An Expeditious Preparation of 15-Membered Nitrogen-Containing Olefinic and Benzo Macrocycles

Rosa M. Sebastián,*[a] Marcial Moreno-Mañas,[a] and Adelina Vallribera[a]

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(*E*,*E*)-1,6,11-Tris(arenesulfonyl)-3,4-benzo-1,6,11-triazacyclopentadeca-8,13-dienes (**2**) and 1,6,11-tris(arenesulfonyl)-3,4;8,9;13,14-tribenzo-1,6,11-triazacyclopentadecanes (**3**) were prepared from arenesulfonamides, *trans*-1,4-dibromobutene, and 1,2-bis(bromomethyl)benzene. They form unstable complexes with silver tetrafluoroborate.

Introduction

Supporting Information for this article, consisting of spectra of reported compounds, is available (see also footnote on the first page of this article).

Nitrogen-containing 15-membered macrocycles featuring internal double bonds are rare.[1] The few examples known from other groups contain only one double bond, and the key step in their preparation is metathesis.[2]

We are interested in the preparation and organometallic chemistry of 15-membered triolefinic macrocycles, and have described macrocycles **1a** (Figure 1), containing three non-coordinating nitrogen atoms. Compounds **1a** coordinate Pd^0, Pt^0, and Ag^I [3] through their olefinic double bonds. Their palladium complexes function as catalysts or precatalysts in Suzuki couplings,[3a] hydroarylation of alkynes,[3] butadiene telomerization,[4] and in Heck reactions.[5]

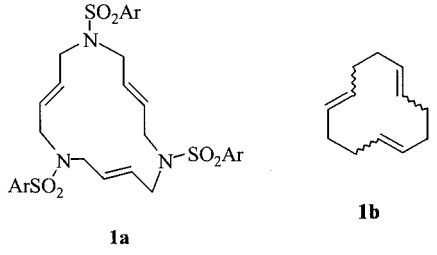
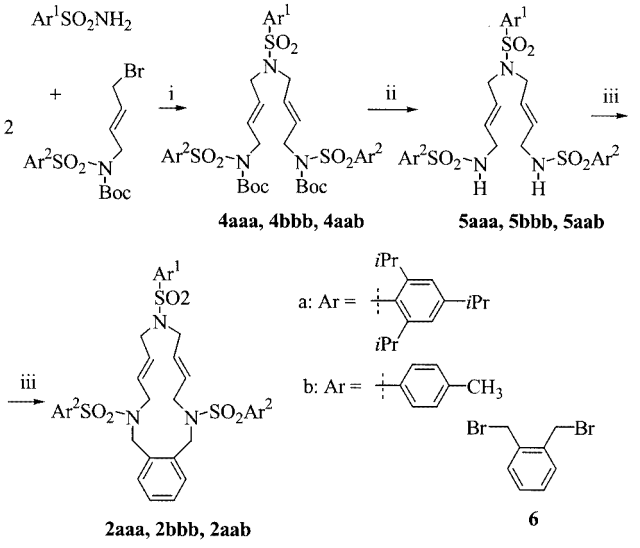


Figure 1. Previously described products

Macrocycles **1a** are easily made by any of three different routes that converge in *trans*-1,4-dibromobutene and arenesulfonamides as starting materials. The concentration of reagents is frequently a crucial problem in the preparation of macrocycles, and high-dilution techniques are frequently adopted. This, though, is not the case with macrocycles **1a**.[3f] It should be noted that the sulfonamide moiety has non-coordinating nitrogen atoms and that the sulfonamides are not incorporated as protecting groups for the secondary amines. Instead, the sulfonamide permits tuning of such properties of the macrocycle as solubility in organic solvents (Ar = 2,4,6-triisopropylphenyl), crystallinity for X-ray diffraction (Ar = 4-tolyl and others), and visibility for chromatographic recovery (Ar = ferrocenyl).

Macrocycles **1a** are reminiscent of the 12-membered carbocyclic cyclododeca-1,5,9-trienes (**1b**) formed by trimerization of butadiene and have an important organometallic chemistry. Their Ni^0 complexes have thus played fundamental roles in catalysis and in organonickel chemistry.[6]



Scheme 1. Preparation of macrocycles **2**; i.- K_2CO_3, refluxing CH_3CN, see ref.[3b] ii.- TFAA, CH_2Cl_2, room temp, see ref.[3b] iii.- **6** (2 mol), K_2CO_3, refluxing CH_3CN.

[a] Department of Chemistry, Universitat Autònoma de Barcelona
Cerdanyola, 08193-Barcelona, Spain
Fax: (internat.) +34-935/811265
E-mail: rosamaria.sebastian@uab.es
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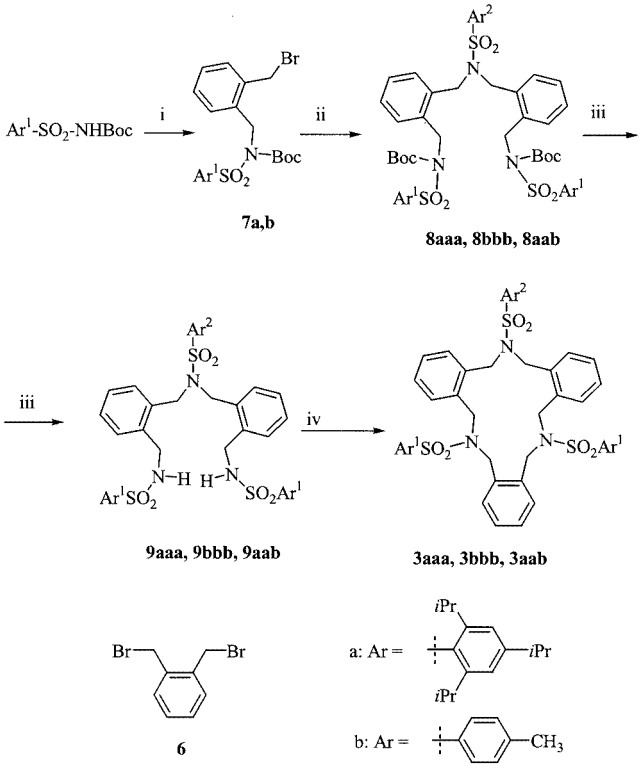
The rich organometallic chemistry of compounds **1a**, the facility of their preparation, the potential for tuning of their properties through variation of sulfonamides, and the catalytic properties of the metallic complexes motivated us to launch a project aimed at access to a broad selection of structures related to **1a**.

Here we present the preparation of (*E*,*E*)-1,6,11-tris-(arenesulfonyl)-3,4-benzo-1,6,11-triazacyclopentadeca-8,13-dienes (**2**, Scheme 1) and 1,6,11-tris(arenesulfonyl)-3,4,8,9,13,14-tribenzo-1,6,11-triazacyclopentadecanes (**3**, Scheme 2). Compounds similar to **3**, with sulfur and phosphorus in place of nitrogen, have been prepared by routes different[7] from that proposed here.



Scheme 2. Preparation of macrocycles **3**; i.- **6** (4 mol), K_2CO_3, refluxing CH_3CN; ii $Ar^2SO_2NH_2$ (1/2 mol), K_2CO_3, refluxing CH_3CN; iii.- TFAA, CH_2Cl_2, room temp; iv.- **6** (1 mol) K_2CO_3, refluxing CH_3CN.

Results and Discussion

Our preparation of macrocycles **2** is versatile, permitting the introduction of different aryl groups at different synthetic steps. Products **4bbb** and **5bbb** are known,[3b] while all other compounds **4** and **5** were prepared similarly (Scheme 1). The cyclization step proceeds excellently, the formation of higher cycles and/or polymers not being a problem.

Tribenzomacrocycles **3** are also easily prepared by controlled condensations of 1,2-bis(bromomethyl)benzene (**6**) with Boc-protected arenesulfonamides in the first step to afford compounds **7**, and with bis-sulfonamides **9** in the last step (Scheme 2). Once more, the cyclization step works very well, higher rings and polymers formation not being a problem. Introduction of different arenes at different steps confers versatility on the preparation.

The extreme simplicity of this modular synthesis also relies upon the availability of starting materials. Appropriate selection of sulfonamides permits the properties of the macrocycles, such as solubility, to be tuned. Moreover, the nitrogen atoms in **2** and in **3** are non-coordinating, the coordinating ability, if any, being concentrated in the olefinic and benzo moieties.

Macrocycles **2** and **3** exhibit very weak coordinating ability towards silver(I) tetrafluoroborate[8,9] and none towards silver triflate or Pd^0. Mixing of equimolar amounts of **2** or **3** and $AgBF_4$ in refluxing acetone, followed by evaporation, gave residues that were discrete compounds rather than mixtures, as evidenced by very different mps and different NMR spectra. However, isolation for further studies failed due to instability. Macrocycles **2aaa**, **2bbb**, **3aaa**, and **3aab** were treated with $Cr(CO)_6$ in refluxing di-*n*-butyl ether under inert atmosphere. In all cases extremely insoluble complexes were formed. Each of them showed two strong infrared peaks in the 1898±6 and 1972±4 cm^{-1} regions, as required for trigonal-pyramidal complexes of the $L_3Cr(CO)_3$ type. Peaks at *m*/*z* values corresponding to the molecular weight were detected for the complexes **2bbb-Cr(CO)$_3$** and **3aab-Cr(CO)$_3$** by HRMS, but the extreme insolubility of these complexes prevented any further studies.

Conclusion

Easy, versatile, and efficient preparations of 15-membered triazamacrocycles containing internal olefins or fused benzene rings, starting from easily available materials, are described. The macrocycles coordinate silver very weakly. Cr^0 complexes are too insoluble for further studies.

Experimental Section

General Remarks: Melting points were determined with a Kofler apparatus and are uncorrected. IR spectra were recorded with a Nicolet FT-IR 510 ZDX. NMR spectra were recorded with a Bruker-Analytik AC 250 instrument. ^1H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at δ = 7.26 and tetramethylsilane at δ = 0.00, and ^{13}C NMR (62.5 MHz) are reported relative to chloroform at δ = 77.00 and tetramethylsilane at δ = 0.0. Mass spectra (EIMS) were obtained with a Hewlett−Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV; relevant data are listed as *m*/*z* (%). MALDI-TOF spectra were recorded on a BIFLEX spectrometer (Bruker-Franzen Analytik) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using 19 kV acceleration voltage. Matrices (α-cyanocinnamic acid) were prepared at 5 mg/mL in THF. Analytes were dissolved at concentrations between 0.1 and 5 mg/mL in THF or chloroform. Elemental analyses were determined at the "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona".

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (4aaa): This com-

pound was prepared in 97% yield as for **4bbb**. M.p. 66−68 °C. IR (KBr): $\tilde{\nu}$ = 2961, 1728, 1369, 1338, 1153 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.21 (s, 18 H), 1.26 (complex absorption, 54 H), 2.93 (sept, *J* = 6.9 Hz, 3 H), 3.85 (d, *J* = 5.0 Hz, 4 H), 3.93 (sept, *J* = 6.7 Hz, 4 H), 4.18 (sept, *J* = 6.7 Hz, 2 H), 4.42 (d, *J* = 4.5 Hz, 4 H), 5.65−5.95 (m, 4 H), 7.15 (s, 4 H), 7.19 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.3, 23.3, 24.2, 24.6, 27.5, 29.0, 33.9, 46.0, 46.1, 83.2, 123.1, 123.6, 127.8, 130.1, 130.9, 134.0, 149.9, 150.6, 151.3, 152.6, 152.7 ppm. $C_{63}H_{99}N_3O_{10}S_3$ (1154.7): calcd. C 65.53, H 8.64, N 3.64; found C 65.54, H 8.76, N 3.62, S 8.11.

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris[(4-methylphenyl)-sulfonyl]-1,6,11-triazaundeca-3,8-diene (4bbb): See ref.[3b]

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-6-[(4-methylphenyl)sulfonyl]-1,11-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (4aab): This compound was prepared in 71% yield as for **4bbb**. M.p. 64−66 °C. IR (KBr): $\tilde{\nu}$ = 2962, 1728, 1369, 1338, 1158 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20 (s, 18 H), 1.26 (d, *J* = 6.8 Hz, 24 H), 1.27 (d, *J* = 6.9 Hz, 12 H), 2.44 (s, 3 H), 2.93 (sept, *J* = 6.9 Hz, 2 H), 3.87 (d, *J* = 6.3 Hz, 4 H), 3.91 (sept, *J* = 6.8 Hz, 4 H), 4.38 (d, *J* = 5.0 Hz, 4 H), 5.65 (dt, *J* = 15.4, 6.2 Hz, 2 H), 5.80 (dt, *J* = 15.4 and 5.0 Hz, 2 H), 7.15 (s, 4 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.2, 23.3, 24.2, 27.5, 28.9, 33.9, 46.0, 47.6, 83.3, 123.1, 127.0, 127.6, 129.5, 129.7, 133.9, 137.1, 142.7, 149.9, 150.6, 152.8 ppm. $C_{55}H_{83}N_3O_{10}S_3$ (1042.5): calcd. C 63.37, H 8.02, N 4.03; found C 63.30, H 8.08, N 4.05.

(*E*,*E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (5aaa): This compound was prepared in 99% yield as for **5bbb**. M.p.144−146 °C. IR (KBr): $\tilde{\nu}$ = 3273, 2960, 1152 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.23−1.30 (complex absorption, 54 H), 2.92 (sept, *J* = 6.9 Hz, 1 H), 2.93 (sept, *J* = 6.9, 2 H), 3.56 (t, *J* = 5.7 Hz, 4 H), 3.72 (d, *J* = 5.7 Hz, 4 H), 4.08 (sept, *J* = 6.9 Hz, 2 H), 4.18 (sept, *J* = 6.7 Hz, 4 H), 4.62 (t, *J* = 6.2 Hz, 2 H), 5.58 (dt, *J* = 15.3 and 6.2 Hz, 2 H), 5.69 (dt, *J* = 15.3 and 5.7 Hz, 2 H), 7.17 (s, 2 H), 7.19 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.2, 23.3, 24.5, 24.6, 29.0, 29.3, 33.9, 43.9, 46.3, 123.5, 123.6, 127.6, 130.6, 130.7, 131.9, 150.0, 151.2, 152.6, 153.0 ppm. $C_{53}H_{83}N_3O_6S_3$ (954.5): calcd. C 66.70, H 8.76, N 4.40, S 10.08; found C 66.66, H 8.86, N 4.41, S 9.99.

(*E*,*E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (5bbb): See ref.[3b]

(*E*,*E*)-6-[(4-Methylphenyl)sulfonyl]-1,11-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (5aab): This compound was prepared in 74% yield as for **5bbb**. M.p. 150−152 °C. IR (KBr): $\tilde{\nu}$ = 3344, 2960, 1323, 1161 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (d, *J* = 6.9 Hz, 24 H), 1.28 (d, *J* = 6.9 Hz, 12 H), 2.45 (s, 3 H), 2.93 (sept, *J* = 6.9 Hz, 2 H), 3.52 (t, *J* = 5.7 Hz, 4 H), 3.72 (d, *J* = 5.9 Hz, 4 H), 4.14 (sept, *J* = 6.9 Hz, 4 H), 4.55 (d, *J* = 6.4 Hz, 2 H), 5.47 (dt, *J* = 15.5, 5.9 Hz, 2 H), 5.62 (dt, *J* = 15.5, 5.7 Hz, 2 H), 7.18 (s, 4 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.2, 23.3, 24.6, 29.3, 33.8, 43.8, 48.0, 123.5, 126.9, 127.6, 129.5, 129.8, 131.9, 136.8, 143.3, 150.0, 152.6 ppm. $C_{45}H_{67}N_3O_6S_3$ (842.2): calcd.C 64.17, H 8.02, N 4.99, S 11.42; found C 64.06, H 8.24, N 4.96, S 11.16.

(*E*,*E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-3,4-benzo-1,6,11-triazacyclopentadeca-8,13-diene (2aaa). General Method: A solution of **5aaa** (0.50 g, 0.24 mmol) and dibromo compound **6** (0.14 g, 0.52 mmol) in acetonitrile (75 mL) was added dropwise to a suspension of potassium carbonate (0.36 g, 2.6 mmol) in refluxing acetonitrile (75 mL). The mixture was heated at reflux overnight and filtered. The filtrate was evaporated and the residue was chromatographed through a column of silica gel with cyclohexane/ethyl acetate (9:1) as eluent to afford **2aaa** as a white solid (0.53 g, 97%). M.p. 90−92 °C. IR (KBr): $\tilde{\nu}$ = 2959, 1320, 1153 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.16−1.28 (complex absorption, 54 H), 2.88 (sept, *J* = 6.9 Hz, 1 H), 2.89 (sept, *J* = 6.9, 2 H), 3.80 (m, 8 H), 4.09 (sept, *J* = 6.7 Hz, 2 H), 4.11 (sept, *J* = 6.7 Hz, 4 H), 4.39 (apparent s, 4 H), 5.57 (dt, *J* = 15.6, 5.4 Hz, 2 H), 5.68 (dt, *J* = 15.6, 6.1 Hz, 2 H), 7.12 (s, 2 H), 7.16 (s, 4 H), 7.27 (double m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.2, 24.4, 24.7, 28.9, 29.4, 33.9, 53.7, 46.3, 49.4, 123.6, 123.8, 127.1, 127.3, 130.4, 130.8, 132.7, 133.2, 151.2, 153.0, 153.1 ppm. MALDI-TOF MS: *m*/*z* = 1055.6 [M + H], 1079.1 [M + Na], 1095 [M + K]. $C_{61}H_{89}N_3O_6S_3$ (1056.6): calcd. C 69.34, H 8.49, N 3.98; found C 69.59, H 9.12, N 3.71.

(*E*,*E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-3,4-benzo-1,6,11-triazacyclopentadeca-8,13-diene (2bbb): This compound was prepared in 68% yield as for **2aaa**. M.p. 102−104 °C. IR (KBr): $\tilde{\nu}$ = 1340, 1161 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.43 (s, 3 H), 2.47 (s, 6 H), 3.43 (d, *J* = 5.4 Hz, 4 H), 3.66 (d, *J* = 6.5 Hz, 4 H), 4.35 (apparent s, 4 H), 5.20 (dt, *J* = 15.4, 5.4 Hz, 2 H), 5.36 (dt, *J* = 15.4, 6.5 Hz, 2 H), 7.23−7.35 (m, 6 H), 7.37 (d, *J* = 8.2 Hz, 4 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 49.2, 49.8, 50.8, 126.8, 127.1, 127.2, 127.5, 128.1, 129.5, 129.6, 131.1, 134.1, 135.5, 143.4 ppm. MALDI-TOF MS: *m*/*z* = 742.4 [M + Na], 758.4 [M + K]. FAB-HRMS: *m*/*z* = 720.22 [M + H], 737.23 [M + NH_4]. $C_{37}H_{41}N_3O_6S_3$ (719.9): calcd. C 61.73, H 5.74, N, 5.84; found C 61.44, H 6.34; N 5.36.

(*E*,*E*)-11-[(4-Methylphenyl)sulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)sulfonyl]-3,4-benzo-1,6,11-triazacyclopentadeca-8,13-diene (2aab): This compound was prepared in 85% yield as for **2aaa**. M.p. 84−86 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2927, 1153 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (d, *J* = 6.9 Hz, 24 H), 1.28 (d, *J* = 6.7 Hz, 12 H), 2.46 (s, 3 H), 2.69 (sept, *J* = 6.7, 2 H), 3.73 (d, *J* = 5.7 Hz, 4 H), 3.84 (d, *J* = 6.5 Hz, 4 H), 4.12 (sept, *J* = 6.9 Hz, 4 H), 4.38 (apparent s, 4 H), 5.52 (dt, *J* = 15.6, 5.7 Hz, 2 H), 5.74 (dt, *J* = 15.6, 6.5 Hz, 2 H), 7.19 (s, 4 H), 7.20−7.31 (m, 4 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.66 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.2, 23.3, 24.7, 26.7, 29.4, 33.9, 43.8, 46.5, 51.1, 123.9, 126.8, 127.1, 127.3, 127.6, 129.6, 130.8, 132.8, 132.9, 135.6, 143.3, 151.2, 153.2. ESI-MS: *m*/*z* = 943 (M), 961 [M + NH_4]. $C_{53}H_{73}N_3O_6S_3$ (944.4): calcd. (+ 1/2 cyclohexane) C 68.18, H 8.07, N 4.26, S 9.75; found C 68.07, H 8.26, N 4.22, S 9.59.

***N*-(2-Bromomethylbenzyl)-*N*-(*tert*-butyloxycarbonyl)-(2,4,6-triisopropyl)benzenesulfonamide (7a). General Method:** A mixture of *N*-Boc-(2,4,6-triisopropyl)benzenesulfonamide (5.00 g, 13 mmol), 1,2-bis(bromomethylbenzene), **6**, (14.34 g, 52 mmol), anhydrous potassium carbonate (2.70 g, 19 mmol), and acetonitrile (200 mL) was heated at reflux for 14 h. After the mixture had cooled, the solids were filtered off and the filtrate was evaporated. The residue was chromatographed through a silica gel column with ethyl acetate/hexanes mixtures of increasing polarity. Excess **6** was eluted first, followed by **7a** (5.63 g, 76%). M.p. 140−142 °C. IR (KBr): $\tilde{\nu}$ = 2965, 1718, 1368, 1337, 1153 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.16 (s, 9 H), 1.30 (d, *J* = 6.8 Hz, 6 H), 1.33 (d, *J* = 6.8 Hz, 12 H), 2.97 (sept, *J* = 6.8 Hz, 1 H), 4.06 (sept, *J* = 6.8 Hz, 2 H), 4.70 (s, 2 H), 5.22 (s, 2 H), 7.20−7.40 (m, 3 H), 7.23 (s, 2 H), 7.70 (d, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 24.1, 25.0, 28.1, 29.9, 31.9, 34.7, 45.9, 84.4, 124.0, 127.9, 128.2, 129.9,

130.6, 134.1, 135.0, 136.8, 150.9, 151.4, 153.8 ppm. $C_{28}H_{40}BrNO_4S$ (566.6): calcd. C 59.36, H 7.12, N 2.47, S 5.66; found C 59.62, H 7.16, N 2.55, S 5.37,

***N*-(2-Bromomethylbenzyl)-*N*-(*tert*-butyloxycarbonyl)-4-methylbenzenesulfonamide (7b):** This compound was prepared in 77% yield as for **7a**. M.p. 109−110 °C. IR (KBr): $\tilde{\nu}$ = 1719, 1353, 1173, 1152 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.35 (s, 9 H), 2.46 (s, 3 H), 4.67 (s, 2 H), 5.24 (s, 2 H), 7.24−7.42 (m, 4 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.4, 27.6, 31.0, 46.3, 84.4, 127.3, 127.4, 127.9, 128.9, 130.1, 134.6, 136.2, 136.6, 144.1, 150.8 ppm. $C_{20}H_{24}BrNO_4S$ (454.4): calcd. C 52.87, H 5.32, N 3.08, S 7.06; found C 53.03, H 5.44, N 3.10, S 6.82.

1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris-[(2,4,6-triisopropylphenyl)sulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (8aaa): This compound was prepared in 69% yield as for **8bbb** (vide infra). M.p. 73−75 °C. IR (KBr): $\tilde{\nu}$ = 2961, 2929, 1729, 1369, 1338, 1154. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.11 (s, 18 H), 1.28 (d, *J* = 6.9 Hz, 36 H), 1.33 (d, *J* = 6.5 Hz, 18 H), 2.95 (sept, *J* = 6.5 Hz, 3 H), 3.93 (sept, *J* = 6.9 Hz, 4 H), 4.30 (sept, *J* ca. 6.8 Hz, 2 H), 4.63 (s, 2 H), 4.79 (s, 2 H), 6.97 (d, *J* = 6.9 Hz, 2 H), 7.12−7.32 (m, 10 H), 7.60 (d, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.3, 24.2, 24.8, 26.6 (cyclohexane), 27.4, 29.1, 29.8, 33.9, 33.9, 45.7, 46.0, 52.1, 83.3, 123.2, 123.6, 123.9, 127.0, 127.4, 129.5, 127.8, 128.9, 132.1, 133.4, 133.9, 135.8, 136.0, 150.3, 150.6, 152.8 ppm. $C_{71}H_{103}N_3O_{10}S_3$ (1254.8): calcd. (+ 3/2 C_6H_{12}) C 69.58, H 8.83, N 3.04, S 6.97; found C 69.83, H 9.03, N 3.20, S 6.75.

1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris-[(4-methylphenyl)sulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (8bbb). General Method: A mixture of 4-methylbenzenesulfonamide (0.19 g, 1.10 mmol), bromo compound **7b** (1.00 g, 2.20 mmol), anhydrous potassium carbonate (0.91 g, 6.6 mmol), and acetonitrile (30 mL) was heated at reflux for 14 h. After the mixture had cooled, the solids were filtered off and the filtrate was evaporated. The residue was chromatographed through a silica gel column with ethyl acetate/cyclohexane (3:7) to afford **8bbb** in 93% yield (1.00 g), taking into account that **8bbb** crystallized with one mol of cyclohexane. M.p. 63−65 °C. IR (KBr): $\tilde{\nu}$ = 2927, 1729, 1359, 1157 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.32 (s, 18 H), 1.44 (s, 12 H, cyclohexane), 2.43 (s, 6 H), 2.47 (s, 3 H), 4.45 (s, 4 H), 4.95 (s, 4 H), 7.12 (m, 8 H), 7.25 (d, *J* = 8.3 Hz, 4 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 7.60 (d, *J* = 8.3 Hz, 4 H), 7.79 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 26.7 (cyclohexane), 27.6, 46.5, 50.0, 84.1, 127.0, 127.3, 127.7, 128.8, 129.0, 129.6, 132.7, 135.4, 135.6, 136.7, 143.4, 143.9, 150.8 ppm. $C_{47}H_{55}N_3O_{10}S_3$ (918.2): calcd. (+ C_6H_{12}) C 63.51, H 6.73, N 4.19, S 9.59; found C 63.04, H 6.88, N 4.12, S 9.48.

1,11-Bis(*tert*-butyloxycarbonyl)-6-[(4-methylphenyl)sulfonyl]-1,11-bis)[(2,4,6-triisopropylphenylsulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (8aab): This compound was prepared in 82% yield as for **8bbb**. M.p. 85−87 °C. IR (KBr): $\tilde{\nu}$ = 2961, 2927, 1728, 1369, 1338, 1158 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.14 (s, 18 H), 1.30 (t, *J* = 6.7 Hz, 36 H), 2.48 (s, 3 H), 2.96 (sept, *J* = 6.7 Hz, 2 H), 4.00 (sept, *J* = 6.7 Hz, 4 H), 4.55 (s, 4 H), 4.99 (s, 4 H), 6.92 (dd, *J* = 7.6, 1.0 Hz, 2 H), 7.05 (dt, *J* = 7.3, 1.1 Hz, 2 H), 7.18 (s, 4 H), 7.20 (dt, *J* = 7.3 and 1.1 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.47 (dd, *J* = 7.6, 1.0 Hz, 2 H), 7.84 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 23.3, 24.3, 26.7, 27.4, 29.1, 34.0, 46.0, 49.4, 83.3, 123.2, 126.8, 127.2, 127.3, 127.8, 129.0, 129.5, 132.2, 133.8, 135.6, 136.1, 143.1, 150.3, 150.7, 152.9 ppm. $C_{63}H_{87}N_3O_{10}S_3$ (1142.6): calcd. C 66.23, H 7.67, N 3.68, S 8.42; found C 66.12, H 8.01, N 3.67, S 8.15.

1,6,11-Tris-[(2,4,6-triisopropylphenyl)sulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (9aaa): This compound was prepared in 75% yield as for **9bbb** (vide infra). M.p. 87−89 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2927, 1601, 1317, 1152 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (d, *J* = 6.7 Hz, 24 H), 1.29 (d, *J* = 6.9 Hz, 12 H), 1.30 (d, *J* = 6.7 Hz, 12 H), 1.33 (d, *J* = 6.9 hz, 6 H), 1.46 (s, cyclohexane), 2.46 (sept, *J* = 6.9 Hz, 3 H), 3.74 (d, *J* = 6.2 Hz, 4 H), 4.06 (sept, *J* = 6.7 Hz, 4 H), 4.20 (sept, *J* = 6.7 Hz, 2 H), 4.56 (s, 4 H), 4.80 (t, *J* = 6.2 Hz, 2 H), 7.06−7.28 (m, 14 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.3, 23.3, 24.6, 24.7, 26.7, 29.3, 29.7, 33.9, 43.6, 45.9, 123.5, 124.0, 127.6, 128.0, 128.9, 129.1, 131.6, 132.3, 133.7, 134.3, 150.2, 150.9, 152.5, 153.1 ppm. $C_{61}H_{87}N_3O_6S_3$ (1054.6): calcd. (+ C_6H_{12}) C 70.67, H 8.76, N, 3.69; found C 71.29, H 9.40, N 3.52.

1,6,11-Tris-[(4-methylphenyl)sulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (9bbb), General Method: Trifluoroacetic acid (10 mL) was added to a solution of **8bbb** (0.87 g, 0.95 mmol) in dichloromethane (10 mL). The mixture was stirred at room temp for 7 h and the solvents were evaporated to dryness. The residue was partitioned between dichloromethane and water. The organic layer was dried with anhydrous Na_2SO_4 and the solvents were evaporated to afford practically pure **9bbb** (0.68 g, 100% yield). A sample for elemental analysis was chromatographed through a column of silica gel with cyclohexane/ethyl acetate (3:8). M.p. 76−78 °C. IR (KBr): $\tilde{\nu}$ = 3268, 1334, 1321, 1161 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.43 (s, 6 H), 2.49 (s, 3 H), 3.86 (d, *J* = 6.2 Hz, 4 H), 4.30 (s, 4 H), 4.97 (d, *J* = 6.2 Hz, 2 H), 7.30 (m, 8 H), 7.28 (d, *J* = 8.3 Hz, 4 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.66 (d, *J* = 8.3 Hz, 4 H), 7.74 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 21.3, 44.2, 49.2, 126.9, 127.2, 127.7, 127.8, 129.3, 129.4, 129.8, 133.8, 134.1, 135.2, 136.3, 143.2, 143.6 ppm. $C_{37}H_{39}N_3O_6S_3$ (717.9): calcd. C 61.90, H 5.48, N 5.85; found C 62.37, H 5.82, N 5.52.

6-[(4-Methylphenyl)sulfonyl]-1,11-bis[(2,4,6-triisopropylphenyl)sulfonyl]-3,4;8,9-dibenzo-1,6,11-triazaundecane (9aab): This compound was prepared in 95% yield as for **9bbb**. M.p. 66−68 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2927, 1600, 1329, 1161 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.29 (t, *J* = 6.9 Hz, 26 H), 1.46 (cyclohexane), 2.51 (s, 3 H), 2.95 (sept, *J* = 6.9 Hz, 2 H), 3.96 (d, *J* = 6.2 Hz, 4 H), 4.12 (sept, *J* = 6.9 Hz, 4 H), 4.44 (br. s, 4 H), 4.78 (t, *J* = 6.2 Hz, 2 H), 6.95−7.21 (m, 12 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 23.3, 24.6, 26.6 (cyclohexane), 29.4, 33.9, 44.0, 49.6, 123.5, 127.3, 127.6, 127.8, 129.2, 129.5, 129.8, 131.9, 134.2, 134.4, 135.1, 143.6, 150.0, 152.5 ppm. $C_{53}H_{71}N_3O_6S_3$ (942.4): calcd. C 67.55, H 7.59, N 4.46; found C 68.04, H 8.00, N 4.30.

1,6,11-Tris-[(2,4,6-triisopropylphenyl)sulfonyl]-3,4;8,9;13,14-tribenzo-1,6,11-triazacyclopentadecane (3aaa): This compound was prepared in 81% yield as for **3bbb** (vide infra). M.p. 200−201 °C. IR (KBr): $\tilde{\nu}$ = 2942, 1596, 1458, 1360, 1156, 1049, 762 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (d, *J* = 6.7 Hz, 36 H), 1.28 (d, *J* = 6.9 Hz, 18 H), 2.93 (sept, *J* = 6.9 Hz, 3 H), 4.03 (sept, *J* = 6.7 Hz, 6 H), 4.21 (s, 12 H), 7.12 (m, 6 H), 7.17 (s, 6 H), 7.30 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 23.3, 24.6, 29.6, 33.8, 46.3, 123.9, 127.6, 128.5, 131.9, 133.3, 150.8, 153.1. ESI-MS: *m*/*z* = 1155.1 (M). $C_{69}H_{93}N_3O_6S_3$ (1156.7): calcd. C 71.65, H 8.10, N 3.63; found C 71.55, H 8.16, N 3.48.

1,6,11-Tris-[(4-methylphenyl)sulfonyl]-3,4;8,9;13,14-tribenzo-1,6,11-triazacyclopentadecane (3bbb). General Method: A mixture of **9bbb** (1.77 g, 2.47 mmol), dibromo compound **6** (0.68 g, 2.47 mmol), and acetonitrile (75 mL) was added dropwise (2 h) to anhydrous potassium carbonate (1.71 g) in refluxing acetonitrile (75 mL). The mix-

ture was stirred for 24 h (^{1}H NMR monitoring). After the mixture had cooled, the solids were filtered off and the filtrate was evaporated to afford **3bbb** (0.30 g). Solid **3bbb** precipitated before evaporation, however, so the filtered solids were extracted several times with hot chloroform, and the chloroform was evaporated to afford more **3bbb** (total yield 79%). M.p. 271−272 °C. IR (KBr): $\tilde{\nu}$ = 1339, 1164 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.50 (s, 9 H), 4.11 (s, 12 H), 7.03−7.12 (m, 12 H), 7.36 (d, *J* = 8.2 Hz, 6 H), 7.69 (d, *J* = 8.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 48.5, 127.0, 127.3, 127.6, 128.9, 129.5, 129.7, 130.4, 133.4, 134.4, 135.5, 143.4. ESI-MS: *m*/*z* = 819.9 (M), 839.0 [M + NH_4], 857.0 (M +2NH_4). FAB HRMS: *m*/*z* = $C_{45}H_{45}N_3O_6S_3$ + H: calcd. 820.255748; found 820.256.

11-[(4-Methylphenyl)sulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)-sulfonyl]-3,4;8,9;13,14-tribenzo-1,6,11-triazacyclopentadecane (3aab): This compound was prepared in 97% yield as for **3bbb**. M.p. 222 °C. IR (KBr): $\tilde{\nu}$ = 2959, 2919, 1600, 1456, 1362, 1323, 1163, 1154, 766 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (d, *J* = 6.7 Hz, 24 H), 1.28 (d, *J* = 6.9 Hz, 12 H), 2.52 (s, 3 H), 2.93 (sept, *J* = 6.9 Hz, 2 H), 3.93 (s, 4 H), 4.04 (sept, *J* = 6.7 Hz, 4 H), 4.23 (s, 4 H), 4.29 (s, 4 H), 7.00−7.30 (m, 12 H), 7.19 (s, 4 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.61 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.3, 23.3, 24.6, 29.6, 33.9, 45.6, 45.8, 49.6, 123.9, 127.2, 127.3, 127.4, 127.6, 127.9, 128.6, 129.3, 129.6, 132.3, 133.1, 133.4, 133.5, 134.8, 143.5, 150.7, 153.0. ESI MS: *m*/*z* = 1043.7 (M), 1060.5 [M + NH_4]. FAB HRMS: *m*/*z* = 1044.504 [M + H]. $C_{61}H_{77}N_3O_6S_3$ (1044.5): calcd. C 70.15, H 7.43, N 4.02; found C 70.55, H 7.76, N 3.93.

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