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Nanometre-sized Macrocyclic Oligoamides by Iterative Synthesis

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Abstract. New nanometre-sized macrocyclic tosylaza[3_n]paracyclophanes have been synthesized by means of an iterative synthetic strategy using linear building blocks with up to four benzene units. The formation of the open-chain difunctionalized linear molecules was achieved by a three step reaction sequence including nucleophilic substitution and transformation of the terminal ester groups to the corresponding dialcohol and dibromide. The final intermolecular macrocyclizations were carried out by reaction of open chained dibromides and bis(tosylamides) to obtain nanosize macrocyclic oligotosylamides in 31–50% yield. Highly symmetrical tosylaza[3_n]paracyclophanes containing up to seven benzene units and up to 49 ring members (n = 5–7) were obtained. Also described is the preparation of 30–90-membered paracyclophanes containing biphenyl or terphenyl units.

Key words: large rings, nanocycles, paracyclophanes, macrocycles, sulfonamides

1. Introduction

Macrocyclic and in particular cyclophane chemistry [1, 2] plays an important role in supramolecular chemistry [3] and in nanochemistry [4]. One of the most popular fields in macrocyclic chemistry comprises [1_n]metacyclophanes known as calix[n]arenes [5]. This originates from their easy preparation and their suitability to form an anchor group for affixing ligand arms with the aim of guest complexation [6]. This should hold for some other cyclophane skeletons as well if the prerequisites of easy preparation and refunctionalization are applicable. This was the intention of the project that emerged from earlier studies to prepare the hitherto unknown [0_n]paraphenylenes **1** [7] and ultralarge biphenylophanes **2a–d** [8]. Today many research groups are working on the synthesis of very large "giganto-" and "ultracycles" ($\geq$50 and $\geq$100 ring members, respectively) [9, 10]. More recently Oda *et al.* described many-membered paraphenylene skeletons like **3a, b** [11] (Figure 1). Sanders *et al.* and Höger *et al.* used large ring triple bond spacered macrocycles for guest inclusion [12].

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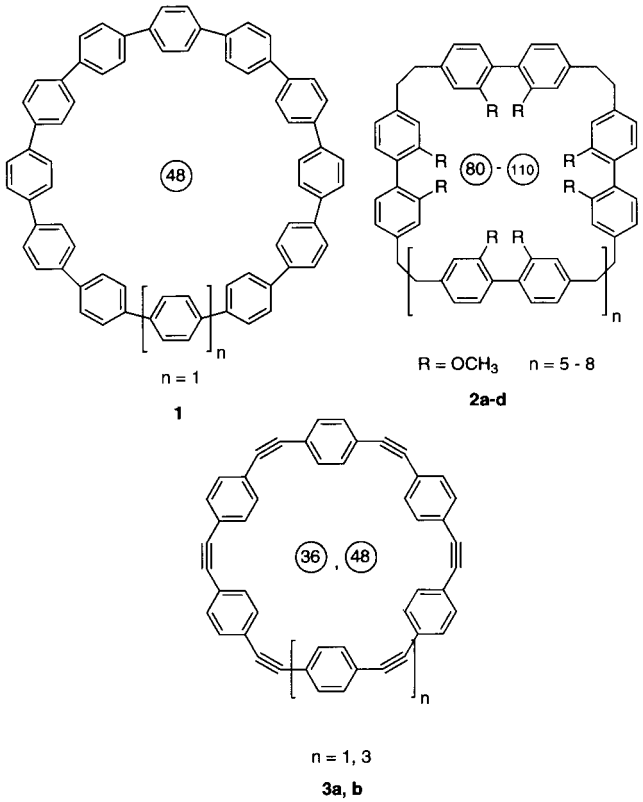

Figure 1. Macrocycles **1–3** with a paracyclophane skeleton.

One problem faced in the synthesis of "nanocycles" [13] based on paracyclophane structural elements are the usually observed low yields since a high-membered ring formation is often a side-reaction [10] in a synthesis designed to produce smaller macrocycles. In addition, the separation of these large rings from an oligomeric mixture of rings is also difficult.

We report here on the first synthesis of macrocyclic oligotosylamides with up to 49 ring members (cf. **33**) based on a paracyclophane framework by an iterative synthetic method [14] using difunctionalized open chain building blocks (cf. **17**). Furthermore we describe the formation of new mixed biphenylobenzenophanes with up to 90 ring members (cf. **4**).

2. Experimental

Chemicals were purchased from Merck, Fluka and Aldrich and were used as received. Di- and trichloromethane were distilled and dried over 4 Å molecular sieve before use. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride. Yields refer to chromatographically and spectroscopically homogeneous materials.

All reactions were monitored by thin-layer chromatography (TLC; silica gel 60 F_{254} Merck 1.05554). 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". Infrared spectra were recorded on an FT-IR-spectrometer (Perkin Elmer Model 1600, Norwalk, Connetticut, USA). GC-MS spectra were recorded on a gas chromatograph HP 5890 Series II and a mass spectrometer HP 5898 A (EI-MS) spectra from Hewlett Packard Company (Palo Alto, California, USA). Fast-atom bombardment (FAB-MS) spectra were obtained on a Kratos Concept 1 H spectrometer (Kratos, Manchester, UK); *m*-nitrobenzyl alcohol (NBA) was the matrix. With a Micromass Tof spec E (Micromass, Manchester, UK) we recorded our MALDI-TOF spectra; 2,5-dihydroxybenzoic acid (DHB) was the matrix. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM 250 (250 MHz (^{1}H), 62.9 MHz (^{13}C)) or a Bruker AM 400 (400 MHz (^{1}H), 100.6 MHz (^{13}C)) spectrometer at room temperature in commercial deuterated solvents (the internal reference was the residual undeuterated solvent). The following abbreviations are 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).

Ethyl 4-[*N*-benzyloxycarbonyl-*N*-(4-tolylsulfonyl)aminomethyl]benzoate 8: A suspension of potassium carbonate (13.80 g, 0.10 mol), ethyl 4-bromomethylbenzoate **7** (12.16 g, 50.00 mmol) and *N*-(4-tolylsulfonyl)benzylcarbamate (TsNHZ; 16.80 g, 55.00 mmol) in dry DMF (400 mL) was stirred for 72 hours under an argon atmosphere. The solvent was evaporated and the remaining residue treated with trichloromethane (300 mL). The undissolved components were removed by filtration, and the filtrate was washed twice with NaCl-solution (100 mL) and twice with water (100 mL), dried (Na_2SO_4), filtered, concentrated and recrystallized from acetone to yield colourless crystals.

R_f = 0.58 (trichloromethane); 18.71 g (67% yield); M.p. 116 °C; MALDI-TOF (DHB): *m/z* = 490.8 $[M + Na]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.39 (t, ^{3}J = 7 Hz, 3 H; CH_3O), 2.37 (s, 3 H; Ts—CH_3), 4.38 (q, ^{3}J = 7 Hz, 2 H; OCH_2), 5.07 (s, 2 H; NCH_2), 5.09 (s, 2 H; OCH_2Ph), 7.02–7.19 (m, 5 H; Ar—H), 7.28 (d, ^{3}J = 8 Hz, 2 H; Ar—H), 7.42 (d, ^{3}J = 8 Hz, 2 H; Ar—H), 7.55 (d, ^{3}J = 8 Hz, 2 H; Ar—H), 7.98 (d, ^{3}J = 8 Hz, 2 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 14.8 ($\underline{C}H_3CH_2O$), 21.7 (Ts-CH_3), 49.2 (NCH_2), 60.9 (OCH_2), 69.7 (OCH_2Ph), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 129.4 (CH), 129.9 (CH), 130.1 (Cq), 130.2 (CH), 134.2 (Cq), 136.1 (Cq), 142.0 (Cq), 144.9 (Cq), 152.5 (CO), 166.2 (CO).

Ethyl 4-[*N*-(4-tolylsulfonyl)aminomethyl]benzoate 9: A suspension of **8** (5.14 g, 11.00 mmol), and catalyst (1.00 g, 10%-palladium on carbon) in trichloromethane (50 mL) was stirred at room temperature for six hours under a hydrogen atmosphere (3.5–4.5 bar). The suspension was filtered through celite,

and the filtrate evaporated to give a colourless substance, which was purified by column chromatography (silica gel, trichloromethane).

R_f = 0.24 (trichloromethane); 3.52 g (96% yield); M.p. 140 °C; GC-MS: *m/z* (%) = 333 $[M]^+$, 288 $[M - C_2H_5O]^+$, 260 $[M - CO_2C_2H_5]^+$, 178 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.37 (t, ^{3}J = 7 Hz, 3 H; $C\underline{H}_3CH_2O$), 2.41 (s, 3 H; Ts-CH_3), 4.16 (d, ^{3}J = 6 Hz, 2 H; NCH_2), 4.34 (q, ^{3}J = 7 Hz, 2 H; OCH_2), 5.12 (t, ^{3}J = 6 Hz, 1 H; NH), 7.26 (m, 4 H; Ar—H), 7.73 (d, ^{3}J = 8 Hz, 2 H; Ts—H), 7.91 (d, ^{3}J = 8 Hz, 2 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 14.6 ($\underline{C}H_3CH_2O$), 21.7 (Ts—CH_3), 47.0 (NCH_2), 61.2 (OCH_2), 127.3 (CH), 127.7 (CH), 129.9 (CH), 130.0 (CH), 131.1 (Cq), 136.9 (Cq), 141.6 (Cq), 143.8 (Cq), 166.4 (CO); $C_{17}H_{19}NO_4S{\cdot}0.5H_2O$. Calcd.: C 59.63, H 5.89, N 4.10, S 9.37; found: C 60.16, H 5.66, N 4.02, S 9.50.

4,4′-Bis[*N*-acetyl-*N*-(4-tolylsulfonyl)aminomethyl]biphenyl 22: A suspension of potassium carbonate (2.76 g, 20.00 mmol), 4,4′-bis(bromomethyl)biphenyl **21** (1.03 g, 3.00 mmol), and *N*-acetyl-4-tolylsulfonamide (2.13 g, 10.00 mmol) in dry DMF (50 mL) was stirred for 48 hours under an argon atmosphere. The solvent was evaporated and the remaining residue treated with trichloromethane (50 mL). The undissolved components were removed by filtration, and the filtrate was washed twice with water (50 mL), dried (Na_2SO_4), filtered, and concentrated to give a colourless substance, which was recrystallized from acetone to yield colourless crystals.

R_f = 0.78 (dichloromethane/methanol 20 : 1); 1.43 g (79% yield); M.p. 210 °C; FAB-MS (NBA): *m/z* = 643.1 $[M + K]^+$, 604.0 $[M]^+$, 450.0 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $[D_6]$DMSO): δ = 2.23 (s, 6 H; Ac-CH_3), 2.39 (s, 6 H; Ts-CH_3), 5.01 (s, 4 H; NCH_2), 7.32 (m, 8 H; Ar—H), 7.48 (d, ^{3}J = 8 Hz, 4 H; Ts—H), 7.69 (d, ^{3}J = 8 Hz, 4 H; Ts—H).

4,4′-Bis[*N*-(4-tolylsulfonyl)aminomethyl)]biphenyl 23: A suspension of diamide **22** (1.43 g, 2.37 mmol), and potassium carbonate (2.76 g, 20 mmol) in 105 mL solvent mixture (100 mL methanol/5 mL water) was refluxed for 7 hours. The solvent was evaporated and the remaining residue treated with water (100 mL) to dissolve the inorganic salts. The undissolved product was obtained by filtration, drying, and recrystallization from acetone.

R_f = 0.45 (dichloromethane/methanol 20 : 1); 1.11 g (90% yield); M.p. 242 °C; MALDI-TOF (DHB): *m/z* = 580.6 $[M + K + Na]^+$, 558.6 $[M + K]^+$, 542.8 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 559.0 $[M + K]^+$, 520.0 $[M]^+$, 365.0 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $[D_6]$DMSO): δ = 2.36 (s, 6 H; Ts—CH_3), 4.00 (s, 4 H; NCH_2), 7.32 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.37 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.54 (d, ^{3}J = 8 Hz, 4 H; Ts—H), 7.72 (d, ^{3}J = 8 Hz, 4 H; Ts—H); ^{13}C-NMR (62.9 MHz, $[D_6]$DMSO): δ = 21.0 (Ts—CH_3), 45.9 (NCH_2), 126.4 (CH), 126.6 (CH), 128.2 (CH), 129.6 (CH), 136.9 (Cq), 137.9 (Cq), 138.7 (Cq), 142.5 (Cq); $C_{28}H_{28}N_2O_4S_2{\cdot}0.5H_2O$. Calcd.: C 63.49, H 5.52, N 5.29, S 12.11; found: C 63.89, H 5.45, N 5.08, S 11.70.

***N*,*N*-Bis[4-(ethoxycarbonyl)benzyl)-4-tolylsulfonamide 10:** A suspension of potassium carbonate (7.00 g, 50.72 mmol), amide **9** (3.33 g, 10.00 mmol), and

bromide **7** (2.43 g, 10.00 mmol) in dry DMF (200 mL) was stirred for 72 hours under an argon atmosphere. The solvent was evaporated and the remaining residue treated with trichloromethane (250 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4), and concentrated to yield a colourless substance, which was purified by column chromatography (silica gel, trichloromethane).

R_f = 0.55 (trichloromethane); 3.87 g (78% yield); M.p. 122 °C; MALDI-TOF (DHB): *m/z* = 518.1 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 496.1 $[M + H]^+$, 450.1 $[M - OC_2H_5]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.36 (t, ^3J = 7 Hz, 6 H; $C\underline{H}_3CH_2O$), 2.45 (s, 3 H; Ts—CH_3), 4.02 (s, 4 H; NCH_2), 4.03 (q, ^3J = 7 Hz, 4 H; OCH_2), 7.08 (d, ^3J = 8 Hz, 4 H; Ar—H), 7.32 (d, ^3J = 8 Hz, 2 H; Ts—H), 7.75 (d, ^3J = 8 Hz, 2 H; Ts—H), 7.86 (d, ^3J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 14.5 ($\underline{C}H_3CH_2O$), 21.7 (Ts—CH_3), 50.9 (NCH_2), 61.2 (OCH_2), 127.4 (CH), 128.5 (CH), 129.9 (CH), 130.1 (CH), 130.1 (Cq), 137.2 (Cq), 140.7 (Cq), 143.9 (Cq), 166.3 (CO); $C_{27}H_{29}NO_6S$. Calcd.: C 65.44, H 5.90, N 2.83, S 6.47; found: C 65.06,H 5.91, N 2.64, S 6.59.

***N,N*-Bis[4-(hydroxymethyl)benzyl)-4-tolylsulfonamide 11:** A suspension of diester **10** (2.47 g, 5.00 mmol), and lithium borohydride (1.00 g, 46.00 mmol) in dry THF (150 mL) was refluxed for 15 hours under an argon atmosphere. The cooled mixture was evaporated. Water (50 mL) was added to the remaining residue and the suspension was stirred for 30 min at room temperature to dissolve the inorganic salts. The alcohol remained undissolved, was filtered, washed with water (50 mL), dried, and used for the next step without further purification.

1.89 g (92% yield); M.p. 120 °C; MALDI-TOF (DHB): *m/z* = 434.7 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 412.1 $[M + H]^+$; ^{1}H-NMR (250 MHz, $[D_6]$DMSO): δ = 2.42 (s, 3 H; Ts—CH_3), 4.11 (s, 4 H; NCH_2), 4.42 (s, 4 H; OCH_2), 6.84 (d, ^3J = 8 Hz, 2 H; Ts—H), 6.97 (d, ^3J = 8 Hz, 2 H; Ts–H), 7.18 (d, ^3J = 8 Hz, 4 H; Ar—H), 7.60 (d, ^3J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (62.9 MHz, $[D_6]$DMSO): δ = 21.6 (Ts—CH_3), 51.2 (NCH_2), 65.0 (OCH_2), 127.1 (CH), 127.3 (CH), 128.9 (CH), 129.9 (CH), 135.2 (Cq), 137.3 (Cq), 140.1 (Cq), 143.5 (Cq).

***N,N*-Bis[4-(bromomethyl)benzyl)-4-tolylsulfonamide 12:** A suspension of alcohol **11** (2.06 g, 5.00 mmol) and PBr_3 (9.68 mL, 0.10 mol) in dry trichloromethane (200 mL) was refluxed for 48 hours under an argon atmosphere. The cooled mixture was poured into ice-water (100 mL) and stirred for one hour. The organic layer was separated, washed three times with concentrated $NaHCO_3$-solution (50 mL), dried (Na_2SO_4), filtered, and evaporated to yield a colourless substance, which was purified by column chromatography (silica gel, trichloromethane/acetone 50 : 1).

R_f = 0.62 (trichloromethane/acetone 50 : 1); 2.42 g (90% yield); M.p. 112 °C; MALDI-TOF (DHB): *m/z* = 561.2 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 1074.9 $[2 M + H]^+$, 537.9 $[M]^+$, 457.9 $[M - Br]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 3 H; Ts-CH_3), 4.27 (s, 4 H; NCH_2), 4.42 (s, 4 H; $BrCH_2$), 7.00 (d, ^3J = 8 Hz, 4 H; Ar—H), 7.19 (d, ^3J = 8 Hz, 4 H; Ar—H), 7.31 (d, ^3J = 8 Hz, 2 H; Ts—H), 7.72 (d, ^3J = 8 Hz, 2 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts—CH_3),

33.2 ($BrCH_2$), 50.9 (NCH_2), 127.2 (CH), 129.0 (CH), 129.1 (CH), 129.8 (CH), 136.1 (Cq), 137.2 (Cq), 137.2 (Cq), 143.5 (Cq); $C_{23}H_{23}Br_2NO_2 \cdot 0.5H_2O$. Calcd.: C 50.57, H 4.43, N 2.56, S 5.87; found: C 50.48, H 4.23, N 2.34, S 6.45.

1,4-Bis[*N*-(4-(ethoxycarbonyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl] benzene 14: A suspension of potassium carbonate (13.80 g, 0.10 mol), 1,4-bis[*N*-(4-tolylsulfonyl)aminomethyl)]benzene **13** (6.67 g, 15.00 mmol), and bromide **7** (7.29 g, 30.00 mmol) in dry DMF (300 mL) was stirred for 72 hours under an argon atmosphere. The solvent was evaporated and the remaining residue treated with trichloromethane. The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4), and concentrated to give a crude oil, which was purified by recrystallization from acetone to yield colourless crystals.

R_f = 0.62 (trichloromethane); 6.92 g (60% yield); M.p. 150 °C; MALDI-TOF (DHB): *m/z* = 791.2 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 769.2 $[M + H]^+$, 723.1 $[M - OC_2H_5]^+$, 613.1 [M − Ts]; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.33 (t, ^{3}J = 7 Hz, 6 H; $C\underline{H}_3CH_2O$), 2.45 (s, 6 H; Ts—CH_3), 4.20 (s, 4 H; NCH_2), 4.23 (s, 4 H; NCH_2), 4.27 (q, ^{3}J = 7 Hz, 4 H; OCH_2), 6.86 (s, 4 H, Ar—H), 7.04 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.32 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.72 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.84 (d, ^{3}J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 14.4 ($\underline{C}H_3CH_2O$), 21.7 (Ts—CH_3), 50.6 (NCH_2), 51.0 (NCH_2), 61.1 (OCH_2), 127.3 (CH), 128.4 (CH), 128.9 (CH), 129.7 (CH), 129.9 (Cq), 130.0 (CH), 135.2 (Cq), 137.3 (Cq), 141.1 (Cq), 143.8 (Cq), 166.3 (CO); $C_{42}H_{44}N_2O_8S_2 \cdot 0.5\ H_2O$. Calcd.: C 64.85, H 5.83, N 3.60, S 8.24; found: C 64.88, H 5.82, N 3.50, S 8.61.

1,4-Bis[*N*-(4-(hydroxymethyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl] benzene 15: A suspension of diester **14** (1.54 g, 2.00 mmol), and lithium borohydride (1.00 g, 46.00 mmol) in dry THF (150 mL) was refluxed for 15 hours under an argon atmosphere. The cooled mixture was evaporated. Water (50 mL) was added to the remaining residue and the suspension was stirred for 30 min at room temperature to dissolve the inorganic salts. The alcohol remained undissolved, was filtered, washed with water (50 mL), dried, and used for the next step without further purification.

1.23 g (90% yield); M.p. 152 °C; MALDI-TOF (DHB): *m/z* = 723.1 $[M + K]^+$, 707.1 $[M + Na]^+$, 691.2 $[M + Li]^+$; FAB-MS (NBA): *m/z* = 691.3 $[M + Li]^+$, 667.2 $[M - OH]^+$, 649.3 $[M - 2\ OH]^+$; ^{1}H-NMR (250 MHz, $[D_6]$DMSO): δ = 2.41 (s, 6 H; Ts—CH_3), 4.18 (s, 8 H; NCH_2), 4.42 (s, 4 H; OCH_2), 6.91 (s, 4 H; Ar—H), 6.97 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.16 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.42 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.75 (d, ^{3}J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (62.9 MHz, $[D_6]$DMSO): δ = 21.8 (Ts—CH_3), 50.4 (NCH_2), 50.5 (NCH_2), 62.6 (OCH_2), 126.3 (CH), 127.1 (CH), 128.0 (CH), 128.2 (CH), 129.9 (CH), 134.4 (Cq), 135.3 (Cq), 136.8 (Cq), 141.8 (Cq), 143.3 (Cq).

1,4-Bis[*N*-(4-(bromomethyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl]benzene 16: A suspension of alcohol **15** (2.05 g, 3.00 mmol), and PBr_3 (9.68 mL, 0.10 mol) in dry trichloromethane (200 mL) was refluxed for 48 hours under an

argon atmosphere. The cooled mixture was poured into ice-water (100 mL) and stirred for one hour. The organic layer was separated, washed three times with concentrated $NaHCO_3$-solution (100 mL), dried (Na_2SO_4), filtered, and evaporated to yield a colourless substance, which was purified by column chromatography (silica gel, trichloromethane/acetone 60 : 1).

R_f = 0.60 (trichloromethane/acetone 60 : 1); 2.24 g (92% yield); M.p. 154 °C; MALDI-TOF (DHB): *m/z* = 850.0 $[M + K]^+$, 834.0 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 811.1 $[M + H]^+$, 731.1 $[M - Br]^+$, 655.0 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 6 H; Ts—CH_3), 4.22 (s, 4 H; NCH_2), 4.24 (s, 4 H; NCH_2), 4.40 (s, 4 H; $BrCH_2$), 6.88 (s, 4 H; Ar—H), 6.96 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.18 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.30 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.71 (d, ^{3}J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts—CH_3), 33.1 ($BrCH_2$), 50.5 (NCH_2), 50.8 (NCH_2), 127.3 (CH), 128.7 (CH), 129.0 (CH), 129.1 (CH), 129.9 (CH), 135.2 (Cq), 136.2 (Cq), 137.3 (Cq), 137.4 (Cq), 143.6 (Cq); $C_{38}H_{38}Br_2N_2O_4S_2 \cdot CHCl_3$. Calcd.: C 52.88, H 4.39, N 3.13, S 7.17; found: C 52.36, H 4.47, N 3.17, S 6.94.

***N*,*N*-Bis[4-(*N*-(4-(ethoxycarbonyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl)benzyl]-4-tolyl-sulfonamide 17:** A suspension of potassium carbonate (13.80 g, 0.10 mol), amide **9** (1.20 g, 3.60 mmol), and bromide **12** (0.97 g, 1.80 mmol) in dry DMF (250 mL) was stirred for 72 hours under an argon atmosphere. The solvent was evaporated, and the remaining residue treated with trichloromethane (100 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4) and concentrated to yield a colourless substance, which was purified by column chromatography (silica gel, trichloromethane/acetone 50 : 1).

R_f = 0.60 (trichloromethane/acetone 50 : 1); 0.97 g (52% yield); M.p. 92 °C; MALDI-TOF (DHB): *m/z* = 1080.7 $[M + K]^+$, 1064.8 $[M + Na]^+$, 889.4 $[M - Ts]^+$; FAB-MS (NBA): *m/z* = 1042.4 $[M + H]^+$, 996.3 $[M - OC_2H_5]^+$, 886.4 [M − Ts]; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, ^{3}J = 7 Hz, 6 H; $C\underline{H}_3CH_2O$), 2.39 (s, 9 H; Ts—CH_3), 4.06 (s, 4 H; NCH_2), 4.16 (s, 4 H; NCH_2), 4.19 (s, 4 H; NCH_2), 4.22 (q, ^{3}J = 7 Hz, 4 H; OCH_2), 6.72 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 6.82 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 6.96 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.24 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 7.64 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 7.77 (d, ^{3}J = 8 Hz, 4 H; Ar—H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 14.3 ($\underline{C}H_3CH_2O$), 21.6 (Ts—CH_3), 24.8 (Ts—CH_3), 49.9 (NCH_2), 50.8 (NCH_2), 51.2 (NCH_2), 61.0 (OCH_2), 127.2 (CH), 127.2 (CH), 128.3 (CH), 128.7 (CH), 128.8 (Cq), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 135.0 (Cq), 135.3 (Cq), 137.0 (Cq), 137.5 (Cq), 141.1 (Cq), 143.5 (Cq), 143.7 (Cq), 166.2 (CO); $C_{57}H_{59}N_3O_{10}S_3 \cdot H_2O$. Calcd.: C 64.57, H 5.80, N 3.96, S 9.07; found: C 64.68, H 5.68, N 3.75, S 9.00.

***N*,*N*-Bis[4-(*N*(4-(hydroxymethyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl) benzyl]-4-tolyl-sulfonamide 18:** A suspension of diester **17** (0.97 g, 0.93 mmol), and lithium borohydride (2.00 g, 92.00 mmol) in dry THF (100 mL) was refluxed for 15 hours under an argon atmosphere. The cooled mixture was evaporated. Water (50 mL) was added to the remaining residue and the suspension was stirred for 30

minutes at room temperature to dissolve the inorganic salts. The alcohol remained undissolved, was filtered, washed with water (50 mL), dried, and used for the next step without further purification.

0.85 g (96% yield); MALDI-TOF (DHB): *m/z* = 997.3 $[M + K]^+$, 980.3 $[M + Na]^+$, 964.4 $[M + Li]^+$, 804.4 $[M - Ts]^+$; FAB-MS (NBA): *m/z* = 958.1 $[M + H]^+$, 922.3 $[M - 2\ OH]^+$, 802.2 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $[D_6]$DMSO): δ = 2.41 (s, 9 H; Ts—CH_3), 4.13 (s, 4 H; NCH_2), 4.15 (s, 4 H; NCH_2), 4.17 (s, 4 H; NCH_2), 4.41 (d, ^{3}J = 5 Hz, 4 H; OCH_2), 5.14 (t, ^{3}J = 5 Hz, 2 H; OH), 6.84 (s, 8 H; Ar—H), 6.95 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.13 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.40 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 7.72 (d, ^{3}J = 8 Hz, 6 H; Ts—H); ^{13}C-NMR (62.9 MHz, $[D_6]$DMSO): δ = 21.0 (Ts—CH_3), 50.4 (NCH_2), 50.5 (NCH_2), 62.5 (OCH_2), 126.2 (CH), 127.0 (CH), 128.0 (CH), 128.1 (CH), 129.8 (CH), 134.3 (Cq), 135.3 (Cq), 136.7 (Cq), 141.7 (Cq), 143.3 (Cq).

***N*,*N*-Bis[4-(*N*-(4-(bromomethyl)benzyl)-*N*-(4-tolylsulfonyl)amino-methyl) benzyl]-4-tolyl-sulfonamide 19:** A suspension of alcohol **18** (0.85 g, 0.89 mmol), and PBr_3 (19.36 mL, 0.20 mol) in dry trichloromethane (100 mL) was refluxed for 48 hours under an argon atmosphere. The cooled mixture was poured into ice-water (100 mL) and stirred for one hour. The organic layer was separated, washed three times with concentrated $NaHCO_3$-solution (100 mL), dried (Na_2SO_4), filtered, and evaporated to give a colourless substance, which was purified by column chromatography (silica gel, trichloromethane/acetone 20 : 1).

R_f = 0.80 (trichloromethane/ethanol 20 : 1); 0.86 g (89% yield); M.p. 102 °C; MALDI-TOF (DHB): *m/z* = 1124.1 $[M + K]^+$, 1106.1 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 1125.3 $[M + K]^+$, 1084.1 $[M]^+$, 928.2 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 9 H; Ts—CH_3), 4.18 (s, 4 H; NCH_2), 4.21 (s, 4 H; NCH_2), 4.22 (s, 4 H; NCH_2), 4.39 (s, 4 H; $BrCH_2$), 6.86 (s, 8 H; Ar—H), 6.95 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.14 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.28 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 7.72 (d, ^{3}J = 8 Hz, 6 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts—CH_3), 33.1 ($BrCH_2$), 50.4 (NCH_2), 50.5 (NCH_2), 50.8 (NCH_2), 127.2 (CH), 128.7 (CH), 129.0 (CH), 129.1 (CH), 129.9 (CH), 135.3 (Cq), 136.2 (Cq), 137.3 (Cq), 137.4 (Cq), 143.6 (Cq); $C_{53}H_{53}Br_2N_3O_6S_3 \cdot (CH_3)_2CO$. Calcd.: C 58.99, H 5.21, N 3.68, S 8.42; found: C 59.58, H 5.20, N 3.86, S 8.86.

2,11,20,29-Tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,4)benzeno(1, 4)benzeno[3.3](1,4)benzeno(3,3′)biphenylo⟨4⟩phane 28: 1,4-Bis[*N*-(*N*-(4-tolylsulfonyl)aminomethyl)benzyl-*N*-(4-tolylsulfonyl)aminomethyl]benzene **25** (50 mg, 0.05 mmol), and 3,3′-bis(bromomethyl)biphenyl **26** (17 mg, 0.05 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (200 mL) under an argon atmosphere. The mixture was then stirred for a further 72 hours. The solvent was evaporated, and the remaining residue treated with dichloromethane. The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (20 mL), dried

(Na_2SO_4), concentrated, and purified by column chromatography (silica gel, trichloromethane/acetone 100 : 1) to yield a colourless substance.

R_f = 0.31 (trichloromethane/acetone 100 : 1); 29 mg (50% yield); M.p. 105 °C; MALDI-TOF (DHB): *m/z* = 1207.6 $[M + K]^+$, 1191.6 $[M + Na]^+$, 1015.6 $[M - Ts]^+$; FAB-MS (NBA): *m/z* = 1013.4 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 6 H; Ts—CH_3), 2.46 (s, 6 H; Ts—CH_3), 3.92 (s, 4 H; NCH_2), 4.02 (s, 4 H; NCH_2), 4.16 (s, 4 H; NCH_2), 4.19 (s, 4 H; NCH_2), 6.61 (s, 4 H; Ar—H), 6.73 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 6.84 (d, ^{3}J = 8 Hz, 8 H; Ts—H), 7.22 (d, ^{3}J = 8 Hz, 4 H; Ar–H), 7.35 (d, ^{3}J = 8 Hz, 8 H; Ts—H), 7.70 (m, 8 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts—CH_3), 23.0 (Ts—CH_3), 50.8 (NCH_2), 51.6 (NCH_2), 127.2 (CH), 127.3 (CH), 127.3 (CH), 128.6 (CH), 128.6 (CH), 128.8 (CH), 129.9 (CH), 135.0 (Cq), 135.1 (Cq), 135.3 (Cq), 136.4 (Cq), 136.9 (Cq), 140.0 (Cq), 143.7 (Cq); $C_{66}H_{64}N_4O_8S_4 \cdot 2\ CH_2Cl_2$. Calcd.: C 60.98, H 5.11, N 4.18; found: C 61.15, H 5.73, N 3.94.

2,11,20,29-Tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,4)benzeno(1,4)benzeno[3.3](1,4)benzeno(4,4′)-*o*-terphenylo⟨4⟩phane 29: The diamide **25** (50 mg, 0.05 mmol), and the 4,4′-bis(bromomethyl)-*o*-terphenyl **27** (21 mg, 0.05 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (200 mL) under an argon atmosphere. The mixture was then stirred for a further 72 hours. The solvent was evaporated, and the remaining residue treated with dichloromethane (50 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, trichloromethane/acetone 100 : 1) to yield a colourless substance.

R_f = 0.28 (trichloromethane/acetone 100 : 1); 26 mg (41% yield); M.p. 115 °C; MALDI-TOF (DHB): *m/z* = 1283.7 $[M + K]^+$, 1267.8 $[M + Na]^+$, 1091.8 $[M - Ts]^+$; FAB-MS (NBA): *m/z* = 1098.5 $[M - Ts]^+$, 933.4 $[M - 2\ Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 6 H; Ts—CH_3), 2.46 (s, 6 H; Ts—CH_3), 4.10 (s, 8 H; NCH_2), 4.11 (s, 4 H; NCH_2), 4.13 (s, 4 H; NCH_2), 6.73 (s, 4 H; Ar—H), 6.78 (s, 12 H; Ar—H), 6.99 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.30 (m, 12 H; Ar—H), 7.70 (m, 8 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts—CH_3), 23.0 (Ts—CH_3), 23.8 (Ts—CH_3), 50.2 (NCH_2), 51.2 (NCH_2), 127.3 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 128.7 (CH), 128.8 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 133.8 (Cq), 135.2 (Cq), 135.5 (Cq), 136.8 (Cq), 137.2 (Cq), 139.9 (Cq), 141.0 (Cq), 143.5 (Cq), 143.7 (Cq); $C_{72}H_{68}N_4O_8S_4$. Calcd. C 69.43, H 5.51, N 4.56; found: C 69.44, H 6.41, N 4.70.

2,11,20,29,38-Pentakis(4-tolylsulfonyl)-2,11, 20,29,38-pentaaza[3.3](1,4)benzeno(1,4)benzeno[3.3](1,4)benzeno(1,4)benzeno[3.0](1,4)benzeno(1,4)benzeno⟨6⟩phane 30: The diamide **23** (26 mg, 0.05 mmol), and the dibromide **19** (54 mg, 0.05 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (400 mL) under an argon atmosphere.

The mixture was then stirred for a further 72 hours. The solvent was evaporated and the remaining residue treated with dichloromethane (50 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, trichloromethane/acetone 100 : 1) to yield a colourless substance.

R_f = 0.33 (trichloromethane/acetone 100 : 1); 31 mg (43% yield); M.p. 164 °C; MALDI-TOF (DHB): *m/z* = 1481.6 $[M + K]^+$, 1465.6 $[M + Na]^+$, 1288.6 $[M - Ts]^+$; FAB-MS (NBA): *m/z* = 1442.6 $[M + H]^+$, 1286.5 $[M - Ts]^+$, 1130.5 $[M - 2\ Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 9 H; Ts—CH_3), 2.47 (s, 6 H; Ts—CH_3), 3.97 (s, 4 H; NCH_2), 4.05 (s, 4 H; NCH_2), 4.10 (s, 4 H; NCH_2), 4.15 (s, 8 H; NCH_2), 6.73 (s, 8 H; Ar—H), 6.75 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 6.84 (d, ^{3}J = 8 Hz, 6 H; Ts—H), 6.93 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.15 (d, ^{3}J = 8 Hz, 4 H; Ar—H), 7.30 (m, 8 H; Ar–H), 7.70 (m, 8 H; Ar—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.8 (Ts—CH_3), 50.1 (NCH_2), 50.5 (NCH_2), 50.9 (NCH_2), 51.8 (NCH_2), 52.0 (NCH_2), 126.5 (CH), 127.3 (CH), 127.4 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 129.9 (CH), 130.0 (CH), 130.0 (CH), 135.1 (Cq), 135.1 (Cq), 135.3 (Cq), 135.4 (Cq), 135.5 (Cq), 136.8 (Cq), 137.3 (Cq), 137.4 (Cq), 139.4 (Cq), 143.7 (Cq), 143.8 (Cq); $C_{81}H_{79}N_5O_{10}S_5 \cdot CHCl_3$. Calcd.: C 63.04, H 5.16, N 4.48, S 10.26; found: C 63.01, H 5.51, N 4.26, S 9.83.

2,11,20,29,38-Pentakis(4-tolylsulfonyl)-2,11,20,29,38-pentaaza[3.3.3.3.3](1,4)benzeno⟨5⟩phane 31: The diamide **25** (99 mg, 0.1 mmol) and the dibromide **12** (54 mg, 0.1 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (400 mL) under an argon atmosphere. The mixture was then stirred for a further 72 hours. The solvent was evaporated and the remaining residue treated with dichloromethane (100 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (50 mL), dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, trichloromethane/ethanol 30 : 1) to give a colourless oil.

R_f = 0.52 (trichloromethane/ethanol 20 : 1); 42 mg (31% yield); MALDI-TOF (DHB): *m/z* = 1388.2 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 1367.5 $[M + H]^+$, 1210.4 $[M - Ts]^+$, 1054.2 $[M - 2\ Ts]^+$, 898.5 $[M - 3\ Ts]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 15 H; Ts—CH_3), 4.05 (s, 20 H; NCH_2), 6.78 (s, 20 H; Ar—H), 7.34 (d, ^{3}J = 8 Hz, 10 H; Ts—H), 7.71 (d, ^{3}J = 8 Hz, 10 H; Ts—H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 22.0 (Ts—CH_3), 51.0 (NCH_2), 127.6 (CH), 128.9 (CH), 130.2 (CH), 135.6 (Cq), 137.3 (Cq), 144.0 (Cq); $C_{75}H_{75}N_5O_{10}S_5 \cdot 2.5\ CH_2Cl_2$. Calcd.: C 58.95, H 5.11, N 4.44, S 10.15; found: C 59.37, H 5.27, N 4.07, S 10.41.

2,11,20,29,38,47-Hexakis(4-tolylsulfonyl)-2,11,20,29,38,47-hexaaza[3.3.3.3.3.3](1,4)benzeno⟨6⟩phane 32: The diamide **25** (99 mg, 0.10 mmol) and the dibromide **16** (81 mg, 0.10 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (400 mL) under an argon atmosphere. The mixture was then stirred for a further 72 hours. The

solvent was evaporated and the remaining residue treated with dichloromethane (100 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (100 mL), dried (Na_2SO_4), and concentrated to yield a colourless substance, which was purified by column chromatography (silica gel, trichloromethane/ethanol 30 : 1).

R_f = 0.32 (trichloromethane/ethanol 30 : 1); 65 mg (40% yield); M.p. 238 °C; MALDI-TOF (DHB): *m/z* = 1662.4 $[M + Na]^+$; FAB-MS (NBA): *m/z* = 1641.1 $[M + H]^+$, 1483.5 $[M - Ts]^+$, 1330.6 $[M - 2\ Ts]^+$; IR (KBr, cm^{-1}): ν = 2921.4 (s), 1721.6 (m), 1596.1 (m), 1446.5 (m), 1332.7 (vs), 1156.0 (vs), 1090.7 (vs), 916.0 (s), 813.7 (s), 759.6 (s), 654.4 (s); ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 18 H; Ts—CH_3), 4.07 (s, 24 H; NCH_2), 6.79 (s, 24 H; Ar—H), 7.33 (d, ^{3}J = 8 Hz, 12 H; Ts—H), 7.71 (d, ^{3}J = 8 Hz, 12 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.8 (Ts—CH_3), 50.6 (NCH_2), 127.3 (CH), 128.8 (CH), 130.0 (CH), 135.3 (Cq), 137.3 (Cq), 143.7 (Cq); $C_{90}H_{90}N_6O_{12}S_5 \cdot 2\ CH_2Cl_2$. Calcd.: C 61.12, H 5.13, N 4.65, S 10.64; found: C 61.50, H 5.53, N 4.31, S 10.15.

2,11,20,29,38,47,56-Heptakis(4-tolylsulfonyl)-2,11,20,29,38,47,56-heptaaza [3.3.3.3.3.3.3](1,4)benzeno⟨7⟩phane 33: The diamide **25** (69 mg, 0.07 mmol) and the dibromide **19** (76 mg, 0.07 mmol) were each dissolved in dry DMF (50 mL). These solutions were added dropwise and simultaneously over 83 hours to a suspension of cesium carbonate (1.63 g, 5.00 mmol) in dry DMF (300 mL) under an argon atmosphere. The mixture was then stirred for a further 72 hours. The solvent was evaporated and the remaining residue treated with dichloromethane (50 mL). The undissolved inorganic salts were removed by filtration, the filtrate was washed with water (20 mL), dried (Na_2SO_4), and concentrated to yield a colourless oil, which was purified by column chromatography (silica gel, trichloromethane/acetone 100 : 1).

R_f = 0.39 (trichloromethane/acetone 100 : 1); 54 mg (40% yield); MALDI-TOF (DHB): *m/z* = 1951.9 $[M + K]^+$, 1935.1 $[M + Na]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.48 (s, 21 H; Ts—CH_3), 4.06 (s, 28 H; NCH_2), 6.77 (s, 28 H; Ar—H), 7.27 (d, ^{3}J = 8 Hz, 14 H; Ts—H), 7.65 (d, ^{3}J = 8 Hz, 14 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.5 (Ts–CH_3), 50.5 (NCH_2), 127.2 (CH), 128.6 (CH), 129.8 (CH), 135.2 (Cq), 137.1 (Cq), 143.6 (Cq); $C_{105}H_{105}N_7O_{14}S_7$. Calcd.: C 65.91, H 5.54, N 5.12; found: C 65.77, H 5.53, N 4.43.

Paracyclophanes 4, 35–39: The dibromide **34** (1.32 g, 5.00 mmol) was dissolved in dry DMF (250 mL). This solution was added dropwise over 2 hours to a suspension of cesium carbonate (4.90 g, 15 mmol) and diamide **23** (2.60 g, 5.00 mmol) in dry DMF (200 mL) under an argon atmosphere. The mixture was further stirred for 110 hours. The solvent was evaporated and the remaining residue treated with dichloromethane. The undissolved inorganic salts were removed by filtration, the filtrate was washed with water, dried (Na_2SO_4), and concentrated. Four cyclic products were isolated by column chromatography (silica gel, trichloromethane/acetone 30 : 1).

2,11,26,35-Tetrakis(4-tolylsulfonyl)-2,11,26,35-tetraaza[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo⟨4⟩phane 35: R_f = 0.65 (trichloromethane/acetone 30 : 1); 0.40 g (13% yield); M.p. >280 °C; MALDI-TOF (DHB): *m/z* = 1271.1 $[M + Na]^+$, 1245.6 $[M]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 6 H; Ts—CH_3), 2.46 (s, 6 H; Ts—CH_3), 4.15 (s, 8 H; NCH_2), 4.17 (s, 8 H; NCH_2), 6.85 (s, 8 H; Ar—H), 6.97 (d, ^{3}J = 8 Hz, 8 H; Ts—H), 7.26–7.36 (m, 16 H, Ar—H), 7.73 (d, ^{3}J = 8 Hz, 8 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts—CH_3), 50.6 (NCH_2), 50.7 (NCH_2), 126.8 (CH), 127.4 (CH), 129.0 (CH), 130.0 (CH), 135.1 (Cq), 137.5 (Cq), 139.7 (Cq), 143.6 (Cq); $C_{72}H_{68}N_4O_8S_4 \cdot CH_2Cl_2$. Calcd.: C 65.90, H 5.30, N 4.21, S 9.64; found: C 65.43, H 5.24, N 4.06, S 8.97.

2,11,26,35,50,59-Hexakis(4-tolylsulfonyl)-2,11,26,35,50,59-hexaaza[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo⟨6⟩phane 36: R_f = 0.64 (trichloromethane/acetone 30 : 1); 0.28 g (9% yield); M.p. >280 °C; MALDI-TOF (DHB): *m/z* = 1869.1 $[M]^+$, 1713.1 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.46 (s, 18 H; Ts—CH_3), 4.12 (s, 12 H; NCH_2), 4.16 (s, 12 H; NCH_2), 6.81 (s, 12 H; Ar—H), 6.96 (d, ^{3}J = 8 Hz, 12 H; Ts—H), 7.26–7.35 (m, 24 H, Ar—H), 7.73 (d, ^{3}J = 8 Hz, 12 H; Ts—H); ^{13}C—NMR (62.9 MHz, $CDCl_3$): δ = 21.6 (Ts—CH_3), 50.5 (NCH_2), 50.7 (NCH_2), 126.6 (CH), 127.2 (CH), 129.0 (CH), 129.8 (CH), 135.0 (Cq), 137.2 (Cq), 139.4 (Cq), 143.5 (Cq); $C_{108}H_{102}N_6O_{12}S_6 \cdot CHCl_3$. Calcd.: C 65.91; H 5.23; N 4.23; S 9.67; found: C 65.96, H 5.35, N 4.00, S 9.02.

2,11,26,35,50,59,74,83-Octakis(4-tolylsulfonyl)-2,11,26,35,50,59,74,83-octaaza[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo⟨8⟩phane 37: R_f = 0.62 (trichloromethane/acetone 30 : 1); 93 mg (3% yield); colourless oil; MALDI-TOF (DHB): *m/z* = 2513.6 $[M + Na]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 24 H; Ts—CH_3), 4.24 (s, 16 H; NCH_2), 4.27 (s, 16 H; NCH_2), 6.88 (s, 16 H; Ar—H), 7.04 (d, ^{3}J = 8 Hz, 16 H; Ts—H), 7.28–7.37 (m, 32 H, Ar—H), 7.72 (d, ^{3}J = 8 Hz, 16 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (Ts—CH_3), 50.5 (NCH_2), 50.5 (NCH_2), 127.2 (CH), 128.8 (CH), 129.2 (CH), 130.0 (CH), 135.2 (Cq), 137.7 (Cq), 140.0 (Cq), 143.6 (Cq); $C_{144}H_{136}N_8O_{16}S_8 \cdot 1.5\ CHCl_3$. Calcd.: C 65.50, H 5.20, N 4.20, S 9.60; found: C 65.47, H 5.34, N 3.93, S 8.95.

2,11,26,35,50,59,74,83,98,107-Decakis(4-tolylsulfonyl)-2,11,26,35,50,59,74,83, 98,107-decaaza[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo⟨10⟩phane 4: R_f = 0.61 (trichloromethane/acetone 30 : 1); 62 mg (2% yield); colourless oil; MALDI-TOF (DHB): *m/z* = 3137.5 $[M + Na]^+$, 2982.4 $[M - Ts + Na]^+$, 2958.4 $[M - Ts]^+$; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 30 H; Ts—CH_3), 4.24 (s, 20 H; NCH_2), 4.26 (s, 20 H; NCH_2), 6.94 (s, 20 H; Ar—-H), 7.04 (d, ^{3}J = 8 Hz, 20 H; Ts–H), 7.27–7.36 (m, 40 H, Ar—H), 7.71 (d, ^{3}J = 8 Hz, 20 H; Ts—H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.8 (Ts—CH_3), 50.5 (NCH_2), 50.6 (NCH_2), 127.5 (CH), 128.9 (CH), 129.1 (CH), 130.0 (CH),

135.1 (Cq), 137.7 (Cq), 140.0 (Cq), 143.6 (Cq); $C_{180}H_{170}N_{10}O_{20}S_{10}\cdot 2.5\ CHCl_3$. Calcd.: C 64.24, H 5.10, N 4.10, S 9.40; found: C 64.05, H 5.10, N 3.95, S 9.11.

2,11,26,35,50,59,74,83,98,107,122,131-Dodecakis(4-tolylsulfonyl)-2,11,26, 35,50,59,74,83,98,107,122,131-dodecaaza[3.3](1, 4)benzeno(4,4′)biphenylo[3.3] (1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno (4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′) biphenylo⟨12⟩phane 38: MALDI-TOF (DHB): *m/z* = 3745.8 $[M]^+$

2,11,26,35,50,59,74,83,98,107,122,131,146,155-Tetradecakis(4-tolylsulfonyl)-2,11,26,35,50,59,74,83,98,107,122,131,146,155-tetradecaaza[3.3](1,4)benzeno (4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′) biphenylo[3.3](1,4)benzeno(4,4′)biphenylo[3.3](1,4)benzeno(4,4′)biphenylo [3.3](1,4)benzeno(4,4′)biphenylo[3.3](1, 4)benzeno(4,4′)biphenylo⟨14⟩phane 39: MALDI-TOF (DHB): *m/z* = 4365.8 $[M + Na]^+$

3. Results and Discussion

The strategy involves the preparation of open-chain molecules based on bis(methylene)tosylamide bridged *p*-substituted benzene units with terminal ester groups (**10**, **14** and **17**) and subsequent functional group transformation to the corresponding dialcohol (**11**, **15** and **18**) and dibromide. The formation of the final products was realized by macrocyclizations of the dibromides based on linear tosylamides (**12**, **16** and **19**), biphenyl (**26**) and terphenyl (**27**) with bistosylamides based on biphenyl (**23**) or a larger linear molecule (**25**). In this way we synthesized paracyclophanes (**31–33**) and cyclophanes containing biphenyl or terphenyl (**28–30**) with up to 49 ring members and seven benzene units in 31–50% macrocyclization yield. We also prepared 36-, 54-, 72- and 90-membered mixed biphenylobenzenophanes (**4**, **35–37**). The 90-membered nanocycle **4** with approximately 4 nm diameter in the extended conformation is the largest isolated paracyclophane described here (Figure 2).

In an oligomeric mixture of macrocycles, which we could not separate, the 108- and 126-membered ultracycles **38** and **39** can be detected by MALDI-TOF-MS and TLC.

The synthesis of the monofunctionalized tosylamide **9** follows similar steps as the synthesis of the already known 2,4-bis[*N*-(4-tolylsulfonyl)aminomethyl]-1,5-bis(ethoxycarbonyl)benzene and 3,5-bis[(4-tolylsulfonylamino)methyl]benzoic acid ethylester, which are important precusors in the synthesis of di- and tetrafunctionalized molecular ribbons [14]. The overall yield for this four step sequence was 38% (Figure 3).

The smallest difunctionalized linear molecule **10** in this series containing two benzene units is formed by the reaction of bromide **7** and tosylamide **9** in 78% yield. Subsequently, the derivatization of the terminal ester groups resulted in the corresponding dialcohol **11** and dibromide **12** [15] (Figure 4). Furthermore, we synthesized diester **14** containing three benzene units in 60% yield using the

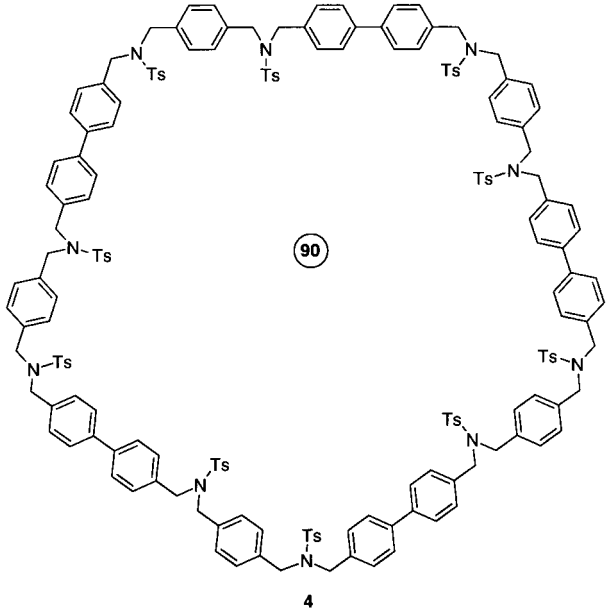

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Figure 2. 90-membered biphenylobenzenophane **4**.

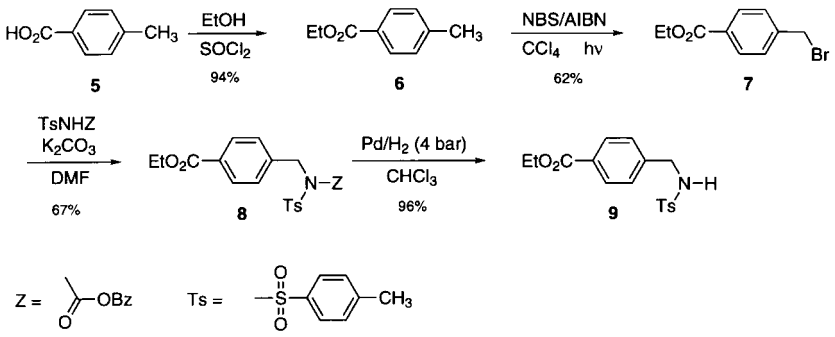

Figure 3. Synthesis of monofunctionalized diamide **9**.

bromide **7** and 1,4-bis[*N*-(4-tolylsulfonyl)aminomethyl]benzene **13** [14]. Transformation to alcohol **15** and bromide **16** succeeded again in similar yields as those obtained in the preparation of **11** and **12** (Figure 4). The linear tosylamides **17**-**19** containing four benzene units are second generation molecules in the iterative synthetic sequence. The diester **17** was prepared in 52% yield, derivatization to the dialcohol **18** and the dibromide **19** was achieved in 96% and 89% yield, respectively (Figure 4).

In addition to the linear dibromides **12**, **16** and **19** we used 3,3′-bis(bromomethyl)biphenyl **26** and 4,4′-bis(bromomethyl)-*o*-terphenyl **27** [16] as the first group of macrocyclization precursors. As a second group we used linear

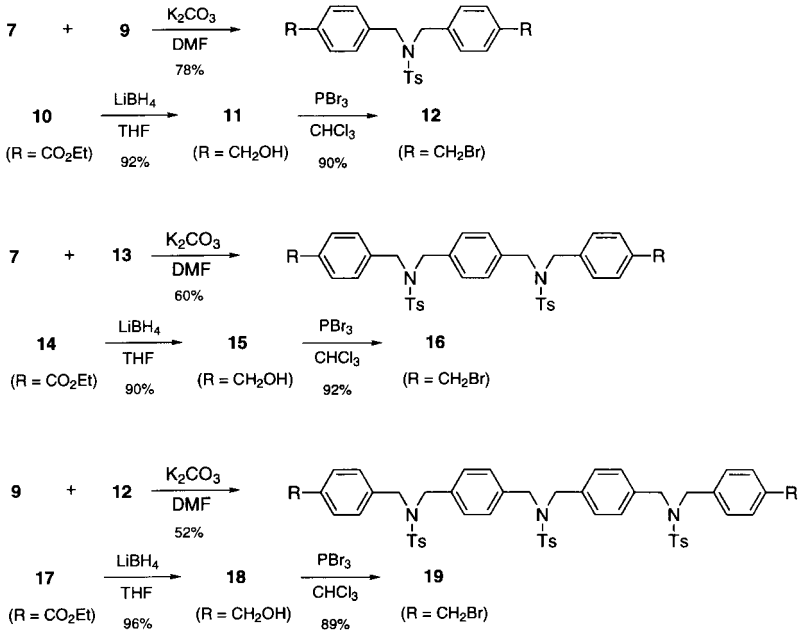

Figure 4. Preparation and derivatization of difunctionalized molecular threads containing two to four benzene units.

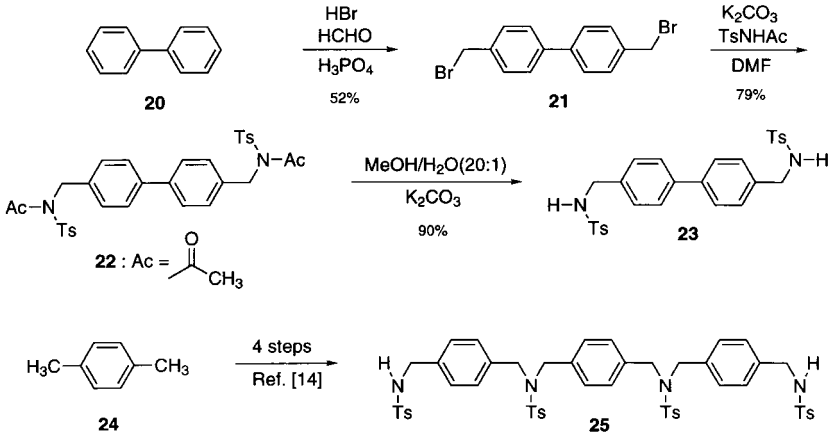

Figure 5. Synthesis of bis(tosylamides) **23** and **25** used in final macrocyclizations.

bistosylamides **25** [14] (four steps, overall yield 6%) and 4,4′-dimethylbiphenyl-based **23** [17] (three steps, overall yield 37%; Figure 5).

Macrocyclizations to nanometre-sized cyclophanes were carried out under high-dilution conditions [18] by simultaneous and dropwise addition of the cyclization precursors to a suspension of cesium carbonate [19] in DMF.

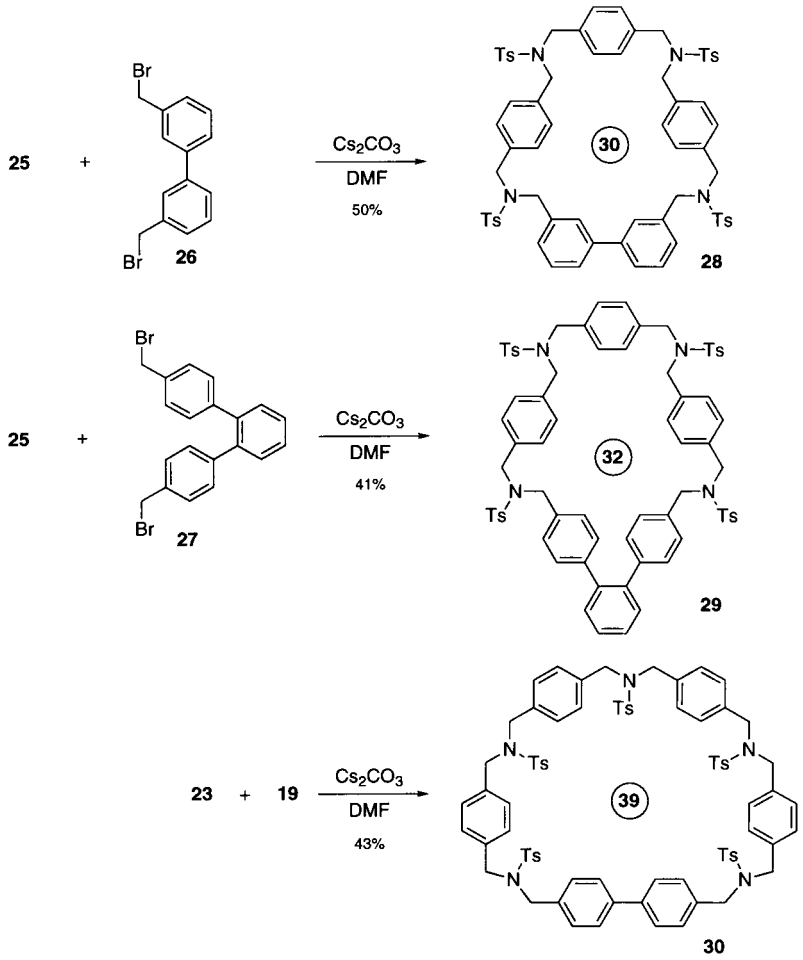

Figure 6. Formation of nano-sized macrocycles **28**, **29** and **30**.

The 30- and 32-membered rings **28** (50%) and **29** (41%) were obtained by the macrocyclization of bromides **26** and **27**, respectively, with tosylamide **25**. Bromide **19** and tosylamide **23** yielded the *all*-paracyclophane **30** (43%, Figure 6).

The highly symmetrical [3_n]paracyclophanes containing tosylamide bridges that are presented here showed only five ^{1}H-NMR signals independent of the number of ring members. The problem of distinguishing each macrocycle was solved by FAB and MALDI-TOF mass spectrometry. A one-pot synthesis of these cyclophanes was carried out using 1,4-bis(bromomethyl)benzene **34**, tosylamide, and NaH, but only 28-membered [3_4] paracyclophane [20] and smaller cycles could be isolated. Thus, the following directed syntheses were carried out (Figure 7):

The macrocyclization of the 35-membered [3_5]paracyclophane **31** using bromide **12** [15] and amide **25** succeeded in 31% yield. For the 42-membered [3_6]paracyclophane **32** we macrocyclized (40% yield) the molecular threads **16**

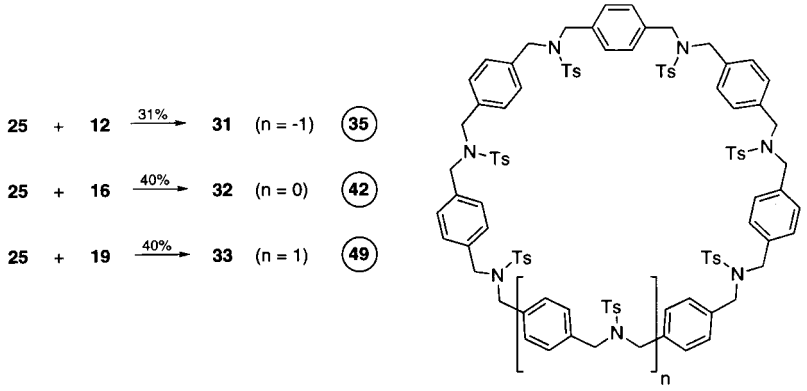

Figure 7. Preparation of highly symmetrical 35-, 42- and 49-membered [3_n]paracyclophanes **31–33** (n = 5–7).

and **25** which have the same size but complementary functionalities (Figure 7). The biggest bis(methylene)tosylamide bridged [3_n]paracyclophane **33** known to date was prepared from bromide **19** and amide **25** (n = 7, 40% yield; Figure 7). Higher cyclic products could not be separated.

The advantage of our synthetic strategy for cyclophane systems is that even cyclophanes with mixed building blocks of variable ring size and rigidity can be prepared and isolated relatively easily. Macrocycles of this type are no longer only side-products in the synthesis of smaller cycles and thus easier to isolate because of higher yields and since no mixture of similar cyclic oligomers has to be separated.

The formation of new "mixed" nanocyclic biphenylobenzenophanes was achieved by the following modified cyclization method: Without use of high-dilution conditions 1,4-bis(bromomethyl)benzene **34** [21] was added dropwise to a suspension of tosylamide **23** and cesium carbonate in DMF. The idea was to favour larger linear intermediate molecules and hence higher cyclic products [14]. By means of MALDI-TOF we detected open chain bistosylamides of variable length and a mixture of macrocycles. We were able to separate four different paracyclophanes (**4, 35–37**) containing 36, 54, 72 and 90 ring members. Also a mixture including two ultracycles **38** and **39**, 108- and 126-membered, was isolated (n = 0–5; Figure 8).

4. Conclusions

The synthetic strategy described demonstrates a route to linear thread molecules with variable length up to nanometric size and subsequently macrocycles with a paracyclophane framework, which can be varied in size and rigidity. In the future it should be possible to elongate the molecular threads by affixing additional benzene units to obtain subsequently even larger ring systems. The yields should be high enough to allow further derivatizations at the bridges. Detosylation [22]

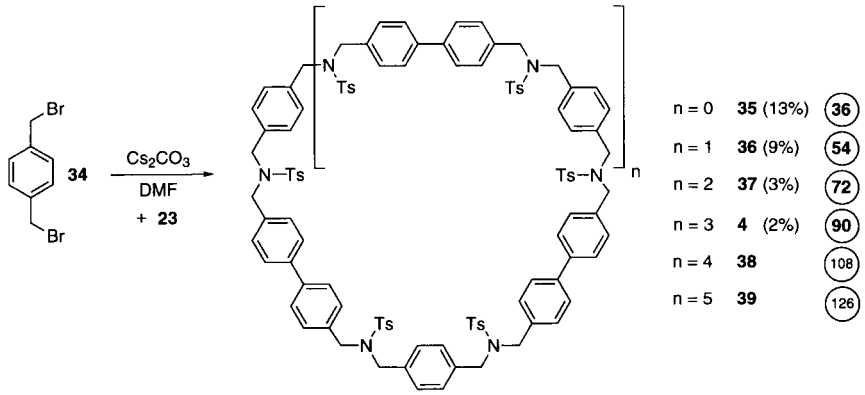

Figure 8. Synthesis leading to "mixed" benzene-biphenyl nanocycles **4** and **35–39**.

to free secondary oligoamines, nitrosation and N_2O-extrusion [23] would lead to [2_n]paracyclophane hydrocarbons. The detosylation of [3_4]paracyclophanes [20] has already been achieved in good yields. If the adaptation to larger ring molecules is possible, further inter- and intramolecular bridges could be incorporated in order to obtain macrooligocyclic skeletons [24] or new molecular belts [14], tubes [25], or networks. Functional groups in the free arene positions could lead to molecules similar to calixarenes but based on paracyclophanes [6, 26]. By means of the variations presented here it should be possible to produce macrocyclic cavities with new material properties similar to those of the cyclodextrins or to obtain chemoselective sensing [27]. Orientating studies in this direction are promising [28].

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