Synthesis of Upper and Lower Rim Binaphthyl Bridged Calix[4]arenes: New Potential Chiral Hosts for Molecular Recognition and Catalysis

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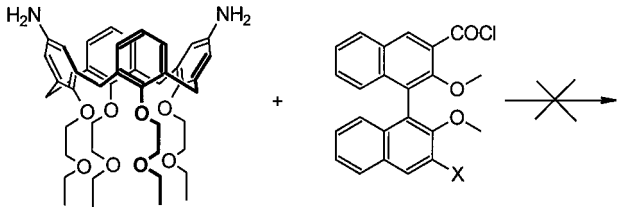
New chiral upper and lower rim (*R*)-binaphthyl-bridged calix[4]arenes in the *cone* conformation (**5**, **10**, **11**, **15**, **17**, **18**) have been synthesized by exploiting the selective functionalization of the calix[4]arene skeleton. The conformational properties of the new hosts in $CDCl_3$ and DMSO-d_6 have been clarified by dynamic NMR measurements, and their complexation properties toward neutral molecules, alkali metal, and silver(I) cations have been explored. The upper rim binaphthyl-bridged calix[4]arene **5** is able to form a 1:1 complex with Ag^+ in $CDCl_3$:CD_3OD 1:1 v/v solution, where the silver cation is encapsulated into the apolar cavity. The determined association constant (log $K = 3.51$) is substantially higher than for unbridged calix[4]arenes in the *cone* conformation. These new macrobicyclic compounds are potential hosts for chiral recognition and catalysis.

Introduction

The design and synthesis of new ligands for chiral recognition and catalysis is an area of current interest both in supramolecular chemistry[1] and organic synthesis.[2] In the modern design of asymmetric reagents and catalysts the reaction center is often surrounded by a chiral moiety and a recognition site, the latter controlling the substrate selectivity and the former the stereoselectivity of the process.[3] Among the most popular chiral building blocks used, binaphthyl derivatives offer a wide range of possibilities. Cram has used binaphthyl-derived crown ethers for the separation of amino acid esters,[4] Diederich et al. synthesized binaphthyl-derived cyclophanes to complex quinine derivatives[5] and pyranosides[6] whereas Hamilton et al. used binaphthyl-containing clefts to bind tartaric acid derivatives.[7] Chiral reagents and catalysts for stereoselective transformations, based on binaphthyl derivatives, are also well-known.[8]

Calixarenes and especially calix[4]arenes are widely used in supramolecular chemistry for the selective recognition of ions and neutral molecules.[9] Therefore it seemed attractive to link the binaphthyl moiety to calix[4]arenes in order to synthesize new chiral ligands. Very recently, Kubo et al. reported on the colorimetric recognition of chiral amines by a binaphthyl-containing calix[4]arene crown ether.[10] In this paper we report our results on the synthesis and preliminary binding studies of several calix[4]arenes bridged either at the upper rim (aromatic nuclei) or at the lower rim (phenolic OH groups) with binaphthyl chiral units.[11]

Scheme 1



1 **2** X = H **3** X = COCl

Results and Discussion

Upper Rim Bridged Calix[4]arenes. Initially we attempted the synthesis of upper rim binaphthyl bridged calix[4]arenes, by the reaction of the diaminocalix[4]arene **1** with dichloride (*R*,*S*)-**3**, using a number of classical experimental procedures for the acylation of amines, but without any success (Scheme 1). However, the reaction of the diamine **1** with several monofunctional acylating agents except **2**, runs smoothly.[11]

Suspecting that the failure of this reaction could be ascribed to unfavorable electronic and steric effects in the reaction of **1** and binaphthol derivatives, we have performed a similar reaction using the diamine **4**, having a CH_2 spacer between the aromatic ring and the amino group. While in our preliminary communication[11] this

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[‡] University of Parma.
[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

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(10) Kubo, Y.; Maeda, S.; Tokite, S.; Kobo, M. *Nature* **1996**, *382*, 522.

(11) Preliminary communication of some part of these results: Pinkhassik, E.; Stibor, I.; Havlicek, V. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1182.

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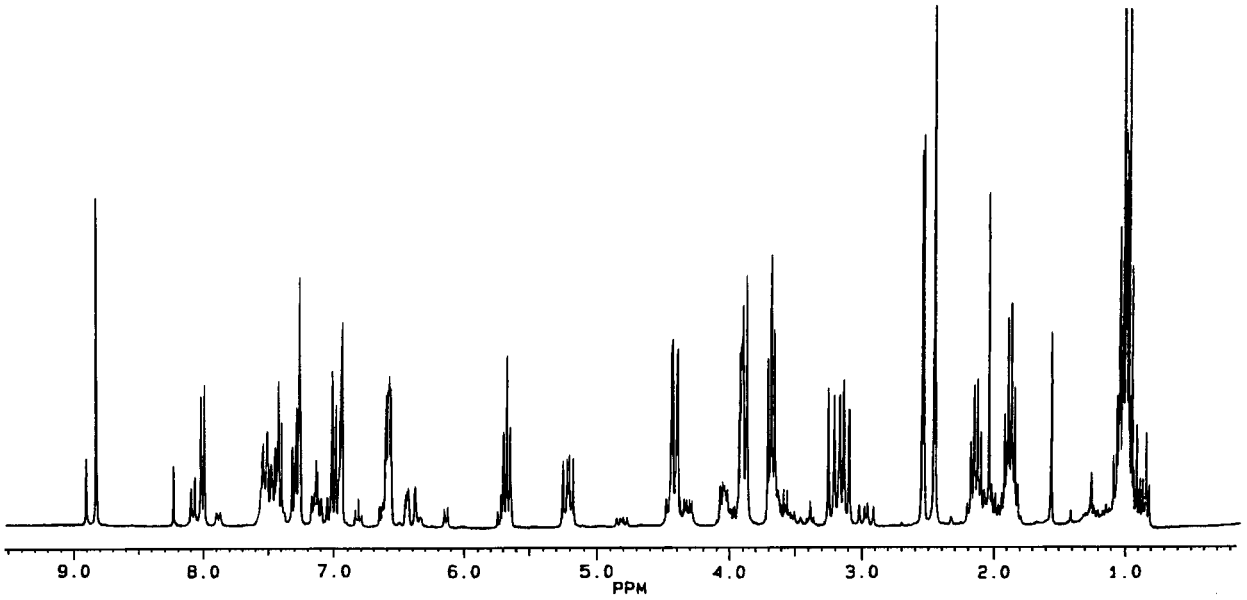
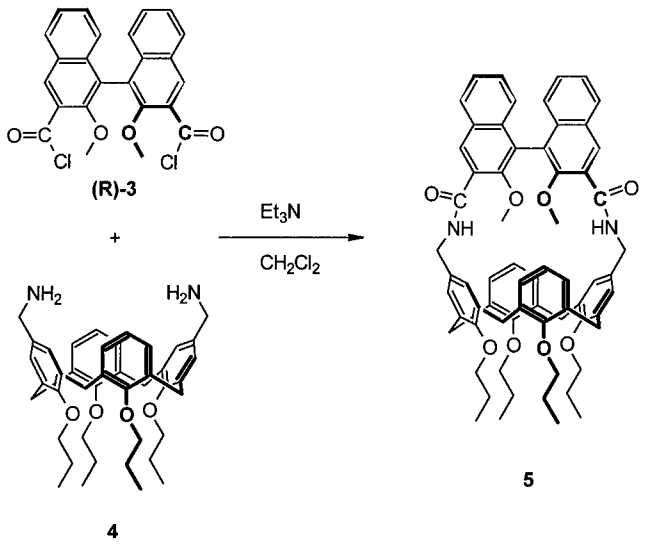


Figure 1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5** at 25 °C.

Scheme 2



reaction was performed using a high-dilution technique, now we have found that the dropwise addition of a solution of dichloride (*R*)-**3** to a solution of the diamine **4** in the presence of a base leads to optically active **5** in 33% yield (Scheme 2).

The calixarene moiety in the compound **5** is fixed in the *cone* conformation as it is in its precursor **4**. However, the ^{1}H NMR spectrum of **5** shows that all signals are split in a ratio of approximately 1:10 indicating the presence of two compounds, very close in structure (Figure 1).

Careful chromatographic purification, GPC and HPLC analyses coupled with MS data, allow us to rule out the presence of compounds having different molecular weights. In particular we did not find any evidence for the formation of 2 + 2 coupling products, which could in principle be formed in the cyclization reaction.[12] As we deal with a single compound, the splitting of the ^{1}H NMR signals must be ascribed to the presence of two stable conformations of the compound **5** in solution. To gain more insight into the structure and conformational behavior of **5**, we performed dynamic ^{1}H NMR experiments in DMSO-d_6 solution. Although Figure 2 shows

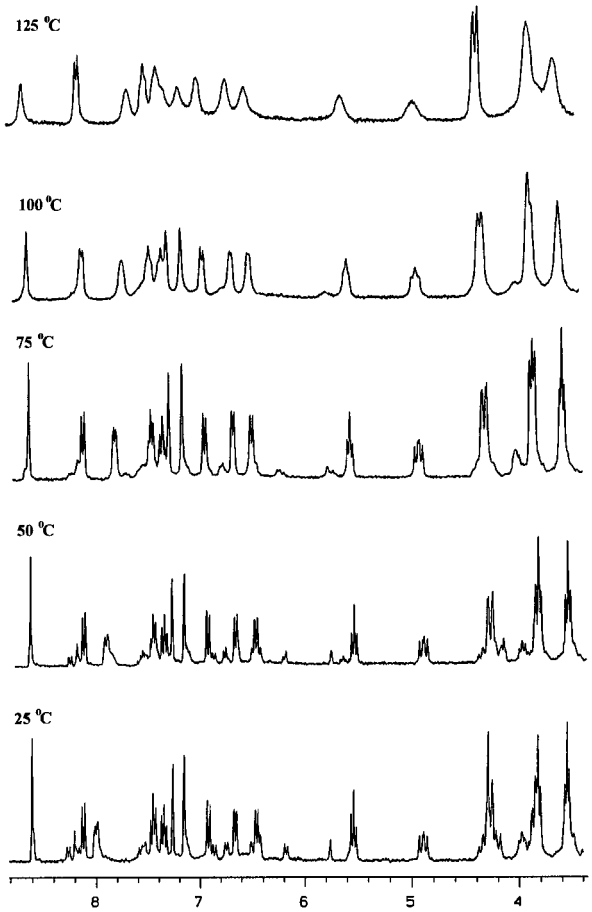
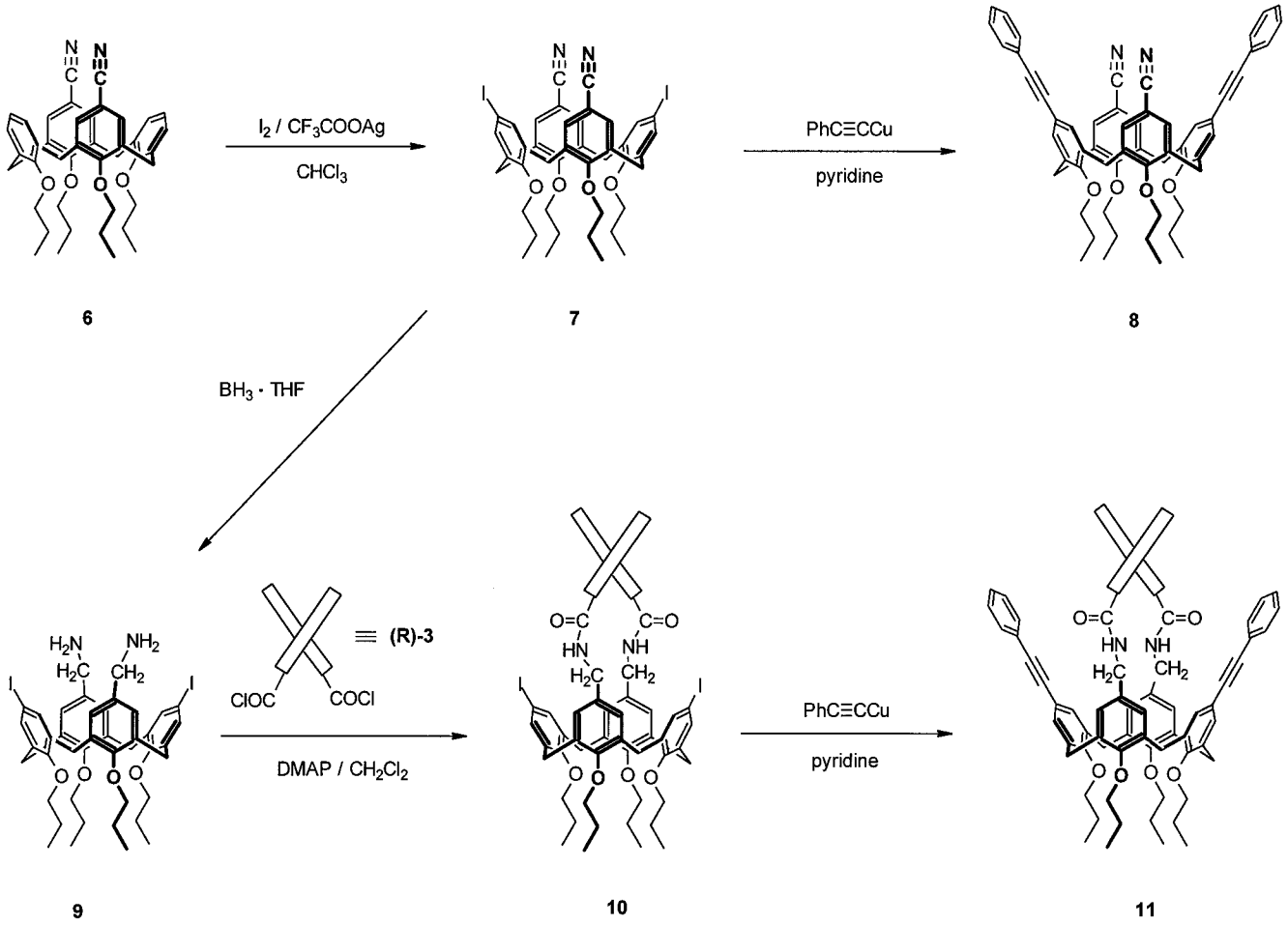


Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5** (δ 3.5−8.8 region) at different temperatures.

only the low field part of the ^{1}H NMR spectrum, a similar behavior can also be observed for other signals.

(12) Such 2 + 2 condensation processes have been previously observed in calix[4]arene chemistry: (a) Kraft, D.; van Loon, J.-D.; Owens, M.; Verboom, W.; Vogt, W.; McKervey, M. A.; Böhmer, V.; Reinhoudt, D. N. *Tetrahedron Lett.* **1990**, *31*, 4941. (b) Beer, P. D.; Keefe, A. D.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3675. (c) Asfari, Z.; Weiss, J.; Pappalardo, S.; Vicens, J. *Pure Appl. Chem.* **1993**, *65*, 585.

Scheme 3



At $T > 75$ °C the splitting of all sets of signals disappears and only one signal is observed for each type of protons, thus indicating that the two conformations are in fast exchange between them. A possible explanation of this behavior can be attributed to a restricted rotation around the bond between the amide carbon and the binaphthyl moiety. Because of the symmetry of the ^{1}H NMR spectrum of the major conformer, we are inclined to think that both its carbonyl groups point toward the exterior of the macrocyclic cavity, being coplanar with the naphthyl nuclei. In the minor component one carbonyl group could be tilted out of the plane causing an upfield shift of the adjacent H-4 (or H-4′) naphthyl proton, which in fact absorbs at $\delta = 8.23$ ppm instead of $\delta = 8.80$ ppm found in the major component or $\delta = 8.88$ ppm observed for the binaphthyl-amide derivatives **12** and **14**. In the receptor **5** the *para* positions of two opposite calix[4]arene aromatic nuclei are still available for further functionalization. One attractive possibility was to extend the aromatic walls by introducing two phenylacetylene groups in these free positions, thus creating a more shielded cleftlike cavity. We therefore synthesized the diiododicyanocalix[4]arene **7** using the recently published I_2/CF_3COOAg protocol for iodination of calix[4]arenes[13] and submitted **7** to a model coupling reaction with cuprous phenylacetylide[14] obtaining **8** in 76% yield (Scheme 3).

Since this last reaction was successful, compound **7** was reduced to the corresponding diamine **9**, which was condensed with binaphthol dichloride (*R*)-**3** to give **10**. The yield of the cyclization step (17%) is lower than that obtained with the unsubstituted diamine **4**, and this can be ascribed to steric hindrance to the ring closure, caused by bulky iodine atoms. The reaction of cuprous phenylacetylide with **10** in refluxing pyridine gave the optically active cleftlike receptor **11** (Scheme 3). We also tried to enlarge the dimension of the chiral cavity by elongating the spacer between the calixarene and the binaphthyl unit. The reaction of glycine methyl ester hydrochloride with binaphthol diacid chloride (*R*)-**3** in CH_2Cl_2 in the presence of *N*,*N*-dimethylaminopyridine (DMAP) as a base gave the diester **12** in 88% yield, which was quantitatively hydrolyzed to the diacid **13** (Scheme 4).

The conversion of the diacid **13** to diacid chloride was tried with several methods ($SOCl_2$, $(COCl)_2$, PCl_5) but it failed in all cases in our hands. Therefore, we have chosen another method of activation of carboxyl group using 1,1′-carbonyldiimidazole (CDI).[15] Prior to cyclization we have performed a model coupling of **13** with *n*-propylamine. The diacid **13** was treated with CDI in THF for 0.5 h, and then the equivalent amount of *n*-propylamine was added, giving **14** in excellent yield (Scheme 4). The cyclization was performed in similar conditions and gave the desired product **15** with the extended chiral cavity (Scheme 4). ^{1}H NMR analyses revealed that, as found for compound **5**, also in the case

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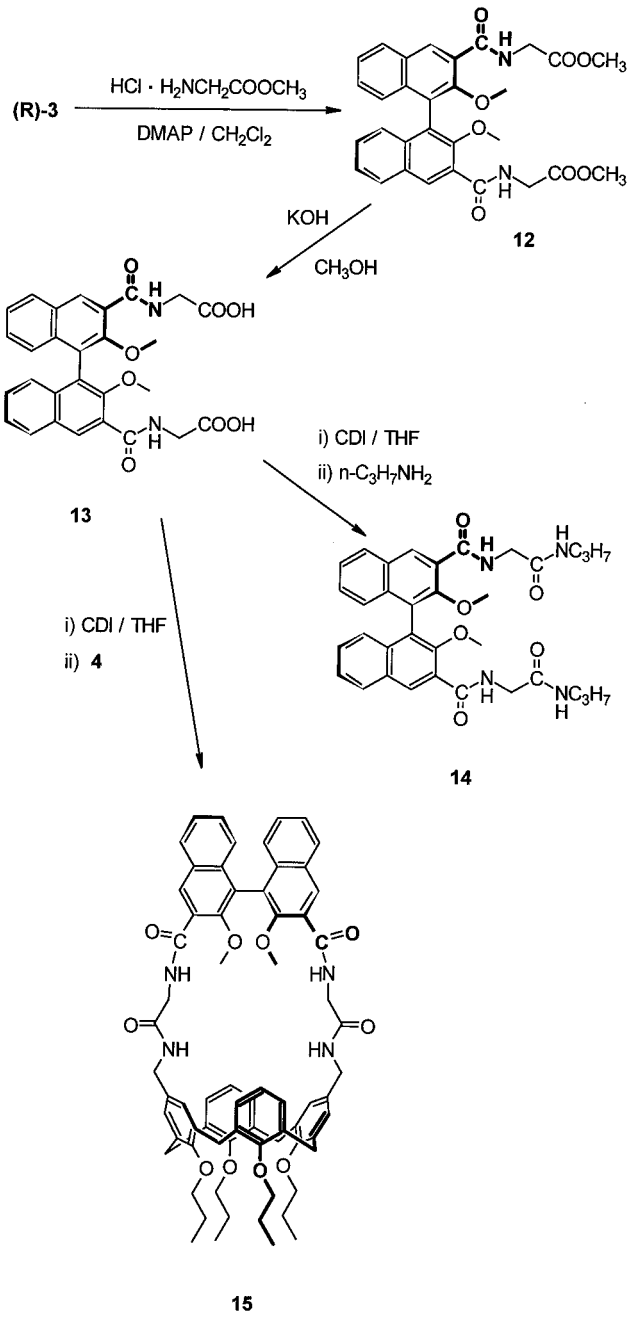
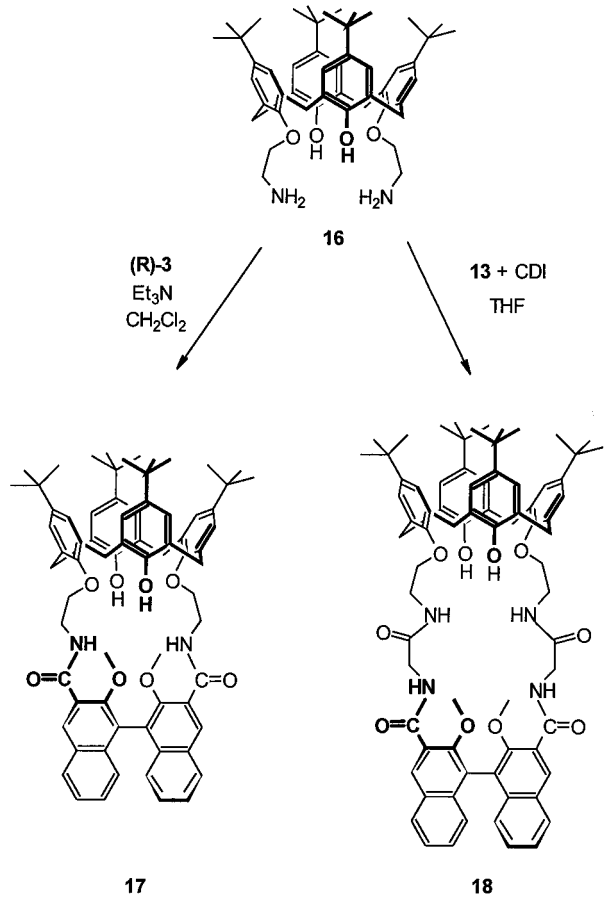
Scheme 4



Scheme 5



of compounds **10**, **11**, and **15** a major and a minor conformer are present in solution.

Lower Rim Bridged Calix[4]arenes. To link our binaphthyl bridge at the lower rim of calix[4]arene we have chosen the diamine **16** since it can be obtained in good yield from *p-tert*-butylcalix[4]arene.[16] The cyclization was performed by dropwise addition of the solution of dichloride (*R*)-**3** to the solution of the diamine **16** and triethylamine in dichloromethane (Scheme 5).

The yield of the macrocyclization to compound **17** (56%) proves that no severe steric strain is created during the ring closure step because of the large ring formed and of the high flexibility of the alkyl chains bearing the amino groups.[17] The diacid **13** was treated with CDI for 0.5 h in THF, and then it was added dropwise to the solution of diamine **16** in THF to give **18** in 17% yield (Scheme 5). Conformational features of the calix[4]arene skeleton were not altered by capping it with the binaphthyl bridge at the lower rim. Both bridged calix[4]arenes **17** and **18** possess a *pinched cone*[9] conformation as is evidenced by their ^{1}H NMR spectra.

Complexation Studies. Complexation tests were performed with a series of neutral molecules, ammonium salts, and metal ions. Two methods were used in this study: extraction of a substrate from solid phase into a $CDCl_3$ solution of the receptor in $CDCl_3$ and ^{1}H NMR titration in solution.

Concerning neutral molecules, complexation was observed only in CCl_4 with compound **5** and guests having acidic C−H groups such as nitromethane ($K_{ass.} = 16\ M^{-1}$) and acetonitrile ($K_{ass.} = 7\ M^{-1}$). The upfield shifts experienced by the methyl groups upon complexation indicate that the guests are included in the calix[4]arene apolar cavity. Contrary to what was observed with other lower rim bridged calix[4]arenes (calixcrowns[18] and calixspherands[19]), no complexation occurs between alkali

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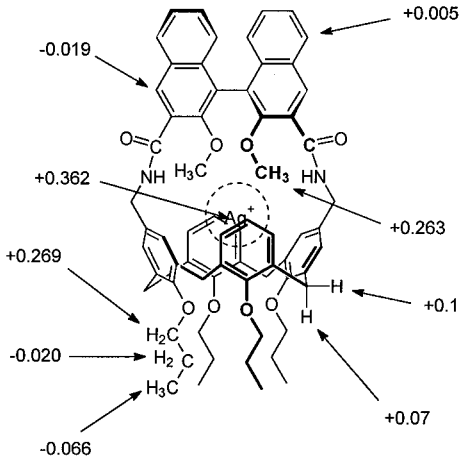

Figure 3. Complexation induced shifts (CIS) experienced by the protons of calixarene **5** upon addition of CF_3COOAg in $CDCl_3$:CD_3OD (1:1 = v/v).

metal cations and our new binaphthyl bridged calix[4]-arenes. Interestingly, the silver cation is strongly and selectively complexed by the ligand **5**. Addition of CF_3-$COOAg$ to a $CDCl_3$:CD_3OD (1:1 v/v) solution of ligand **5** causes substantial changes in the ^1H NMR spectrum of the ligand. First of all, the signals of the minor conformer of **5** are gradually reduced until they disappear thus indicating that only the major conformer is able to complex the metal cation. This confirms the results of the dynamic ^1H NMR experiments on **5** (vide supra), which indicated the presence of two conformational isomers in solution and shows that the conformational equilibrium between the two conformers can be affected by the Ag^+ cation. At room-temperature we do not observe separate signals for complexed and uncomplexed host **5** but simply gradual complexation-induced shifts (CIS), which indicates that the complexation/decomplex-ation process is fast on the NMR time scale. The CIS experienced by the calixarene protons (Figure 3) are similar to those observed previously by Shinkai et al. with simpler systems,[20] thus indicating that the silver cation is sandwiched between the two unsubstituted aromatic rings of the *cone* calixarene, whose para-H experience the largest downfield shift upon complexation. Nonlinear least-squares analysis of the ^1H NMR data using several protons as probes, allowed to establish a log $K_{ass.} = 3.51$ for this complex.[21] This value is substantially higher than that found by Shinkai et al. for *n*-propyl derivatives of calix[4]arene and *p-tert*-butylcalix[4]arene in the *cone* conformation (log $K_{ass.} = 2.96$ and 2.66, respectively) in a less polar solvent ($CDCl_3$:CD_3OD 4:1 v/v).[20] This can be due to higher rigidity of the calix[4]arene cavity in **5**, induced by the upper rim bridging, in comparison with the simple *cone* calix[4]arene which experience a residual $C_{2v} \leftrightarrow C_{2v}$ interconversion, in solution.[22] It is also possible that the stabilization of the Ag^+ complex of the ligand **5** can be partly ascribed to the participation of the binaphthyl OCH_3 groups, which also experience a substantial downfield shift upon complexation.

Recently a catalytic asymmetric allylation of aldehydes using a chiral silver(I) BINAP complex has been reported.[23] The formation of a strong Ag^+ complex in the chiral cavity offered by **5** makes this ligand also attractive for chiral catalysis studies, which are now in progress in our laboratories.

Experimental Section

General Procedures. Dichloromethane was distilled over CaH_2 and stored over 3 Å molecular sieves before use. THF was freshly distilled from potassium benzophenone. All other reagents and solvents were of reagent grade quality, obtained from commercial suppliers, and used without purification. Chemical shifts are expressed in ppm from TMS. Compounds **1**,[24] **2**,[25] **3**,[26] **4**,[27] and **16**[16] were synthesized according to literature procedures.

General Method for the Cyclization of Calix[4]arene-diamines 4, 9, 16 with Binaphthyl (*R*)-3.

A solution of acyl chloride (*R*)-**3** (453 mg, 1 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise to a solution of calix[4]-arenediamine (1 mmol) and triethylamine (2.2 mmol) in dry CH_2Cl_2 (35 mL) at room temperature during 2 h. The reaction mixture was washed with 1 N HCl (2 × 50 mL) and water (50 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the solid residue was submitted to the column chromatography (silica gel, CH_2Cl_2/acetone, 20:1, v/v).

Compound 5. Yield 33%, mp > 270 °C. ^1H NMR ($CDCl_3$) δ: (main conformer) 8.85 (s, 2H), 8.04 (d, 2H, $J = 8$ Hz), 7.56 (d, 2H, $J = 8$ Hz), 7.45 (t, 2H, $J = 7.5$ Hz), 7.32 (t, 2H, $J = 7.5$ Hz), 7.17 (t, 2H, $J = 7.5$ Hz), 7.02 (d, 2H, $J = 8$ Hz), 6.97 (s, 2H), 6.61 (t, 2H, $J = 6$ Hz), 4.43 and 4.42, 3.20 and 3.13 (d, 2H, $J = 12$ Hz), 3.90 and 3.69 (t, 4H, $J = 7.5$ Hz), 2.47 (s, 6H), 2.24−1.78 (m, 8H), 1.03 and 0.99 (t, 6H, $J = 7.5$ Hz). FAB HRMS *m/e*: 1016.497 (M^+) rel intensity 100%. For $C_{66}H_{68}N_2O_8$ calculated: 1016.498. Anal. Calcd for $C_{66}H_{68}N_2O_8$: C, 77.93; H, 6.74. Found: C, 77.54; H, 6.49. $[\alpha]^{25}_{589}$ (*c* 0.04, CH_2Cl_2).

Compound 10. Yield 17%. ^1H NMR ($CDCl_3$) (main conformer) δ 8.80 (s, 2H), 8.00 (d, 2H, J = 7.5 Hz), 7.70 (d, 2H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.5 Hz), 7.32 (t, 2H, J = 7.5 Hz), 7.15, 7.12, 7.03 and 6.87 (s, 2H), 4.36 (d, 4H, H = 12 Hz), 3.88−3.72 (m, 8H), 3.17 and 3.10 (d, 2H, J = 12 Hz), 2.65 (s, 6H), 2.18−1.79 (m, 8H), 1.02 and 0.96 (t, 6H, J = 7.5 Hz). MS (CI) *m/e* 1269.0 [$(M + H)^+$]. Anal. Calcd for $C_{66}H_{66}N_2I_2O_8$. $[\alpha]^{25}_{589}$ (*c* 0.02, CH_2Cl_2)

Compound 17. Yield 56%. mp > 220 °C. ^1H NMR ($CDCl_3$) δ 9.06 (t, 2H, $J = 5.5$ Hz), 8.82 (s, 2H), 8.07 (d, 2H, $J = 7.5$ Hz), 7.50 (t, 2H, $J = 7.5$ Hz), 7.39 (t, 2H, $J = 7.5$ Hz), 7.30 (d, 2H, $J = 7.5$ Hz), 7.04 (s, 4H), 6.63 (s, 2H), 6.62 (s, 2H), 6.02 (s, 2H), 4.36−4.0 (m, 10 H), 3.82−3.78 (m, 2H), 3.32 (d, 4H $J = 13$ Hz), 3.17 (s, 6H), 1.29 (s, 18H), 0.83 (s, 18H). MS−FAB *m/e* 1101.581 ($M^+ + H$). Anal. Calcd for $C_{72}H_{80}N_2O_8$: C, 78.51; H, 7.32. Found: C, 78.92; H, 7.12. $[\alpha]^{25}_{589}$ (*c* 0.065, CH_2Cl_2)

5,17-Dicyano-11,23-diiodo-25,26,27,28-tetrapropoxycalix-[4]arene (7). To a suspension of CF_3COOAg (200 mg, 0.88 mmol) in $CHCl_3$ (10 mL) was added a solution of **6** (128 mg, 0.2 mmol) in $CHCl_3$ (15 mL), the cloudy solution was refluxed for 25 min, and then I_2 (220 mg, 0.88 mmol) was added. After 1 h, the precipitated AgI was filtered off, and the solution was treated with 20% aqueous $Na_2S_2O_5$ solution until the violet color had disappeared. The organic layer was separated and washed twice with water, dried over Na_2SO_4, and evaporated to afford a yellow solid which was purified by crystallization (CH_2Cl_2/CH_3OH); yield 144 mg (81%). ^1H NMR ($CDCl_3$) δ 7.20 and 6.82 (s, 4H), 4.36 and 3.13 (d, 4H), 3.87 and 3.81 (t, 4H, $J = 7.5$ Hz), 1.96−1.78 (m, 8H), 1.03 and 0.93 (t, 6H, $J = 7.5$

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Hz). MS (CI) 894.4 (M^+). Anal. Calcd for $C_{42}H_{44}N_2I_2O_4$: C, 56.39; H, 4.96. Found: C, 56.25; H, 4.99.

5,17-Dicyano-11,23-bis(phenylethynyl)-25,26,27,28-tetrapropoxycalix[4]arene (8). A mixture of **7** (618 mg, 0.805 mmol) and cuprous phenylacetylide (530 mg, 3.22 mmol) in dry pyridine (15 mL) was stirred at reflux in an inert atmosphere for 24 h. The reaction mixture was cooled, poured to 50 mL of 1 N HCl, and extracted with dichloromethane (30 mL). The organic layer was washed with 1 N HCl and water and dried, and the solvent was evaporated. The residue was triturated with petroleum ether to give 443 mg (76%) of grayish solid. mp 248 °C (CH_2Cl_2/CH_3OH). ^{1}H NMR ($CDCl_3$) δ 7.61−7.28 (m, 10H), 7.23 (s, 4H), 6.74 (s, 4H), 4.43 and 3.19 (d, 4H, J = 13.5 Hz), 3.98 and 3.79 (t, 4H, J = 7 Hz), 2.02−1.82 (m, 8H), 1.08 and 0.93 (t, 6H, J = 7 Hz). MS (CI) 842.9 (M^+). Anal. Calcd for $C_{58}H_{54}N_2O_4$: C, 82.63; H, 6.46. Found: C, 82.47; H, 6.52.

5,17-Bis(aminomethyl)-11,23-diiodo-25,26,27,28-tetrapropoxycalix[4]arene (9). To a solution of **7** (100 mg, 0.11 mmol) in dry THF (5 mL) was added dropwise BH_3 (1 M in THF, 2 mL, 2 mmol) under nitrogen. The reaction mixture was then heated at 70 °C for 7 h. After being cooled, the solution was carefully quenched by the addition of water, and the mixture was stirred for 30 min at room temperature. The solvent was then distilled off, and the solid residue was heated to reflux for 3 h in 6 N HCl (10 mL). After being cooled, the acidic solution was evaporated to dryness in vacuo. 2 N NaOH (10 mL) was added to the reaction flask, and the product was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over $MgSO_4$, and the solvent was evaporated to dryness to give **9** (82 mg, 81%). mp = 170 °C dec. ^{1}H NMR ($CDCl_3$) δ 7.08 (s, 4H), 6.50 (s, 4H), 4.38 and 3.09 (d, 4H, J = 13 Hz), 3.86 and 3.78 (t, 4H, J = 7.5 Hz), 3.52 (s, 4H), 1.98−1.82 (m, 8H), 1.06−0.92 (m, 12H). MS (CI) 902.6 (M^+). Anal. Calcd for $C_{42}H_{52}I_2N_2O_4 \cdot 1.25H_2O$: C, 54.52; H, 5.81. Found: C, 54.43; H, 5.96.

Compound 11. A mixture of **10** (40 mg, 0.032 mmol), cuprous phenylacetylide (21 mg, 0.128 mmol), and dry pyridine (3 mL) was stirred at reflux in an inert atmosphere for 24 h. The reaction mixture was cooled, poured to 10 mL of 1 N HCl, and extracted with dichloromethane (10 mL). The organic layer was washed with 1 N HCl and water and dried, and the solvent was evaporated. The residue was submitted to preparative TLC (silica gel, CH_2Cl_2/acetone, 20:1, v/v) to give 28 mg (72%) of **11**. ^{1}H NMR ($CDCl_3$) (main conformer) δ 8.74 (s, 2H, ArH), 8.06 (d, 2H, J = 7.5 Hz), 7.69 (d, 2H, J = 7.5 Hz), 7.63−7.22 (m, 14H), 7.15, 7.12, 7.03 and 6.98 (4s, 8H), 4.43 (d, 4H, H = 12 Hz), 3.93−3.77 (m, 8H), 3.24 and 3.17 (2d, 4H, J = 12 Hz), 2.43 (s, 6H), 2.18−1.79 (m, 8H), 1.02 and 0.96 (2t, 12H, J = 7.5 Hz). MS (CI) 1216.2 (M^+). Anal. Calcd for $C_{82}H_{76}N_2O_8$: C, 80.89; H, 6.29. Found: C, 80.42; H, 6.33.

(*R*)-2,2′-Dimethoxy-3,3′-bis[[(methoxycarbonyl)methyl]carbamoyl]-1,1′-binaphthylene (12). A mixture of (*R*)-**3** (1.00 g, 2.28 mmol), glycine methyl ester hydrochloride (800 mg, 8.98 mmol), and DMAP (1.53 g, 12.5 mmol) in dry ether (30 mL) was stirred at room temperature for 24 h. The reaction mixture was then washed with 1 N HCl (2 × 30 mL) and water (30 mL) and dried, and the solvent was evaporated. The residue was submitted to column chromatography (silica gel/CH_2Cl_2) to give 1.09 g (88%) of white product. ^{1}H NMR ($CDCl_3$) δ 8.88 (s, 2H), 8.56 (br t, 2H), 8.04 (d, 2H, J = 7.5 Hz), 7.47 (t, 2H, J = 7.5 Hz), 7.35 (t, 2H, J = 7.5 Hz), 7.09 (d, 2H, J = 7.5 Hz), 4.54−4.14 (m, 4H), 3.77 and 3.42 (s, 6H). MS (CI) *m/e* 544.8 (M^+). Anal. Calcd for $C_{30}H_{28}N_2O_8$: C, 66.17; H, 5.18. Found: C, 66.06; H, 5.11.

(*R*)-2,2′-Dimethoxy-3,3′-bis[(carboxymethyl)carbamoyl]-1,1′-binaphthalene (13). Diester **12** (800 mg, 1.47 mmol) was added to a solution of KOH (825 mg, 14.7 mmol) in CH_3OH (40 mL) and the resulting yellow solution was stirred for 3 h at room temperature. Then methanol was evaporated, the solid residue was dissolved in water (30 mL) and concentrated HCl was added to the solution till pH 1. White precipitate was filtered on a buchner, washed with water and dried to give 714 mg (94%) of **13**. ^{1}H NMR (acetone-d_6) 8.75 (s, 2H), 8.54 (br t, 2H), 8.16 (d, 2H, J = 7.5 Hz), 7.55 (t, 2H, J = 7.5 Hz), 7.42 (t, 2H, J = 7.5 Hz), 7.14 (d, 2H, J = 7.5 Hz), 4.38−4.28 (m, 4H), 3.50 (s, 6H). MS (CI) 517 (M^+). Anal. Calcd for $C_{28}H_{24}N_2O_8$: C, 65.11; H, 4.68. Found: C, 64.98; H, 4.61.

(*R*)-2,2′-Dimethoxy-3,3′-bis[[[(*N*-propylamino)carbonyl]methyl]carbamoyl]-1,1′-binaphthalene (14). Diacid **13** (50 mg, 0.097 mmol) was added to the solution of carbonyldiimidazole (32 mg, 0.2 mmol) in dry THF (1 mL). After being stirred for 30 min, propylamine (12 mg, 0.2 mmol) was added. After stirring overnight at room temperature, the reaction mixture was poured into 10 mL of 1 N HCl and extracted with dichloromethane (15 mL). The organic layer was separated, washed with water (2 × 10 mL), and dried, and the solvent was evaporated to give 56 mg (97%) of product. ^{1}H NMR ($CDCl_3$) δ 8.88 (s, 2H), 8.64 (t, 2H), 8.06 (d, 2H, J = 8 Hz), 7.50 (t, 2H, J = 8 Hz), 7.37 (t, 2H, J = 8 Hz), 7.11 (d, 2H, J = 8 Hz), 6.17 (bs, 2H), 4.35−4.05 (m, 4H), 3.39 (s, 6H), 3.35−3.20 (m, 4H), 1.65−1.45 (m, 4H), 0.93 (t, 6H, J = 7.5 Hz). MS (CI) 598.7 (M^+). Anal. Calcd for $C_{34}H_{38}N_4O_6$: C, 68.21; H, 6.40. Found: C, 68.34; H 6.37.

General Method for the Cyclization of Calix[4]arenediamines 4 and 16 with Binaphthyl 13. Diacid **13** (100 mg, 0.194 mmol) was added to a solution of carbonyldiimidazole (64 mg, 0.4 mmol) in dry THF (10 mL). After being stirred for 30 min at room temperature, a solution of calix[4]arenediamine (0.194 mmol) in dry THF (10 mL) was added dropwise during approximately 1 h. The solvent was evaporated to dryness, the residue was dissolved in CH_2Cl_2 and washed with 1 N HCl (2 × 20 mL) and water (20 mL) and dried over $MgSO_4$. The solvent was evaporated to dryness, and the solid residue was subjected to preparative TLC (silica gel, CH_2Cl_2:CH_3OH 10:1 v/v).

Compound 15. Yield 4%. ^{1}H NMR ($CDCl_3$) (main conformer) δ 8.67 (s, 2H), 7.98 (d, 2H, J = 7.5 Hz), 7.84 (br t, 2H), 7.49 (t, 2H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.5 Hz), 7.21 (d, 2H, J = 7.5 Hz), 7.13 (t, 2H, J = 7.5 Hz), 4.33 (d, 4H, J = 13.5 Hz), 4.52−4.18 (m, 4H), 3.95 and 3.61 (t, 4H, J = 7.5 Hz), 3.12 and 3.01 (d, 2H, J = 12 Hz), 3.03 (s, 6H), 2.04−1.76 (m, 8H), 1.02 and 0.89 (t, 6H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 169.3, 167.5, 157.5, 156.1, 153.4, 137.7, 136.9, 135.5, 134.1, 133.9, 133.8, 131.8, 131.0, 130.2, 129.8, 129.4, 128.8, 128.2, 128.0, 126.8, 126.2, 122.1, 77.99, 77.24, 63.13, 45.08, 44.29, 31.70, 31.57, 31.48, 24.08, 23.66, 11.30, 10.61. MS (CI) 1130.7 (M^+).

Compound 18. Yield 17%. ^{1}H NMR ($CDCl_3$) δ 8.97 (br t, 2H), 8.82 (s, 2H), 8.78 (s, 2H), 8.66 (br t, 2H), 8.00 (d, 2H, J = 7.5 Hz), 7.44 (t, 2H, J = 7.5 Hz), 7.31 (t, 2H, J = 7.5 Hz), 7.17−6.98 (m, 10H), 4.50−4.18 (m, 12H), 3.84−3.54 (m, 4H), 3.51 (s, 6H), 3.41 (d, 4H, J = 13 Hz), 1.27 and 1.16 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 169.45, 166.00, 154.63, 149.88, 149.20, 148.96, 143.80, 136.20, 134.10, 133.78, 130.77, 130.23, 129.05, 128.63, 128.28, 127.22, 128.63, 126.47, 126.43, 126.29, 126.11, 126.00, 76.24, 62.82, 44.13, 40.16, 34.90, 34.57, 33.36, 32.61, 32.23, 31.88. CI MS 1214.6 (M^+). Anal. Calcd for $C_{76}H_{86}N_4O_{10}$: C, 75.10; H, 7.13. Found: C, 75.16; H, 6.73.

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