SYNTHESIS OF NEW CHIRAL LIGANDS BY CAPPING OF CALIX[4]ARENE DERIVATIVES

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Calix[4]arene derivatives are used as a scaffold for the attachment of chiral substituents. Calix[4]arenes having either lower or upper rim capped with chiral binaphtholic species **5** and **6**, as well as new biscalix[4]arenodiaza-18-crown-6 (**8**), have been synthesized.
Key words: Calixarenes; Binaphthols; Chiral ligands.

Chiral recognition[1] is an important and attractive area of research grown with the development of chemistry of weak interactions, host–guest complexes or, in other words, supramolecular chemistry[2,3]. Among a large number of hosts designed so far, calixarenes[4–6] have attracted special attention. Due to their availability and a broad range of possible chemical modifications, they were even considered[6] to be"macrocycles with (almost) unlimited possibilities". Chiral calix[4]arenes** are of two types. Calixarenes can be converted into chiral derivatives by the introduction of a chiral substituent[6–18]. They can also be prepared as inherently chiral macrocycles due to their nonplanar molecular structure[6,19]. Recently calix[4]arenes capped on lower-rim with racemic biaryls have been used for recognition of butylamines[20]. This has prompted us to disclose our synthetic results obtained when trying to cap the calix[4]arene skeleton by axially-chiral binaphthol unit and to synthesize a new tail-to-tail biscalix[4]arene.

This paper reports on the synthesis of a new class of chiral calix[4]arene-based ligands, using axially chiral substituted 2,2′-dihydroxy-1,1′-binaphthalene (binaphthol) as a chiral substituent. Symmetrically substituted binaphthols have been known for a long time and have been incorporated into a number of interesting chiral ligands[21–25].

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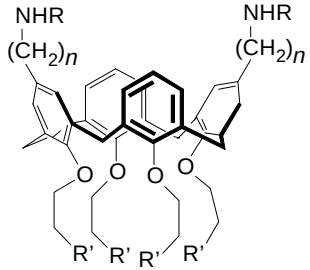
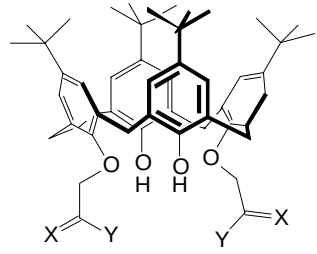
**The name calix[4]arene is used instead of 1,3,5,7-tetrabenzenecyclooctophane-1^2,3^2,5^2,7^2-tetrol.

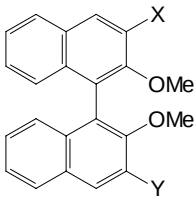
The recently developed[26–29] facile synthesis of non-symmetrically substituted binaphthols has opened the way for the design and synthesis of new chiral ligands[30]. The synthetic protocol developed for preparation of binaphthol-containing ligands (see below) allows us to synthesize new biscalix[4]arene derivatives **7**, **8** with connected lower-rims. The additional macrocycle thus formed resembles the well-known diaza-18-crown-6.



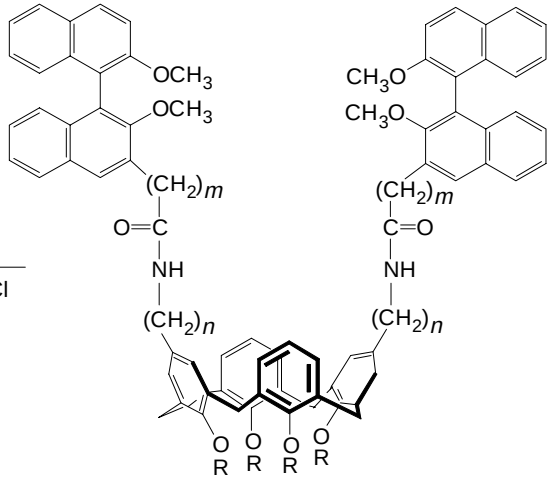
1	R	R'	*n*
a	H	OEt	0
b	H	Me	1
c	PhCO	OEt	0
d	L-BocAla	OEt	0
e	tetra-*O*-acetyl-D-ribonyl	OEt	0



2	X	Y
a	2H	NH_2
b	O	Cl



3	X	Y
a	COCl	COCl
b	COCl	H
c	COOH	H
d	CH_2COOCH_3	H
e	CH_2COOH	H
f	CH_2COCl	H



4	R	*m*	*n*
a	$CH_2CH_2CH_3$	0	0
b	$CH_2CH_2OCH_2CH_3$	1	1
c	$CH_2CH_2CH_3$	1	1

RESULTS AND DISCUSSION

At the beginning of our work we have tried to couple calixarenediamine[31] **1a** with dichloride[23] **3a** using a number of common experimental protocols for acylation of amines but without any success. In all experiments only the starting materials have been isolated (the binaphtholic species isolated was the corresponding diacid). We suspected that the failure could be attributed to the strain in the desired capped product and attempted the same reaction with monoacyl chloride[28] **3b** but again without any success. The carbonyl group directly attached to the binaphthol moiety seems to be uncapable of the reaction with diamine **1a**. This fact was repeatedly confirmed by many experiments also for the reaction of both **3a** and **3c** with **1a**. The very same reaction using benzoyl chloride in pyridine, Boc-phenylalanine (DCC coupling[32]) as well as the reaction with chloride of tetra-*O*-acetyl-D-ribonic acid furnished the desired amides **1c**, **1d** and **1e** in yields 82, 47, and 95%, respectively.

On the other hand, if at least one functional group is separated from either calix[4]arene or binaphthol moieties by a methylene spacer, the reaction proceeds smoothly. Thus coupling **1b** (ref.[33]) with **3b** gave **4a** (54%), **1a** with **3f** gave **4b** (46%), and **1b** with **3f** gave **4c** (57%). The new binaphthalenes **3d–3f** have been prepared by standard synthetic procedures.

Having the synthetic method in hands we attempted the upper-rim capping when treating **1b** with both (*R*,*S*)-**3a** and (*R*)-**3a** under high-dilution technique yielding racemic **5** as well as chiral (–)-**5** in 14% (racemic) and 12% (chiral) yields, respectively.

The modelling of this molecule using CPK models as well as program HYPERCHEM™ has shown that the aromatic rings of the binaphthol unit are almost parallel with the adjacent calixarene aromatic nuclei and form a kind of a very narrow molecular cleft. The lower-rim capping of the disubstituted diaminocalix[4]arene **2** (ref.[34]) proceeded even better. Again, the high-dilution technique was applied and (±)-**6** and (–)-**6** were obtained in 31 and 27% yield, respectively. The MS-analysis has proved that the reaction really furnished the 1 : 1 coupling product (Fig. 1), as confirmed by high resolution EI-MS with M^+ ion with *m/z* 1 016.497 and relative intensity 100% (for $C_{66}H_{68}N_2O_8$ calculated 1 016.498. The most abundant "binaphthyl-containing" acylium fragment ion, *m/z* 384.1240 and relative intensity 50% (for $C_{24}H_{18}NO_4$ calculated 384.1236) was also observed in the daughter-ion linked scan of the protonated molecule (FAB mode) as the base peak. For **6**, $M^+ - H$ ion appeared at *m/z* 1 101.581, relative intensity 5.5% (for $C_{72}H_{81}N_2O_8$ calculated 1 101.599). The charged binaphthyl-related fragment *m/z* 453 (40%) formed by *p-tert*-butylcalix[4]arene rejection, is the most intense peak in daughter-ion linked scan of the corresponding protonated molecule. We have not observed even traces of 2 : 2 coupling products.

Next, we turned our attention to tail-to-tail coupling of two calix[4]arenes. Thus, treatment of the diamine **2a** with known diacyl dichloride **2b** (ref.[34]) furnished diamide **7** in

21% yield. The subsequent reduction with borane–tetrahydrofuran complex solution yielded the desired diamine **8** in 80% yield.

Compound **5** was tested for complexation with neutral molecules in tetrachloromethane by the ^{1}H NMR technique. The stability constants were determined using a standard titration protocol. Complexes were formed with nitromethane (K = 16 mol^{-1}) and acetonitrile (K = 7 mol^{-1}). The product **5** exists in two forms with very similar NMR spectra,

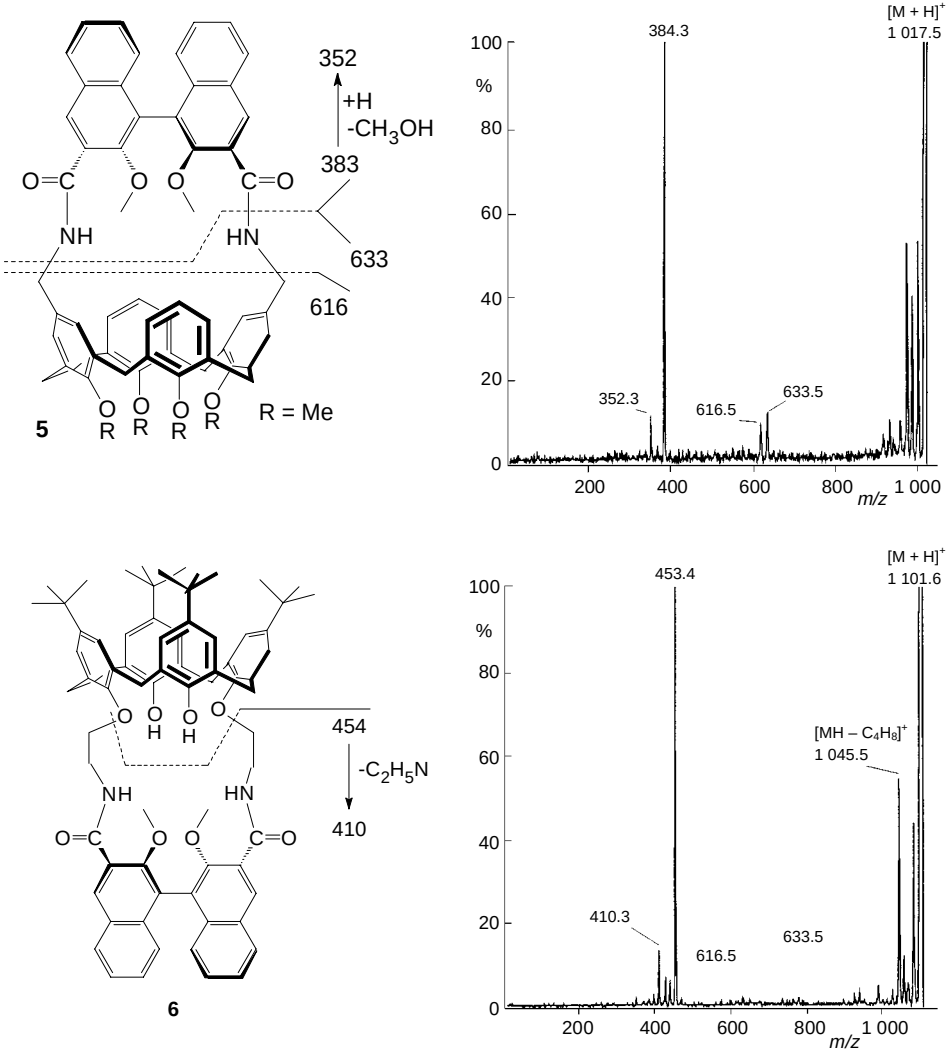
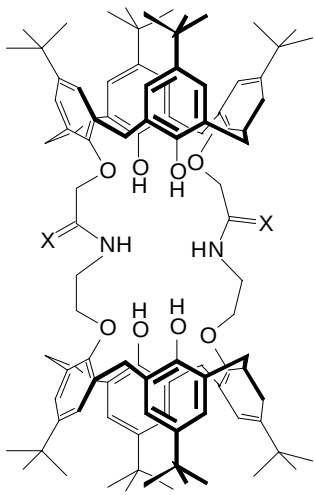


FIG. 1
Structures and FAB-MS of capped calix[4]arenes **5** (R = $CH_3CH_2CH_2$–) and **6**

probably differing in orientation of the amide groups. This phenomenon is now studied in detail. The NMR data have justified the inclusion-type complexation. No detectable inclusion was observed for the following substrates: chloroacetonitrile, dimethylformamide, methyl acetate, acetone, methanol, butylamine, benzene, toluene, pyridine, nitrobenzene, and benzonitrile.



	X
7	O
8	2H

In conclusion, we have developed a method for binaphthol-capping of calix[4]arene moiety on the lower- as well as the upper-rim. In addition, we have synthesized a new biscalixarene crown-type macrocycle.

EXPERIMENTAL

Temperature data are uncorrected, the isolated compounds have been dried in vacuo for 8 h (or overnight), solvents were evaporated on a rotatory evaporator at 40 °C. NMR spectra (δ, ppm; *J*, Hz) with TMS as internal standard were recorded on the Varian Gemini 300 HC spectrometer in $CDCl_3$ at 298 °C. All mass spectra were recorded on the double-focusing instrument Finnigan MAT 90 (Finnigan MAT, Brement, Germany) of BE geometry. For fast atom bombardment (FAB) ionisation the standard saddle field gun (Ion Tech Ltd, Teddington, England) was operated at 2 mA current and 6 kV energy using xenon as bombarding gas (10^{-3} Pa). *meta*-Nitrobenzyl alcohol (Aldrich) was used as a matrix. The liquid nitrogen baffle was mounted on the ion source to cool the FAB volume during the operation. The calibration was performed with Ultramark 1600F (PCR Inc., Gainesville, U.S.A.) as a standard. The products of collisionally activated decompositions in the first field-free region of the instrument were analyzed by daughter-ion linked scan (B/E constant) using manufacturer's software. The collision gas (He) pressure was adjusted for 50% attenuation of the primary ion beam, with collision cell voltage maintained at the ground potential. The mass range was scanned at a rate of 5 amu/s and conventional resolution of the instrument was adjusted to 2 000 (10% valley definition). For high-resolution measurements a rotatable FAB target was used with sample deposited on one side and Ultramark 1600F as a standard on the other side. For the peak-matching procedure the instrument was tuned to a resolution of 10 000 (10% valley definition). Positive-ion electron impact spectrum of **5**

was recorded at 70 eV ionizing energy, source temperature 200 °C, emission current 0.5 mA, accelerating voltage 5 kV, direct inlet, DIP temperature 300 °C. Sample was dosed in microgram amount for evaporation. High resolution measurements were carried out by the peak-matching method using Ultramark 1600F as a standard. The instrument was tuned to a resolution of 8 000 (10% valley definition).

Calix[4]arene **1c**

To a stirred solution of **1a** (ref.[31], 50 mg, 0.067 mmol) and triethylamine (0.02 ml, 0.14 mmol) in dry benzene (1 ml) the solution of benzoyl chloride (50 mg, 0.14 mmol) in dry benzene (1 ml) was added dropwise at room temperature. After one hour the reaction mixture was diluted with 5 ml of benzene, washed with aqueous 1 M HCl and water, dried, and evaporated. The residue was submitted to the preparative (silica gel, $CHCl_3$–acetone 10 : 1) TLC to give **1c** (52 mg, 82%). ^{1}H NMR spectrum: 7.72–7.16 m, 10 H (H arom.); 6.87 s, 4 H (H arom.); 6.79 d, 4 H, J = 7 (H arom.); 6.68 t, 2 H, J = 7 (H arom.); 4.54 d and 3.18 d, 8 H, J = 13.3 (4 × $ArCH_2Ar$); 4.20 t and 4.09 t, 8 H, J = 5.5 (4 × $ArOCH_2$); 3.89 t and 3.85 t, 8 H, J = 5.5 (4 × $ArOCH_2C\mathbf{H}_2O$); 3.57 q and 3.55 q, 8 H, J = 5.5 (4 × $OC\mathbf{H}_2CH_3$); 1.23 t and 1.22 t, 12 H, J = 5.5 (4 × $OCH_2C\mathbf{H}_3$).

Calix[4]arene **1d**

A solution of **1a** (ref.[31], 50 mg, 0.067 mmol), L-Boc-alanine (26 mg, 0.14 mmol) and DCC (18 mg, 0.14 mmol) in dry DMF (5 ml) was stirred for 24 h at room temperature. The solvent was evaporated and the residue was submitted to the preparative HPLC (20 × 2 cm column Tessek C-18, 10 μm, methanol–water 9 : 1) to give **1d** (34 mg, 47%). ^{1}H NMR spectrum: 8.71 s, 2 H (2 × NH); 7.13 d and 6.93 d, 4 H, J = 7 (H arom.); 6.82 t, 2 H, J = 7 (H arom.); 4.48 d, 4.47 d and 3.21 d, 3.07 d, 8 H, J = 13.5 (4 × $ArCH_2Ar$); 4.35–3.8 m, 10 H (2 × $NHC\mathbf{H}CH_3$, 4 × $ArOCH_2$); 3.87 t and 3.75 t, 8 H, J = 6 (4 × $ArOCH_2C\mathbf{H}_2$); 3.57 q and 3.51 q, 8 H, J = 7 (4 × $OC\mathbf{H}_2CH_3$); 1.46 s, 18 H (2 × *t*-Bu); 1.32 bd, 6 H (2x $NHCHC\mathbf{H}_3$); 1.24 t and 1.16 t, 12 H, J = 7 (4 × $OCH_2C\mathbf{H}_3$).

Calix[4]arene **1e**

Tetra-*O*-acetyl-D-ribonic acid chloride (48 mg, 0.14 mmol) was added to a stirred solution of **1a** (ref.[31], 50 mg, 0.07 mmol) and triethylamine (0.02 ml, 0.14 mmol) in dry benzene (1 ml) at room temperature. The reaction was monitored by TLC and was found to be complete within 4 h. The solvent was evaporated and the residue submitted to the preparative TLC (silica gel, $CHCl_3$–ethanol 10 : 1) to give **1e** (88 mg, 95%). ^{1}H NMR spectrum: 7.74 s, 2 H (H arom.); 7.37 s, 4 H (H arom.); 6.52–6.36 m, 2 H (2 × $C\mathbf{H}OCOCH_3$); 5.66–5.56 m, 2 H (2 × $C\mathbf{H}OCOCH_3$); 5.48–5.40 m, 2 H (2 × $C\mathbf{H}OCOCH_3$); 4.50 d, 4 H, J = 13 (4 × H_{ax} of $ArCH_2Ar$); 4.40–4.30 m, 4 H (2 × $C\mathbf{H}_2OCOCH_3$); 4.18 t and 4.05 t, 8 H, J = 7 (4 × $ArOCH_2$); 3.85 t and 3.81 t, 8 H, J = 7 (4 × $ArOCH_2C\mathbf{H}_2O$); 3.58–3.46 m, 8 H (4 × $OC\mathbf{H}_2CH_3$); 3.14 d and 3.13 d, 4 H, J = 13 (4 × H_{eq} of $ArCH_2Ar$); 2.27 s, 2.07 s, 2.06 s, 1.81 s, 24 H (8 × CH_3CO); 1.22 t and 1.18 t, 12 H, J = 7 (4 × $OCH_2C\mathbf{H}_3$).

Methyl 2-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)acetate (**3d**)

A solution of 2,2′-dimethoxy-1,1′-binaphthalene-3-carbonyl chloride[28] (1.0 g, 2.65 mmol) in dry benzene (20 ml) was added dropwise to a solution of diazomethane (2.8 g, 67 mmol) in ether (100 ml) at –5 °C. The mixture was allowed to warm to room temperature, stirred for 2 h, excess of diazomethane was decomposed by careful addition of acetic acid in dry benzene. Solvents were evaporated to give 1.02 g of yellowish crude diazoketone that was used without purification in the next step.

Silver oxide (65 mg) in methanol (3 ml) was added portionwise to refluxing suspension of crude diazoketone (0.65 g, 1.7 mmol) in methanol (30 ml) and reaction mixture was stirred at reflux for 3 h, then activated charcoal was added and all solids were filtered off. The filtrate was evaporated to dryness to give 0.55 g (84%) of methyl 2-(2,2′-dimethoxy-1,1′-binaphthalen-3-yl)acetate (**3d**). ^{1}H NMR spectrum: 8.01 d, 1 H, *J* = 9 (H arom.); 7.91–7.81 m, 2 H (H arom.); 7.47 d, 1 H, *J* = 9 (H arom.); 7.41–7.09 m, 7 H (H arom.); 3.91 s, 2 H (ArC**H**$_2$COOCH$_3$); 3.81 s, 3 H (ArOCH$_3$); 3.74 s, 3 H (ArCH$_2$COOC**H**$_3$); 3.30 s, 3 H (ArOCH$_3$).

2-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)acetic Acid (**3e**)

A mixture of methyl ester **3d** (0.52 g, 1.35 mmol) and 10% methanolic KOH (50 ml) was refluxed for 5 h. After evaporation of MeOH, water (50 ml) was added to the residue and the solution was acidified with concentrated HCl to give 0.45 g (90%) of the desired acid as a white precipitate. ^{1}H NMR spectrum (CD_3SOCD_3): 8.13 d, 1 H, *J* = 9 (H arom.); 7.98–7.88 m, 3 H (H arom.); 7.66 d, 1 H, *J* = 9 (H arom.); 7.40 t, 1 H, *J* = 7.5 (H arom.); 7.34 t, 1 H, *J* = 7.5 (H arom.), 7.24 t, 2 H, *J* = 7.5 (H arom.); 6.93 t, 2 H, *J* = 9 (H arom.); 3.79 s, 2 H (ArC**H**$_2$COOH); 3.78 s, 3 H (ArOCH$_3$); 3.23 s, 3 H (ArOCH$_3$).

2-(2,2′-Dimethoxy-1,1′-binaphthalen-3-yl)acetic Acid Chloride (**3f**)

A mixture of acid **3e** (200 mg, 0.52 mmol), thionyl chloride (1 ml) and dry benzene (2.5 ml) was refluxed for 3 h and evaporated to dryness to give 206 mg (98%) of crude acid chloride, that was used without purification in the next step.

Calix[4]arenes **4**. General Procedure

The solution of chloride **3** (0.2 mmol) in dry dichloromethane (5 ml) was added dropwise to a stirred solution of a diamine **1** (0.1 mmol) and triethylamine (22 mg, 0.22 mmol) in dry dichloromethane (5 ml) at room temperature. After completion of the addition (within 15–30 min) the reaction mixture was stirred for another 15 min, washed with 1 M HCl (10 ml), water (2 × 10 ml), and dried. Solvent was evaporated and the residue was submitted to the preparative TLC (silica gel, chloroform–acetone 10 : 1) to give the product.

Calixarene **4a** was prepared from **1b** and **3b** in 54% yield. ^{1}H NMR spectrum: 8.78 s, 2 H (H arom.); 8.06–7.02 m, 30 H (H arom.); 6.71 s, 4 H (H arom.); 5.78 s, 2 H (2 × CONH); 4.41 d and 3.17 d, 8 H, *J* = 13 (4 × ArC**H**$_2$Ar); 3.86 t and 3.63 t, 8 H, *J* = 7.5 (4 × ArOC**H**$_2$); 3.51 s, 4 H (2 × ArC**H**$_2$NH); 3.26 s and 3.16 s, 12 H (4 × ArOCH$_3$); 2.26–1.72 m, 8 H (4 × OCH$_2$C**H**$_2$CH$_3$); 1.02 t and 0.97 t, 12 H, *J* = 7.5 (4 × OCH$_2$CH$_2$C**H**$_3$).

Calixarene **4b** was prepared from **1a** and **3f** in 46% yield. ^{1}H NMR spectrum: 8.02–7.04 m, 30 H (H arom. and CONH); 6.72 s, 4 H (H arom.); 4.48 d and 3.16 d, 8 H, *J* = 13 (4 × ArC**H**$_2$Ar); 4.19 t and 4.10 t, 8 H, *J* = 5.5 (4 × ArOC**H**$_2$CH$_2$); 3.89 t and 3.84 t, 8 H, *J* = 5.5 (4 × ArOCH$_2$C**H**$_2$O); 3.61 s, 4 H (2 × ArCH$_2$CO); 3.56 q and 3.54 q, 8 H, *J* = 5.5 (4 × OC**H**$_2$CH$_3$); 3.19 s and 3.06 s, 12 H (4 × ArOCH$_3$); 1.22 t and 1.21 t, 12 H, *J* = 5.5 (4 × OCH$_2$C**H**$_3$).

Calixarene **4c** was prepared from **1b** and **3f** in 57% yield. ^{1}H NMR spectrum: 8.04–7.02 m, 28 H (H arom.); 6.94 s, 4 H (H arom.); 5.43 s, 2 H (2 × CONH); 4.40 d and 3.16 d, 8 H, *J* = 13 (4 × ArCH$_2$Ar); 3.87 t and 3.68 t, 8 H, *J* = 7.5 (4 × ArOC**H**$_2$CH$_2$CH$_3$); 3.58 s, 4 H (2 × ArCH$_2$CO); 3.51 s and 3.37 s, 12 H (4 × ArOCH$_3$); 3.47 s, 4 H (2 × ArCH$_2$NH); 2.23–1.72 m, 8 H (4 × OCH$_2$C**H**$_2$CH$_3$); 1.04 t and 1.01 t, 12 H, *J* = 7.5 (4 × OCH$_2$CH$_2$C**H**$_3$).

Macrocyclization. General Procedure for Synthesis of Ligands **5**, **6**, **7**

Solutions of a diamine (0.1 mmol) in dry benzene (5 ml) and an acyl chloride (0.1 mmol) in dry benzene (5 ml) were added simultaneously via two motor-driven syringes to a stirred solution of triethylamine (22 mg, 0.22 mmol) in dry benzene (100 ml) at the reflux in an inert atmosphere. The addition time was approximately 3.5 h. The reaction mixture was cooled, evaporated to dryness, and the solid residue was submitted to column or preparative thin layer chromatography (silica gel and eluent specified below).

Ligand (±)-**5** was isolated by preparative TLC (R_F 0.7, chloroform–acetone 10 : 1) in 14% yield. M.p. >270 °C. For $C_{66}H_{68}N_20_8$ (1 017.3) calculated: 77.93% C, 6.74% H; found: 77.32% C, 6.51% H. ^{1}H NMR spectrum: 8.85 s, 2 H (H arom.); 8.04 d, 2 H, J = 8 (H arom.); 7.56 d, 2 H, J = 8 (H arom.); 7.45 t, 2 H, J = 7.5 (H arom.); 7.32 t, 2 H, J = 7.5 (H arom.); 7.17 t, 2 H, J = 7.5 (H arom.); 7.02 d, 2 H, J = 8 (H arom.); 6.97 s, 2 H (H arom.); 6.61 t, 2 H, J = 6 (H arom.); 4.43 d and 4.42 d, 3.20 d and 3.13 d, 8 H , J = 12 (4 × $ArCH_2Ar$); 3.90 t and 3.69 t, 8 H, J = 7.5 (2 × $ArOCH_2$); 2.47 s, 6 H (2 × $ArOCH_3$); 2.24–1.78 m, 8 H (4 × $OCH_2C\mathbf{H}_2CH_3$); 1.03 t and 0.99 t, 12 H, J = 7.5 (4 × $OCH_2CH_2C\mathbf{H}_3$). Mass spectrum (EI), *m/z* (rel. int.): 1 016.497 (M+, 100). For $C_{66}H_{68}N_20_8$ calculated: 1 016.498.

Ligand (–)-**5** was isolated using the same procedure in 12% yield, having identical spectral data. For $C_{66}H_{68}N_20_8$ (1 017.3) calculated.: 77.93% C, 6.74% H; found: 77.54% C, 6.49% H. $[\alpha]_{589}^{25}$ –50° (dichloromethane, *c* 0.04).

Ligand **6** was isolated by preparative TLC (R_F 0.5, chloroform–acetone 20 : 1) in 31% yield. M.p. >220 °C. For $C_{72}H_{80}N_2O_8$ (1 101.4) calculated: 78.52% C, 7.32% H; found: 78.92% C, 7.12% H. ^{1}H NMR spectrum: 9.06 t, 2 H, J = 5.5 (NH); 8.82 s, 2 H (H arom.); 8.07 d, 2 H, J = 7.5 (H arom.); 7.50 t, 2 H, J = 7.5 (H arom.); 7.39 t, 2 H, J = 7.5 (H arom.); 7.30 d, 2 H, J = 7.5 (H arom.); 7.04 s, 4 H (H arom.); 6.63 s, 2 H (H arom.); 6.62 s, 2 H (H arom.); 6.02 s, 2 H (H arom.); 4.36–4.0 m, 10 H (4 × H_{ax} of $ArCH_2Ar$ and 2 × $ArOCH_2$); 3.82–3.78 m, 2 H ($ArOCH_2$); 3.32 d, 4 H, J = 13 (4 × H_{eq} of $ArCH_2Ar$); 3.17 s, 6 H (2 × $ArOCH_3$); 1.29 s, 18 H (2 × *t*-Bu); 0.83 s, 18 H (2 × *t*-Bu). Mass spectrum (FAB), *m/z* (rel. int., %): 1 101.581 (M^+ + H, 5.5). For $C_{72}H_{81}N_2O_8$ calculated: 1 101.599.

Ligand (–)-**6** was isolated using the same procedure in 27% yield, having identical spectral data. For $C_{72}H_{80}N_2O_8$ (1 101.4) calculated: 78.52% C, 7.32% H; found: 78.74% C, 7.16% H. $[\alpha]_{589}^{25}$ –92.3° (dichloromethane, *c* 0.065).

Ligand **7** was isolated by column chromatography with chloroform as eluent. TLC: R_F 0.6, chloroform–acetone 10 : 1. M.p. 219 °C. For $C_{96}H_{122}N_2O_{10}$ (1 464.1) calculated: 78.76% C, 8.40% H; found: 78.96% C, 8.57% H. ^{1}H NMR spectrum: 9.01 t, 2 H (2 × NH); 8.56 s, 2 H (2 × ArO**H**); 7.04 s, 4 H (H arom.); 6.96 s, 4 H (H arom.); 6.95 s, 4 H (H arom.); 6.74 s, 4 H (H arom.); 6.51 s, 2 H (2 × ArO**H**); 4.53 s, 4 H (2 × OCH_2CO); 4.3–4.1 m, 16 H (2 × OCH_2CH_2N and 8 × H_{ax} of $ArCH_2Ar$); 3.24 d and 3.20 d, 8 H, J = 13 (8 × H_{eq} of $ArCH_2Ar$); 1.33, 1.24, 1.12, 0.92, 4 s, 72 H (8 × *t*-Bu). Mass spectrum (FAB), *m/z* (rel. int., %): 1 463.914 (M^++ H, 20). For $C_{96}H_{123}N_2O_{10}$ calculated 1 463.918.

Ligand **8**. To a solution of **7** (50 mg, 0.034 mmol) in dry THF (5 ml), 1 M BH_3 in THF (2 ml, 2 mmol) was added dropwise under nitrogen. The reaction mixture was then stirred at 70 °C for 7 h. After being cooled, the solution was carefully hydrolyzed by addition of water (5 ml) and the solvent was distilled off. The residue was refluxed for 8 h with 6 M HCl (20 ml). The acidic solution was evaporated to dryness in vacuo. 2 M NaOH (5 ml) was added to the residue and the mixture was extracted with dichloromethane (2 × 10 ml). The organic solution was dried over $MgSO_4$ and evaporated to dryness to give 39 mg (80%) of a white solid. M.p. >190 °C (decomp.). For $C_{96}H_{128}N_2O_8$ (1 438.1) calculated: 80.18% C, 8.97% H; found: 80.38% C, 8.83% H. ^{1}H NMR spectrum: 7.07 s, 4 H (4 × ArO**H**); 7.05 s and 7.03 s, 16 H (H arom.); 4.38 d and 3.39 d, 16 H, J = 13 (8 × $ArCH_2Ar$); 4.24 t, 8 H, J = 6 (4 × $ArOCH_2$); 3.55 t, 8 H, J = 6 (4 × NCH_2); 1.26 s and 1.15 s, 72 H (8 × *t*-Bu).

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