5 Hz, outer $OCH_2O$), 6.02 (4 H, d, $J$ = 7.5 Hz, outer $OCH_2O$), 6.78 (4 H, s, ArH on bowl), 6.82 (12 H, s, ArH on bowl), 7.06 (4 H, d, $J$

= 6.8 Hz, H$^c$ of binaphthyl bridge), 7.14 (32 H, m, ArH on feet), 7.21 (48 H, m, ArH on feet), 7.50 (4 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge), 8.05 (4 H, d, $J$ = 8.3 Hz, H$^f$ of binaphthyl bridge), 8.19 (8 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2561, M$^+$), 2563 (40), 2475 (100). Anal. Calcd for $C_{167}H_{156}O_{25}\cdot H_2O$ (2581): C, 77.71; H, 6.17. Found: C, 77.43; H, 6.17.

**1⊙5-Methyl-2-hexanone.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol) and 2 mL of 5-methyl-2-hexanone at 130 °C for 48 h gave 19 mg (95% yield) of **1**⊙5-methyl-2-hexanone: $^1$H NMR $\delta$ −2.28 (3 H, d, $J$ = 7.0 Hz, guest $CH_3$), −2.14 (3 H, d, $J$ = 7.0 Hz, guest $CH_3$), −1.49 (3 H, d, $J$ = 7.0 Hz, guest $CH_3$), 1.83 (6 H, br s, bridge $OCH_2CH_2$), 2.01 (6 H, m, bridge $OCH_2CH_2$), 2.34 (4 H, m, $CH_2CH_2Ph$), 2.46 (8 H, m, $CH_2CH_2Ph$), 2.46 (4 H, m, $CH_2CH_2Ph$), 2.53 (4 H, m, $CH_2CH_2Ph$), 2.66 (12 H, br s, $CH_2CH_2Ph$), 3.62 (6 H, m, bridge $OCH_2CH_2$), 4.20 (6 H, m, bridge $OCH_2CH_2$), 4.20 (2 H, m, inner $OCH_2O$), 4.30 (2 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 4.49 (6 H, m, inner $OCH_2O$), 4.92 (2 H, t, $J$ = 5.4 Hz, methine), 4.98 (6 H, m, methine), 4.98 (2 H, partially hidden, naphthyl $CH_2$), 5.75 (6 H, t, $J$ = 6.0 Hz, outer $OCH_2O$), 5.94 (2 H, br s, outer $OCH_2O$), 6.76 (8 H, m, ArH on bowl), 7.06 (2 H, d, H$^c$ of binaphthyl bridge), 7.15 (16 H, m, ArH on feet), 7.21 (24 H, m, ArH on feet), 7.51 (2 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge), 8.05 (2 H, d, $J$ = 8.0 Hz, H$^f$ of binaphthyl bridge), 8.18 (4 H, s, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2587, M$^+$), 2587 (20), 2476 (100). Anal. Calcd for $C_{169}H_{158}O_{25}$ (2589): C, 78.40; H, 6.15. Found: C, 78.13; H, 6.01.

**1⊙3-Hexanone.** Application of procedure A to **1**⊙$CHCl_3$ (20 mg, 7.7 $\mu$mol) and 2 mL of 3-hexanone at 130 °C for 48 h gave 16 mg (82% yield) of **1**⊙3-hexanone: $^1$H NMR $\delta$ −3.15 (6 H, m, guest $CH_3$), −0.33 (2 H, m, guest $CH_2$), 1.87 (6 H, br s, bridge $OCH_2CH_2$), 2.01 (6 H, m, bridge $OCH_2CH_2$), 2.34 (4 H, m, $CH_2CH_2Ph$), 2.46 (8 H, m, $CH_2CH_2Ph$), 2.46 (4 H, m, $CH_2CH_2Ph$), 2.53 (4 H, m, $CH_2CH_2Ph$), 2.67 (12 H, br s, $CH_2CH_2Ph$), 3.68 (6 H, m, bridge $OCH_2CH_2$), 3.89 (2 H, d, $J$ = 7.2 Hz, inner $OCH_2O$), 4.15 (6 H, m, bridge $OCH_2CH_2$), 4.15 (6 H, m, inner $OCH_2O$), 4.35 (2 H, d, $J$ = 8.5 Hz, naphthyl $CH_2$), 4.38 (2 H, hidden, methine), 4.98 (6 H, m, methine), 4.98 (2 H, hidden, naphthyl $CH_2$), 5.12 (2 H, d, $J$ = 7.2 Hz, outer $OCH_2O$), 5.91 (4 H, t, $J$ = 5.4 Hz, outer $OCH_2O$), 6.02 (2 H, br s, outer $OCH_2O$), 6.80 (8 H, m, ArH on bowl), 7.05 (2 H, d, H$^c$ of binaphthyl bridge), 7.15 (16 H, m, ArH on feet), 7.21 (24 H, m, ArH on feet), 7.48 (2 H, t, $J$ = 7.2 Hz, H$^e$ of binaphthyl bridge), 8.01 (2 H, d, $J$ = 8.0 Hz, H$^f$ of binaphthyl bridge), 8.19 (4 H, m, H$^a$ and H$^b$ of binaphthyl bridge); FAB MS *m/e* (2573, M$^+$), 2576 (10), 2475 (100). Anal. Calcd for $C_{168}H_{156}O_{25}\cdot H_2O$ (2593): C, 77.82; H, 6.14. Found: C, 77.79; H, 6.13.

**8,8a,11a,12,40,41,42,43-Octahydro-10,10-dimethyl-1,19,27,29,54,56,64,81-octaphenethyl-35,48-(epoxybutanoxy)-21,25:58,62-dimethano-2,53:18,30-dimetheno-3,52,17,31-(methynoxybutanoxymethyno)-1*H*,19*H*,27*H*,29*H*,54*H*,56*H*-bis[1,3]benzodioxocino[9,8-*d*:9′,8′-*d*′]-bis[1,3]benzodioxocino[9′,10′:17,18;10″,9‴:25,26][1,3]dioxolo[4′,5′:21,22][1,3,6,11,14,16,19,24]octaoxacyclohexacosino[4,5-*j*:13,12-*j*′]bis-[1,3]benzodioxocin [(*SS*)-2⊙$Me_2$NCOMe]. Procedure D.** A mixture of diol **5** (100 mg, 0.045 mmol), 30 mL of DMA, 1 g of $Cs_2CO_3$, and 42 mg (0.09 mmol) of (*S*,*S*)-(−)-1,4-di-*O*-tosyl-2,3-*O*-isopropylidene-L-threitol (**4**) was stirred at 70 °C for 24 h under argon, and 63 mg (0.14 mmol) of ditosylate **4** was added. After another 24 h of stirring at 70 °C, the solvent was removed in vacuo and the residue was dissolved in $CHCl_3$. The remaining solids were filtered through a 1 cm pad of Celite, and the solvent was rotary evaporated and concentrated to ∼2 mL and poured into 100 mL of MeOH. The precipitate that formed was filtered and chromatographed on a preparative TLC plate with $CHCl_3$ to give 61 mg (58% yield) of **2**⊙$Me_2$NCOMe: $^1$H NMR $\delta$ −1.78 (3 H, s, guest $CH_3$), −0.67 (3 H, s, guest $CH_3$), 1.38 (6 H, s, $CH_3$ on bridge), 1.54 (3 H, s, guest $CH_3$), 1.88 (6 H, d, bridge $OCH_2CH_2$), 2.15 (6 H, m, bridge $OCH_2CH_2$), 2.48 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.55 (6 H, m, bridge $OCH_2CH_2$), 3.58 (2 H, m, CH on the tartrate bridge, partially hidden), 4.17 (6 H, br s, bridge $OCH_2CH_2$), 4.20 (2 H, m, $CH_2$ on the tartrate bridge, hidden), 4.22 (4 H, t, $J$ = 7.6 Hz, inner $OCH_2O$, partially hidden), 4.33 (4 H, t, $J$ = 7.6 Hz, inner $OCH_2O$), 4.70 (2 H, d, $J$ = 11.2 Hz, $CH_2$ on the tartrate bridge), 4.80 (8 H, m, methine), 5.81 (8 H, m, outer $OCH_2O$), 6.84 (8 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2408, M$^+$), 2410.8 (100). Anal. Calcd for $C_{151}H_{149}NO_{27}$ (2410): C, 75.26; H, 6.23. Found: C, 75.01; H, 6.26.

**2⊙$Me_2$SO.** Application of procedure D to 100 mg (0.045 mmol) of diol **5**, 30 mL of DMSO, 1 g of $Cs_2CO_3$, and 105 mg (0.23 mmol) of ditosylate **4** gave 59 mg (55% yield) of **2**⊙$Me_2$SO after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −0.68 (3 H, s, guest $CH_3$), −0.54 (3 H, s, guest $CH_3$), 1.38 (6 H, s, $CH_3$ on bridge), 1.89 (6 H, m, bridge $OCH_2CH_2$), 2.19 (6 H, m, bridge $OCH_2CH_2$), 2.50 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.57 (8 H, m, bridge $OCH_2CH_2$), 3.57 (2 H, m, CH on the tartrate bridge, hidden), 4.11 (2 H,dd, $J$ = 7.5 Hz, $CH_2$ on the tartrate bridge), 4.20 (6 H, hidden, bridge $OCH_2CH_2$), 4.20 (8 H, m, inner $OCH_2O$), 4.69 (2 H, d, $J$ = 12.0 Hz, $CH_2$ on the tartrate bridge), 4.84 (8 H, m, methine), 5.85 (8 H, m, outer $OCH_2O$), 6.85 (8 H, s, ArH on bowl), 7.16 (16 H, m, ArH on feet), 7.22 (24 H, m, ArH on feet); FAB MS *m/e* (2399, M$^+$), 2402 (100). Anal. Calcd for $C_{149}H_{146}O_{27}S$ (2401): C, 74.54; H, 6.13. Found: C, 74.82; H, 6.11.

**2⊙*N*-Methylpyrrolidinone.** Application of procedure D to 100 mg (0.045 mmol) of diol **5**, 30 mL of NMP, 1 g of $Cs_2CO_3$, and 105 mg (0.23 mmol) of **4** gave 59 mg (55% yield) of **2**⊙NMP after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −1.04 (2H, m, guest $CH_2$), −1.01 (3 H, s, guest $CH_3$), −0.77 (3 H, br s, guest $CH_2$), 1.39 (6 H, s, $CH_3$ on bridge), 1.89 (6 H, m, bridge $OCH_2CH_2$), 2.10 (6 H, m, bridge $OCH_2CH_2$), 2.49 (16 H, m, $CH_2CH_2Ph$), 2.68 (16 H, m, $CH_2CH_2Ph$), 3.67 (8 H, m, bridge $OCH_2CH_2$), 3.81 (2 H, t, CH on the tartrate bridge), 4.22 (2 H, hidden, $CH_2$ on the tartrate bridge), 4.22 (6 H, hidden, bridge $OCH_2CH_2$), 4.22 (4 H, t, hidden, inner $OCH_2O$), 4.36 (4 H, t, $J$ = 7.1 Hz, inner $OCH_2O$), 4.61 (2 H, d, $J$ = 11.3 Hz, $CH_2$ on the tartrate bridge), 4.84 (8 H, m, methine), 5.81 (8 H, m, outer $OCH_2O$), 6.85 (8 H, br s, ArH on bowl), 7.16 (16 H, m, ArH on feet), 7.22 (24 H, m, ArH on feet); FAB MS *m/e* (2420, M$^+$), 2421 (100). Anal. Calcd for $C_{152}H_{149}NO_{27}$ (2422): C, 75.38; H, 6.20. Found: C, 75.44; H, 6.15.

**2 (Empty).** Application of procedure D to 100 mg (0.045 mmol) of diol **5**, 30 mL of dimethylformamide, 1 g of $Cs_2CO_3$, and 105 mg (0.23 mmol) of **4** gave 58 mg (56% yield) of empty **2** after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ 1.37 (6 H, s, $CH_3$ on bridge), 1.88 (6 H, m, bridge $OCH_2CH_2$), 2.14 (6 H, m, bridge $OCH_2CH_2$), 2.50 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.58 (8 H, m, bridge $OCH_2CH_2$), 3.58 (2 H, m, CH on the tartrate bridge, hidden), 4.11 (2 H, dd, $J$ = 7.5 Hz, $CH_2$ on the tartrate bridge), 4.19 (6 H, hidden, bridge $OCH_2CH_2$), 4.19 (8 H, m, inner $OCH_2O$), 4.64 (2 H, d, $J$ = 12.0 Hz, $CH_2$ on the tartrate bridge), 4.83 (8 H, m, methine), 5.89 (8 H, br s, outer $OCH_2O$), 6.91 (8 H, s, ArH on bowl), 7.16 (16 H, m, ArH on feet), 7.22 (24 H, m, ArH on feet); FAB MS *m/e* (2321, M$^+$), 2323 (100). Anal. Calcd for $C_{147}H_{140}O_{26}$ (2323): C, 76.02; H, 6.08. Found: C, 76.07; H, 6.22.

**2⊙Methyl Ethyl Ketone. Procedure E.** A flask equipped with a reflux condenser was charged with 20 mL of methyl ethyl ketone and 20 mg of **2**(empty) (8.2 $\mu$mol). The resulting solution was heated at reflux under argon for 48 h and then concentrated to a volume of *ca*. 3 mL on a rotovap. This solution was poured into 30 mL of MeOH. The precipitate that formed was filtered and chromatographed on a preparative TLC plate with $CHCl_3$ to give 19 mg (95% yield) of **2**⊙-methyl ethyl ketone: $^1$H NMR $\delta$ −2.83 (3 H, t, $J$ = 7.2 Hz, guest $CH_3$), −1.91 (3 H, s, guest $CH_3$), 0.37 (2 H, q, guest $CH_2$), 1.39 (6 H, s, $CH_3$ on bridge), 1.90 (6 H, d, bridge $OCH_2CH_2$), 2.19 (6 H, m, bridge $OCH_2CH_2$), 2.50 (16 H, m, $CH_2CH_2Ph$), 2.70 (16 H, m, $CH_2CH_2Ph$), 3.55 (6 H, m, bridge $OCH_2CH_2$), 3.58 (2 H, m, CH on the tartrate bridge, partially hidden), 4.05 (4 H, t, $J$ = 7.6 Hz, inner $OCH_2O$), 4.11 (4 H, t, $J$ = 7.6 Hz, inner $OCH_2O$), 4.23 (6 H, br s, bridge $OCH_2CH_2$), 4.27 (2 H, m, $CH_2$ on the tartrate bridge), 4.73 (2 H, d, $J$ = 11.2 Hz, $CH_2$ on the tartrate bridge), 4.82 (8 H, m, methine), 5.89 (8 H, m, outer $OCH_2O$), 6.84 (6 H, s, ArH on bowl), 6.86 (2 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2393, M$^+$), 2396 (90), 2323 (100). Anal. Calcd for $C_{151}H_{148}O_{27}$ (2395): C, 75.73; H, 6.23. Found: C, 75.81; H, 5.97.

**2⊙Ethyl Acetate.** Application of procedure E to **2** (empty) (20 mg, 8.2 $\mu$mol) and 20 mL of ethyl acetate gave 18 mg (93% yield) of **2**⊙-ethyl acetate: $^1$H NMR $\delta$ −2.24 (3 H, s, guest $CH_3$), −2.11 (3 H, t, $J$ = 7.0 Hz, guest $CH_3$), 1.39 (6 H, s, $CH_3$ on bridge), 1.90 (6 H, d, bridge $OCH_2CH_2$), 2.17 (6 H, m, bridge $OCH_2CH_2$), 2.50 (16 H, m, $CH_2CH_2Ph$), 2.70 (16 H, m, $CH_2CH_2Ph$), 3.61 (6 H, m, bridge $OCH_2CH_2$), 3.61 (2 H, hidden, CH on the tartrate bridge), 4.19 (8 H, m, inner $OCH_2O$), 4.19 (6 H, m, bridge $OCH_2CH_2$), 4.27 (2 H, hidden, $CH_2$ on the tartrate bridge), 4.68 (2 H, d, $J$ = 11.2 Hz, $CH_2$ on the

tartrate bridge), 4.88 (8 H, m, methine), 5.85 (8 H, m, outer $OCH_2O$), 6.84 (6 H, s, ArH on bowl), 6.86 (2 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2409, $M^+$), 2410.7 (90), 2322.6 (100). Anal. Calcd for $C_{151}H_{148}O_{28}$ (2411): C, 75.23; H, 6.19. Found: C, 75.12; H, 6.33.

**2⊙(±)-1,2-Propanediol.** Application of procedure A to **2** (empty) (20 mg, 8.2 $\mu$mol) and 1 mL of (±)-1,2-propanediol and 1 mL of $Ph_2O$ gave 18 mg (93% yield) of **2**⊙(±)-1,2-propanediol as a 1:1 mixture of diastereomeric complexes: $^1$H NMR $\delta$ −2.14 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), −2.06 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), −0.04 (2 H, t, guest $CH_2$), −0.14 (2 H, t, guest $CH_2$), 0.89 (1 H, d, guest OH), 1.02 (1 H, d, guest OH), 1.37 (12 H, s, $CH_3$ on bridge), 1.91 (12 H, d, bridge $OCH_2CH_2$), 2.12 (12 H, m, bridge $OCH_2CH_2$), 2.49 (32 H, m, $CH_2CH_2Ph$), 2.69 (32 H, m, $CH_2CH_2Ph$), 3.61 (12 H, m, bridge $OCH_2$-$CH_2$), 3.61 (4 H, hidden, CH on the tartrate bridge), 4.22 (4 H, hidden, $CH_2$ on the tartrate bridge), 4.22 (16 H, m, inner $OCH_2O$), 4.22 (12 H, m, bridge $OCH_2CH_2$), 4.63 (4 H, d, $J$ = 11.3 Hz, $CH_2$ on the tartrate bridge), 4.83 (16 H, m, methine), 5.84 (16 H, m, outer $OCH_2O$), 6.85 (12 H, s, ArH on bowl), 6.87 (4 H, s, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet); FAB MS *m/e* (2397, $M^+$), 2398.2 (100). Anal. Calcd for $C_{150}H_{148}O_{28}$ (2399): C, 75.11; H, 6.22. Found: C, 74.71; H, 5.95.

**2⊙(±)-2-Butanol.** Application of procedure A to **2** (empty) (20 mg, 8.2 $\mu$mol), 1 mL of (±)-2-butanol, and 1 mL of $Ph_2O$ at 160 °C for 48 h gave 18 mg (93% yield) of **2**⊙(±)-2-butanol as a 1.4:1 mixture of diastereomeric complexes.

Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 167 mg (2.3 mmol) of (±)-2-butanol, and 105 mg (0.23 mmol) of ditosylate **4** gave 22 mg (39% yield) of **2**⊙-(±)-2-butanol as a 1.1:1 mixture of diastereomeric complexes after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −2.90 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −2.83 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −2.55 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), −2.45 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), 0.83 (2 H, m, guest OH), 1.38 (12 H, s, $CH_3$ on bridge), 1.91 (12 H, d, bridge $OCH_2CH_2$), 2.14 (12 H, m, bridge $OCH_2CH_2$), 2.49 (32 H, m, $CH_2CH_2Ph$), 2.69 (32 H, m, $CH_2CH_2Ph$), 3.61 (12 H, m, bridge $OCH_2CH_2$), 3.61 (4 H, hidden, CH on the tartrate bridge), 4.16 (4 H, hidden, $CH_2$ on the tartrate bridge), 4.16 (16 H, m, inner $OCH_2O$), 4.16 (12 H, br s, bridge $OCH_2CH_2$), 4.67 (4 H, d, $J$ = 11.1 Hz, $CH_2$ on the tartrate bridge), 4.83 (16 H, m, methine), 5.85 (16 H, m, outer $OCH_2O$), 6.83 (12 H, s, ArH on bowl), 6.85 (4 H, s, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet), FAB MS *m/e* (2395, $M^+$), 2396.3 (70). Anal. Calcd for $C_{151}H_{150}O_{27}\cdot H_2O$ (2415): C, 75.10; H, 6.34. Found: C, 75.09; H, 6.39.

**2⊙(+)-2-Butanol.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 167 mg (2.3 mmol) of (+)-2-butanol, and 105 mg (0.23 mmol) of **4** gave 19 mg (35% yield) of **2**⊙(+)-2-butanol after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −2.89 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −2.45 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), 0.86 (1 H, d, guest OH), 1.38 (6 H, s, $CH_3$ on bridge), 1.90 (6 H, d, bridge $OCH_2CH_2$), 2.16 (6 H, m, bridge $OCH_2CH_2$), 2.48 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.60 (6 H, t, $J$ = 8.3 Hz, bridge $OCH_2CH_2$), 3.60 (2 H, hidden, CH on the tartrate bridge), 4.10 (2 H, d, $J$ = 7.2 Hz, $CH_2$ on the tartrate bridge), 4.17 (8 H, m, inner $OCH_2O$), 4.22 (6 H, br s, bridge $OCH_2CH_2$), 4.68 (2 H, d, $J$ = 11.1 Hz, $CH_2$ on the tartrate bridge), 4.81 (8 H, m, methine), 5.85 (8 H, m, outer $OCH_2O$), 6.84 (6 H, s, ArH on bowl), 6.86 (2 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2395, $M^+$), 2396.3 (70). Anal. Calcd for $C_{151}H_{150}O_{27}\cdot H_2O$ (2415): C, 75.10; H, 6.34. Found: C, 75.19; H, 6.36.

**2⊙(−)-2-Butanol.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$ , 167 mg (2.3 mmol) of (−)-2-butanol, and 105 mg (0.23 mmol) of **4** gave 20 mg (37% yield) of **2**⊙(−)-2-butanol after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −2.83 (3 H, t, $J$ = 7.1 Hz, guest $CH_3$), −2.55 (3 H, d, $J$ = 6.1 Hz, guest $CH_3$), 0.82 (1 H, d, guest OH), 1.38 (6 H, s, $CH_3$ on bridge), 1.91 (6 H, d, bridge $OCH_2CH_2$), 2.14 (6 H, m, bridge $OCH_2CH_2$), 2.49 (16 H, m, $CH_2CH_2Ph$), 2.69 (16 H, m, $CH_2CH_2Ph$), 3.60 (6 H, t, $J$ = 8.7 Hz, bridge $OCH_2CH_2$), 3.60 (2 H, hidden, CH on the tartrate bridge), 4.10 (2 H, dd, $J$ = 8.2, 7.2 Hz, $CH_2$ on the tartrate bridge), 4.20 (8 H, m, inner $OCH_2O$), 4.23 (6 H, br s, bridge $OCH_2$-$CH_2$), 4.67 (2 H, d, $J$ = 11.1 Hz, $CH_2$ on the tartrate bridge), 4.83 (8 H, m, methine), 5.85 (8 H, m, outer $OCH_2O$), 6.83 (6 H, s, ArH on bowl), 6.85 (2 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2395, $M^+$), 2396.3 (70). Anal. Calcd for $C_{151}H_{150}O_{27}$ (2397): C, 75.67; H, 6.31. Found: C, 75.74; H, 6.32.

**2⊙(±)-2-Methyl-1-butanol.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 205 mg (2.3 mmol) of (±)-2-methyl-1-butanol, and 105 mg (0.23 mmol) of **4** gave 18 mg (33% yield) of **2**⊙(±)-2-methyl-1-butanol as a 1:1 mixture of diastereomeric complexes after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −2.90 (3 H, t, guest $CH_3$), −2.77 (3 H, t, guest $CH_3$), −1.61 (3 H, d, $J$ = 6.5 Hz, guest $CH_3$), −1.56 (3 H, d, $J$ = 6.5 Hz, guest $CH_3$), −0.60 (8 H, m, guest $CH_2$), 1.37 (12 H, s, $CH_3$ on bridge), 1.89 (12 H, d, bridge $OCH_2CH_2$), 2.09 (12 H, m, bridge $OCH_2CH_2$), 2.49 (32 H, m, $CH_2CH_2Ph$), 2.69 (32 H, m, $CH_2CH_2Ph$), 3.66 (12 H, m, bridge $OCH_2CH_2$), 3.74 (4 H, partially hidden, CH on the tartrate bridge), 4.19 (4 H, hidden, $CH_2$ on the tartrate bridge), 4.19 (16 H, m, inner $OCH_2O$), 4.35 (12 H, br s, bridge $OCH_2CH_2$), 4.59 (4 H, d, $J$ = 9.6 Hz, $CH_2$ on the tartrate bridge), 4.83 (16 H, m, methine), 5.80 (16 H, m, outer $OCH_2O$), 6.84 (12 H, s, ArH on bowl), 6.87 (4 H, s, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet); FAB MS *m/e* (2409, $M^+$), 2411 (100). Anal. Calcd for $C_{152}H_{152}O_{27}$ (2411): C, 75.73; H, 6.35. Found: C, 75.47; H, 6.42.

**2⊙(±)-2-Pentanol.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 205 mg (2.3 mmol) of (±)-2-pentanol, and 105 mg (0.23 mmol) of **4** gave 22 mg (40% yield) of **2**⊙(±)-2-pentanol as a 1.2:1 mixture of diastereomeric complexes after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −2.72 (12 H, m, guest $CH_3$), −0.17 to −0.82 (8 H, m, guest $CH_2$), 0.65 (1 H, m, guest OH), 0.73 (1 H, m, guest OH), 1.38 (12 H, s, $CH_3$ on bridge), 1.91 (12 H, d, bridge $OCH_2CH_2$), 2.14 (12 H, m, bridge $OCH_2CH_2$), 2.49 (32 H, m, $CH_2CH_2Ph$), 2.69 (32 H, m, $CH_2CH_2$-Ph), 3.78 (12 H, m, bridge $OCH_2CH_2$), 3.61 (4 H, hidden, CH on the tartrate bridge), 4.20 (4 H, hidden, $CH_2$ on the tartrate bridge), 4.20 (16 H, m, inner $OCH_2O$), 4.20 (12 H, m, bridge $OCH_2CH_2$), 4.61 (4 H, d, $J$ = 11.1 Hz, $CH_2$ on the tartrate bridge), 4.83 (16 H, m, methine), 5.85 (16 H, m, outer $OCH_2O$), 6.83 (12 H, s, ArH on bowl), 6.85 (4 H, s, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet); FAB MS *m/e* (2409, $M^+$), 2411.8 (100). Anal. Calcd for $C_{152}H_{152}O_{27}$ (2411): C, 75.73; H, 6.35. Found: C, 75.67; H, 6.07.

**2⊙(±)-5-Methyl-2-hexanol.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 167 mg (2.3 mmol) of (±)-2-hexanol, and 105 mg (0.23 mmol) of **4** gave 22 mg (39% yield) of **2**⊙(±)-5-methyl-2-hexanol as a 1.2:1 mixture of diastereomeric complexes after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −3.11 (6 H, m, guest $CH_3$), −2.39 (3 H, d, $J$ = 6.0 Hz, guest $CH_3$), −2.03 (3 H, d, $J$ = 6.0 Hz, guest $CH_3$), −1.25 (3 H, d, $J$ = 6.0 Hz, guest $CH_3$), −0.96 (3 H, d, $J$ = 6.0 Hz, guest $CH_3$), 1.01 (1 H, m, guest OH), 1.08 (1 H, m, guest OH), 1.38 (12 H, s, $CH_3$ on bridge), 1.90 (24 H, d, bridge $OCH_2CH_2$), 2.49 (32 H, m, $CH_2CH_2$-Ph), 2.69 (32 H, m, $CH_2CH_2Ph$), 3.90−4.55 (12 H, m, bridge $OCH_2$-$CH_2$), 3.90−4.55 (4 H, hidden, CH on the tartrate bridge), 3.90−4.55 (4 H, hidden, $CH_2$ on the tartrate bridge), 3.90−4.55 (16 H, m, inner $OCH_2O$), 3.90−4.55 (12 H, m, bridge $OCH_2CH_2$), 4.83 (4 H, hidden, $CH_2$ on the tartrate bridge), 4.83 (16 H, m, methine), 5.78 (16 H, m, outer $OCH_2O$), 6.85 (12 H, m, ArH on bowl), 6.85 (4 H, s, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet); FAB MS *m/e* (2437, $M^+$), 2439 (100). Anal. Calcd for $C_{154}H_{156}O_{27}$ (2439): C, 75.84; H, 6.45. Found: C, 76.15; H, 6.50.

**2⊙3-Hexanone.** Application of procedure A to **2** (empty) (20 mg, 8.2 $\mu$mol) and 1 mL of 3-hexanone at 130 °C for 48 h gave 19 mg (94% yield) of **2**⊙3-hexanone: $^1$H NMR $\delta$ −3.10 (6 H, m, guest $CH_3$), −0.39 (2 H, m, guest $CH_2$), 0.46 (2 H, m, guest $CH_2$), 0.90 (2 H, m, guest $CH_2$), 1.38 (6 H, s, $CH_3$ on bridge), 1.89 (6 H, d, bridge $OCH_2CH_2$), 2.03 (6 H, m, bridge $OCH_2CH_2$), 2.49 (16 H, m, $CH_2CH_2$-Ph), 2.68 (16 H, m, $CH_2CH_2Ph$), 3.81 (6 H, m, bridge $OCH_2CH_2$), 3.94 (2 H, t, CH on the tartrate bridge), 4.23 (8 H, m, inner $OCH_2O$), 4.23 (6 H, m, bridge $OCH_2CH_2$), 4.33 (2 H, d, $J$ = 7.1 Hz, $CH_2$ on the tartrate bridge), 4.51 (2 H, d, $J$ = 8.3 Hz, $CH_2$ on the tartrate bridge), 4.83 (8 H, m, methine), 5.80 (8 H, m, outer $OCH_2O$), 6.81 (6 H, s, ArH on bowl), 6.83 (2 H, s, ArH on bowl), 7.17 (16 H, m, ArH on feet), 7.23 (24 H, m, ArH on feet); FAB MS *m/e* (2421, $M^+$), 2424

(95), 2323 (100). Anal. Calcd for $C_{153}H_{152}O_{27}$ (2423): C, 75.85; H, 6.32. Found: C, 75.67; H, 6.16.

**2⊙(±)Methyl Phenyl Sulfoxide.** Application of procedure D to 50 mg of diol **5** (0.023 mmol), 5 mL of HMPA, 0.5 g of $Cs_2CO_3$, 322 mg (2.3 mmol) of (±)-methyl phenyl sulfoxide, and 105 mg (0.23 mmol) of **4** gave 18 mg (33% yield) of **2**⊙(±)-methyl phenyl sulfoxide as a 1:1 mixture of diastereomeric complexes after preparative plate chromatography with $CHCl_3$: $^1$H NMR $\delta$ −1.15 (3 H, s, guest $CH_3$), −1.14 (3 H, s, guest $CH_3$), 1.56 (12 H, s, $CH_3$ on bridge), 1.87 (24 H, br s, bridge $OCH_2CH_2$), 2.51 (32 H, m, $CH_2CH_2Ph$), 2.69 (32 H, m, $CH_2CH_2Ph$), 3.81 (4 H, partially hidden, CH on the tartrate bridge), 4.02 (16 H, m, inner $OCH_2O$), 4.26 (24 H, m, bridge $OCH_2CH_2$), 4.84 (16 H, m, methine), 5.37 (4H, m, guest), 5.63 (16 H, m, outer $OCH_2O$), 6.50 (4H, m, guest), 6.93 (16 H, m, ArH on bowl), 7.17 (32 H, m, ArH on feet), 7.23 (48 H, m, ArH on feet); FAB MS *m*/*e* (2461, $M^+$), 2464 (100). Anal. Calcd for $C_{154}H_{148}O_{27}S$ (2463): C, 75.10; H, 6.06. Found: C, 74.79; H, 5.80.

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