Linear and Macrocyclic Molecular Thread, Ribbon and Belt Assemblies of Nanometric Scale

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Abstract: The hitherto longest molecular thread-belt assemblies **8**, **29**, **32** and **43** based on benzene-connected [3.3]metacyclophane units were prepared by means of a repetitive synthetic method. The preparation of difunctionalized [3.3]metacyclophane units (**14**, **22**, **26**) succeeded in good yields by an iteration sequence including the cyclization to the cyclophane skeleton and the derivatization of the ester groups. The covalent linkage of the [3.3]metacyclophane belt parts to the thread part leads to higher product yields compared to cyclophane belts only. The final intermolecular macrocyclizations are done by reaction of diamide, dithiol or dibromide functionalized belt fragments to obtain a minimum of single bridged benzene units in the macrocyclic thread-belt assemblies ("pseudobelts").

Keywords: Cyclophanes, macrocycles, molecular ribbons, nanostructures, repetitive synthesis

Introduction

In supramolecular chemistry[1] and especially in nanochemistry[2] macrocyclic and concave hydrocarbons play an important role. Nanometric scale molecules are fascinating due to their often appealing architecture, high symmetry and host-guest interactions. Efforts on the way to $[0]_n$-paraphenylenes[3] **1** have been reported. Concrete belt shaped hydrocarbons like **2** and **5** had been postulated more than ten years ago[4]. At present several research groups are working on the synthesis of belt shaped molecules and particularly belt shaped hydrocarbons[5] like **3** and **4**, yet no genuine cyclic polyacene has been prepared[6] so far (Figure 1).

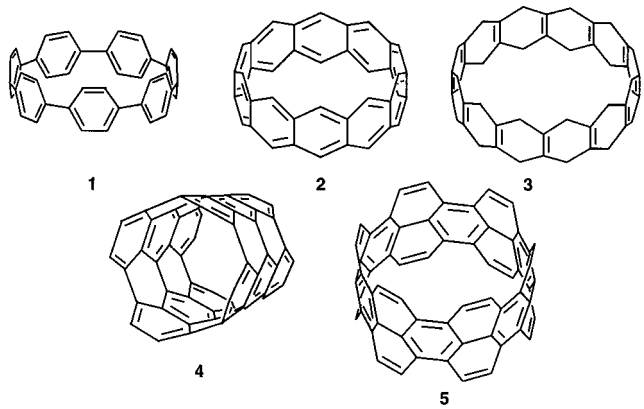
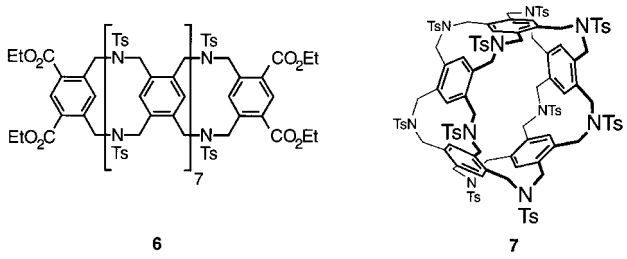


Figure 1 Belt-shaped synthetic targets **1–5**

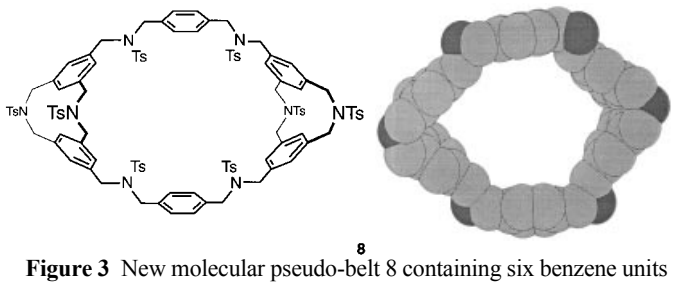
One possible strategy for the synthesis of molecular belts starts with the formation of molecular ribbons based on [3.3]metacyclophane units, which can then be macrocyclized making use of four functional groups. For that we developed a repetitve synthetic strategy[7]. Following this we prepared structure-perfect molecular ribbons like **6** with up to nine benzene units[8] and molecular belts like **7** containing five benzene units[9] (Figure 2). Mass spectrometry revealed molecular belts with up to 30 benzene units[9], but their separation met with difficulties. As a consequence it seems that avoiding oligomeric macrocycles by structure directed synthesis of every single belt is the better choice presently.



6 7

Figure 2 Longest known tetrafunctionalized molecular ribbon **6** and molecular belt **7**

A problem on the way to longer molecular belts was the final macrocyclization step with low yields due to the high number of covalent bonds which have to be formed[9,10]. The new strategy described here bases on the following consideration: The substitution of one or more [3.3]metacyclophane[11] bridges by single bridges of the same character should result in higher flexibility and solubility of the macrocycle. Two times covalently linking of difunctionalized belt fragments (that can include [3.3]metacyclophane units) should also lead to higher yields of the macrocycle as the formation of cyclization by-products is prevented. Furthermore, the preparation of the belt precursors is then carried out more easily and in good yields. According to space filling models the mixed thread-belt macrocycles still look very similar to molecular belts and like those we described earlier[9] (cf. Figure 3). The waist of the molecular belt is hardly seen by looking on space filling models. Yet with increasing number of single-bridged benzene units the ribbon structure is hampered. In the following we report on the preparation of the first examples of such tied molecular pseudo-belts based on [3.3]metacyclophane units including the longest yet synthesized and fully characterized molecular "pseudo-



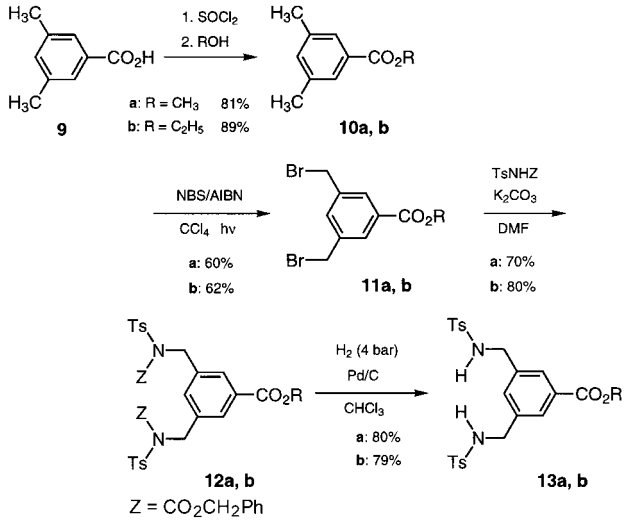
8

Figure 3 New molecular pseudo-belt 8 containing six benzene units

beltane"[12] **8** containing six benzene rings connected in the 38-membered macrocycle (Figure 3).

Results and Discussion

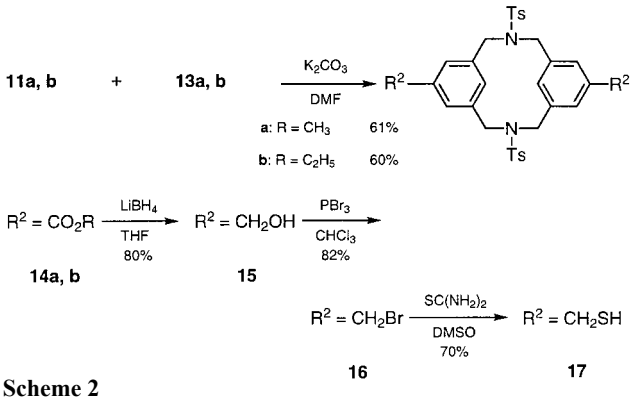
The synthesis of the monofunctionalized diamide **13** follows similar steps as the synthesis of the corresponding difunctionalized diamide 2,4-bis[*N*-(4-tolylsulfonyl)aminomethyl]-1,5-bis(ethoxycarbonyl)benzene formerly prepared in 14% yield[7,8,13], but as anticipated (see introduction) the total yield is more than twice as high (**13**: 35%, Scheme 1).



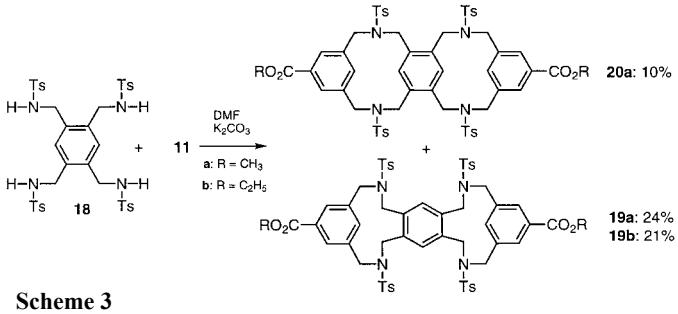
Scheme 1

The intermolecular cyclization of dibromide **11** and diamide **13** to the 6,15-difunctionalized metacyclophane skeleton **14** with terminal ester groups succeeded under high-dilution conditions[14] in 60–61% yield. The cyclization of dibromide **11** with TosNHNa[15] afforded the cyclophane unit in one step only, but in lower yields. In connection with the formation of the 12-membered [3.3]metacyclophane ring system the derivatization of the terminal ester group lead to the corresponding alcohol **15**, bromide **16** and thiol **17** (Scheme 2).

The synthesis of [3.3]metacyclophane ribbons including three to five benzene units was succeeded using the known procedures adapted from the synthesis of the tetrafunctionalized molecular ribbons (cf. **6**). By double intermolecular cyclization of dibromide **11** and 1,2,4,5-tetrakis[*N*-(4-tolylsulfonyl)aminomethyl]benzene[9] **18** we obtained the *meta/meta*-cyclophane **19b** in 10% yield and *meta/para*-cyclophane **20** in 21–24% yield (Scheme 3). Separation of the isomeric mixture is possible by extraction of **20** in ethyl acetate (residue: **19**).

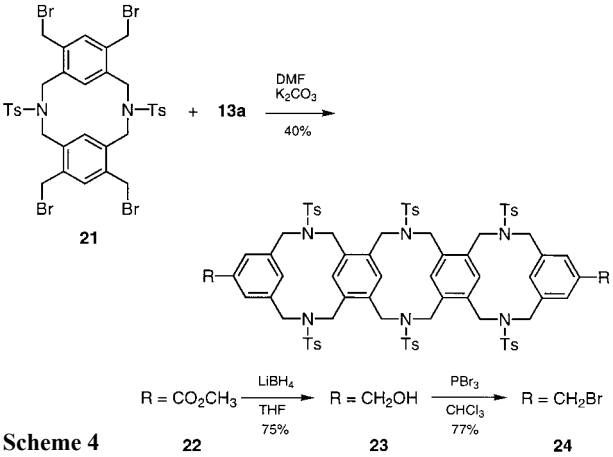


Scheme 2



Scheme 3

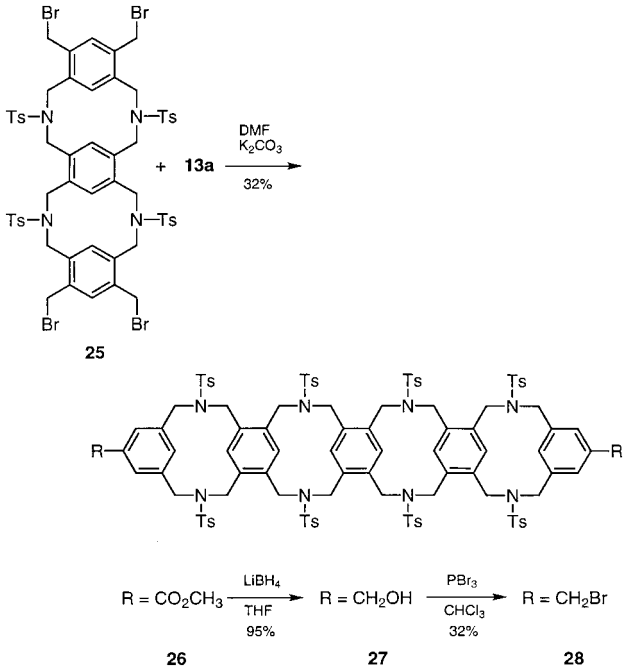
The cyclophanes **22–24** and **26–28** containing four and five benzene units respectively are the first examples in the series of difunctionalized molecular ribbons where the repetition sequence is used twice. The cyclophane tetrabromides **21**[13] and **25**[7–9] are obtained after one complete repetitive reaction sequence of intermolecular cyclization, reduction and bromination in the synthesis sequence of tetrafunctionalized molecular ribbons. The difunctionalized [3.3][3.3][3.3]cyclophane **22** is prepared in 40% yield from diamide **13a** and cyclophane tetrabromide **21** (Scheme 4). The yields for the derivatization reactions to



Scheme 4

dialcohol **23** and dibromide **24** of this cyclophane are as high as in the [3.3]cyclophane system **14**.

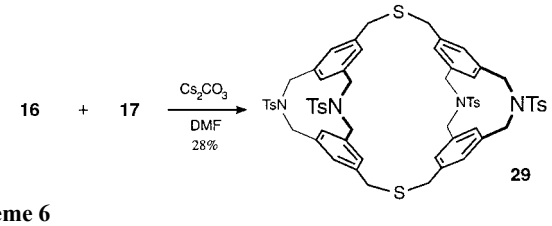
[3.3][3.3][3.3][3.3]Cyclophane **26** with a sequence of five benzene units is formed by the reaction of tetrabromide **25** and diamide **13a** (Scheme 5). The solubility of this cyclophane diester is low and only after derivatization to the corresponding dibromide **28** a characterization was possible.



Scheme 5

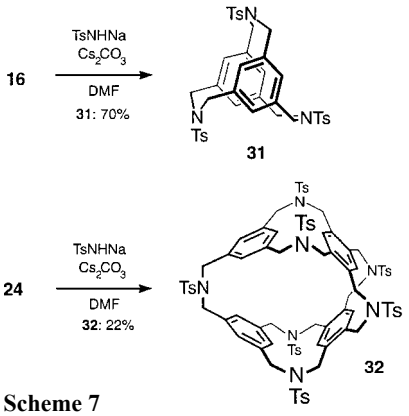
In the final macrocyclizations generating pseudobeltanes (cf. **8**, **29**, **32**, **38**, **40**, **41** and **43**) always a difunctionalized cyclophane bromide (**16** and **24**) is used as one of the cyclization compounds reacting intramolecularly with TsNHNa (Scheme 7) or intermolecularly with a dithiol (Scheme 6) or diamide (Schemes 9, 10 and 12), both of which can include cyclophane units.

Pseudobeltane **29** containing four benzene units can be prepared under high-dilution conditions in 28% yield from the cyclophane dibromide **16** and the cyclophane dithiol **17**. A comparison to 3% macrocyclization yield using tetrafunctionalized cyclophane units[13] to generate beltane **30**[9,10,13] demonstrates the advantage of this new approach (Scheme 6).



Scheme 6

Intramolecular cyclization of dibromide **16** and dibromide **24** using TsNHNa leads to pseudobeltanes **31**[16] and **32** containing two and four benzene units (Scheme 7).



Scheme 7

There is only little difference in the belt shape as one compares the space filling-models of pseudobeltanes **29** and **32** and completely cyclophane bridged beltanes **30**[9,13] and **33** generated from tetrafunctionalized molecular ribbons (Figure 4). Single bridges in parts of the belt are seemingly only of low influence for the gross appearence.

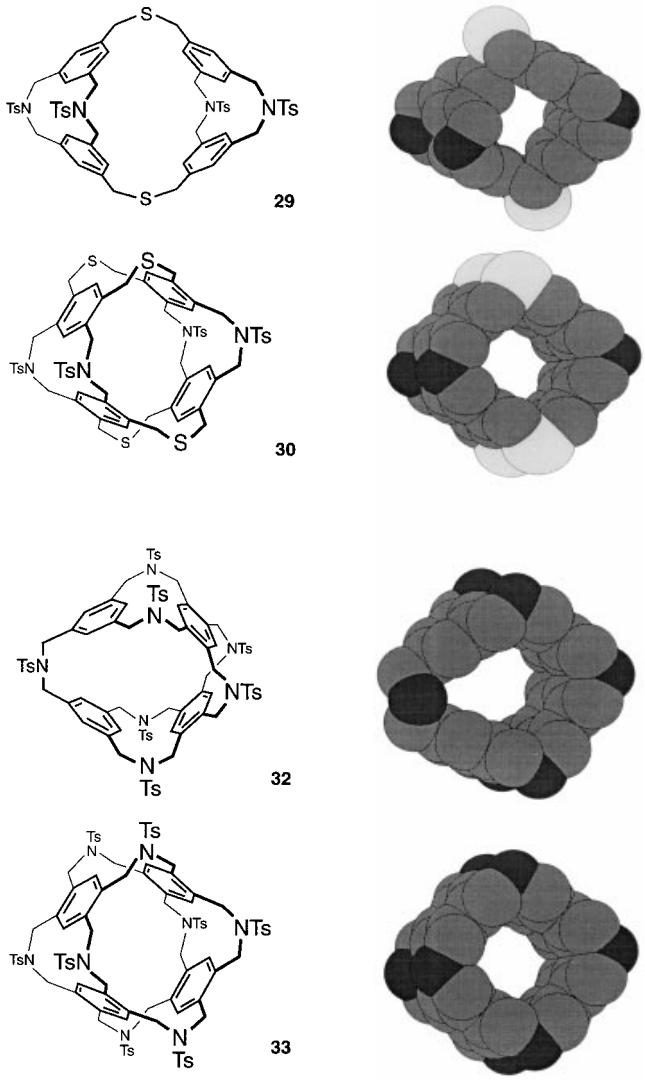
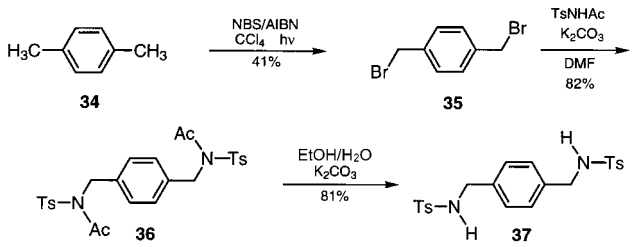


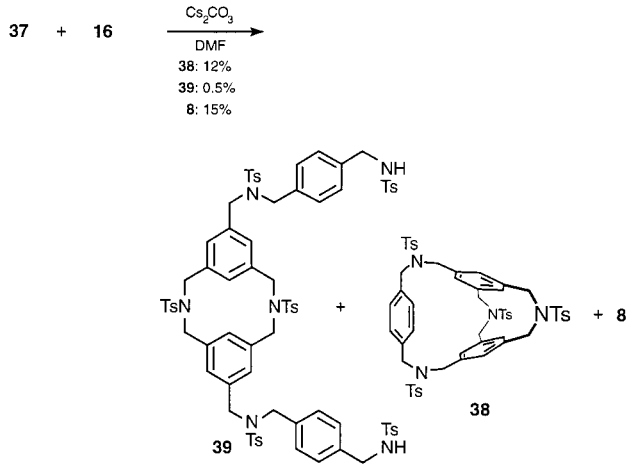
Figure 4 Space filling models of pseudobeltanes **29, 32** in comparison to beltanes **30, 33**

The smallest intermolecular possibility for macrocyclization to benzene based pseudobeltanes is the cyclization with the *p*-xylene-bis(tosylamide) **37**. The yield of this amide is even 10% higher than the yield of the known durene based tetraamide **18**[9] to generate tetrafunctionalized molecular ribbons and genuine belts[9,13,17] derived from these (Scheme 8).



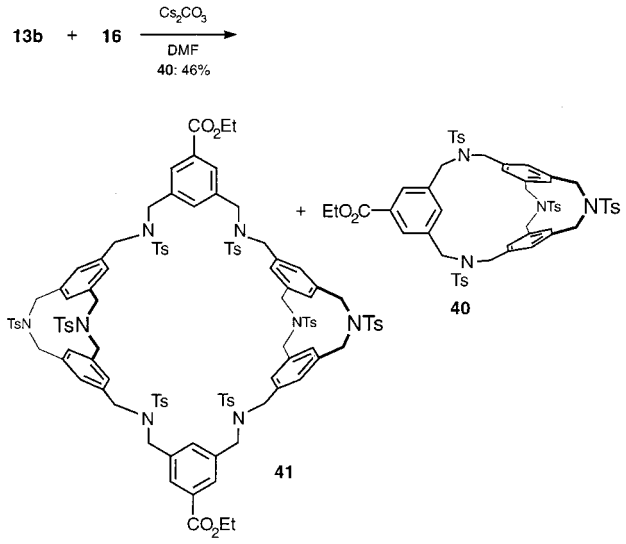
Scheme 8

In contrast to published procedures the following final macrocyclization was not carried out under high-dilution conditions by simultaneous and dropwise addition of the cyclization components to a suspension of potassium carbonate in DMF. In this case the cyclophane dibromide **16** is added dropwise to a suspension of the diamide **37** and caesium carbonate in DMF[18]. The idea was to build up an intermediate spaced diamide to favour a 2:2-cyclization product. Three products were isolated (Scheme 9): The 1:1-cyclization product **38**, a pseudobeltane containing three benzene units (12%), the cyclophane-spaced open diamide **39** (0.5%), and the 2:2-cyclization product **8**, a pseudobeltane containing six benzene units (15%). This pseudobeltane **8** is the biggest yet synthesized tied molecular belt by the synthetic strategy described.



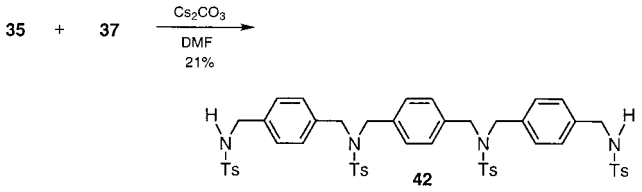
Scheme 9

Under analogous conditions the amide **13b** and bromide **16** were macrocylized to yield the pseudobeltanes **40** and **41** containing three and six benzene units with exocyclic ester groups (Scheme 10). The 2:2-cyclization product **41**, a pseudobeltane containing six benzene units, could not be isolated, but detected by mass spectrometry (MALDI and FAB).



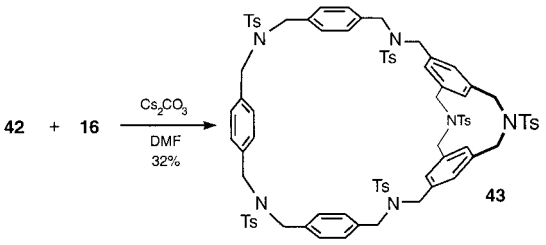
Scheme 10

A molecular belt **43** with a size of five benzene units we prepared with a new thread-like bistosylamide precursor **42** containing three benzene units. This precursor **42** can be synthesized in only four steps (Scheme 11).



Scheme 11

In the cyclophane series the tosylamide function could only be prepared in low yields following repetitive sequences of steps that failed in the preparation of longer molecular ribbons and belts[9,13,19]. In this former strategy we carried out one cyclization step to form the cyclophane skeleton and a sequence of reactions to refunctionalize the terminal functional groups. An advantage of the synthesis of the thread-like bis(tosylamide) **42** is that the skeleton and the tosylamide function is obtained in only one step adding the dibromide **35** dropwise to a suspension of the diamide **37** and caesium carbonate in DMF. Formation of cyclic side ([3.3]-and [3.3.3.3]paracyclophane) products was observed (MS, *vide infra*). Additionally it was not necessary to use the less soluble and less stable dithiol compounds in the final cyclization. The preparation of the



Scheme 12

molecular belt **43** with a size of five benzene units was successful in 32% macrocyclization yield (Scheme 12) using this new toslyamide **42** compared to 9% for a fourfold covalent linkage using tetrafunctionalized cyclophane precursors[9]. The 2:2-cyclization product, a pseudobeltane containing ten benzene units, could not be found.

In all reactions leading to large ring molecules like **8** and **26,** side products, especially higher cyclic oligomers, were formed and detected by MALDI-MS in the crude product, but the isolation was not successful. Formation of catenanes and polycondensed networks was not observed.

Conclusions

The synthetic strategy presented here demonstrates a route to tied molecular pseudobeltanes based on difunctionalized [3.3]cyclophane units. All procedures are carried out in good yields compared to the preparation of tetrafunctionalized ribbons and belts. The synthesis of spaced bis(tosylamides) is a key step to obtain longer cyclizable molecules in less steps and in good total and macrocyclization yields. Due to the higher flexibility of these corded up belts further reactions should be possible. The detosylation[20] of the connecting bridges, the nitrosation of the resulting free secondary amine, the extrusion of N_2O[21] and subsequent reduction will lead to belt shaped hydrocarbons based on [2.2]metacyclophane units.

Pseudobelts of the types described above are of interest as host molecules having cavities of the size of cyclodextrins. Substituting benzene units by biphenyl or terphenyl building blocks should lead to longer molecular pseudobeltanes, and, after cyclization, to larger cavities inside. Such variations should make it possible to produce concave macrocyclic host molecules that fulfill the size requirement for a given guest. The aim will be to tune structure-property relationships ending up with new material properties[22], e.g. periodically arranged molecular tubes filled with known guests, e.g. from the cyclodextrins or chemoselective sensing.

Chemicals were purchased from Merck, Fluka and Aldrich and were used as received. DMF, CH_2Cl_2, and $CHCl_3$ were destilled and dried over 4 Å molecular sieve before use. THF was distilled from $LiAlH_4$ [indicator: Ph_3CH (red)]. Yields refer to chromatographically and spectroscopically homogeneous materials. All reactions were monitored by TLC carried out on aluminum sheets precoated with silica gel 60 F_{254} (Merck 1.05554). The sheets were visualized by UV light (λ = 254 nm). Column chromatography was carried out on silica gel 60 (Merck 15101). Melting points were determined on a Kofler microscope heater (Reichert, Wien) and are not corrected. Microanalyses were performed by the Microanalytical Department at the "Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn". IR spectra were recorded on a FT-IR-spectrometer (Perkin-Elmer Model 1600). GC/MS spectra were recorded on HP 5890 Serie II gas chromatograph and HP 5898 A (EI-MS) mass spectrometer from Hewlett Packard. Fast-atom bombardment (FAB-MS) mass spectra were obtained using a Kratos Concept 1 H spectrometer. The matrix used was *m*-nitrobenzyl alcohol (NBA). MALDI-TOF spectra were recorded on a Micromass Tof spec E spectrometer using 2,5-dihydroxybenzoic acid (DHB) as a matrix. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 [250 MHz (^1H), 62.9 MHz (^{13}C)] or a Bruker AM 400 [400 MHz (^1H), 100.6 MHz (^{13}C)] spectrometer at r.t. (20 °C) in commercial deuterated solvents (internal reference was the residual undeuterated solvent: $CHCl_3$, δ = 7.27; DMSO-d_6, δ = 2.5; DMF-d_6, δ = 2.74, 2.91, 8.05; CD_2Cl_2, δ = 5.31). The following abbrevations were used to indicate NMR-multiplicities and IR-intensities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); vs (very strong), s (strong), m (medium), w (weak).

1,4-Bis[*N*-acetyl-*N*-(4-tolylsulfonyl)aminomethyl]benzene (36)
A suspension of K_2CO_3 (82.93 g, 0.60 mol), 1,4-bis(bromomethyl)benzene (**35**;[23] 31.68 g, 0.12 mol) and *N*-acetyl-4-tolylsulfonamide (TsNHAc; 63.96 g, 0.60 mol) in anhyd DMF (500 mL) was stirred for 48 h under argon atmosphere. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (500 mL). The undissolved components were removed by filtration, and the filtrate was washed twice with H_2O, dried (Na_2SO_4), filtered, and concentrated to give a colourless substance, which was recrystallized from acetone to yield colourless crystals; R_f 0.79 ($CHCl_3$/acetone, 20:1); 52.02 g (82%); mp 194 °C.

FAB-MS (NBA): *m/z* = 567.1 $[M + K]^+$, 529.1 $[M + H]^+$.

^1H NMR (250 MHz, DMSO-d_6): δ = 2.21 (s, 6 H, Ac-CH_3), 2.38 (s, 6 H, Ts-CH_3), 5.06 (s, 4 H, NCH_2), 7.36 (s, 4 H, Ar-H), 7.45 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.68 (d, ^3J = 8 Hz, 4 H Ts-H).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 21.1 (Ts-CH_3), 24.3 (Ac-CH_3), 49.2 (NCH_2), 126.6 (CH), 127.7 (CH), 129.8 (CH), 136.1 (Cq), 139.2 (Cq), 144.8 (Cq), 170.8 (CO).

Anal. $C_{26}H_{26}N_2O_6S_2 \cdot 0.5\ H_2O$: calcd. C 58.08, H 5.44, N 5.21; found C 57.85, H 5.48, N 5.18.

1,4-Bis[(4-tolylsulfonylamino)methyl)]benzene (37)
A suspension of **36** (21.15 g, 40 mmol) and K_2CO_3 (49.76 g, 0.36 mol) in a mixture of EtOH (1 L) and H_2O (50 mL) was refluxed for 7 h. The solvent was evaporated, and the remaining residue treated with H_2O (250 mL) to dissolve the inorganic salts. The undissolved product was obtained by filtration; evaporation and recrystallization from acetone; R_f 0.75 ($CHCl_3$/MeOH, 20:1); 14.40 g (81%); mp 221 °C.

MALDI-TOF (DHB): *m/z* = 483.7 $[M + K]^+$.

FAB-MS (NBA): *m/z* = 483.1 $[M + K]^+$, 445.1 $[M + H]^+$.

^1H NMR (250 MHz, DMSO-d_6): δ = 2.38 (s, 6 H, Ts-CH_3), 4.04 (s, 4 H, NCH_2), 7.06 (s, 4 H, Ar-H), 7.36 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.70 (d, ^3J = 8 Hz, 4 H, Ts-H).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 22.1 (Ts-CH_3), 45.9 (NCH_2), 126.6 (CH), 127.5 (CH), 129.6 (CH), 136.7 (Cq), 137.8 (Cq), 142.6 (Cq).

Anal. $C_{22}H_{22}N_2O_4S_2 \cdot C_2H_5OH$: calcd. C 59.00, H 5.76, N 5.73, S 13.12; found C 59.20, H 5.34, N 6.07, S 13.13.

1,4-Bis[*(N*-(4-tolylsulfonyl)aminomethyl)benzyl-*N*-(4-tolylsulfonyl)aminomethyl]benzene (42)
The dibromide **35** (0.79 g, 3.00 mmol) was dissolved in anhyd DMF (50 mL). This solution was added dropwise over 6 h to a suspension of Cs_2CO_3 (5.91 g, 18.00 mmol) and diamide **37** (8.00 g, 18.00 mmol) in anhyd DMF (250 mL) under argon atmosphere. The suspension was then stirred for further 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (300 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated to give a colourless substance, which was purified by column chromatogra-

phy (silica gel, $CHCl_3$/MeOH, 20:1); R_f 0.32 ($CHCl_3$/MeOH, 20:1); 0.62 g (21%); mp 96°C.

MALDI-TOF (DHB): *m/z* = 1013.7 $[M + Na]^+$.

FAB-MS (NBA): *m/z* = 991.2 $[M]^+$, 835.3 $[M – Ts]^+$, 679.4 $[M – 2 Ts]^+$.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.35 (s, 6 H, Ts-CH_3), 2.41 (s, 6 H, Ts-CH_3), 3.86 (d, ^3J = 6 Hz, 4 H, NCH_2), 4.06 (s, 4 H, NCH_2), 4.16 (s, 4 H, NCH_2), 6.88 (s, 4 H, Ar-H), 6.90 (d, ^3J = 8 Hz, 4 H, Ar-H), 7.07 (d, ^3J = 8 Hz, 4 H, Ar-H), 7.34 (d, ^3J = 8 Hz, 4 H, Ar-H), 7.42 (d, ^3J = 8 Hz, 4 H, Ar-H), 7.65 (d, ^3J = 8 Hz, 4 H, Ar-H), 7.73 (d, ^3J = 8 Hz, 4 H, Ar-H), 8.02 (t, ^3J = 6 Hz, 2 H, NH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.9 (Ts-CH_3), 21.0 (Ts-CH_3), 45.7 (NCH_2), 50.3 (NCH_2), 50.4 (NCH_2), 126.5 (CH), 127.0 (CH), 127.4 (CH), 128.1 (CH), 128.2 (CH), 129.6 (CH), 129.9 (CH), 135.0 (Cq), 135.3 (Cq), 136.7 (Cq), 136.9 (Cq), 137.8 (Cq), 142.6 (Cq), 143.3 (Cq).

3,5-Bis[*N*-benzyloxycarbonyl-*N*-(4-tolylsulfonyl)aminomethyl)]benzoic Acid Alkyl Esters 12a,b

A suspension of K_2CO_3 (14.00 g, 0.10 mol), 3,5-bis(bromomethyl)benzoic acid alkyl ester (**11**;[24] 25 mmol, 8.05 g **11a**/8.40 g **11b**) and *N*-(4-tolylsulfonyl)benzylcarbamate (TsNHZ; 16.79 g, 55 mmol) in anhyd DMF (500 mL) was stirred for 72 h under argon atmosphere. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (300 mL). The undissolved components were removed by filtration, and the filtrate was washed twice with brine and twice with H_2O, dried (Na_2SO_4), filtered, and concentrated to give a crude oil, which was recrystallized from MeOH to yield colourless crystals.

Methyl Ester 12a

R_f 0.64 ($CHCl_3$/acetone, 20:1); 13.50 g (70%); mp 128°C.

FAB-MS (NBA): *m/z* = 771.1 $[M + H]^+$, 739.2 $[M – OCH_3]^+$, 605.1 $[M – OCH_3 – Z]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.38 (s, 6 H, Ts-CH_3), 3.88 (s, 3 H, OCH_3), 5.04 (s, 4 H, NCH_2), 5.09 (s, 4 H, O*C*H_2Ph), 7.14–7.32 (m, 10 H, Ar-H), 7.11 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.55 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.61 (t, ^4J = 2 Hz, 1 H, Ar-H), 7.97 (d, ^4J = 2 Hz, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts-CH_3), 46.1 (NCH_2), 52.2 (OCH_3), 69.2 (O*C*H_2Ph), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.3 (CH), 130.9 (Cq), 132.3 (CH), 134.3 (Cq), 136.0 (Cq), 137.8 (Cq), 144.6 (Cq), 152.2 (CO), 166.3 (CO).

Anal. $C_{40}H_{38}N_2O_{10}S_2$: calcd. C 62.32, H 4.97, N 3.63; found C 62.17, H 4.90, N 3.59.

Ethyl Ester 12b

R_f 0.68 ($CHCl_3$/acetone, 20:1); 15.70 g (80%); mp 119°C.

FAB-MS (NBA): *m/z* = 786.0 $[M + H]^+$, 739.2 $[M – OC_2H_5]^+$, 605.1 $[M – OC_2H_5 – Z]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 7 Hz, 3 H, CH_3CH$_2$O), 2.39 (s, 6 H, Ts-CH_3), 4.34 (q, ^3J = 7 Hz, 2 H, OCH_2), 5.04 (s, 4 H, NCH_2), 5.07 (s, 4 H, O*C*H_2Ph), 7.10–7.34 (m, 10 H, Ar-H), 7.11 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.58 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.60 (t, ^4J = 2 Hz, 1 H, Ar-H), 7.98 (d, ^4J = 2 Hz, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4 (*C*H_3CH$_2$O), 21.7 (Ts-CH_3), 49.5 (NCH_2), 61.2 (OCH_2), 69.3 (OCH_2Ph), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.3 (CH), 131.3 (Cq), 132.3 (CH), 134.5 (Cq), 136.1 (Cq), 137.8 (Cq), 144.7 (Cq), 152.4 (CO), 166.0 (CO). Anal. $C_{41}H_{40}N_2O_{10}S_2$: calcd. C 62.74, H 5.14, N 3.57, S 8.17; found C 62.47, H 5.15, N 3.46, S 8.12.

3,5-Bis[(4-tolylsulfonylamino)methyl]benzoic Acid Alkyl Esters 13a, b

A suspension of **12** (5 mmol, 3.85 **12a**/3.92 g **12b**) and catalyst (0.5 g, 10%-Pd on carbon) in $CHCl_3$ (100 mL) was stirred at r.t. for 6 h under an H_2 atmosphere (4 bar). The suspension was filtered through Celite and the filtrate was evaporated to give a colourless oil, which was purified by column chromatography (silica gel, $CHCl_3$/acetone, 10:1).

Methyl ester 13a

R_f 0.14 ($CHCl_3$/acetone, 20:1); 2.11 g (80%); mp 180°C.

FAB-MS (NBA): *m/z* = 525.1 $[M + Na]^+$, 503.1 $[M]^+$, 347.1 $[M – Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.39 (s, 6 H, Ts-CH_3), 3.87 (s, 3 H, OCH_3), 4.05 (br, 4 H, NCH_2), 7.24 (t, ^4J = 2 Hz, 1 H, Ar-H), 7.31 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.56 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.65 (d, ^4J = 2 Hz, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.1 (Ts-CH_3), 46.1 (NCH_2), 52.0 (OCH_3), 126.8 (CH), 127.8 (Cq), 129.5 (CH), 130.2 (Cq), 131.7 (CH), 136.8 (Cq), 137.7 (CH), 143.3 (Cq), 166.7 (CO).

Anal. $C_{24}H_{26}N_2O_6S_2$•2 H_2O: calcd. C 53.51, H 5.61, N 5.20; found C 53.17, H 5.11, N 5.17.

Ethyl ester 13b

R_f 0.18 ($CHCl_3$/acetone, 20:1); 2.02 g (79%); mp 151°C.

FAB-MS (NBA): *m/z* = 539.1 $[M + Na]^+$, 517.1 $[M]^+$, 361.1 $[M – Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, ^3J = 7 Hz, 3 H, CH_3CH$_2$O), 2.40 (s, 6 H, Ts-CH_3), 4.06 (d, ^3J = 6 Hz, 4 H, NCH_2), 4.30 (q, ^3J = 7 Hz, 2 H, OCH_2), 5.18 (t, ^3J = 6 Hz, 2 H, NH) , 7.27 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.31 (t, ^4J = 2 Hz, 1 H, Ar-H), 7.70 (d, ^3J = 8 Hz, 4 H, Ts-H), 7.72 (d, ^4J = 2 Hz, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4 (*C*H_3CH$_2$O), 21.6 (Ts-CH_3), 46.7 (NCH_2), 61.4 (OCH_2), 127.2 (CH), 128.4 (Cq), 129.9 (CH), 131.2 (Cq), 131.7 (CH), 136.7 (Cq), 137.5 (CH), 143.8 (Cq), 165.9 (CO).

Anal. $C_{25}H_{28}N_2O_6S_2$: calcd. C 58.12, H 5.46, N 5.42, S 12.41; found C 58.07, H 5.49, N 5.40, S 12.15.

6,15-Bis(alkoxycarbonyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacyclophanes 14a, b

The diamide (4 mmol, 2.01 g **13a**/2.07 g **13b**) and the dibromide (4 mmol, 1.29 g **11a**/1.34 g **11b**) were each dissolved in anhyd DMF (50 mL). These solutions were added dropwise and simultaneously over 23 h to a suspension of K_2CO_3 (5.03 g, 40 mmol) in anhyd DMF (350 mL) under argon atmosphere. The mixture was stirred at 20°C for further 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (200 mL).The undissolved inorganic salts were removed by filtration, the filtrate was washed with water, dried (Na_2SO_4), concentrated and purified by recrystallization from EtOAc to yield a colourless solid.

6,15-Bis(methoxycarbonyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacyclophane 14a

R_f 0.47 (CH_2Cl_2/acetone, 20:1); 1.61 g (61%); mp 184°C.

FAB-MS (NBA): *m/z* = 663.1 $[M]^+$, 631.1 $[M – OCH_3]^+$, 507.1 $[M – Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.49 (s, 6 H; Ts-CH_3), 3.80 (s, 6 H; OCH_3), 4.05 (br, 8 H; NCH_2), 7.40 (s, 4 H; Ar-H), 7.42 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.65 (s, 2 H; Ar-H), 7.80 (d, ^3J = 8 Hz, 4 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts-CH_3), 52.1 (OCH_3), 54.5 (NCH_2), 127.2 (CH), 129.2 (Cq), 130.3 (CH), 130.4 (Cq), 135.8 (Cq), 136.0 (CH), 137.2 (Cq), 144.1 (CH), 166.1 (CO).

Anal. $C_{34}H_{34}N_2O_8S_2$•0.5 $CHCl_3$: calcd. C 56.52, H 4.74, N 3.87; found C 55.91, H 4.70, N 3.66.

6,15-Bis(ethoxycarbonyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza-[3.3]metacyclophane 14b

R_f 0.52 (CH_2Cl_2/acetone, 20:1); 1.74 g (60%).

FAB-MS (NBA): *m/z* = 691.1 $[M]^+$, 645.1 $[M - OCH_2CH_3]^+$, 535.1 $[M - Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, ^3J = 7 Hz, 6 H; CH_3CH$_2$O), 2.49 (s, 6 H; Ts-CH_3), 4.24 (q, ^3J = 7 Hz, 4 H; OCH_2), 4.36 (br, 8 H; NCH_2), 7.37 (s, 4 H; Ar-H), 7.40 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.50 (s, 2 H; Ar-H), 7.82 (d, ^3J = 8 Hz, 4 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3 (*C*H$_3$CH$_2$O), 21.7 (Ts-CH_3), 54.4 (NCH_2), 61.0 (OCH_2), 127.3 (CH), 129.0 (Cq), 130.3 (CH), 130.6 (Cq), 135.9 (Cq), 136.0 (CH), 137.0 (Cq), 144.1 (CH), 165.6 (CO).

6,15-Bis(hydroxymethyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacyclophane (15)

A suspension of **14** (3 mmol, 1.99 g **14a**/2.07 g **14b**) and $LiBH_4$ (1.00 g, 46 mmol) in anhyd THF (200 mL) was refluxed for 24 h under argon atmosphere. The cooled mixture was evaporated in vacuo. H_2O (50 mL) was added to the remaining residue and the suspension was stirred for 30 min at r.t. to dissolve the inorganic salts. The alcohol remained undissolved and was filtered, washed with H_2O, and dried. The compound was used in the next step without further purification; 1.51 g (80%); mp 248 °C.

FAB-MS (NBA): *m/z* = 607.1 $[M]^+$, 451.1 $[M - Ts]^+$.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.47 (s, 6 H; Ts-CH_3), 4.21 (d, ^3J = 7 Hz, 4 H; OCH_2), 4.24 (br, 8 H; NCH_2), 5.08 (t, ^3J = 7 Hz, 2 H; OH), 6.70 (s, 4 H; Ar-H), 7.10 (s, 2 H, Ar-H), 7.49 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.84 (d, ^3J = 8 Hz, 4 H; Ts-H).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 21.1 (Ts-CH_3), 54.0 (NCH_2), 62.6 (OCH_2), 125.9 (Cq), 126.9 (CH), 130.2 (CH), 131.5 (Cq), 135.2 (CH), 136.2 (CH), 141.9 (Cq), 143.4 (Cq).

6,15-Bis(bromomethyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]-metacyclophane (16)

A suspension of alcohol **15** (2.42 g, 4 mmol) and PBr_3 (19.36 mL, 0.20 mol) in anhyd $CHCl_3$ (250 mL) was refluxed for 48 h under argon atmosphere. The cooled mixture was poured into ice-water (200 mL)and stirred for 1 h. The organic layer was separated, washed with concd $NaHCO_3$ solution (3 × 100 mL), dried (Na_2SO_4), filtered, and evaporated to yield a colourless substance, which was purified by column chromatography (silica gel, $CHCl_3$/acetone, 50:1); R_f 0.62 ($CHCl_3$/acetone, 50:1); 2.40 g (82%); mp 239 °C.

MALDI-TOF (DHB): *m/z* = 754.9 $[M + Na]^+$, 732.9 $[M]^+$.

FAB-MS (NBA): *m/z* = 757.2 $[M + Na]^+$, 733.0 $[M]^+$, 577.0 $[M - Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.48 (s, 6 H; Ts-CH_3), 4.22 (s, 4 H; $BrCH_2$), 4.28 (br, 8 H; NCH_2), 6.80 (s, 4 H; Ar-H), 7.16 (s, 2 H; Ar-H), 7.48 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.78 (d, ^3J = 8 Hz, 4 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts-CH_3), 33.5 ($BrCH_2$), 54.7 (NCH_2), 127.2 (CH), 128.8 (CH), 130.3 (CH), 131.0 (Cq), 133.4 (Cq), 136.0 (CH), 137.5 (Cq), 144.0 (Cq).

Anal. $C_{32}H_{32}Br_2N_2O_4S_2$•2 H_2O: calcd. C 50.01, H 4.72, N 3.64, S 8.34; found C 50.38, H 4.31, N 3.51, S 8.13.

6,15-Bis(thiomethyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]-metacyclophane (17)

A solution of the dibromide **16** (147 mg, 0.2 mmol) and thiourea (31 mg, 0.2 mmol) in DMSO (10 mL) was stirred for 24 h under argon atmosphere. Aq 10% NaOH solution (10 mL) was added dropwise during a few minutes at 0 °C and the mixture was further stirred 1 h. With half concentrated HCl a colourless substance precipitated at pH 1. The thio compound **17** remained undissolved, was filtered and used without further purification; R_f 0.19 ($CHCl_3$/acetone, 20:1); 89 mg (70%).

FAB-MS (NBA): *m/z* = 650.0 $[M + Na]^+$, 637.1 $[M]^+$, 603.0 $[M - H_2S]^+$, 567.9 $[M - 2\ H_2S]^+$, 481.8 $[M - Ts]^+$.

6,24-Bis(alkoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-hexaaza[3.3](1,3)(1,2)[3.3](4,5)(1,3)benzeno⟨3⟩phane (19a, 19b) and 6,24-Bis(methoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-hexaaza[3.3](1,3)(1,3)[3.3]-(4,6)(1,3)benzeno-(3)-phane (20a)

The tetraamide **18**[9] (3 mmol, 2.43 g) and the dibromide (6 mmol, 1.93 g **11a**/2.02 g **11b**) were each dissolved in anhyd DMF (50 mL). These solutions were added dropwise and simultaneously over 8 h to a suspension of K_2CO_3 (3.00 g, 22 mmol) in anhyd DMF (500 mL) under argon atmosphere. The mixture was stirred for further 18 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (300 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated. The mixture was purified by recrystallization from acetone. The *meta/para*-isomers (**19a**/**19b**) were obtained by extraction with $CHCl_3$. The residue was the *meta/meta*-isomer (**20a**). The ethyl ester **20b** could not be isolated.

***meta/para*-6,24-Bis(methoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-hexaaza[3.3](1,3)(1,2)[3.3](4,5)(1,3)-benzeno⟨3⟩phane (19a)**

0.84 g (24%); mp >280 °C.

FAB-MS (NBA): *m/z* = 1169.1 $[M + K]^+$, 1153.1 $[M + Na]^+$, 1131.3 $[M + H]^+$, 1013.2 $[M - Ts]^+$.

IR (KBr): ν = 2962 (s), 1718 (vs), 1598 (s), 1434 (m), 1339 (s), 1261 (s), 1218 (s), 1161 (s), 1090 (vs), 1010 (s), 888 (m), 803 (m), 663 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.50 (s, 12 H; Ts-CH_3), 3.62 (d, ^2J = 14 Hz, 4 H; NCH_2), 3.68 (d, ^2J = 14 Hz, 4 H; NCH_2), 3.80 (d, ^2J = 14 Hz, 4 H; NCH_2), 3.97 (s, 6 H; OCH_3), 4.39 (d, ^2J = 14 Hz, 4 H; NCH_2), 5.48 (s, 2 H; Ar-H), 6.15 (s, 2H; Ar-H), 7.41 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.74 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.80 (s, 4 H; Ar-H).

***meta/meta*-6,24-Bis(methoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)-benzeno⟨3⟩phane (20a)**

0.33 g (10%); mp >280 °C.

FAB-MS (NBA): *m/z* = 1169.1 $[M + K]^+$, 1153.1 $[M + Na]^+$, 1131.3 $[M + H]^+$, 1013.2 $[M - Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.48 (s, 12 H; Ts-CH_3), 3.7–4.7 (br, 22 H; NCH_2 and OCH_3), 7.17 (s, 2 H; Ar-H), 7.33 (s, 2 H; Ar-H), 7.40 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.71 (s, 4 H; Ar-H), 7.76 (d, ^3J = 8 Hz, 8 H; Ts-H).

***meta/para*-6,24-Bis(ethoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-hexaaza[3.3](1,3)(1,2)[3.3](4,5)(1,3)benzeno(3)phane (19b)**

0.68 g (21%); mp >280 °C.

FAB-MS (NBA): *m/z* = 1197.3 $[M + K]^+$, 1181.3 $[M + Na]^+$, 1159.3 $[M + H]^+$, 1113.3 $[M - OCH_2CH_3]^+$, 1003.3 $[M - Ts]^+$, 849.3 $[M - 2\ Ts]^+$.

IR (KBr): ν = 2969 (m), 1723 (vs), 1679 (m), 1592 (m), 1432 (m), 1342 (s), 1260 (s), 1213 (s), 1161 (s), 1090 (vs), 1010 (s), 880 (m), 809 (m), 666 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 7 Hz, 6 H; CH_3CH$_2$O), 2.48 (s, 12 H; Ts-CH_3), 3.63 (d, ^2J = 14 Hz, 4 H; NCH_2), 3.76 (d, ^2J = 14 Hz, 4 H; NCH_2), 3.81 (d, ^2J = 14 Hz, 4 H; NCH_2), 4.39 (d, ^2J = 14 Hz, 4 H; NCH_2), 4.40 (q, ^3J = 7 Hz, 4 H; OCH_2), 5.48 (s, 2 H; Ar-H), 6.16 (s, 2 H; Ar-H), 7.40 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.75 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.79 (s, 4 H; Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4 (CH_3CH_2O), 21.6 (Ts-CH_3), 50.3 (NCH_2), 52.2 (NCH_2), 61.3 (OCH_2), 127.5 (CH), 128.7 (Cq), 130.2 (CH), 131.2 (Cq), 132.4 (CH), 133.2 (CH), 134.4 (Cq), 135.1 (Cq), 137.2 (Cq), 144.0 (CH), 165.9 (CO).

6,36-Bis(methoxycarbonyl)-2,11,20,29,32,41-hexakis(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)-(1,3)[3.3)-(4,6)(1,3)benzeno⟨4⟩phane (22)

The diamide **13a** (2.00 mmol, 1.01 g) and the tetrabromide **21** (1.00 mmol, 1.01 g) were each dissolved in anhyd DMF (50 mL). These solutions were added dropwise and simultaneously over 83 h to a suspension of K_2CO_3 (3.00 g, 22 mmol) in anhyd DMF (500 mL) under argon atmosphere. The mixture was stirred for further 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (100 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4), concentrated and purified by (silica gel, $CHCl_3$/acetone, 15:1) to yield a colourless substance; R_f 0.47 ($CHCl_3$/acetone, 15:1); 0.60 g (40%); mp 252°C.

FAB-MS (NBA): *m/z* = 1622.2 $[M + Na]^+$, 1600.3 $[M + H]^+$, 1568.2 $[M – OCH_3]^+$, 1443.2 $[M – Ts]^+$, 1289.2 $[M – 2 Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.46 (s, 6 H; Ts-CH_3), 2.49 (s, 12 H; Ts-CH_3), 3.74 (s, 6 H; OCH_3), 4.00–5.50 (br, 24 H; ArCH_2), 6.45 (s, 2 H; Ar-H), 6.79 (s, 2 H; Ar-H), 7.34 (s, 2 H; Ar-H), 7.55 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.82 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.91 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.98 (d, ^3J = 8 Hz, 8 H; Ts-H), 8.38 (s, 4 H; Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.3 (Ts-CH_3), 21.4 (Ts-CH_3), 52.2 (OCH_3), 61.4 (NCH2), 128.1 (CH), 128.6 (CH), 130.1 (Cq),130.3 (Cq), 130.7 (CH), 130.8 (CH), 131.8 (Cq), 133.2 (Cq), 136.7 (Cq), 136.9 (Cq), 137.2 (Cq), 144.4 (Cq), 166.3 (CO).

Anal. $C_{82}H_{82}N_6O_{16}S_6$•1.5 $CHCl_3$: calcd. C 55.36, H 4.65, N 4.72; found C 55.73, H 4.70, N 4.48.

6,36-Bis(hydroxymethyl)-2,11,20,29,32,41-hexakis(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3)-(4,6)(1,3)benzeno⟨4⟩phane (23)

A suspension of **22** (0.48 g, 0.3 mmol) and $LiBH_4$ (0.50 g, 23 mmol) in anhyd THF (200 mL) was refluxed for 24 h under argon atmosphere. The cooled mixture was evaporated in vacuo. H_2O (50 mL) was added to the remaining residue and the suspension was stirred for 30 min at r.t. to dissolve the inorganic salts. The alcohol remained undissolved and was filtered, washed with H_2O, and dried. The compound was used in the next step without further purification; 0.35 g (75%).

FAB-MS (NBA): *m/z* = 1549.3 $[M + Li]^+$, 1543.3 $[M + H]^+$, 1387.3 $[M – Ts]^+$, 1233.3 $[M – 2 Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 12 H; Ts-CH_3), 2.49 (s, 6 H; Ts-CH_3), 4.19 (s, 4 H; OCH_2), 4.25–5.30 (br, 24 H; ArCH_2), 6.33 (br, 2 H; Ar-H), 6.42 (br, 2 H; Ar-H), 6.82 (br, 2 H; Ar-H), 6.91 (br, 4 H; Ar-H), 7.38 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.45 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.76 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.79 (d, ^3J = 8 Hz, 8 H; Ts-H).

6,36-Bis(bromomethyl)-2,11,20,29,32,41-hexakis(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3)-(4,6)(1,3)benzeno⟨4⟩phane (24)

A suspension of the alcohol **23** (0.3 g, 0.2 mmol) and PBr_3 (9.72 mL, 0.10 mol) in anhyd $CHCl_3$ (200 mL) was refluxed for 72 h under argon atmosphere. The cooled mixture was poured into ice-water (100 mL) and stirred for 1 h. The organic layer was separated, washed with concd $NaHCO_3$ solution (3 × 100 mL), dried (Na_2SO_4), filtered, and evaporated to yield a colourless substance, which was purified by column chromatography (silica gel, $CHCl_3$/acetone, 15:1); R_f 0.64 ($CHCl_3$/acetone, 15:1); 0.25 g (77%); mp 186°C.

FAB-MS (NBA): *m/z* = 1669.2 $[M + H]^+$, 1589.3 $[M – Br]^+$, 1513.2 $[M – Ts]^+$, 1359.2 $[M – 2 Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.46 (s, 12 H; Ts-CH_3), 2.48 (s, 6 H; Ts-CH_3), 4.04 (s, 4 H; CH_2Br), 4.25–5.30 (br, 24 H; ArCH_2), 6.31 (s, 2 H; Ar-H), 6.50 (s, 2 H; Ar-H), 6.59 (s, 4 H; Ar-H), 6.88 (s, 2 H; Ar-H), 7.37 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.45 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.79 (d, ^3J = 8 Hz, 12 H; Ts-H).

^{13}C NMR (62.9 MHz, DMF-d_7): δ = 21.3 (Ts-CH_3), 21.4 (Ts-CH_3), 29.4 (CH_2Br), 61.5–55.5 (NCH_2), 128.1 (CH), 128.6 (CH), 129.0 (CH), 130.7 (CH), 130.8 (CH), 131.7 (Cq), 132.6 (Cq),134.4 (CH), 134.7 (CH), 136.0 (Cq), 136.5 (Cq), 137.1 (Cq), 138.1 (Cq), 138.5 (Cq), 144.4 (Cq), 144.6 (Cq).

6,48-Bis(methoxycarbonyl)-2,11,20,29,32,41,44,53-octakis(4-tolylsulfonyl)-2,11,20,29,32,41,-44,53-octaaza[3.3](1,3)(1,3)-[3.3](4,6)(1,3)[3.3)(4,6)(1,3)[3.3)(4,6)(1,3)benzeno⟨5⟩phane (26)

The diamide **13a** (1.00 mmol, 0.51 g) and the tetrabromide **25** (0.5 mmol, 0.67 g) were each dissolved in anhyd DMF (50 mL). These solutions were added dropwise and simultaneously over 83 h to a suspension of K_2CO_3 (4.18 g, 30 mmol) in anhyd DMF (200 mL) under argon atmosphere. The mixture was stirred for further 48 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (100 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4), concentrated and purified by (silica gel, $CHCl_3$/acetone, 15:1) to yield a colourless solid; R_f 0.44 ($CHCl_3$/acetone, 15:1); 0.33 g (32%); mp >280°C.

FAB-MS (NBA): *m/z* = 2105.4 $[M + K]^+$, 2068.5 $[M + H]^+$, 1913.5 $[M – Ts]^+$, 1757.5 $[M – 2 Ts]^+$.

6,48-Bis(hydroxymethyl)-2,11,20,29,32,41,44,53-octakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)-[3.3](4,6)-(1,3)[3.3)(4,6)(1,3)[3.3)(4,6)(1,3)benzeno⟨5⟩phane (27)

A suspension of **26** (0.18 g, 0.09 mmol) and $LiBH_4$ (0.20 g, 9 mmol) in anhyd THF (150 mL) was refluxed for 18 h under argon atmosphere. The cooled mixture was evaporated in vacuo. H_2O (100 mL) was added to the remaining residue and the suspension was stirred for 30 min at r.t. to dissolve the inorganic salts. The alcohol remained undissolved and was filtered, washed with H_2O, and dried. The compound was used without further purification; 0.17 g (95%); mp >280°C.

6,48-Bis(bromomethyl)-2,11,20,29,32,41,44,53-octakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)[3.3]-(4,6)-(1,3)[3.3)(4,6)(1,3)[3.3)(4,6)(1,3) benzeno⟨5⟩phane (28)

A suspension of alcohol **27** (0.17 g, 0.09 mmol) and PBr_3 (5.00 mL, 52 mmol) in anhyd $CHCl_3$ (100 mL) was refluxed for 96 h under argon atmosphere. The cooled mixture was poured into ice-water and stirred for 1 h. The organic layer was separated, washed three times with concd $NaHCO_3$ solution, dried (Na_2SO_4), filtered, and evaporated to yield a colourless solid, which was purified by column chromatography (silica gel, $CHCl_3$/acetone, 15:1); R_f 0.63 ($CHCl_3$/acetone, 15:1); 65 mg (35%); mp >280°C.

FAB-MS (NBA): *m/z* = 2139.1 $[M + H]^+$, 1983.1 $[M – Ts]^+$.

^{1}H NMR (250 MHz, CD_2Cl_2): δ = 2.49 (s, 24 H; Ts-CH_3), 3.00–5.30 (br, 36 H; ArCH_2), 6.24 (s, 2 H; Ar-H), 6.41 (s, 2 H; Ar-H), 6.60 (s, 4 H; Ar-H). 6.84 (s, 2 H; Ar-H), 6.91 (s, 2 H; Ar-H), 7.43 (d, ^3J = 8 Hz, 16 H; Ts-H), 7.79 (d, ^3J = 8 Hz, 16 H; Ts-H).

2,11,20-Tris(4-tolylsulfonyl)-2,11,20-triaza[3.3.3](1,3,5)benzeno⟨2⟩phane (31)

The dibromide **17** (140 mg, 0.19 mmol) was dissolved in anhyd DMF (50 mL). This solution was added dropwise over 1 h to a suspension of Cs_2CO_3 (1.63 g, 5.00 mmol) and TsNHNa (0.45 g, 1.00 mmol) in anhyd DMF (100 mL) under argon atmosphere at

90 °C. The mixture was further stirred for 24 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (150 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated. The product was purified by recrystallization from dioxane; R_f 0.52 ($CHCl_3$/acetone 20:1); 98 mg (70%); mp >280 °C.

FAB-MS (NBA): *m/z* = 742.1 $[M + H]^+$, 587.1 $[M – Ts]^+$.

IR (KBr): ν = 3030.3 (m), 2960.5 (w), 2910.8 (w), 2855.0 (m),1460.0 (m), 1335.1 (s), 1160.8 (vs), 1095.4 (s), 922.3 (m), 811.1 (m), 777.6 (m), 667.1 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.49 (s, 9 H; Ts-CH_3), 4.08–4.66 (br, 12 H; NCH_2), 6.92 (s, 6 H; Ar-H), 7.40 (d, ^3J = 8 Hz, 6 H; Ts-H) , 7.77 (d, ^3J = 8 Hz, 6 H; Ts-H).

2,11,20,29,32,41,44-Heptakis(4-tolylsulfonyl)-2,11,20,29,32,41,44-heptaaza[3.3](1,3) (1,3)[3.3](4,6)(1,3)[3.3)(4,6)(1,3)[3](5,5)-benzeno⟨4⟩phane (32)

The dibromide **24** (250 mg, 0.15 mmol) was dissolved in anhyd DMF (50 mL). This solution was added dropwise over 2 h to a suspension of Cs_2CO_3 (4.90 g,15 mmol) and TsNHNa (1.34 g, 3 mmol) in anhyd DMF (200 mL) under argon atmosphere at 90 °C. The mixture was further stirred for 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (150 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated. The product was isolated by column chromatography (silica gel, $CHCl_3$/acetone, 15:1); R_f 0.48 ($CHCl_3$/acetone, 15:1); 55 mg (22%); mp >280 °C.

FAB-MS (NBA): *m/z* = 1679.2 $[M + H]^+$, 1522.2 $[M – Ts]^+$, 1368.2 $[M – 2 Ts]^+$.

^1H NMR (400 MHz, CD_2Cl_2): δ = 2.34 (s, 3 H; Ts-CH_3), 2.40 (s, 6 H; Ts-CH_3), 2.43 (s, 12 H; Ts-CH_3), 3.50–5.00 (br, 28 H; NCH_2), 6.69 (s, 4 H; Ar-H), 6.99 (s, 2 H; Ar-H), 7.04 (s, 2 H; Ar-H), 7.05 (s, 2 H; Ar-H), 7.42–7.44 (br, 14 H; Ts-H), 7.63–7.75 (br, 14 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4 (Ts-CH_3), 21.6 (Ts-CH_3), 51.4–55.4 (NCH_2), 126.7.1 (Cq), 127.5 (CH), 127.7 (CH), 128.3 (CH), 129.6 (CH), 130.4 (CH), 132.7 (Cq), 133.2 (Cq), 134.7 (CH), 135.4 (Cq), 136.2 (Cq), 136.8 (Cq), 144.3 (Cq), 144.4 (Cq).

Anal. $C_{87}H_{87}N_7O_{17}S_7$: calcd. C 62.23, H 5.22, N 5.84; found C 62.07, H 5.15, N 5.69.

Pseudobeltanes 38, 8 and Cyclophane Spaced Diamide (39)

The dibromide **16** (440 mg, 0.6 mmol) was dissolved in anhyd DMF (250 mL). This solution was added dropwise over 6 h to a suspension of Cs_2CO_3 (4.90 g, 15 mmol) and diamide **37** (267 mg, 0.6 mmol) in anhyd DMF (350 mL) under argon atmosphere. The mixture was further stirred for 110 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (200 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated. All three products were isolated by column chromatography (1. filter column: silica gel, $CHCl_3$/acetone, 10:1; 2. column: silica gel, $CHCl_3$/acetone, 50:1).

2,11,20,29-Tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,3)-(1,3)[3](5,5)[3](1,4) benzeno⟨3⟩phane (38)

R_f 0.53 ($CHCl_3$/acetone, 50:1); 73 mg (12%); mp 205 °C.

MALDI-TOF (DHB): *m/z* = 1037.3 $[M + Na]^+$.

FAB-MS (NBA): *m/z* = 1015.3 $[M]^+$, 859.3 $[M – Ts]^+$.

IR (KBr): ν = 2922.3 (m), 2856.3 (m), 1597.8 (m), 1438.0 (m), 1336.3 (s), 1158.3 (vs), 1091.4 (vs), 915.3 (m), 814.1 (m), 757.6 (s), 657.1 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 6 H; Ts-CH_3), 2.48 (s, 6 H; Ts-CH_3), 3.76 (s, 4 H; NCH_2), 3.00–5.20 (br, 8 H; NCH_2), 6.81 (s, 4 H; Ar-H), 7.25 (s, 2 H; Ar-H), 7.26 (s, 4 H; Ar-H), 7.34 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.40 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.68 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.78 (d, ^3J = 8 Hz, 4 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts-CH_3), 22.4 (Ts-CH_3), 54.5 (NCH_2), 55.0 (NCH_2), 126.9 (Cq), 128.0 (CH), 129.9 (CH), 130.1 (CH), 130.2 (CH), 133.4 (Cq), 133.9 (Cq), 134.7 (Cq), 143.6 (Cq), 144.0 (CH).

Anal. $C_{54}H_{54}N_4O_8S_4 \cdot H_2O$: calcd. C 62.77, H 5.46, N 5.42, S 12.41; found C 62.79, H 5.48, N 5.01, S 12.30.

2,11,20,29,32,41,44,53-Octakis(4-tolylsulfonyl)-2,11,20,29,32,-41,44,53-octaaza[3.3](1,3)(1,3)[3.3](1,3)(1,3)[3](5,5)[3](5.5)[3]-(1,4)[3](1,4)benzeno⟨6⟩phane (8)

R_f 0.45 ($CHCl_3$/acetone, 50:1); 92 mg (15%); mp > 300 °C.

MALDI-TOF (DHB): *m/z* = 2052.3 $[M + Na]^+$.

FAB-MS (NBA): *m/z* = 2030.6 $[M]^+$, 1875.5 $[M – Ts]^+$, 1719.5 $[M – 2 Ts]^+$, 1563.4 $[M – 3 Ts]^+$, 1407.4 $[M – 4 Ts]^+$.

IR (KBr): ν = 2923.9 (s), 2861.0 (m), 1597.1 (s), 1437.4 (s), 1331.9 (vs), 1159.4 (vs), 1087.0 (vs), 915.3 (m), 812.6 (s), 761.0 (s), 662.2 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 12 H; Ts-CH_3), 2.52 (s, 12 H; Ts-CH_3), 3.76 (d, ^2J = 12 Hz, 8 H; NCH_2), 3.20–5.80 (br, 16 H; NCH_2), 6.54 (s, 4 H; Ar-H), 6.85 (s, 8 H; Ar-H), 7.25 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.31 (s, 8 H; Ar-H), 7.42 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.57 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.80 (d, ^3J = 8 Hz, 8 H; Ts-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts-CH_3), 21.8 (Ts-CH_3), 48.2 (NCH_2), 48.5 (NCH_2), 127.2 (CH), 127.3 (CH), 129.5 (Cq), 129.9 (CH), 130.4 (CH), 134.7 (CH), 135.7 (Cq), 138.5 (Cq), 143.4 (Cq), 143.9 (Cq).

Anal. $C_{108}H_{108}N_8O_{16}S_8 \cdot 2\ H_2O$: calcd. C 62.77, H 5.46, N 5.42, S 12.41; found C 62.77, H 5.37, N 5.31, S 12.38.

6,15-Bis[(*N*-(4-tolylsulfonyl)aminomethyl)benzyl-*N*-(4-tolylsulfonyl)aminomethyl]-2,11-diaza[3.3]metacyclophane (39)

R_f 0.39 ($CHCl_3$/acetone, 10:1); 2 mg (0.5%).

MALDI-TOF (DHB): *m/z* = 1481.6 $[M + Na]^+$.

2,11,32,41-Tetrakis(4-tolylsulfonyl)-20,29-dithia-2,11,32,41-tetraaza[3.3](1,3)(1,3)[3.3](1,3) (1,3)[3](5,5)[3](5,5)benzeno⟨4⟩phane (29)

The dithiol **17** (64 mg, 0.1 mmol) and the dibromide **16** (73 mg, 0.1 mmol) were each dissolved in anhyd DMF (50 mL). This solutions were added dropwise and simultaneously over 83 h to a suspension of Cs_2CO_3 (1.63 g, 5.00 mmol) in anhyd DMF (500 mL) under argon atmosphere. The mixture was stirred for further 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (250 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4), concentrated and purified by column chromatography (silica gel, $CHCl_3$/MeOH, 30:1) to give a colourless oil; R_f 0.35 ($CHCl_3$/MeOH, 20:1); 34 mg (28%); mp 197 °C.

MALDI-TOF (DHB): *m/z* = 1341.0 $[M + Cs]^+$, 1293.2 $[M + Na + K]^+$, 1249.4 $[M + K]^+$, 1232.4 $[M + Na]^+$.

FAB-MS (NBA): *m/z* = 1210.5 $[M + H]^+$, 900.4 $[M – 2 Ts]^+$.

IR (KBr): ν = 2922.0 (m), 1700.0 (m), 1598.1 (m), 1445.5 (m), 1334.8 (s), 1157.2 (vs), 1093.2 (s), 914.9 (m), 880.4 (s), 814.5 (m), 771.7 (m), 664.5 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 12 H; Ts-CH_3), 2.72 (br, 8 H; SCH_2), 4.30 (br, 16 H; NCH_2), 6.79 (s, 8 H; Ar-H), 7.38 (s, 4

H; Ar-H), 7.39 (d, ^3J = 8 Hz, 8 H; Ts-H), 7.77 (d, ^3J = 8 Hz, 8 H; Ts-H).

Anal. $C_{64}H_{64}N_4O_8S_6$•$CHCl_3$: calcd. C 58.75, H 4.93, N 4.22; found C 58.28, H 5.19, N 4.61.

Pseudobeltanes 40 and 41

The dibromide **16** (150 mg, 0.2 mmol) was dissolved in anhyd DMF (100 mL). This solution was added dropwise over 18 h to a suspension of Cs_2CO_3 (1.67 g, 5.00 mmol) and diamide **13b** (104 mg, 0.2 mmol) in anhyd DMF (150 mL) under argon atmosphere. The mixture was further stirred for 72 h. The solvent was evaporated, and the remaining residue treated with $CHCl_3$ (200 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4) and concentrated. Product **40** was isolated by column chromatography (silica gel, $CHCl_3$/acetone, 50:1) to yield a colourless oil.

6-Ethoxycarbonyl-2,11,20,29-Tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,3)(1,3)[3](5,5)[3](1,3)benzeno⟨3⟩phane (40)

R_f 0.33 ($CHCl_3$/acetone, 50:1); 99 mg (46%).

MALDI-TOF (DHB): *m/z* = 1219.6 $[M + Cs]^+$, 1205.6 $[M + Cs - CH_3]^+$, 1111.7 $[M + Na]^+$,1065.6 $[M - CH_3]^+$.

FAB-MS (NBA): *m/z* = 1219.2 $[M + Cs]^+$, 1205.8 $[M + Cs - CH_3]^+$, 1087.2 $[M]^+$,1065.1 $[M - CH_3]^+$,1041.2 $[M - OCH_2CH_3]^+$, 931.2 $[M - Ts]^+$, 755.2 $[M - 2\ Ts]^+$.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7 Hz, 3 H, CH_3CH_2O), 2.42 (s, 6 H; Ts-CH_3), 2.46 (s, 6 H; Ts-CH_3), 3.69 (s, 4 H; NCH_2), 3.98 (br, 8 H; NCH_2), 4.22 (q, ^3J = 7 Hz, 2 H, CH_2O), 6.50 (br, 4 H; Ar-H), 6.61 (br, 2 H; Ar-H), 7.22 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.37 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.65 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.78 (d, ^3J = 8 Hz, 4 H; Ts-H), 7.82 (s, 2 H; Ar-H), 7.90 (s, 1 H; Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4 (CH_3CH_2O), 21.6 (Ts-CH_3), 49.9 (NCH_2), 54.9 (NCH_2), 61.2 (OCH2), 125.1 (Cq), 126.9 (CH), 127.4 (CH), 129.9 (CH), 130.1 (CH), 130.5 (Cq), 131.6 (Cq), 132.0 (Cq), 134.9 (Cq), 136.2 (Cq), 135.3 (CH), 135.7 (CH), 134.7 (Cq), 143.6 (Cq), 143.7 (CH), 143.8 (CH), 166.1 (CO).

Anal. $C_{57}H_{59}N_4O_{10}S_4$•H_2O: calcd. C 61.94, H 5.47, N 5.07, S 11.60; found C 62.03, H 5.69, N 4.44, S 11.16.

6,48-Bis(ethoxycarbonyl)-2,11,20,29,32,41,44,53-octakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)-[3.3]-(1,3)-(1,3)[3](5,5)[3](5.5)[3](1,3)[3] (1,3)benzeno⟨6⟩phane (41)

R_f 0.30 ($CHCl_3$/acetone, 50:1).

MALDI-TOF (DHB): *m/z* = 2308.7 $[M + Cs]^+$, 2292.6 $[M + Cs - CH_3]^+$, 2174.2 $[M]^+$. FAB-MS (NBA): *m/z* = 2306.2 $[M + Cs]^+$, 2292.2 $[M + Cs - CH_3]^+$, 2019.6 $[M - Ts]^+$, 2005.6 $[M - Ts - CH_3]^+$.

2,11,20,29,32,41-Hexakis(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1.3)(1.3)[3](5.5)[3] (1,4)[3](1,4)[3](1,4)benzeno⟨5⟩phane (43)

The dibromide **16** (220 mg, 0.3 mmol) was dissolved in anhyd DMF (300 mL). This solution was added dropwise over 13 h to a suspension of the diamide **42** (293 mg, 0.3 mmol) and Cs_2CO_3 (1.63 g, 5.00 mmol) in anhyd DMF (400 mL) under argon atmosphere. The mixture was further stirred for 72 h. The solvent was evaporated, and the remaining residue treated with CH_2Cl_2 (200 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with H_2O, dried (Na_2SO_4), concentrated and purified by column chromatography (silica gel, $CHCl_3$/EtOH, 30:1) to give a colourless substance; R_f 0.57 ($CHCl_3$/EtOH, 30:1); 152 mg (32%); mp 174°C.

MALDI-TOF (DHB): *m/z* = 1600.6 $[M + K]^+$, 1583.6 $[M + Na]^+$.

FAB-MS (NBA): *m/z* = 1561.4 $[M + H]^+$, 1405.5 $[M - Ts]^+$, 1251.5 $[M - 2\ Ts]^+$, 1095.3 $[M - 3\ Ts]^+$, 844.2 $[M - 4\ Ts]^+$.

IR (KBr): ν = 2919.8 (s), 1597.3 (m), 1444.3 (m), 1335.7 (vs), 1156.6 (vs), 1091.2 (vs), 908.7 (s), 814.0 (s), 767.2 (s), 656.8 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.37 (s, 6 H; Ts-CH_3), 2.42 (s, 6 H; Ts-CH_3), 2.47 (s, 6 H; Ts-CH_3), 3.65 (s, 4 H; NCH_2), 3.82 (s, 4 H; NCH_2), 4.00 (s, 8 H; NCH_2), 4.00–4.70 (br, 8 H; NCH_2), 6.62 (s, 2 H; Ar-H), 6.64 (d, ^3J = 8 Hz, 4 H; Ar-H), 6.70 (s, 4 H; Ar-H), 6.86 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.26 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.28 (s, 4 H; Ar-H), 7.30 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.42 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.56 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.71 (d, ^3J = 8 Hz, 4 H; Ar-H), 7.79 (d, ^3J = 8 Hz, 4 H; Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4 (Ts-CH_3), 21.5 (Ts-CH_3), 21.6 (Ts-CH_3), 49.4 (NCH_2), 49.6 (NCH_2), 51.2 (NCH_2), 54.7 (NCH_2), 126.9 (CH), 127.1 (CH), 127.2 (CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 130.2 (CH), 132.5 (Cq), 134.0 (Cq), 134.8 (CH), 135.4 (CH), 135.7 (Cq), 136.0 (Cq), 136.2 (Cq), 136.4 (Cq) 136.5 (Cq), 137.8 (Cq), 143.4 (Cq), 143.5 (Cq), 143.8 (Cq).

Anal. $C_{84}H_{84}N_6O_{12}S_6$•2.5 CH_2Cl_2: calcd. C 58.56, H 5.06, N 4.74, S 10.84; found C 58.91, H 5.08, N 4.76, S 10.84.

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