matograph. Pressure reactions were done inside a 100-mL stainless steel Parr autoclave equipped with a teflon reaction chamber and a teflon-coated magnetic stirrer bar.

^{13}C NMR spectra were recorded on a Varian FT 80 instrument equipped with a low temperature unit.

Formylation Reactions at High Pressure. A 100-mL stainless steel autoclave fitted with a Teflon insert was charged with the aromatic substrate (usually 20 mmol) and the required amount of CF_3SO_3H or $CF_3SO_3H + SbF_5$(1:1) diluted in 10 mL of Freon-113 was added slowly with cooling under dry nitrogen. The autoclave was sealed and CO (1200 psi) was then introduced.

For the reactions with $CF_3SO_3H + HF + BF_3$, the aromatic substrate and triflic acid were placed in the autoclave and the required amount of liquid HF was then added and the autoclave was sealed while still at or below -30 °C. BF_3 and CO were then introduced as described above. After 3.5 h at room temperature (1 h in competitive experiments) the autoclave was depressurized and opened, and the reaction mixture was quenched in ice/bicarbonate, twice extracted in CH_2Cl_2, and dried ($MgSO_4$). Products were analyzed by GC and GC-MS.

Formylation at Atmospheric Pressure. The aromatic substrate, CF_3SO_3H, and HF were placed into a 50-mL Teflon reactor equipped with a Teflon coated magnetic stirrer bar, cooled to dry ice/acetone temperature, and then saturated with BF_3. The temperature was then allowed to rise slowly to 0 °C with efficient stirring. The reaction mixture was then again saturated with BF_3 at 0 °C. Thereafter CO was passed through the reaction mixture with efficient mixing for 3.5 h before quenching and GC analysis.

Mass Spectroscopic Data. Ditolylmethane (3 isomers): *m/e* 196 (M), 181 (M - Me, 100%), 166 (M - 2Me), 165 (M - 2Me - H^+), 104 (M - C_6H_5Me), 91, 77. Ditolylmethanol (3 isomers): *m/e* 224 (M, 100%), 209 (M - Me), 195 (M - CHO), 181, 166, 165, 104, 91, 77. Ditalylacetic acid: *m/e* 240 (M), 195 (M - COOH, 100%), 181, 166, 121, 119, 91, 77.

Acknowledgment. We thank Dr. K. Chan and E. Watson of USC, School of Pharmacy, for GC-MS analysis. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Registry No. C_6H_5Me, 108-88-3; 1,3,5-$C_6H_3Me_3$, 108-67-8; *o*-$C_6H_4Me_2$, 95-47-6; *m*-$C_6H_4Me_2$, 108-38-3; *p*-$C_6H_4Me_2$, 106-42-3; C_6H_5Et, 100-41-4; MeC_6H_4CHO, 1334-78-7; $Et_2C_6H_3CHO$, 95364-36-6; CO, 630-08-0; $Me_3C_6H_2CHO$, 70679-68-4; *p*-tolualdehyde, 104-87-0; *o*-tolualdehyde, 529-20-4; *m*-tolualdehyde, 620-23-5; ditolylmethane, 1335-47-3; ditolylacetaldehyde, 95364-33-3; ditolylacetic acid, 95462-21-8; tritolylmethane, 59645-11-3; 2,4,6-trimethylbenzaldehyde, 487-68-3; *o*-xylenecarboxaldehyde, 95364-34-4; *m*-xylenecarboxaldehyde, 95364-35-5; 2,5-dimethylbenzaldehyde, 5779-94-2; ethylbenzaldehyde, 53951-50-1.

Host-Guest Complexation. 33. Search for New Chiral Hosts[1]

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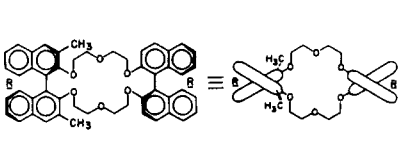
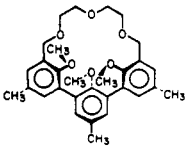
Nine new macrocyclic hosts have been designed, synthesized, and examined for their ability to bind alkali metal, ammonium, and alkylammonium cations. Their ring sizes vary from 17- to 24-membered. Five contain axially chiral units, three of which have not previously been incorporated in a host. Their structures are indicated by line formulas in which sequences of letters indicate the units and their points of attachment through which they are incorporated into the macroring. The order of the letters indicates the order of attachment of the units to one another. Chart I identifies the structures associated with the letters and Chart II identifies the structures of hosts **1-9** with the line formulas. The yields in the critical ring-closing reactions ranged from 5% to 80%. Additionally, Chart II also lists five assemblies of units (**10-14**) potentially useful for other host syntheses. Of these, **10** and **11** are chiral due to inhibition of ring inversion, whereas **14** is chiral due to the axial dissymmetry of the binaphthyl unit (B). Attempts to couple in two places 2 mol each of **12**, **13**, and **14** failed. The free energies ($-\Delta G°$ values) in $CDCl_3$ at 25 °C of hosts **1-9** binding the picrate salts of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and *t*-$BuNH_3^+$ were measured. The $-\Delta G°$ values were correlated with the structures of hosts and guests.

The construction of hosts with enforced or semienforced cavities of shapes complementary to a variety of guests has been the subject of the previous papers of this series. To provide for convergently arranged and cooperating binding sites, hosts must be macrocyclic or polymacrocyclic. In reconciling the design of hosts with the feasibility of potential synthetic pathways, it is useful to think in terms of molecular modules whose attachment to one another composes a desired structure. A molecular module is an assembly of units common to a variety of hosts. The points of attachment of the modules place limits on the distances they span and the part-cavities they define. Once their syntheses are developed for use in one host, they can be employed in others. The larger the number of modules that are developed, the greater the variety of cavity shapes available in a synthetic repertory.

One ambition of this research is the design and synthesis of hosts that exhibit high chiral recognition in complexation and catalysis. Hosts have been designed and prepared based on the 1,1'-binaphthyl unit which complex differentially enantiomeric amino acids and esters by factors of up to 30.[2] The same or similar hosts catalyze reactions in which complexed potassium salts of prochiral carbanions serve as nucleophiles to generate chiral products with as high as 99% ee enantiomeric purity.[3] Chorand host I



I



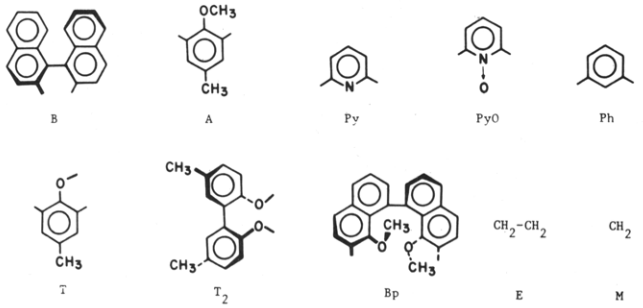
II, A(AMOE)$_2$O

(1) We warmly thank the National Science Foundation, Grant No. CHE 81-09532, for support of this research.

(2) Peacock, S. C.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043-2052.

0022-3263/85/1950-1486$01.50/0

Chart I

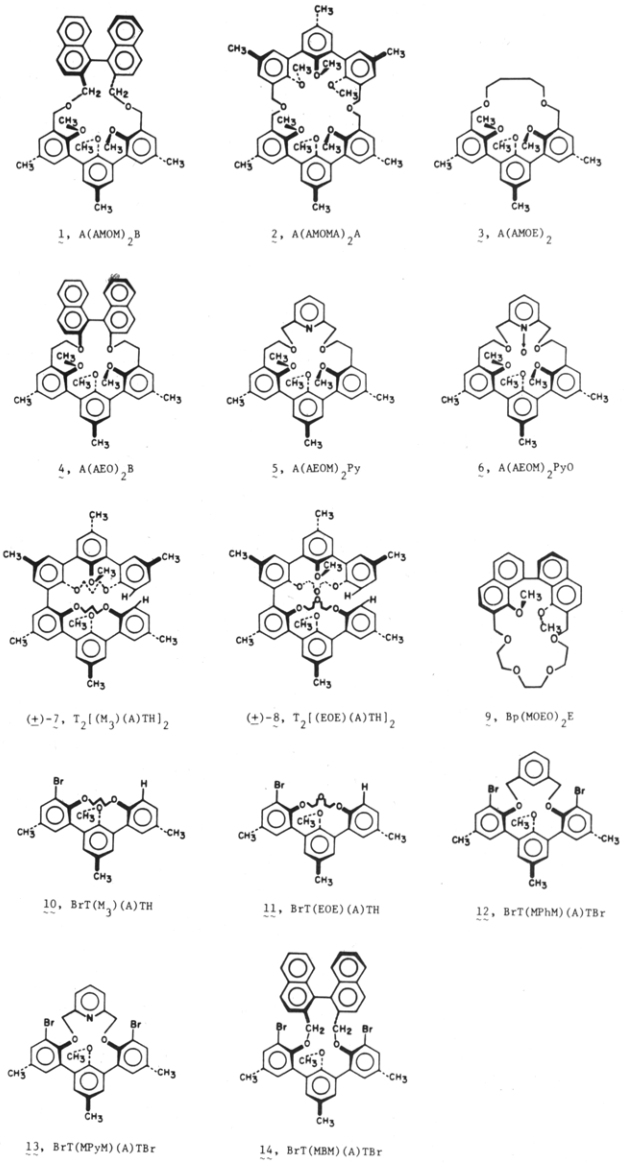


exhibits the highest chiral recognition observed in both complexation and catalysis. Because of its many conformations, most of which are nonbinding, its $-\Delta G°$ values for complexing K^+ and $CH_3NH_3^+$ picrates in $CDCl_3$ saturated with D_2O in $CDCl_3$ at 25 °C are only 8.1[4a] and 4.4 kcal mol^{-1},[4b] respectively. What is worse is the fact that the conformational flexibility allows this system to structurally adapt to unwanted guests and complexes, thus limiting specificity.[2]

The hemispherands,[5] of which A(AMOE)$_2$O (II) is a prototype, are half-preorganized, as a consequence of which they show higher binding and specificity among similar guests (principle of preorganization).[7] Thus II gives $-\Delta G°$ values of 11.8 and 8.2 kcal mol^{-1} for binding the picrates of K^+ and $CH_3NH_3^+$ in $CDCl_3$ at 25 °C, respectively.[6] Much evidence has accumulated that indicates that high degrees of preorganization and high binding free energies are prerequisites for high specificities with alkali-metal cations as guests.[4a,8] It seems likely that high stereospecificity in binding and catalysis are also going to require higher binding free energies and more preorganization than has yet been realized in chiral hosts.

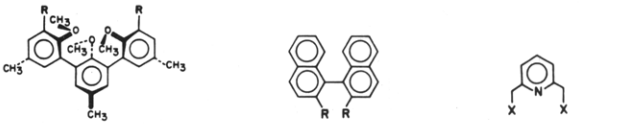
This paper describes the scope and limitations of synthetic sequences leading to new chiral units, modules, and hosts that are more highly preorganized than the catechol and ethylene glycol based units and modules of the chorands. The $-\Delta G°$ values for our nine new hosts binding the alkali metal, ammonium, and alkylammonium cations are reported. The systematic names of these compounds are useless for discussion. Accordingly, line formulas are employed in which capital letters stand for *units and points* of attachment and the *orders of the letters* indicate the orders of bonding of the units to one another. Chart I identifies the letters with the structures and points of attachment of the units. Chart II provides the structures, line formulas, and compound numbers of the hosts **1–9** and the five molecular modules **10–14**. When the hosts or modules are chiral, specific enantiomers are drawn, although in this work we deal only with racemates.

Chart II



Results

Syntheses. Host A(AMOM)$_2$B (**1**) was synthesized by slow addition of a mixture of diol A(ACH$_2$OH)$_2$[6] (**15**) and



dibromide (BrM)$_2$B[9] (**21**) in (CH$_2$)$_4$O to a refluxing mixture of KH and (CH$_2$)$_4$O under high-dilution conditions to give cycle **1** in 28% yield. Attempts to obtain **1** by similar procedures from A(ACH$_2$Br)$_2$[6] (**16**) and (HOM)$_2$B[9] (**20**) failed to give any detectable product. The final step in the ring closure is an S_N2 reaction with a semilinear transition state, M^+ $O^-\cdots C^+\cdots Br^-$. In CPK molecular models of the transition state (III) of the reaction which

(3) Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 625–628.

(4) (a) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106. (b) Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.*, **1981**, *46*, 393–406.

(5) Cram, D. J.; Dicker, I. B.; Lein, G. M.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6827–6828.

(6) Koenig, K. E.; Lein, G. M.; Stückler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553–3566.

(7) Cram, D. J. "Host–Guest Complexation Chemistry, IUPAC Chemistry for the Future"; Grünwald, H., Ed.; Pergamon Press: Oxford, 1984; pp 3–10.

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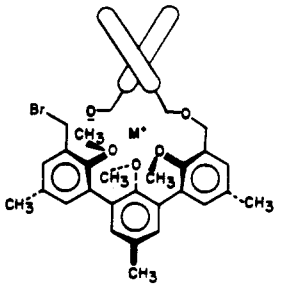
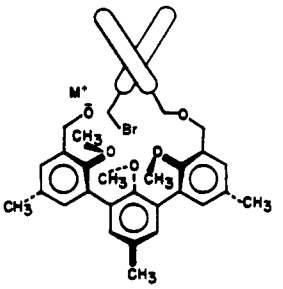
(9) Helgeson, R. C.; Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 3929–3931.



III

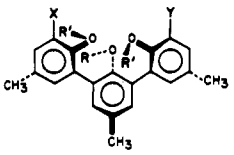


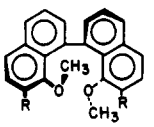
IV

gave 1, the M^+ ion-paired to the nucleophilic oxygen can nicely occupy the cavity to give $1 \cdot M^+$. In models of the transition state for the reaction that failed (IV), the M^+ ion-paired to the nucleophilic oxygen cannot occupy the cavity and at the same time provide a linear transition state. Thus examination of models in constrained systems might provide guidance in the choice of reactions to be used in ring closures. Host **2** was similarly prepared (35%) with $A(ACH_2OH)_2$ (**15**) and $(BrCH_2A)_2A$ (**16**) as starting materials for the ring closure. To determine how small a ring could be closed that included the MAAAM module, $A(AMBr)_2$ (**16**) and 1,4-butanediol were added to $(CH_2)_4O$–NaH under high-dilution conditions. Hemispherand $A(AMOE)_2$ (**3**) was produced, but in only 7% yield. This 17-atom ring in molecular models appears to be close to the lower limit on the number of ring members that can include the MAAAM unit. Models of $A(AMOE)_2$ (**3**) suggest the compound is rather strained. Attempts to close rings by the reactions of $A(AMBr)_2$ (**16**) with 1,2-bis(hydroxymethyl)benzene or (+)-2,3-dimethoxybutane-1,4-diol failed.

Hemispherands **4**–**6** were prepared with $A(AH)_2$[6] (**17**) as starting material. This compound was metalated with *n*-BuLi, and the resulting organometallic was treated with ethylene oxide to give $A(AEOH)_2$ (**18**), 26%, which was tosylated to produce $A(AEOTs)_2$ (**19**), 56%. Attempts to produce $A(AEO)_2B$ (**4**) from 2,2′-dihydroxy-1,1′-binaphthalene [$(HO)_2B$] and $A(AEOTs)_2$ (**19**) with NaH–$(CH_2)_4O$ or NaH–$(CH_3)_2NCHO$ led only to elimination reactions. However, addition of $A(AEOTs)_2$ to a mixture of K_2CO_3–$B(OH)_2$–$(CH_3)_2NCHO$ gave a 5% yield of $A(AEO)_2B$ (**4**). Host $A(AEOM)_2Py$ (**5**) was produced (27%) by slow addition of a mixture of 2,6-pyridinedimethanol[10] [$(HOM)_2Py$ or **23**] and $A(AEOTs)_2$ (**19**) in $(CH_2)_4O$ to $(CH_4)_4O$–NaH under high-dilution conditions. Oxidation of $A(AEOM)_2Py$ (**5**) with *m*-$ClC_6H_4CO_3H$ gave $A(AEOM)_2PyO$ (**6**), 83%.

The synthesis of hosts $T_2[(M_3)(A)TH]_2$ ((±)-**7**) and $T_2[(EOE)(A)TH]_2$ ((±)-**8**) both involved the trisphenol compound $HT[T(H)H]_2$ (**25**) as starting material.[6] Treatment of **25** with 1 mol of CH_3I–K_2CO_3 gave $A[T(H)H]_2$ (**26**), 70%.[11] Apparently the hydroxyl group of the central phenol is more acidic than the terminal phenols, possibly due both to the inductive effect of the two aryls attached to the central phenol and to the two terminal hydroxyl groups hydrogen bonding one another more strongly than do hydroxyls on adjacent aryls (molecular model examination). Bromination of $A[T(H)H]_2$ (**26**) with 1 mol of bromine gave BrT(H)AT(H)H (**27**), 45%, whereas 2 mol gave BrT(H)AT(H)Br (**28**), 88%.[11] When BrT(H)AT(H)H (**27**) was ring closed with 1,3-dibromopropane or diethylene glycol ditosylate under high-dilution conditions (Cs_2CO_3 and $(CH_3)_2NCHO$),[12] modules BrT(M_3)(A)TH (**10**) and BrT(EOE)(A)TH (**11**) were produced in 36% and 60% yields, respectively. Lithiation of BrT(M_3)(A)TH (**10**) with *sec*-BuLi and oxidative coupling of the organometallic produced with $Fe(acac)_3$[13] gave (±)-$T_2[(M)_3(A)TH]_2$ ((±)-**7**, 37%) and *meso*-**7**, both of which were characterized (see below). Similar treatment of BrT(EOE)(A)TH (**11**) gave (±)-$T_2[(EOE)(A)TH]_2$ ((±)-**8**, 17%), which was characterized, but only a trace of *meso*-**8**, characterized only by its mass spectrum. The configurational assignments of **7** and **8** are discussed in a later section.





25, X = Y = R = R′ = H; $HT[T(H)H]_2$
26, X = Y = R′ = H, R = CH_3; $A[T(H)H]_2$
27, X = Br, Y = R′ = H, R = CH_3; BrT(H)AT(H)H
28, X = Y = Br, R′ = H, R = CH_3; BrT(H)AT(H)Br

29, R = H: $Bp(H)_2$
30, R = CO_2Et; $Bp(CO_2Et)_2$
31, R = CH_2OH; $Bp(MOH)_2$
32, R = CH_2Br; $Bp(MBr)_2$
33, R = CHO; $Bp(CHO)_2$
34, R = CH_3; $Bp(CH_3)_2$

Chorand $Bp(MOEO)_2E$ (**9**) was prepared from 1-methoxynaphthalene as starting material. Shirley and Cheng observed that 1-methoxynaphthalene can be lithiated in its 2- or 8-position, depending on the lithiating agent and solvent.[14] Accordingly, 1-methoxynaphthalene was metalated with *t*-BuLi in cyclohexane, and the organometallic was oxidized with $Fe(acac)_3$ in benzene to give $Bp(H)_2$ (**29**), 47%. This new unit was metalated in the two positions ortho to the methoxyl groups with *n*-BuLi (tetramethylethylenediamine in Et_2O), and the resulting organometallic was quenched with ethyl chloroformate to give $Bp(CO_2Et)_2$ (**30**), 45%. This diester was reduced with $LiAlH_4$ to give $Bp(MOH)_2$ (**31**), 74%, which with PBr_3 gave $Bp(MBr)_2$ (**32**), only partially characterized. Two other approaches to $Bp(MOH)_2$ (**31**) and $Bp(MBr)_2$ (**32**) were investigated. When the diorganometallic derived from $Bp(H)_2$ (**29**) was quenched with ethyl formate, $Bp(CHO)_2$ (**33**), 39%, was formed. When the same derivative was quenched with CH_3I, $Bp(CH_3)_2$ (**34**), 69%, was obtained. Reduction of $Bp(CHO)_2$ (**33**) with $NaBH_4$ gave $Bp(MOH)_2$ (**31**), 46%. When $Bp(CH_3)_2$ was treated with *N*-bromosuccinimide, a bad mixture of compounds was produced. Thus the best route to $Bp(MOH)_2$ (**31**) is $Bp(H)_2 \rightarrow Bp(CO_2Et)_2 \rightarrow Bp(MOH)_2$. Demethylation of $Bp(H)_2$ (**29**) gave the parent, 8,8′-dihydroxy-1,1′-binaphthalene (83%).

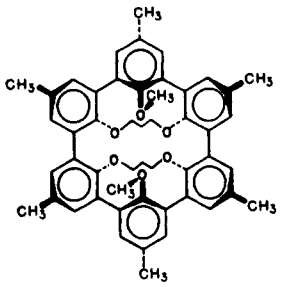
The extreme insolubility of $Bp(MBr)_2$ in a variety of solvents made it a poor candidate for ring-closing reactions. Accordingly, a mixture of $Bp(MOH)_2$ (**31**) and $(TsOEO)_2E$[15] in $(CH_2)_4O$ was added to NaH–$(CH_2)_4O$ under high-dilution conditions to give chorand $Bp(MOEO)_2E$ (**9**) in 46% yield.

Diol BrT(H)AT(H)Br (**28**) served as the starting material for the syntheses of modules **12**–**14** (Chart II). The reactions were carried out in $(CH_3)_2CO$–K_2CO_3–KI under

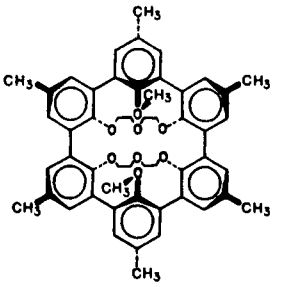
(10) Newcomb, M.; Timko, J. M.; Walba, D. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6392–6398.
(11) We warmly thank Dr. T. Kaneda for first carrying out these reactions.
(12) (a) van Keulen, B. J.; Kellogg, R. M.; Piepers, O. *J. Chem. Soc., Chem. Commun.* **1979**, 285–286. (b) Kruizinga, W. H.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 286–288.
(13) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752–6754.
(14) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251–252.
(15) Marshall, A.; Mobbs, R. H.; Booth, C. *Eur. Polym. J.* **1980**, *16*(2), 881–885.

middle-dilution conditions. From *m*-xylyl dibromide and **28**, BrT(MPhM)(A)TBr (**12**) was obtained in 58% yield. From $(BrM)_2Py$[10] (**24**) and **28**, BrT(MPyM)(A)TBr (**13**) was produced in 80% yield, whereas racemic $(BrM)_2B$[9] (**21**) and **28** gave BrT(MBM)(A)TBr (**14**) in 73% yield.

Attempts that were made to convert each of these three dibromides to their corresponding spherands failed. Colors were produced when **12–14** were treated with alkyllithium, which suggests the formation of benzyl anions subject to Wittig rearrangements.[16] Encouragement to attempt the syntheses of these doubly bridged spherands was derived from our analogous and successful syntheses of **35** and **36**.[17]

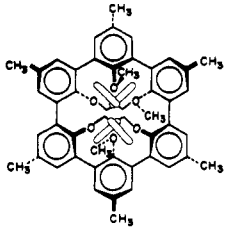


syn-35

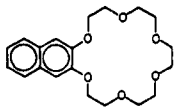


syn-36

Surprisingly **35** and **36** were shown by crystal structure determinations of their Li^+ complexes to have the syn rather than the expected anti configurations.[17b] Molecular models (CPK) of *anti*-**35** and *anti*-**36** can be assembled, as can the models of *anti*-**37** and the anti spherands de-



anti-37



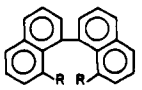
V, $Nap(OEOEO)_2E$

rivable in principle from BrT(MPhM)(A)TBr (**12**) and BrT(MPyM)(A)TBr (**13**). Models of *syn*-**35** and *syn*-**36** can only be assembled if about 15% of the four bridging aryl oxygens are shaved away. However, there is no way to assemble the syn isomer of **37** or those syn spherands based on the T(MPhM)(A)T or T(MPyM)(A)T modules. The mystery of why only *syn*-**35** and *syn*-**36** have been detected has not yet been solved.

Binding Properties of Hosts. The association constants (K_a) and free energies of association ($-\Delta G°$) of cyclic hosts **2–9** were measured by the picrate extraction method.[18] Solutions of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and *t*-$BuNH_3^+$ picrates in D_2O were extracted with $CDCl_3$ in the presence and absence of hosts. The hosts and their complexes are soluble essentially only in the $CDCl_3$ layer. The K_a and $-\Delta G°$ values at 25 °C in $CDCl_3$ saturated with D_2O were calculated from the results and are found in Table I. Those of hemispherand II[6] and chorand V[18] are included for comparison purposes. The binding by host **1** of the above ions was $-\Delta G° < 6$ kcal mol^{-1} and was "off scale" by this method.

Discussion

Structures of Hosts. The compounds of this study involve four types of chiral elements, the 2,2′-disubstituted-1,1′-binaphthyl unit B, the 7,7′-disubstituted-8,8′-dimethoxy-1,1′-binaphthyl unit Bp, and the modules RT-(M_3)(A)TH (e.g., **7** and **10**) and RT(EOE)(A)TH (e.g., **8** and **11**). The barriers to rotation of the naphthyl rings with respect to one another in the B unit are high enough to impart asymmetry to their hosts at ordinary working temperatures.[19] Although the barrier to rotation of the parent phenol of the Bp unit (**38**) is not known, those of



38, R = OH

39, R = CH_3

40, R = CH_2OH

other peri-disubstituted binaphthyls are. Thus **39** and **40** have $-\Delta G^‡$ values for rotation of 30.4 and 29.8 kcal mol^{-1}, respectively,[20] suggesting that the barrier for **38** is in the middle 20s. However, when incorporated in the ring system of $Bp(MOEO)_2E$ (**9**) this barrier should be enlarged by at least 10 kcal mol^{-1}. Molecular models (CPK) of **9** show the ring system is much too small to allow the methoxyl group of one naphthyl to rotate past that hydrogen of the other naphthalene which is ortho to the point of linkage of the two naphthyls. Rotations of the two peri methoxyls past one another is equally inhibited, so enantiomers of **9** should be configurationally stable to high temperatures. For modules RT(M_3)(A)TH or RT-(EOE)(A)TH to enantiomerize, the methoxyl groups of the A units have to undergo ring inversion. Molecular model examination shows such a process is out of the question in the absence of bond-breaking processes. Thus the enantiomers **1**, **4**, **7–11**, and **14** should be configurationally stable at working temperatures.

Proton NMR spectral studies demonstrated that $Bp(MOEO)_2E$ (**9**) is a racemate. When 1 equiv of (–)-$C_6H_5CH(CH_3)NH_3^+B(C_6H_5)_4^-$ was added to **9** in $CDCl_3$, the methoxyl singlet at δ 2.71 of the free host split into two singlets and moved upfield to δ 2.56 and 2.61 due to formation of diastereomeric complexes. Use of racemic salt moved the singlet upfield to a new singlet at δ 2.58. Rapid exchange on the ^1H NMR time scale of enantiomeric guests between enantiomeric hosts accounts for the latter result.

Compounds $T_2[(M_3)(A)TH]_2$ (**7**) and $T_2[(EOE)(A)TH]_2$ (**8**) each combine two like chiral elements and therefore should exist either as enantiomers containing C_2 axes or as a meso isomer containing a mirror plane. Both the racemic and meso forms of $T_2[(M_3)(A)TH]_2$ (**7**) were isolated, characterized, and assigned relative configurations based on the differences in their abilities to bind guests (next section). Unfortunately, both forms bound chiral ammonium salts too poorly to do chiral shift ^1H NMR experiments. The one stereoisomer of $T_2[(EOE)(A)TH]_2$ (**8**) that was isolated and characterized was identified as racemic material (±)-(**8**). Addition of 1 equiv of (–)-

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Table I. Association Constants (K_a) and Binding Free Energies ($-\Delta G°$) of Hosts for Picrate Salt Guests in $CDCl_3$ Saturated with D_2O at 25 °C

host structure	guest cation	K_a, M^{-1}	$-\Delta G°$, kcal mol^{-1}	host structure	guest cation	K_a, M^{-1}	$-\Delta G°$, kcal mol^{-1}
$A(AMOMA)_2A$ (2)	Li	3.5×10^4	6.2	(±)-7	Rb	6.8×10^4	6.6
	Na	1.9×10^5	7.2		Cs	4.1×10^4	6.3
	K	2.2×10^5	7.3		NH_4	1.7×10^4	5.8
	Rb	5.6×10^5	7.8		CH_3NH_3		<5
	Cs	6.5×10^6	9.3		t-$BuNH_3$		<5
	NH_4	1.9×10^5	7.2				
	CH_3NH_3	3.5×10^4	6.2	(±)-$T_2[(EOE)(A)TH]_2$ ((±)-8)	Li	2.9×10^4	6.1
	t-$BuNH_3$		<5		Na	3.1×10^5	7.5
					K	8.5×10^5	8.1
$A(AMOE)_2$ (3)	Li	1.8×10^4	5.8		Rb	5.6×10^5	7.8
	Na		<6		Cs	6.1×10^5	7.9
	K		<6		NH_4	2.2×10^5	7.3
					CH_3NH_3	1.1×10^5	6.9
$A(AEO)_2B$ (4)	Li	6.8×10^4	6.6		t-$BuNH_3$		<5
	Na	1.1×10^8	11.0				
	K	9.6×10^7	10.9	$Bp(MOEO)_2E$ (9)	Li		<6
	Rb	3.9×10^6	9.0		Na		<6
	Cs	5.6×10^5	7.8		K	3.7×10^5	7.6
	NH_4	2.8×10^6	8.8		Rb	8.5×10^5	8.1
					Cs	6.1×10^5	7.9
$A(AEOM)_2Py$ (5)	Li	6.8×10^4	6.6		NH_4	6.1×10^5	7.9
	Na	1.2×10^6	8.3		CH_3NH_3	4.9×10^4	6.4
	K	9.0×10^6	9.5		t-$BuNH_3$	1.2×10^3	3.9
	Rb	2.4×10^6	8.7				
	Cs	6.1×10^5	7.9	$A(AMOE)_2O$ (II)	Li	1.3×10^5	7.0
	NH_4	2.0×10^6	8.6		Na	1.0×10^9	12.3
	CH_3NH_3	1.1×10^5	6.9		K	5.0×10^8	11.8
	t-$BuNH_3$	7.6×10^3	5.3		Rb	4.1×10^7	10.4
					Cs	3.9×10^6	9.0
$A(AEOM)_2PyO$ (6)	Li	1.1×10^4	5.5		NH_4	1.5×10^7	9.8
	Na	6.8×10^4	6.6		CH_3NH_3	1.0×10^6	8.2
	K	1.6×10^5	7.1		t-$BuNH_3$	4.4×10^5	7.7
	Rb	2.9×10^4	6.1				
	Cs	5.7×10^4	6.5	$Nap(OEOEO)_2E$ (V)	Li	2.3×10^4	5.9
	NH_4	8.1×10^4	6.7		Na	1.2×10^6	8.3
	CH_3NH_3	6.4×10^3	5.2		K	8.6×10^7	10.8
	t-$BuNH_3$		<5		Rb	1.1×10^7	9.6
					Cs	1.3×10^6	8.3
(±)-$T_2[(M_3)(A)TH]_2$ ((±)-7)	Li	2.5×10^4	6.0		NH_4	9.9×10^6	9.5
	Na	3.7×10^5	7.6		CH_3NH_3	3.3×10^5	7.5
	K	3.1×10^5	7.5		t-$BuNH_3$	1.1×10^4	6.9

$C_6H_5CH(CH_3)NH_3^+B(C_6H_5)_4^-$ to (±)-8 in $CDCl_3$ moved the ^1H NMR signal of the CH_3O singlet of the free host from δ 3.14 to two higher field singlets at δ 3.07 and 3.06. In addition, one of the $ArCH_3$ singlets at δ 2.33 moved and split into two singlets at δ 2.36 and 2.37. When racemic salt was used in a similar experiment, the methoxy singlet did not split but moved from δ 3.14 to 3.06. The trace of a second isomer of 8 produced in the synthesis was characterized only by its mass spectrum. It was probably *meso*-8.

Examinations of molecular models of $A(AMOM)_2B$ (1), $A(AMOE)_2$ (3), and $A(AEO)_2B$ (4) strongly support the hypothesis that in their more stable conformations, the three CH_3O groups of their A–A–A modules possess the alternate arrangement shown in their drawings. Compound $A(AMOE)_2$ (3) contains a 17-membered ring, and the A–A–A module appears rigid. The other two contain 19-membered rings, and their A–A–A conformations seem equally fixed by the steric requirements of the macroring system and the methoxyl groups. The ^1H NMR spectra reflect the resulting symmetry properties. The ACH_2 protons of $A(AMOM)_2B$ (1) exhibit two AB quartets, whereas those of $A(AMOE)_2$ (3) provide only one AB quartet. The three cycles (1, 3, and 4) appear to be true hemispherands since at least half of the cavity is preorganized for binding.

The macroring of $A(AMOMA)_2A$ is 24-membered and appears flexible enough in models to be a rapidly equilibrating series of conformers. However, ring inversions are not rapid enough to reduce the ACH_2 protons to a singlet. They appear as AB quartets. Compounds A(AEOM)Py (5) and A(AEOM)PyO (6) contain 20-membered macrorings and exist as two conformers that equilibrate rapidly on the human but slowly on the ^1H NMR time scale. The ^1H NMR spectrum (200 MHz) of $A(AEOM)_2Py$ (5) in hexachlorobutadiene showed no coalescence of any protons of either the major or minor conformers when the spectrum was taken at 90 °C. Thus the barrier to interconversion has a value of $\Delta G^‡ > 18.6$ kcal mol^{-1} at 90 °C. In models of either 5 or 6, the alternate arrangement of methoxyl groups in the A–A–A modules does not appear enforced. The complex $A(AEOM)_2Py$·KPic (5·KPic; Pic = picrate) seems to exist as a single conformation (^1H NMR spectrum). Since $Bp(MOEO)_2E$ (9) is chiral and contains a C_2 axis, its $ArCH_2$ protons exist as an AB quartet as well.

A comparison of the ^1H NMR chemical shifts (200 MHz) of the centrally located OCH_3 of the A–A–A module correlates with expectations based on molecular model examination of the compounds containing this moiety. Table II provides these values along with the numbers of atoms included in the macroring. This methyl group is flanked by two aryl groups and is transannular to other aryl groups in many of the cycles. The signals of these protons move upfield due to the shielding provided by the ring currents of these aromatic rings. Open-chain model compound $A(AMBr)_2$ (16) is the most conformationally mobile of the

Table II. Chemical Shifts in ^1H NMR Spectra in $CDCl_3$ of Central CH_3O Protons in A–A–A Modules

compd	δ CH_3O	no. of atoms in macroring
$A(AMBr)_2$ (16)	3.190	no ring
$A(AMOMA)_2A$ (2)	3.033	24
$A(AMOE)_2O$ (II)	2.563	18
$A(AMOE)_2$ (3)	2.422	17
$A(AEOM)_2Py$ (5)	2.434	19
$A(AMOM)_2B$ (1)	2.023	19
$A(AEO)_2B$ (4)	1.772	19
4·LiPic	1.898	19
4·NaPic	1.742	19
4·KPic	1.470	19
4·NH_4Pic	1.344	19

series, and the protons occur at the lowest field (δ 3.190). Cycle $A(AMOMA)_2A$ (2) is 24-membered, and its models show that it is conformationally very mobile as well. This host provides a signal at the next lowest field (δ 3.033). Models of hemispherand $A(AMOE)_2O$ (II), which contains an 18-membered ring, suggest an enforced methoxyl arrangement with relatively little strain, and the signal occurs at δ 2.563. Models of $A(AMOE)_2$ (3, 17-membered ring) indicate the compound is nearly rigid, with the methyl group forced into the faces of the flanking aryls. The signal is moved the furthest upfield (δ 2.422) of those of the simple systems.

Models of $A(AEOM)_2Py$ (5), $A(AMOM)_2B$ (1), and $A(AEO)_2B$ (4), all of which contain 19-membered rings, indicate that the methyl in question is shielded by both the flanking and transannular aromatic rings. The signals are moved even further upfield to δ 2.434, 2.023, and 1.772, respectively. As the guests in the four complexes of $A(AEO)_3B$ (4; see Table II) became larger, the signals shift upfield from δ 1.898 for 4·Li^+ to a high of δ 1.344 for 4·NH_4^+. Model examination shows that the larger the guest, the more the methyl group is forced into the face of the transannular naphthalene ring. Complexes 4·Li^+, 4·Na^+, and 4·K^+ probably possess a nesting structure, whereas 4·NH_4^+ must have a perching structure in which the guest occupies the face of the macroring opposite to that of the central OCH_3 group, as in the crystal structure of $A(AMOE)_2O$·*t*-$BuNH_3^+$.[4a]

Correlation of Structure and Binding. Three of the macrocycles of Chart II contain five ligating oxygens, of which only $A(AEO)_2B$ (4) appears well organized for binding. This host provides a $(-\Delta G°)_{av}$ for the six ions measured (Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+) of about 9.0 kcal mol^{-1}, which compares with $(-\Delta G°)_{av}$ values of 10.1 kcal mol^{-1} for prototypical hemispherand $A(AMOE)_2O$ (II) and 8.7 kcal mol^{-1} for reference chorand $Nap(OEOEO)_2E$ (V) binding the same ions.[6,18] These latter hosts both contain six oxygens distributed rather evenly in 18-membered rings. Thus the preorganization for binding intrinsic to the A–A–A module more than compensates for the loss of one oxygen in $A(AEO)_2B$ (4) as compared to $Nap(OEOEO)_2E$ (V).

The patterns of binding of hemispherands $A(AMOE)_2O$ (4) and $A(AMOE)_2O$ (II) resemble one another, peaking at K^+ and Na^+. Models of $A(AEO)_2B$ (4) show the binaphthyl unit can act as a hinge to provide a cavity adaptable within limits to the sizes of the guest. The only internal groups capable of moving into the cavity are the two methylenes attached to the binaphthyl oxygens. However, strain is generated in the A–A–A unit in models when either one or two of these methylenes occupy the cavity. Thus all five oxygens of $A(AEO)_2B$ (4) appear preorganized for complexation, a fact that accounts for the $-\Delta G°$ values of 11.0 and 10.9 kcal mol^{-1} for the compound binding K^+ and Na^+, respectively. Isomeric cycle $A(AMOM)_2B$ (1) and the 17-membered ring compound $A(AMOE)_2$ (3) exhibit $-\Delta G°$ values of less than 6 kcal mol^{-1} for all eight ions. These results are surprising, since both compounds contain five oxygens that appear in molecular models as well preorganized for binding the smaller ions as $A(AEO)_2B$ (4).

The main structural difference between these strongly and weakly binding hosts is the length of the longest gap between oxygens in models of the binding conformers. In $A(AMOM)_2B$ (1) the enforced gap spanned by the MBM unit is ~2.0 Å and in $A(AMOE)_2$ (3) the enforced gap spanned by the EE module is ~1.5 Å. In the binding conformations of $A(AEO)_2B$ (4) and of $A(AMOE)_2O$ (II), no enforced gaps of greater than 0.5 Å are encountered. This phenomenon has been observed in hosts such as $Ph(MOEOE)_2O$,[21] which contains an 18-membered ring close to $Nap(OEOEO)_2E$ (V) in geometry. The former has a $(-\Delta G°)_{av}$ value of 5.8 kcal mol^{-1} compared to 8.7 kcal mol^{-1} for the latter binding Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+. The enforced gap between oxygens in models of $Ph(MOEOE)_2O$ is ~1.7 Å.

Although hosts $A(AMOMA)_2A$ (2), $A(AEOM)_2Py$ (5), and $A(AEOM)_2PyO$ (6) all contain the A–A–A module, its self-organizing potentialities are somewhat lost by its incorporation into large, flexible macrorings. These three hosts' $(-\Delta G°)_{av}$ values for Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+ are 7.5, 8.3, and 6.4 kcal mol^{-1}, respectively. As expected from its 24-membered ring system and eight binding sites, $A(AMOMA)_2A$ (2) shows maximum binding for Cs^+ at 9.3 kcal mol^{-1}. The host binds Rb^+ with $-\Delta G°$ = 7.3 kcal mol^{-1}. Molecular models of 2 show that a sphere normalized to 3.4-Å diameter (that of Cs^+) can be used to organize the cavity so that the unshared electron pairs of the eight oxygens simultaneously contact the sphere without introducing strain into the system. Host $A(AEOM)_2Py$ (5) containing six binding sites distributed in a 20-membered ring shows peak binding with K^+ ($-\Delta G°$ = 9.5 kcal mol^{-1}), inferior to that of $A(AEO)_2B$ (4) with only five binding sites ($-\Delta G°$ = 10.9 kcal mol^{-1} for K^+). Models of 5 show that a sphere normalized to 2.7-Å diameter (that of K^+) by insertion nicely organizes the cavity but that the free host has many more conformational degrees of freedom than free host 4. Both 4 and 5 contain the same O–E–A–A–A–E–O module. However, the B unit used to close the cycle in 4 provides a much more preorganized cavity than the MPyM module in 5. In models, the oxygen of the PyO unit in $A(AEOM)_2PyO$ (6) protrudes into the cavity in most of the conformations of the macroring. The low binding properties of 6 show that a large organizational burden is put on the guest during complexation. Although the PyO unit undoubtedly possesses intrinsically strong binding potential, a high degree of preorganization appears to be required for this to be realized.

Hosts (±)-$T_2[(M_3)(A)TH]_2$ ((±)-7) and (±)-$T_2[(EOE)(A)TH]_2$ ((±)-8) combine two rigid modules by the ary–aryl bond of the T_2 unit. Molecular models show that in principle, rotation about this bond allows the binding oxygens to approach one another as in rigid spherands, *anti*-35 and *anti*-36, respectively. In practice, the low binding values for (±)-7 and (±)-8 ($-\Delta G°$ values reach a maximum of 7.6 and 8.1 kcal mol^{-1}, respectively) indicate that this ideal geometry is never approached, probably because high nonbonded repulsions between the oxygens of the T_2 units are encountered before the other oxygens are in place. Enormous differences are observed in the binding by (±)-7 and *syn*-35 toward Li^+ ($\Delta(-\Delta G°)$ = 10.8

kcal mol^{-1}) and toward Na^+ ($\Delta(-\Delta G°)$ = 5.7 kcal mol^{-1}) on the one hand and by (±)-**8** and *syn*-**36** toward Li^+ ($\Delta(-\Delta G°)$ = 9.8 kcal mol^{-1}) and toward Na^+ ($\Delta(-\Delta G°)$ = 11.1 kcal mol^{-1}) on the other.[17b] These large differences again point to the importance of preorganization to binding.

The cavity of a CPK molecular model of $Bp(MOEO)_2E$ (**9**) is most ideally organized for binding by insertion of a sphere that normalizes to a diameter of about 3.0 Å, which is close to that of Rb^+. Peak binding is observed for Rb^+ with a $-\Delta G°$ value of 8.1 kcal mol^{-1}, with values for K^+, Cs^+, and NH_4^+ being 7.6, 7.9, and 7.9 kcal mol^{-1}, respectively. Although the oxygens in the Bp unit in **9** are held close together in an enforced conformation, the orbitals of the unshared electron pairs do not converge on the center of the cavity as well as those of the oxygens in $Nap(OEOEO)_2E$ (V), which is a more strongly complexing host. Thus $Nap(OEOEO)_2E$ (V) provides a $\Delta(-\Delta G°)_{av}$ value of 8.7 kcal mol^{-1} for binding Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+, whereas $Bp(MOEO)_2E$ (**9**) gives a value of <7.2 kcal mol^{-1}.

Chiral system $Bp(MOEO)_2E$ (**9**) in models adapts best to hydrogen bonding three hydrogens of NH_4^+ and $CH_3NH_3^+$ to give two linear N^+–H···$O(CH_2)_2$ and one bifurcated N^+–H:::$(OCH_3)_2$ hydrogen bond, as in the crystal structure[4a] of $A(AMOE)_2O$·*t*-$BuNH_3^+$ (the outer two methoxyls bind one hydrogen). The cavity of **9** is ill-shaped for three linear hydrogen bonds. In models of **9**·$CH_3NH_3^+$, two of the six oxygens are somewhat distant from the NH_3^+ group when all three hydrogen bonds are linear, but all six oxygens nicely contact the NH_3^+ group when one hydrogen bond is bifurcated and the other two are linear. This "bifurcated structure" explains the large $\Delta(-\Delta G°)$ = 2.5 kcal mol^{-1} for **9** binding $CH_3NH_3^+$ vs. $(CH_3)_3CNH_3^+$. In the "all-linear" structure, models of neither **9**·$CH_3NH_3^+$ nor **9**·$(CH_3)_3CNH_3^+$ provide nonbonded repulsions between host and guest since the CH_3 and $(CH_3)_3C$ groups perch well above the macroring and away from the chiral barrier. In the "bifurcated structure", the CH_3 and $(CH_3)_3C$ groups more deeply penetrate the cavity, which brings one of the methyls of the latter guest into the space occupied by the face of the naphthalene ring and a second methyl into the space occupied by the CH_3O of the host. Thus **9**·$CH_3NH_3^+$ and **9**·$(CH_3)_3CNH_3^+$ are forced to have different structures with different free energies of binding. This is the type of situation upon which chiral recognition in complexation depends—one diastereomeric complex is forced to have a different structure and free energy than a second.[2] Thus the unusual shape of the Bp unit may find some use in designing hosts for chiral recognition studies.

This investigation indicates that chiral hosts $A(AEO)_2B$ (**4**) and $Bp(MOEO)_2E$ (**9**) are good candidates for studies of chiral recognition in complexation and catalysis. However, the binding powers of chiral systems $A(AMOM)_2B$ (**1**), (±)-$T_2[(M_3)(A)TH]_2$ ((±)-**7**), and (±)-$T_2[(EOE)(A)TH]_2$ (±)-**8**) are too low to encourage further studies. The ring system of $A(AMOMA)_2A$ (**2**) appears to be too flexible and that of $A(AMOE)_2$ (**3**) to be too small and rigid to offer interesting host characteristics.

Experimental Section

General. Benzene was distilled from $LiAlH_4$ before use and CH_2Cl_2 twice from CaH_2, and Et_2O and $(CH_2)_4O$ (THF) were distilled from sodium benzophenone ketyl under N_2. Dimethylformamide (DMF) was distilled under reduced pressure from alumina and was stored under argon over 4-Å molecular sieves. Pyridine was fractionally distilled from solid NaOH and stored over 4-Å sieves, *t*-BuOH was distilled from CaH_2, and toluene and $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (TMEDA) were dried over 4-Å sieves. All diols used for ring closure were dried before use, as was $Fe(acac)_3$ (100 °C at 0.1 mm). Flash chromatography and medium-pressure chromatography were performed on silica gel 60 (E. Merck, particle size 0.040–0.063 mm, 230–400 mesh). Medium-pressure chromatography (120 psi at ca. 10 mL/min) was conducted on either of three Altex columns: 250 mm × 15 mm (column A), 1000 mm × 25 mm (column B), or 600 mm × 25 mm (column C). When solvent gradients were used, their starting and ending solvent compositions are indicated with an arrow showing the direction of the gradient. Medium-pressure columns were packed with the same silica gel as described for flash chromatography. Gravity columns were packed with silica gel 60 (E. Merck, particle size 0.063–0.200 mm) or aluminum oxide (E. Merck, neutral grade, particle size 0.063–0.200 mm, 70–230 mesh ASTM). Gel permeation chromatography was performed on a 20 ft × 0.375 in. (o.d.) column packed with 200 g of 100-Å Styragel (Waters Associates) with CH_2Cl_2 as eluent at flow rates of 3.5–4.0 mL/min. Thin-layer chromatography was conducted on precoated silica gel plates (E. Merck, F_{254}, thickness 0.2 mm). Melting points below 240 °C were measured on a Thomas-Hoover apparatus; those above 240 °C on a Mel-Temp melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 297 spectrometer. Absorbance readings in the UV for association constants were taken on a Gilford Model 252 photometer utilizing a Beckman DU monochromator. The mass spectra were recorded on an AEI Model MS-9 double-focusing spectrometer interfaced by Kratos Co. to a Data General Nova 3. The nuclear magnetic spectra were recorded on either a Bruker WP-200 (200 MHz) spectrometer or a JEOL FX 90Q (90 MHz) spectrometer.

3,5,21,23-Tetrahydro-34,35,36-trimethoxy-8,13,18-trimethyl-10*H*-6,10:11,15:16,20-trimethenodinaphtho[2,1-*c*:1′,2′-*e*][1,8]dioxacyclopentacosin (1). Procedure 1. A flask fitted in series with a reflux-return, diluting and mixing thimble of ~30-mL volume,[17c] a condenser, and a Hershberg addition funnel was dried at 200 °C, flushed with dry argon while hot, and allowed to cool under argon. To this flask were added 0.89 g (4.45 mmol) of a 20% KH dispersion in mineral oil (washed with dry hexane) and 200 mL of dry, freshly distilled THF (solution A). A solution of 0.61 g (1.11 mmol) of dibromide **16**[6] and 0.35 g (1.11 mmol) of [1,1′-binaphthalene]-2,2′-dimethanol[9] (**20**) in 200 mL of dry, freshly distilled THF (solution B) was added to the addition funnel. Solution A was heated to a vigorous reflux. After the reflux-return thimbles were full, slow addition was started and continued for 16 h. The solution was allowed to reflux an additional 36 h. The mixture was cooled, and the solvent was evaporated under reduced pressure. The residue (A) was partitioned between 100 mL of 1 N hydrochloric acid and 100 mL of CH_2Cl_2. The organic layer was washed with 100 mL of water, dried ($MgSO_4$), and evaporated under reduced pressure. The residue (B) was chromatographed through gel permeation column A. The last material eluted was collected (R_v = 175.5 mL). Residue C (the residue after evaporation of the CH_2Cl_2) was eluted over 50 g of silica gel with pentane–CH_2Cl_2 (40:60). The eluted material (R_f 0.15, CH_2Cl_2, silica gel) crystallized from ethanol to give 0.22 g (28%) of **1**: mp 312–314 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.023 (s, inner OCH_3, 3 H), 2.232 (s, inner $ArCH_3$, 3 H), 2.425 and 2.453 (s, $ArCH_3$, 2 × 3 H), 3.206 and 3.254 (s, OCH_3, 2 × 3 H), 3.837 and 4.593 (AB, $ArCH_2$, 2 H, J = 15.5 Hz), 3.996 and 4.684 (AB, $ArCH_2$, 2 H, J = 12.4 Hz), 4.396 and 4.571 (AB, $ArCH_2$, 2 H, J = 11.7 Hz), 4.625 and 5.193 (AB, $ArCH_2$, 2 H, J = 11.5 Hz), 6.95–8.15 (m, ArH, 18 H); MS (16 eV, 230 °C), m/e 700 (M^+). Anal. Calcd for $C_{48}H_{44}O_5$: C, 82.27; H, 6.31. Found: C, 82.03; H, 6.37.

37,38,39,40,41,42-Hexamethoxy-4,9,17,22,27,35-hexamethyl-13,31-dioxaheptacyclo[31.3.1.1^{2,6}.1^{7,11}.1^{15,19}.1^{20,24}.1^{25,29}]-dotetracont-1(37),2,4,6(42),7,9,11(41),15,17,19(40),20,22,24-(39),25,27,29(38),33,35-octadecaene (2). Procedure 1 was followed. Solution A was made by suspending 0.82 g of KH (20% dispersion in oil) in 200 mL of dry, freshly distilled THF. Solution B was prepared by dissolving 0.39 g (0.93 mmol) of **15** and 0.51 g (0.93 mmol) of **16** in 200 mL of dry, freshly distilled THF. The addition and total times of reflux were 24 and 48 h, respectively. Gel permeation chromatography gave a retention volume (R_v) for product of 177 mL. Residue C crystallized from ethanol. The crystals dried in vacuo gave 0.205 g (27%) of host **2**: mp 263–265 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.286 (s, $ArCH_3$, 6 H), 2.337 (s, $ArCH_3$, 12 H), 3.033 (s, OCH_3, 6 H), 3.111 (s, OCH_3, 12 H),

4.301 and 4.880 (AB, $ArCH_2O$, 8 H, J = 11.5 Hz), 7.007 (s, inner ArH, 4 H), 7.050 (br s, ArH, 4 H), 7.260 (br s, ArH, 4 H); MS (16 eV, 230 °C), m/e 808 (M^+). Anal. Calcd for $C_{52}H_{56}O_8$: C, 77.23; H, 6.93. Found: C, 76.98; H, 6.84.

24,25,26-Trimethoxy-4,9,22-trimethyl-13,18-dioxatetracyclo[19.3.1.1^{2,6}.1^{7,11}]hexacosa-1(24),2,4,6(26),7,9,11(25),20,22-nonaene (3). Procedure 1 was followed. Solution A was made by suspending 0.22 g (4.5 mmol) of a 50% NaH dispersion in mineral oil (washed with THF) in 300 mL of THF. Solution B was prepared by dissolving 0.40 g (0.73 mmol) of **16** and 69.0 mg (0.76 mmol) of dry 1,4-butanediol in 250 mL of THF. The addition and total reflux times were 30 and 48 h, respectively. Residue A was extracted with EtOAc, not CH_2Cl_2. Gel permeation chromatography gave R_v = 160 mL. Residue C was eluted on a thick-layer silica gel plate with CH_3OH–CH_2Cl_2. Product **3** (R_f = 0.65 on alumina with CH_2Cl_2) was recovered from the plate and dried in vacuo to give 0.025 g (7%): mp 218–219 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40–1.70 (m, OCH_2CH_2, 4 H), 2.322 (s, $ArCH_3$, 6 H), 2.422 (s, center OCH_3, 3 H), 2.468 (s, $ArCH_3$, 3 H), 3.310 (s, OCH_3, 6 H), 3.40–3.50 (m, OCH_2CH_2, 4 H), 4.365 and 4.743 (AB, $ArCH_2O$, 4 H, J = 11.2 Hz), 7.107 (br s, ArH, 4 H), 7.283 (s, ArH, 2 H); MS (16 eV, 200 °C), m/e 476 (M^+). Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.51; H, 7.56.

3,3″-Bis(2-hydroxy-1-ethyl)-2,2′,2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl (18). A solution of 10.09 g (27.9 mmol) of **17** and 6.5 g (56 mmol) of TMEDA in 350 mL of dry, freshly distilled diethyl ether was prepared under argon, and 43.6 mL of 1.6 M n-BuLi was added. After 3 h, the solution was cooled to 0 °C, and 5.6 mL of dry ethylene oxide in 4 mL of diethyl ether was added. The white suspension that formed was stirred for 12 h. The mixture was washed with 200 mL of water, and the aqueous layer was back-extracted with 100 mL of diethyl ether. The combined organic layers were dried ($MgSO_4$) and chromatographed over 400 g of silica gel. Elution with EtOH–EtOAc–CH_2Cl_2 (2:10:88) gave 3.25 g (26%) of diol **18** as an oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (br s, OH, 2 H), 2.313 (s, $ArCH_3$, 6 H), 2.352 (s, $ArCH_3$, 3 H), 2.930 and 3.882 (A_2X_2, $ArCH_2CH_2O$, 8 H, J = 6.3 Hz), 3.245 (s, $ArOCH_3$, 3 H), 3.452 (s, $ArOCH_3$, 6 H), 7.014 and 7.046 (AB, outer ArH, 4 H, J = 1), 7.144 (s, inner ArH, 2 H); MS (70 eV, 190 °C), m/e 450 (M^+)., Anal. Calcd for $C_{28}H_{34}O_5$: C, 74.64; H, 7.61. Found: C, 74.73; H, 7.77.

3,3″-Bis(2-(tosyloxy)-1-ethyl)-2,2′,2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl (19). Diol **18**, 4.79 g (10.6 mmol), was dissolved in 22 mL of dry pyridine (KOH) and cooled to 5 °C. Recrystallized tosyl chloride (EtOH), 4.66 g (16 mmol), was added, and the suspension was stirred at 0 °C for 1 h and allowed to stand for 24 h at −20 °C. Then an additional 4.66 g of tosyl chloride and 5 mL of pyridine were added, and the resulting solution was left for 5 days at −20 °C. The mixture was poured into 50 mL of ice water. After 0.5 h the mixture was extracted with 300 mL of $CHCl_3$. The organic layer was washed three times with 100-mL portions of 2 N hydrochloric acid, once with 100 mL of water, and twice with 100-mL portions of saturated $KHCO_3$ in water. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The oil, eluted through 200 g of silica gel with Et_2O–CH_2Cl_2, gave 4.54 g (56%) of ditosylate **19** as a white foam: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.269 (s, outer $ArCH_3$, 6 H), 2.349 (s, $ArCH_3$, 3 H), 2.402 (s, O_3SArCH_3, 6 H), 3.342 and 4.262 (A_2X_2, $ArCH_2CH_2O$, 8 H, J = 10.8 Hz), 3.161 (s, $ArOCH_3$, 3 H), 3.342 (s, $ArOCH_3$, 6 H), 6.859 and 7.037 (AB, outer ArH, 4 H, J = 1 Hz), 7.077 (s, inner ArH, 2 H), 7.280 and 7.718 (AB, $O_3SC_6H_4Me$, 8 H, J = 8.2 Hz); MS (70 eV, 190 °C), m/e 572 (M^+ − 186, loss of MeOTs, 12), 386 (M^+ − 2(186), 100), 186 (40); Anal. Calcd for $C_{42}H_{46}S_2O_9$: C, 66.47; H, 6.10. Found: C, 66.52; H, 6.19.

4,5,21,22-Tetrahydro-34,35,36-trimethoxy-8,13,18-trimethyl-10*H*-6,10:11,15:16,20-trimethenodinaphtho[2,1-*b*:1′,2′-*d*][1,6]dioxacyclopentacosin (4). Under dry conditions in an argon atmosphere, 0.4054 g (1.42 mmol) of dry [1,1′-binaphthalene]-2,2′-diol (**22**), 0.783 g (5.80 mmol) of K_2CO_3, and 250 mL of freshly distilled DMF were stirred at 50 °C for 2 h. Into this mixture was cannulated 1.075 g (1.42 mmol) of ditosylate **19** dissolved in 100 mL of DMF. The resulting solution was stirred at 70 °C for 5 days. A small portion of hydrochloric acid in EtOH was added to neutralize the reaction mixture. The solution was concentrated under reduced pressure. The residue was partitioned between 20 mL of CH_2Cl_2 and 20 mL of deionized water. The aqueous phase was removed with a pipet. Another portion of deionized water was added to the organic layer. This solution was vortexed, centrifuged, and separated. This process was repeated five times. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Gel permeation chromatography of the residue (R_v = 141–168 mL) gave an oil, which was subjected to thick-layer chromatography. Product was eluted with Et_2O–CH_2Cl_2 (3:97) and crystallized from ethanol to give, after drying in vacuo, 0.056 g (6%) of **4**: mp 226–228 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.772 (s, inner OCH_3, 3 H), 2.188 (s, inner $ArCH_3$, 3 H), 2.356 and 2.365 (s, outer $ArCH_3$, 2 × 3 H), 3.038 and 3.312 (s, outer OCH_3, 2 × 3 H), 2.30–3.00 and 3.60–4.30 (m, $ArCH_2CH_2O$, 8 H), 6.64–8.00 (m, ArH, 18 H); MS (16 eV, 230 °C), m/e 700 (M^+). Anal. Calcd for $C_{48}H_{44}O_5$: C, 82.27; H, 6.31. Found: C, 82.07; H, 6.39.

Host **4** complexed with lithium picrate gave ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.898 (s, inner OCH_3, 3 H), 2.247 (s, inner $ArCH_3$, 3 H), 2.458 and 2.512 (s, outer $ArCH_3$, 2 × 3 H), 2.70–4.70 (m, $ArCH_2CH_2O$, 8 H), 3.289 and 3.507 (s, outer $ArOCH_3$, 2 × 3 H), 6.20–8.10 (m, ArH, 18 H), 8.857 (s, picrate H, 2 H). Host **4** complexed with sodium picrate gave ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.742 (s, inner OCH_3, 3 H), 2.232 (s, inner $ArCH_3$, 3 H), 2.448 and 2.507 (s, outer $ArCH_3$, 2 × 3 H), 2.60–4.65 (m, $ArCH_2CH_2O$, 8 H), 3.204 and 3.450 (s, outer OCH_3, 2 × 3 H), 6.35–7.70 (m, ArH, 18 H), 8.743 (s, picrate H, 2 H). Host **4** complexed with potassium picrate gave ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.470 (s, inner OCH_3, 3 H), 2.206 (s, inner $ArCH_3$, 3 H), 2.426 and 2.491 (s, outer $ArCH_3$, 2 × 3 H), 2.55–4.75 (m, $ArCH_2CH_2O$, 8 H), 6.48–7.70 (m, ArH, 18 H), 8.857 (s, picrate H, 2 H). Host **4** complexed with ammonium picrate gave ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.344 (s, inner OCH_3, 3 H), 2.196 (s, inner $ArCH_3$, 3 H), 2.413 and 2.491 (s, outer $ArCH_3$, 2 × 3 H), 2.40–4.75 (m, $ArCH_2CH_2O$, 8 H), 3.367 and 3.410 (s, outer OCH_3, 2 × 3 H), 6.40–8.85 (m, ArH, 18 H), 8.880 (s, picrate H, 2 H).

29,31,32-Trimethoxy-4,9,27-trimethyl-14,22-dioxa-30-azapentacyclo[23.3.1.1^{2,6}.1^{7,11}.1^{16,20}]dotriaconta-1(29),2,4,6(32),7,9,11(31),16,18,20(30),25,27-dodecaene (5). Procedure 1 was applied. Solution A was made by suspending 0.29 g (6.0 mmol) of a 50% NaH dispersion in oil with 200 mL of THF. Solution B was prepared by dissolving 0.7804 g (1.73 mmol) of diol **18** and 0.455 g (1.73 mmol) of 2,6-bis(bromomethyl)pyridine (**24**)[10] in 250 mL of THF. The addition and total reflux times were 12 and 48 h, respectively. Residue A was partitioned between 20 mL of CH_2Cl_2 and 20 mL of water. The aqueous layer was removed. Deionized water (20 mL) was added to the organic layer. The solution was vortexed, centrifuged, and separated. The washing with deionized water was repeated six times. The organic layer was dried ($MgSO_4$) and subjected to gel permeation chromatography (R_v = 156 mL). The residue, which was crystallized from ethanol in two crops, gave 0.262 g (27%) of **5**: mp 152 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 24 °C) showed two conformers in a ratio of 6:1. The major conformer is reported in full: δ 2.278 (s, $ArCH_3$, 6 H), 2.359 (s, inner $ArCH_3$, 3 H), 2.434 (s, inner OCH_3, 3 H), 2.55–3.82 (m, $ArCH_2CH_2O$, 8 H), 3.332 (s, OCH_3, 6 H), 4.423 and 4.858 (AB, pyr CH_2O, 4 H, J = 13.7 Hz), 6.885 and 6.950 (two br s, outer ArH, 2 × 2 H), 7.081 (s, inner ArH, 2 H), 7.343 and 7.613 (A_2B, pyr H, 3 H, J = 7.7 Hz). The minor conformer is reported in part: δ 2.323 and 2.342 (s, CH_3), 3.252 (s, OCH_3), 4.327 and 4.571 (AB, pyr CH_2O, 4 H, J = 13.9 Hz). The ^{1}H NMR (200 MHz, hexachlorobutadiene, 90 °C) of **5** showed no coalescence of any protons of the major and minor conformers. A minimum barrier for interconversion was based on the outer OCH_3 shifts; $\Delta\nu$ = 20.9, T_c > 363 K, $\Delta G_c^{\ddagger}$ > 18.6 kcal mol^{-1}. Compound **5**: MS (70 eV, 230 °C), m/e 553 (M^+). Anal. Calcd for $C_{35}H_{39}NO_5$: C, 75.92; H, 7.10. Found: C, 75.84; H, 7.14.

A small amount of host **5** was complexed with potassium picrate in chloroform and crystallized from toluene: mp 278–280 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.985 (s, inner OCH_3, 3 H), 2.346 (s, $ArCH_3$, 6 H), 2.401 (s, inner $ArCH_3$, 3 H), 2.50–4.30 (m, $ArCH_2CH_2O$, 8 H), 3.323 (s, OCH_3, 6 H), 4.166 and 4.610 (AB, pyr CH_2O, 4 H, J = 10.8 Hz), 6.935 (br s, outer ArH, 2 H), 6.982 and 7.453 (A_2B, pyr H, 3 H, J = 7.6 Hz), 7.087 (br s, outer ArH, 2 H), 7.152 (s, center ArH, 2 H), 8.887 (s, picrate H, 2 H).

29,31,32-Trimethoxy-4,9,27-trimethyl-14,22-dioxa-30-azapentacyclo[23.3.1.1^{2,6}.1^{7,11}.1^{16,20}]dotriaconta-1(29),2,4,6(32),7,9,11(31),16,18,20(30),25,27-dodecaene 30-Oxide (6). A

solution of 82.3 mg (0.149 mmol) of host **5** and 0.151 g (0.74 mmol) of 85% *m*-$ClC_6H_4CO_3H$ in 70 mL of CH_2Cl_2 was stirred for 24 h. The reaction mixture was concentrated to 20 mL, transferred to a centrifuge tube, and washed by vortexing with 20 mL of aqueous 0.5 N Na_2SO_3, 20 mL of aqueous 0.5 N NaOH, 20 mL of aqueous 0.5 N $NaHCO_3$, and six 20-mL portions of deionized water. The organic layer was dried ($MgSO_4$), concentrated under reduced pressure, and dried in vacuo. The foam 70.7 mg (84%) of host **6**, had the following properties: ^1H NMR (200 MHz, $CDCl_3$, 24 °C) (two conformations in a ratio of 6:5 for which no shifts coalesced up to 67 °C) δ 2.289, 2.340, 2.359, 2.367 and 2.461 (s, $ArCH_3$ and inner OCH_3), 2.55–3.90 (m, $ArCH_2CH_2O$, 8 H), 3.252 and 3.360 (s, OCH_3, 6 H), 4.619 and 4.742 (minor) and 4.640 and 5.174 (major) (two AB, pyr CH_2O, 4 H, J_{minor} = 17.5 Hz, J_{major} = 16.5 Hz), 6.85–7.40 (m, ArH and pyr H, 9 H); MS (70 eV, 190 °C), *m/e* 569 (M^+). Anal. Calcd for $C_{35}H_{39}NO_6$: C, 73.79; H, 6.90. Found: C, 73.42; H, 6.86.

2′-Methoxy-5,5′,5″-trimethyl[1,1′:3′,3″-terphenyl]-2,2″-diol (26). A mixture of 20 g (0.0625 mol) of trisphenol **25**, 80 mL of acetone, 9.1 g (0.0659 mol) of K_2CO_3, and 9.7 mL (0.156 mol) of CH_3I was stirred under N_2 in the dark for 48 h at 25 °C. The acetone was evaporated under reduced pressure. To the residue was added 200 mL of Et_2O, followed by the slow addition of 80 mL of 1.8 N HCl in water. The mixture was stirred until no solids remained. The organic layer was washed with 100 mL of a saturated solution of NaCl in water, and the solution was extracted with three 320-mL portions and one 280-mL portion of 1.25 N aqueous NaOH. The basic extracts were combined, washed with 200 mL of Et_2O, acidified by dropwise addition of 160 mL of concentrated HCl in water, and extracted with three 200-mL portions of EtOAc. The organic extracts were dried ($MgSO_4$), evaporated under reduced pressure, and dried in vacuo to yield 16.3 g (78%) of **26** as a white foam. For analysis a small sample was molecularly distilled at 300–350 °C (0.1 mmHg) to give **26** as a glass: R_f = 0.19, silica gel, $ClCH_2CH_2Cl$: MS (70 eV, 190 °C), *m/e* 334 (M^+). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.05; H, 6.65.[11]

3,3″-Dibromo-2′-methoxy-5,5′,5″-trimethyl[1,1′:3′,3″-terphenyl]-2,2″-diol (28). To a solution of 35.5 g (0.106 mol) of **26** in 700 mL of $CHCl_3$ stirred at 0 °C was added dropwise (70 min) a solution of 37.3 g (0.233 mol) of Br_2 dissolved in 250 mL of $CHCl_3$. The mixture was stirred an additional 10 min at 0 °C, and a solution 7.5 g of Na_2SO_3 in 300 mL of water was added cautiously. The mixture was warmed to 25 °C, and the organic layer was washed with 500 mL of water, dried ($MgSO_4$), and decolorized with 17.5 g of activated charcoal. The solvent was evaporated under reduced pressure to give 49.8 g of crystalline solid. This material was dissolved in 200 mL of CH_2Cl_2, and 350 mL of hexane was added. The resulting solution was evaporated under reduced pressure until crystals appeared. The mixture was allowed to stand at 25 °C for 15 h, and the product was collected, washed, and dried to give 45.8 g (87.9%) of **28**, mp 174–176 °C. A small sample was recrystallized for analysis from EtOAc: mp 176–177 °C; R_f 0.69, silica gel, $ClCH_2CH_2Cl$; MS (70 eV, 190 °C), *m/e* 490 (M^+). Anal. Calcd for $C_{22}H_{20}O_3Br_2$: C, 53.68; H, 4.10; Br, 32.47. Found: C, 53.78; H, 4.20; Br, 32.54.[11]

1,13-Dibromo-15,28-dihydro-30-methoxy-3,7,11-trimethyl-9,5-metheno-5*H*-dibenzo[*i*,*p*]dinaphtho[2,1-*c*:1′,2′-*e*][1,8]-dioxacycloheptadecin (14). An aluminum foil covered, 500-mL oven-dried flask was cooled under an N_2 atmosphere. In it was prepared a refluxing solution of 2.00 g (4.08 mmol) of **28**, 2.24 g (5.1 mmol) of (*R*,*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthalene (**21**), 1.71 g (10.3 mmol) of KI, 1.41 g (10.2 mmol) of K_2CO_3, and 300 mL of reagent grade acetone. After 12 h at reflux the solution was concentrated under reduced pressure, and the solid residue was extracted with 50- and 75-mL portions of hot CH_2Cl_2. The organic solution was filtered, combined with 50 mL of methanol, and concentrated. Two crops of crystals gave 2.28 g (73%) of module **14**: mp 270 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 2.101, 2.262 and 2.276 (s, $ArCH_3$, 3 × 3 H), 3.172 (s, $ArOCH_3$, 3 H), 3.896 and 4.297 (AB, $ArCH_2O$, 2 H, J = 11.2 Hz), 6.52–8.59 (m, ArH, 18 H); MS (70 eV, 210 °C), *m/e* 770 (M^+ + 2, $^{81}Br^{79}Br$). Anal. Calcd for $C_{44}H_{34}O_3Br_2$: C, 68.58; H, 4.45; Br, 20.74. Found: C, 68.46; H, 4.44; Br, 20.80.

1,13-Dibromo-15,21-dihydro-24-methoxy-3,7,11-trimethyl-9*H*-5,9-metheno-16,20-nitrilodibenzo[*j*,*q*][1,9]dioxacyclooctadecin (13). A mixture of 3.10 g (11.7 mmol) of 2,6-bis(bromomethyl)pyridine[10] (**24**), 4.31 g (8.80 mmol) of **28**, 4.15 g (25.0 mmol) of KI, 3.23 g (23.4 mmol) of K_2CO_3, and 800 mL of reagent grade acetone was flushed with N_2, the container was encased in aluminum foil, and this mixture was refluxed for 4 h. The solvent was concentrated under reduced pressure. The solid residue was extracted with two 150-mL portions of hot CH_2Cl_2 and filtered. The filtrate was mixed with 50 mL of methanol and evaporated to a volume of 30 mL. The crystals that separated were collected, washed, and dried to give 4.18 g (80%) of **13**: mp 232 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.97 (s, inner $ArCH_3$, 3 H), 2.32 (s, outer $ArCH_3$, 6 H), 3.50 (s, $ArOCH_3$, 3 H), 4.72 and 5.14 (AB, $ArCH_2O$, 4 H, J = 10.6 Hz), 6.74 (s, inner ArH, 2 H), 7.19 and 7.39 (AB, outer ArH, 4 H, J = 2.8 Hz), 7.13 and 7.54 (A_2B, pyridine bridge H, 3 H, J = 7.0 Hz); MS (70 eV, 180 °C), *m/e* 593 (M^+). Anal. Calcd for $C_{29}H_{25}Br_2NO_3$: C, 58.51; H, 4.23; Br, 26.85. Found: C, 58.41; H, 4.29; Br, 26.91.

1,13-Dibromo-15,21-dihydro-24-methoxy-3,7,11-trimethyl-9*H*-5,9:16,20-dimethenodibenzo[*j*,*q*][1,9]dioxacyclooctadecin (12). A solution of 11.70 g (23.8 mmol) of **28**, 6.59 g (25.0 mmol) of 1,3-bis(bromomethyl)benzene (Aldrich, purified by distillation), 8.29 g (23.8 mmol) of KI, 7.24 g of K_2CO_3, and 600 mL of reagent grade acetone was refluxed for 30 h under an argon atmosphere. The solution was evaporated to dryness. The residue was extracted with 300 mL of CH_2Cl_2. The organic solution was washed with 50 mL of water and 50 mL of brine and dried ($MgSO_4$). Hexane was added to the solution, and the precipiate that separated was recrystallized from CH_2Cl_2–CH_3OH. The dried crystals were collected to give 8.18 g (58%) of **12**: mp 210–211.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.216 (s, inner $ArCH_3$, 3 H), 2.369 (s, outer $ArCH_3$, 6 H), 3.292 (s, $ArOCH_3$, 3 H), 4.854 and 5.133 (AB, $ArCH_2O$, 4 H, J = 11.7 Hz), 6.991 (s, inner ArH, 2 H), 7.07–7.29 (m, bridge ArH, 4 H), 7.142 and 7.439 (AB, outer ArH, 4 H, J = 1.7 Hz); MS (70 eV, 230 °C), *m/e* 594 (M^+ + 2, 33.8), 592 (M^+, 14.12). Anal. Calcd for $C_{30}H_{26}Br_2O_3$: C, 60.61; H, 4.41; Br, 26.91. Found: C, 60.45; H, 4.41; Br, 26.92.

3-Bromo-2′-methoxy-5,5′,5″-trimethyl[1,1′:3′,1″-terphenyl]-2,2″-diol (27). To a solution of 26.32 g (78.71 mmol) of **26** in 300 mL of $CHCl_3$ cooled to 0 °C was added a solution of 4.0 mL of bromine (78.1 mmol) in 25 mL of $CHCl_3$ dropwise over 30 min. The reaction mixture was stirred at 0 °C for 2.5 h and then at 25 °C for 1 h. The reaction mixture was then washed with 300 mL of water, dried (Na_2SO_4), and concentrated in vacuo. The residue was flash chromatographed (silica gel, 80 × 8.5 cm, 1:1 hexane–CH_2Cl_2) to provide 9.17 g (24%) of dibrominated terphenyl **28**. Further elution with 6:4 dichloromethane–hexane gave the monobromide **26** as a white solid. Some fractions containing both mono- and dibrominated products were combined and rechromatographed under the same conditions to effect complete separation to give **26**, 13.94 g (44%): mp 143.5–145.5 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.32 (s, 3 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 2.40 (s, 3 H, $ArCH_3$), 3.32 (s, 3 H, OCH_3), 6.93–7.36 (m, 7 H, ArH); MS (70 eV, 210 °C), *m/e* 414 (M^+). Anal. Calcd for $C_{22}H_{21}BrO_3$: C, 63.93; H, 5.12; Br, 19.33. Found: C, 64.06; H, 5.09; Br, 19.30.

4-Bromo-7,8-dihydro-19-methoxy-2,12,16-trimethyl-18,14-metheno-6*H*,14*H*-dibenzo[*f*,*m*][1,5]dioxacyclotetradecin (10). A mixture of 5.49 g (13.28 mmol) of monobromide **27** and 8.96 g (27.50 mmol) of Cs_2CO_3 was stirred in 400 mL of freshly distilled DMF at 65 °C for 24 h. To this mixture was added 1.38 mL (13.6 mmol) of 1,3-dibromopropane, and the reaction mixture was stirred at 65–70 °C for 71 h. The DMF was evaporated under reduced pressure, and the residue was partitioned between 500 mL of CH_2Cl_2 and 250 mL of water. The organic layer was dried ($MgSO_4$) and the solvent evaporated in vacuo. The residue was flash chromatographed (silica gel, 40 × 6.5 cm, 1:3 CH_2Cl_2–hexane), to afford 2.15 g (36%) of **10**. Recrystallization of this material from CH_2Cl_2–methanol gave stout, white crystals, 1.65 g (27%): mp 231.5–233 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.78–2.21 (m, 2 H, $OCH_2CH_2CH_2O$), 2.36 (s, 6 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 3.21 (s, 3 H, OCH_3), 3.58–4.10 (m, 4 H, OCH_2), 6.97–7.37 (m, 7 H, ArH); MS (70 eV, 210 °C), *m/e* 452 (M^+). Anal. Calcd for $C_{25}H_{25}BrO_3$: C, 66.23; H, 5.56; Br, 17.62. Found: C, 66.03; H, 5.43; Br, 17.70.

4-Bromo-6,7,9,10-tetrahydro-21-methoxy-2,14,18-trimethyl-20,16-metheno-16*H*-dibenzo[*h*,*o*][1,4,7]trioxacyclo-

hexadecin (11). A mixture of 1.49 g (3.61 mmol) of monobromide **27**, 1.54 g (7.55 mmol) of diethylene glycol ditosylate,[15] 2.46 g (7.55 mmol) of Cs_2CO_3, and 100 mL of DMF was stirred at 65–70 °C for 120 h. Crude product was isolated as in the preparation of **10** and chromatographed (medium pressure, silica gel, column B, 5% Et_2O–CH_2Cl_2) to provide pure **11** as a white foam after drying under vacuum, 1.05 g (60%): ^1H NMR ($CDCl_3$, 200 MHz), δ 2.33 (s, 6 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 3.11 (s, 3 H, OCH_3), 3.47–4.12 (m, 8 H, OCH_2), 6.77–7.37 (m, 7 H, ArH); MS (70 eV, 210 °C), *m/e* 482 (M^+). Anal. Calcd for $C_{26}H_{27}BrO_4$: C, 64.60; H, 5.63; Br, 16.53. Found: C, 64.79; H, 5.61; Br, 16.45.

(±)-7,7′,8,8′-Tetrahydro-19,19′-dimethoxy-2,2′,12,12′,16,16′-hexamethyl-4,4′-bi-18,14-metheno-6*H*,14*H*-dibenzo[*f*,*m*][1,5]dioxacyclotetradecin ((±)-7). To a solution of 1.334 g (2.94 mmol) of terphenyl **10** in 30 mL of dry THF at −78 °C was added 4.49 mmol of *sec*-BuLi in cyclohexane. After the mixture was stirred 15 min at −78 °C, the lithiate suspension was cannulated into a reluxing solution of 2.08 g (5.88 mmol) of $Fe(acac)_3$ in 110 mL of dry benzene. The mixture was refluxed for 2 h and then maintained at 25 °C for an additional 4 h. The mixture was washed with five 150-mL portions of 3 N HCl in water, 150 mL of water, and 75 mL of brine and was dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed (medium pressure, silica gel, column B, 5% ether–hexane → 10% ether–hexane → 20% ether–hexane) to afford the crude sexiphenyl. Recrystallization of this material from CH_2Cl_2–heptane gave pure (±)-**7** as a white crystalline powder: R_f 0.54, silica gel, ether–hexane; 0.405 g (37%); mp 275–277 °C; ^1H NMR ($CDCl_3$) δ 1.55–1.88 (m, 2 H, $OCH_2CH_2CH_2O$), 2.33 (s, 3 H, $ArCH_3$), 2.39 (s, 6 H, $ArCH_3$), 3.20 (s, 3 H, OCH_3), 3.54–4.07 (m, 4 H, OCH_2), 6.90–7.27 (m, 7 H, ArH); ^{13}C NMR ($CDCl_3$, JEOL) δ 20.72 ($ArCH_3$), 20.79 ($ArCH_3$), 30.52 ($OCH_2CH_2CH_2O$), 60.77 (OCH_3), 67.22 (OCH_2), 67.80 (OCH_2), 118.58, 129.08, 129.40, 130.10, 130.46, 130.73, 130.83, 131.12, 131.19, 131.80, 131.85, 131.94, 132.19, 132.57, 133.42, 151.57, 154.87, 155.33; MS (70 eV, 210 °C), *m/e* 746 (M^+). Anal. Calcd for $C_{50}H_{50}O_6$: C, 80.40; H, 6.75. Found: C, 80.19; H, 6.69.

The chromatographic fractions with higher R_f values than (±)-**7** combined and slowly crystallized from CH_2Cl_2–hexane to afford the *meso*-**7** as white needles, 0.131 g (12%): R_f = 0.57, silica gel, 1:1 ether–hexane; mp 282–286 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.53–1.68 (m, 2 H, $OCH_2CH_2CH_2O$), 2.36 (s, 6 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 3.22 (s, 3 H, OCH_3), 3.31–3.96 (m 4 H, OCH_2), 6.91–7.25 (m, 7 H, ArH); MS (70 eV, 210 °C), *m/e* 746 (M^+). Anal. Calcd for $C_{50}H_{50}O_6$: C, 80.40; H, 6.75. Found: C, 80.42; H, 6.81.

(±)-6,6′,7,7′,9,9′,10,10′-Octahydro-21,21′-dimethoxy-2,2′,14,14′,18,18′-hexamethyl-4,4′-bi-20,16-metheno-16*H*-dibenzo[*h*,*o*][1,4,7]trioxacyclohexadecin ((±)-8). To a solution of 1.11 g (2.30 mmol) of terphenyl **11** in 35 mL of dry THF at −78 °C was added 3.5 mmol of *sec*-BuLi in cyclohexane. After the lithiate mixture was stirred for 15 min at −78 °C, it was cannulated into a refluxing solution of 1.64 g (4.64 mmol) of $Fe(acac)_3$ in 115 mL of dry benzene. The resulting mixture was refluxed for 2 h and stirred at 25 °C for an additional 4.5 h. The mixture was cooled and washed with five 100-mL portions of 3 N HCl in water followed by three 100-mL portions of water (or until the aqueous washings became nearly colorless). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed (medium pressure, silica gel, column B, 1:1 ether–hexane) to provide the crude **8** (0.226 g). Recrystallization of this material from CH_2Cl_2–heptane gave white crystals of (±)-**8**, 0.156 g (17%): mp 260.5–262.5 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.33 (s, 3 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 2.37 (s, 3 H, $ArCH_3$), 3.15 (s, 3 H, OCH_3), 3.31–4.05 (m, 8 H, OCH_2), 6.74–7.25 (m, 7 H, ArH); ^{13}C NMR ($CDCl_3$, JEOL) δ 20.60 ($ArCH_3$), 20.77 ($ArCH_3$), 60.94 (OCH_3), 69.40 (OCH_2), 69.77 (OCH_2), 70.52 (OCH_2), 72.83 (OCH_2), 112.42, 128.84, 130.78, 131.00, 131.24, 131.29, 131.68 (all aromatic CH), 129.66, 129.74, 131.97, 132.14, 132.28, 132.45, 132.65, 133.28, 153.24, 154.60, 154.99 (all other aromatic C's); MS (70 eV, 210 °C), *m/e* 806 (M^+). Anal. Calcd for $C_{52}H_{54}O_8$: C, 77.39; H, 6.74. Found: C, 77.44; H, 6.64.

8,8′-Dimethoxy-1,1′-binaphthalene (29). To a solution of 45.89 g (290.1 mmol) of 1-methoxynaphthalene in 150 mL of cyclohexane at 25 °C was added 335 mmol of *t*-BuLi in pentane. The mixture, when maintained at 25 °C for 27.5 h, deposited a thick, white precipitate. The mixture was cooled to 0 °C, and a solution of 157.61 g (446.3 mmol) of $Fe(acac)_3$ in 500 mL of dry benzene was added rapidly. These proportions reflect experience gained in applying this reaction to other systems. Care was taken during the addition because heat was generated and some pentane was volatilized. After the reaction mixture was stirred at 0 °C for 10 min, it, now thick with a rust-colored sludge, was stirred at 25 °C for an additional 18 h. It was then partitioned between 250 mL of ether and 500 mL of 50% hydrochloric acid. The organic phase was washed with a solution of 50 mL of concentrated hydrochloric acid in 250 mL of water followed by three 250-mL portions of water. The combined aqueous layers were extracted with 250 mL of ether, and this organic layer was washed with 250 mL of water. The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure to give a viscous red oil to which was added 250 mL of hexane. After the mixture was allowed to stand at 25 °C for 12 h, crystals deposited, which were filtered, washed with pentane, and dried in vacuo to afford **29** as needles, 21.3 g (47%), mp 157.5–160 °C. A small sample was recrystallized from hexane to give white needles: mp 158–159.5 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.02 (s, 3 H, OCH_3), 6.64 (d of d, 1 H, ArH_7, J_o = 7.6 Hz, J_m = 1.1 Hz), 7.17–7.79 (m, 5 H, ArH); MS (70 eV, 210 °C), *m/e* 314 (M^+). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.08; H, 5.84.

8,8′-Dimethoxy-7,7′-dimethyl-1,1′-binaphthalene (34). To a suspension of 5.87 g (18.67 mmol) of **29** and 6 mL (39.76 mmol) of TMEDA in 300 mL of dry ether stirred under argon at 25 °C was added 52 mmol of *n*-BuLi in hexane. The mixture was stirred at 25 °C for 4.5 h during which time the starting material slowly dissolved and was replaced by a gray-white precipitate. The mixture was cooled to −78 °C, 19 mL (305 mmol) of CH_3I was added, and the reaction mixture was stirred for 10 min at −78 °C followed by 13 h at 25 °C. The mixture was partitioned between 250 mL of ether and 250 mL of water. The aqueous layer was extracted with 250 mL of ether, and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was flash chromatographed (short silica gel column, 5% EtOAc–hexane → CH_2Cl_2) to give the product as a white solid which was recrystallized from hexane to afford pure **34**, 4.41 g (69%): mp 153–154.5 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.28 (s, 3 H, $ArCH_3$), 2.78 (s, 3 H, OCH_3), 7.25–7.80 (m, 3 H, ArH), 7.27 (d, 1 H, ArH_6, J = 8.3 Hz), 7.59 (d, 1 H, ArH_5, J = 8.3 Hz); MS (70 eV, 210 °C), *m/e* 342 (M^+). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.10; H, 6.39.

Diethyl 8,8′-Dimethoxy[1,1′-binaphthalene]-7,7′-dicarboxylate (30). To a suspension of 5.56 g (17.69 mmol) of **29** stirred under argon in 250 mL of dry ether was added 5.4 mL (35.8 mmol) of TMEDA followed by 56 mmol of *n*-BuLi in hexane. After the reaction mixture was stirred 4 h at 25 °C, it was cooled to −78 °C and rapidly quenched with 101 mL (1.06 mol) of ethyl chloroformate. The reaction was stirred at −78 °C for 10 min and then stirred at 25 °C for an additional 14 h. The solvent was evaporated under reduced pressure. Flash chromatography of the residue (silica gel column, 45 × 6 cm, CH_2Cl_2) produced the crude product which was recrystallized from CH_2Cl_2–cyclohexane to afford the diester **30** as fine white crystals, 3.63 g (45%), mp 166–169 °C. A small sample was recrystallized first from 95% ethanol and then from CH_2Cl_2–cyclohexane to give small colorless needles: mp 167–170 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.31 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 2.92 (s, 3 H, OCH_3), 4.29 (q, 2 H, OCH_2CH_3, J = 7.1 Hz), 7.26–7.83 (m, 3 H, ArH), 7.63 (d, 1 H, ArH_5, J = 8.6 Hz), 7.77 (d, 1 H, ArH_6, J = 8.6 Hz); MS (70 eV, 210 °C), *m/e* 458 (M^+). Anal. Calcd for $C_{28}H_{26}O_6$: C, 73.35; H, 5.72. Found: C, 73.22; H, 5.84.

8,8′-Dimethoxy[1,1′-binaphthalene]-7,7′-dicarboxaldehyde (33). To a suspension of 2.05 g (6.52 mmol) of **29** stirred under argon at 25 °C in 90 mL of dry ether was added 2.0 mL (13.25 mmol) of TMEDA. To this mixture was added 19.0 mmol of *n*-BuLi in hexane, and the reaction was maintained at 25 °C for 5 h. The mixture was cooled to −78 °C, and 26 mL (321.8 mmol) of ethyl formate was added in one portion. The solution was stirred at −78 °C for 10 min and then at 25 °C for 30 min. The solvent was evaporated in vacuo, and the residue was partitioned between 200 mL of CH_2Cl_2 and 200 mL of water. The aqueous phase was extracted with 200 mL of ether, and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (medium

pressure, silica gel, column C, CH_2Cl_2) to give the dialdehyde as a solid, 0.930 g (39%). A small sample was recrystallized from benzene to give stout, yellow crystals: mp 230–232 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.99 (s, 3 H, OCH_3), 7.42–7.93 (m, 3 H, ArH), 7.75 (d, 1 H, ArH_5, J = 8.6 Hz), 7.89 (d, 1 H, ArH_6, J = 8.6 Hz), 8.32 (s, 1 H, ArCHO); MS (70 eV, 210 °C), m/e 370 (M^+). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.80; H, 4.91.

8,8′-Dihydroxy-1,1′-binaphthalene (38). To a solution of 5.54 g (17.62 mmol) of **29** in 100 mL of CH_2Cl_2 was added 16.0 g (63.9 mmol) of BBr_3. This mixture was stirred at −78 °C for 30 min followed by an additional 5 h at 25 °C. The reaction mixture was cooled, quenched with water, and partitioned between 250 mL of water and 250 mL of CH_2Cl_2. Th organic phase was dried ($MgSO_4$) and the solvent evaporated in vacuo. The residue was filtered through a short column (silica gel, 1:1 CH_2Cl_2–hexane) to give crude binaphthol, which was recrystallized from 1:1 cyclohexane–hexane to produce pure **38** as fine white needles, 4.19 g (83%): mp 117–119 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.39 (s, 1 H, OH), 6.84 (d of d, 1 H, ArH_7, J_o = 7.4 Hz, J_m = 1.0 Hz), 7.32–7.97 (m, 5 H, ArH); MS (70 eV, 210 °C), m/e 286 (M^+). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.72; H, 4.90.

8,8′-Dimethoxy[1,1′-binaphthalene]-7,7′-dimethanol (31). To a solution of 2.86 g (6.24 mmol) of diester **30** in 250 mL of THF at 0 °C was added 1.20 g (31.62 mmol) of $LiAlH_4$. The reaction mixture was stirred at 0 °C for 1 h and at 25 °C for an additional 2 h. The reaction mixture was then cooled and quenched with 20% NaOH in water. After the mixture was filtered, the collected solid was washed well with ether, and the filtrate was washed with 200 mL of water and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the crude product was recrystallized from benzene–ethanol to give diol **31** as fine needles, 1.73 g (74%): mp 217–219 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.38 (br s, 1 H, OH), 2.70 (s, 3 H, OCH_3), 4.48 (d, 1 H, $ArCH_2OH$, J_{gem} = 12.5 Hz), 4.70 (d, 1 H, $ArCH_2OH$, J_{gem} = 12.5 Hz), 7.34–7.84 (m, 3 H, ArH), 7.38 (d, 1 H, ArH_6, J = 8.3 Hz), 7.67 (d, 1 H, ArH_5, J = 8.3 Hz); MS (70 eV, 210 °C), m/e 374 (M^+). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.89; H, 5.87.

In an alternative synthesis of diol **31**, dialdehyde **33** (0.223 g, 0.060 mmol) was reduced in the usual way with $NaBH_4$ to give diol as fine needles, 0.104 g (46%): mp 217–219 °C, ^1H NMR identical with that of the authentic material.

7,9,10,12,13,15,16,18-Octahydro-5,20-dimethoxy-4,6:19,21-diethenodibenzo[*m*,*p*][1,4,7,10]tetraoxacycloeicosin (9). To a refluxing suspension of 607 mg of 50% NaH in oil (12.65 mmol) in 250 mL of dry THF was added over 66 h under high-dilution conditions a solution of 1.149 g (3.068 mmol) of diol **31** and 1.405 g (3.064 mmol) of triethylene glycol ditosylate[15] in 240 mL of THF. After the addition was completed, the reaction mixture was refluxed for 30 h, cooled, and quenched with water. The mixture was partitioned between 150 mL of ether and 150 mL of water. The aqueous layer was extracted with 200 mL of ether, and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and gel chromatographed. Concentration of the eluate between 141- and 177-mL retention volumes provided the crude cycle, which was passed through a short silica gel filtration column (CH_2Cl_2 → 2% CH_3OH–CH_2Cl_2) to give cycle **9** as a white solid, 0.959 g (64%), pure to ^1H NMR. This material was recrystallized from methanol at −20 °C to give colorless crystals, 0.683 g (46%): mp 133.5–135.5 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.71 (s, 3 H, OCH_3), 3.46–3.60 (m, 6 H, OCH_2CH_2O), 4.47 (d, 1 H, $ArCH_2O$, J_{gem} = 11.4 Hz), 4.63 (d, 1 H, $ArCH_2O$, J_{gem} = 11.4 Hz), 7.34–7.84 (m, 3 H, ArH), 7.50 (d, 1 H, ArH_6, J = 8.4 Hz), 7.68 (d, 1 H, ArH_5, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, JEOL) δ 62.34 (CH_3), 67.53 (OCH_2), 68.63 (OCH_2), 70.43 (OCH_2), 70.74 (OCH_2), 124.49, 124.84, 127.15, 127.26, 127.78, 128.07, 128.49, 134.87, 141.06, 156.23; MS (70 eV, 210 °C), m/e 488 (M^+). Anal. Calcd for $C_{30}H_{32}O_6$: C, 73.75; H, 6.60. Found: C, 73.55; H, 6.72.

Registry No. **1**, 95694-75-0; **2**, 95694-76-1; **2**·Li·picrate, 95723-94-7; **2**·Na·picrate, 95723-96-9; **2**·K·picrate, 95739-50-7; **2**·Rb·picrate, 95723-98-1; **2**·Cs·picrate, 95724-00-8; **2**·NH_4·picrate, 95694-94-3; **2**·CH_3NH_3·picrate, 95694-95-4; **2**·*t*-$BuNH_3$·picrate, 95694-96-5; **3**, 95694-77-2; **3**·Li·picrate, 95724-02-0; **3**·Na·picrate, 95724-04-2; **3**·K·picrate, 95724-06-4; **4**, 95694-78-3; **4**·Li·picrate, 95724-08-6; **4**·Na·picrate, 95724-10-0; **4**·K·picrate, 95724-12-2; **4**·Rb·picrate, 95724-14-4; **4**·Cs·picrate, 95724-16-6; **4**·NH_4·picrate, 95694-97-6; **5**, 95694-79-4; **5**·Li·picrate, 95724-18-8; **5**·Na·picrate, 95724-20-2; **5**·K·picrate, 95724-22-4; **5**·Rb·picrate, 95724-24-6; **5**·Cs·picrate, 95724-26-8; **5**·NH_4·picrate, 95694-98-7; **5**·CH_3NH_3·picrate, 95694-99-8; **5**·*t*-$BuNH_3$·picrate, 95695-00-4; **6**, 95694-80-7; **6**·Li·picrate, 95724-28-0; **6**·Na·picrate, 95724-30-4; **6**·K·picrate, 95724-32-6; **6**·Rb·picrate, 95724-34-8; **6**·Cs·picrate, 95724-36-0; **6**·NH_4·picrate, 95695-01-5; **6**·CH_3NH_3·picrate, 95695-02-6; **6**·*t*-$BuNH_3$·picrate, 95695-03-7; (±)-**7**, 95782-45-9; *meso*-**7**, 73229-33-1; **7**·Li·picrate, 82484-56-8; **7**·Na·picrate, 82484-55-7; **7**·K·picrate, 95724-38-2; **7**·Rb·picrate, 95724-40-6; **7**·Cs·picrate, 95724-42-8; **7**·NH_4·picrate, 95782-48-2; **7**·CH_3NH_3·picrate, 95783-36-1; **7**·*t*-$BuNH_3$·picrate, 95782-49-3; (±)-**8**, 95782-46-0; **8**·Li·picrate, 82489-41-6; **8**·Na·picrate, 82489-39-2; **8**·K·picrate, 95724-44-0; **8**·Rb·picrate, 95724-46-2; **8**·Cs·picrate, 95724-48-4; **8**·NH_4·picrate, 95782-51-7; **8**·CH_3NH_3·picrate, 95782-52-8; **9**, 95694-81-8; **9**·Li·picrate, 95724-50-8; **9**·Na·picrate, 95724-52-0; **9**·K·picrate, 95724-54-2; **9**·Rb·picrate, 95724-56-4; **9**·Cs·picrate, 95724-58-6; **9**·NH_4·picrate, 95695-04-8; **9**·CH_3NH_3·picrate, 95695-05-9; **9**·*t*-$BuNH_3$·picrate, 95695-06-0; **10**, 95694-82-9; **11**, 95694-83-0; **12**, 95694-84-1; **13**, 95723-91-4; **14**, 95694-85-2; **15**, 71128-92-2; **16**, 71128-93-3; **17**, 71128-90-0; **18**, 95694-86-3; **19**, 95694-87-4; (±)-**20**, 78038-79-6; (±)-**21**, 64091-25-4; **22**, 602-09-5; **24**, 7703-74-4; **25**, 71128-89-7; **26**, 73229-34-2; **27**, 95694-88-5; **28**, 73229-35-3; **29**, 82265-47-2; **30**, 95694-89-6; **31**, 95694-90-9; **32**, 95694-91-0; **34**, 95694-92-1; **38**, 95694-93-2; II, 73522-93-7; II·Li·picrate, 95724-60-0; II·Na·picrate, 95724-62-2; II·K·picrate, 95724-64-4; II·Rb·picrate, 95724-66-6; II·Cs·picrate, 95724-68-8; II·NH_4·picrate, 95723-92-5; II·CH_3NH_3·picrate, 95695-07-1; II·*t*-$BuNH_3$·picrate, 95695-08-2; V·Li·picrate, 64799-51-5; V·Na·picrate, 64799-49-1; V·K·picrate, 64851-30-5; V·Rb·picrate, 64822-96-4; V·Cs·picrate, 64799-34-4; V·NH_4·picrate, 64916-33-2; V·CH_3NH_3·picrate, 75640-72-1; V·*t*-$BuNH_3$·picrate, 64916-32-1; 1,4-butanediol, 110-63-4; ethylene oxide, 75-21-8; 1,3-bis(bromomethyl)benzene, 626-15-3; 1,3-dibromopropane, 109-64-8; diethylene glycol ditosylate, 7460-82-4; 1-methoxynaphthalene, 2216-69-5; ethyl chloroformate, 541-41-3; ethyl formate, 109-94-4; triethylene glycol ditosylate, 19249-03-7.