Preparation of Nitrogen-Containing 15-Membered Triolefinic Macrocycles: (*E,E,E*)-1,6,11-Tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes

Silvia Cerezo,[a] Jordi Cortès,[a] David Galvan,[a][‡] Elena Lago,[b] Caroline Marchi,[a] Elies Molins,[b] Marcial Moreno-Mañas,*[a] Roser Pleixats,[a] Javier Torrejón,[a] and Adelina Vallribera[a]

Keywords: Alkenes / Macrocycles / Nitrogen heterocycles / Palladium

Three routes to (*E,E,E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes are described. Optimization of the preparation of key intermediates has opened the way to efficient synthesis of a broad variety of 15-membered, nitrogen-containing triolefinic macrocycles.

Introduction

Nitrogen-containing, 15-membered macrocycles are commonplace.[1,2] However, nitrogen-containing, 15-membered macrocycles featuring internal olefinic double bonds are exceptional. The few known examples contain only one double bond, and the key step for their preparation is metathesis.[3] In 1998 we described the formation of (*E,E,E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes (**1**) (Figure 1) by non-selective, palladium(0)-catalyzed Tsuji–Trost allylation of arenesulfonamides with *cis*-2-butene-1,4-diol dicarbonate.[4] Compounds **1** were present in the complicated reaction mixtures, together with 10- and 20-membered rings and higher macrocycles, as well as open-chain oligomers. Obviously, this Pd-catalyzed reaction could not be considered a synthesis. However, our interest

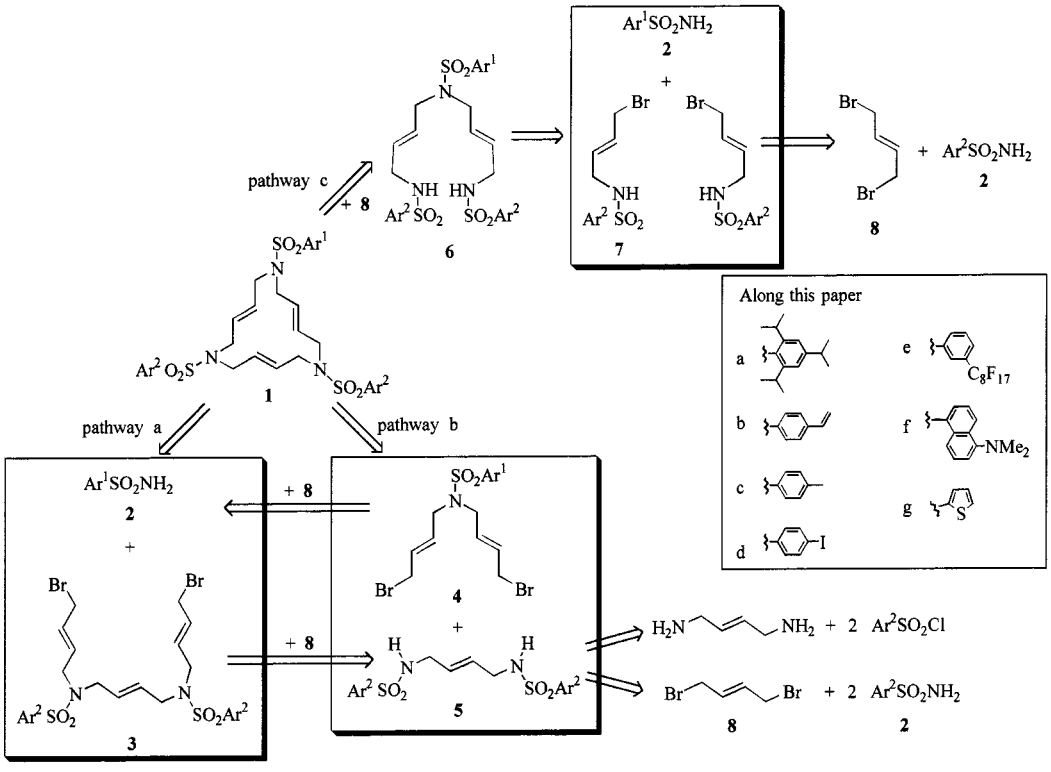

Figure 1. Retrosynthetic analysis for macrocycles **1**

[a] Department of Chemistry,
Universitat Autònoma de Barcelona, Cerdanyola, 08193 Barcelona, Spain
[b] Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193-Cerdanyola, Spain
[‡] Erasmus student from the Université de Reims (France).

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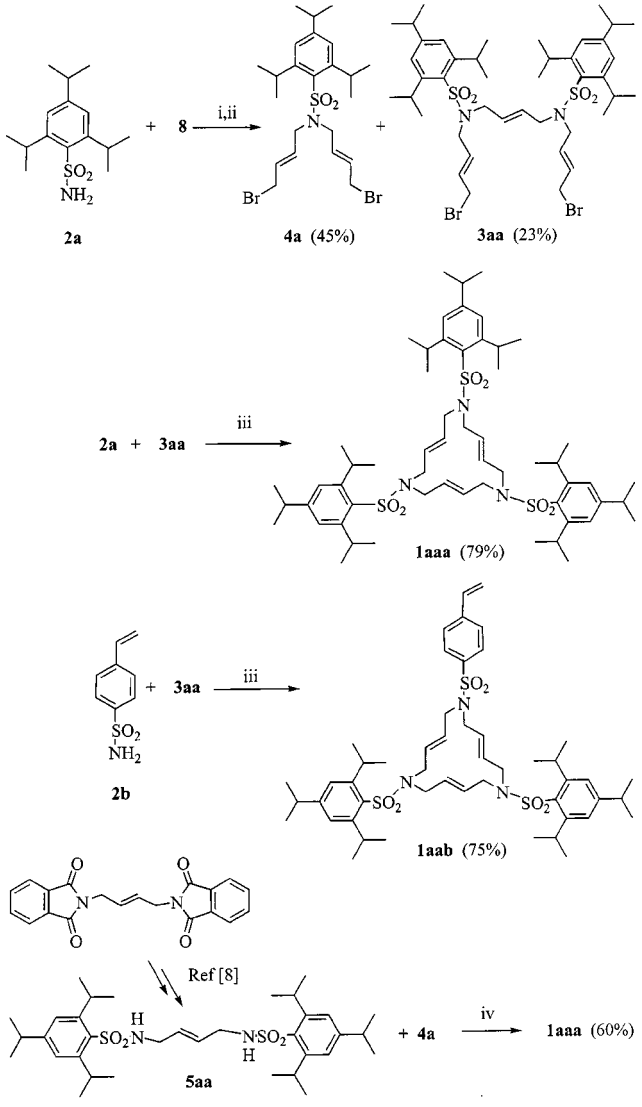
was attracted by the complexing ability of **1** towards palladium(0). Indeed, in some cases, all palladium(0) introduced as a catalyst was recovered in the form of a complex with **1**.[4] Additionally, although complexes $Pd_2(dba)_3$.solvent and $Pd_2(dba)_4$[5] are very well known and their catalytic effect acknowledged, complexes of olefins with palladium(0) are rather scarce.[6–8]

Later, we reported a preparation of **1aaa** (Ar^1 = Ar^2= 2,4,6-triisopropylphenyl) and **1aab** (Ar^1 = 4-vinylphenyl, Ar^2= 2,4,6-triisopropylphenyl) (see Scheme 1). The palladium(0) complex of **1aaa** is an efficient, recoverable catalyst for certain Suzuki-type cross-coupling reactions.[9] Macrocycle **1aab** was copolymerized with styrene and divinylbenzene to afford a functionalized polystyrene, which, once loaded with palladium(0), is also an excellent catalyst for cross-coupling reactions. It could be recovered by simple filtration, without loss of activity.[9]1



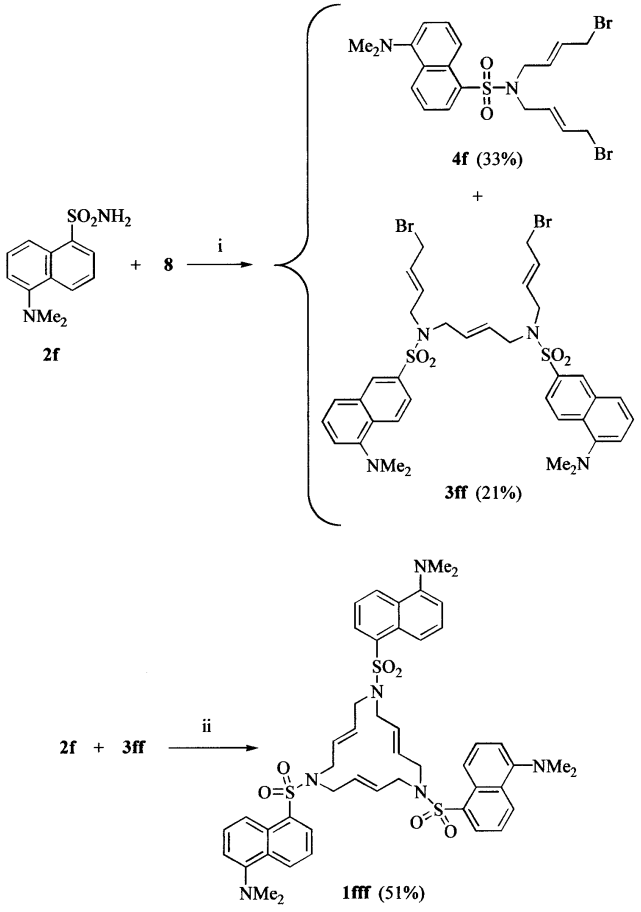
Scheme 1. Preparation of **1aaa** and **1aab** according to ref.[9]; reagents and conditions: i. NaH/DMF, then $BrCH_2CH{=}CHCH_2Br$ (**8**), 90 °C; ii. column chromatography on silica gel; iii. NaH/DMF on **2a** or **2b**, then **3aa**, 90 °C; iv. NaH/DMF on **5aa**, then **4a**

Results and Discussion

Our initial syntheses of **1aaa** and **1aab** are shown in Scheme 1. Reaction of sulfonamide **2a** with *trans*-1,4-dibromo-2-butene (**8**) gave a mixture of monosulfonamide **4a** and bis-sulfonamide **3aa**, in variable ratios, but with the former always predominant. The preparation of macrocycle **1aaa** was first achieved by reaction of the more abundant **4a** with bis-sulfonamide **5aa**, obtained from 2-butene-1,4-diamine[10] (Pathway b, Figure 1). The preparation of **1aaa** and **1aab** from **3aa** and sulfonamides **2a** and **b** (Pathway a, Figure 1) was high-yielding and more straightforward.

Since **3aa** was always obtained as a minor product, we studied variations in experimental conditions in order to invert the ratio **4a**/**3aa**. An experimental plan suggested some approaches which failed for practical experimental reasons. We finally became convinced that we would obtain **3aa**, and compounds **3** in general, by some selective method in which formation of **4** should not be possible.

In the meantime, the use of compounds **3**, separated out of product mixtures, to prepare macrocycles **1** (Scheme 2) continued. Thus, macrocycle **1fff**, featuring three dansyl groups, was prepared by treatment of **2f** with **3ff**, the latter formed as a minor product in the reaction between **2f** and dibromide **8** (Scheme 2).

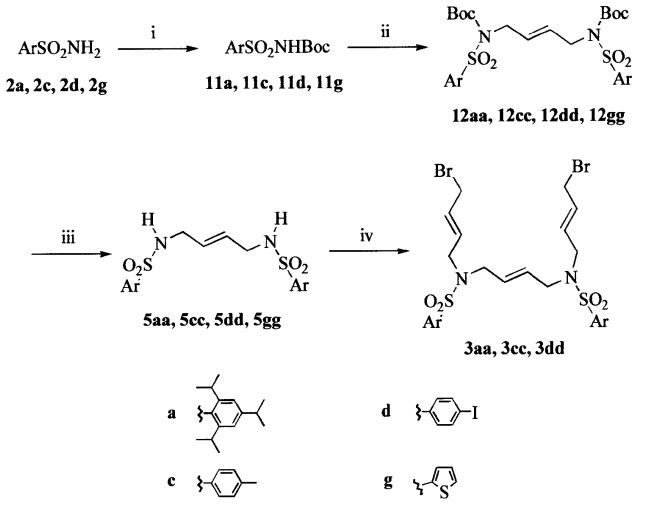


Scheme 2. New application of the old method. Preparation of **1fff**; reagents and conditions: i. K_2CO_3/CH_3CN, **2f**, then **8** (4 equiv.), reflux; ii. K_2CO_3/CH_3CN, reflux

The retrosynthetic analysis for macrocycles **1** is shown in Figure 1. As discussed above, pathway a is preferred to pathway b. Key intermediates **3** could be prepared from **5**, which in turn are accessible, a priori, not only through non-commercial 2-butene-1,4-diamine,[10] but also by treatment of commercially available *trans*-1,4-dibromo-2-butene (**8**) with arenesulfonamides **2**. Conversion of **5** into **3** would require an excess of **8** in order to preserve both bromine atoms in **3**. Formation of **5** by treatment of **2** with the dibromide **8** requires 0.5 equivalents of **8** and some sort of protection or blocking in the sulfonamide[11] to avoid the reaction leading to **4**.

Pathway c was also envisaged. For the preparation of **6**, the NH groups in **7** would need to be protected for the reaction with **2** to be successful. And for the preparation of **7**, protection at the sulfonamide **2** stage would be required, so as to avoid formation of **4**.

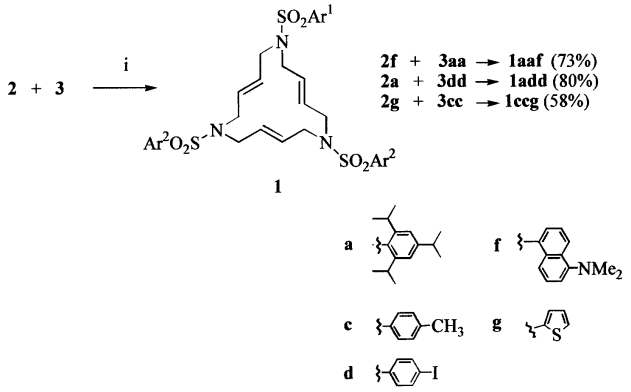
Intermediates **5** and **3**, required for pathway a, were prepared as shown in Scheme 3. Arenesulfonamides **2a**,**c**,**d**, and **g** were protected as *N*-Boc derivatives **11**.[12] Treatment of **11** with 0.5 equiv. of **8** afforded the protected disulfonamides **12**. Elimination of the Boc group resulted in the isolation of **5aa**, **5cc**, **5dd**, and **5gg**. Treatment of **5** with eight equivalents of dibromide **8** in the presence of base afforded the required **3aa**, **3cc**, and **3dd** as the only products. Excess **8** could be removed, and even recovered, by sublimation or co-distillation with water, depending on the reaction scale.



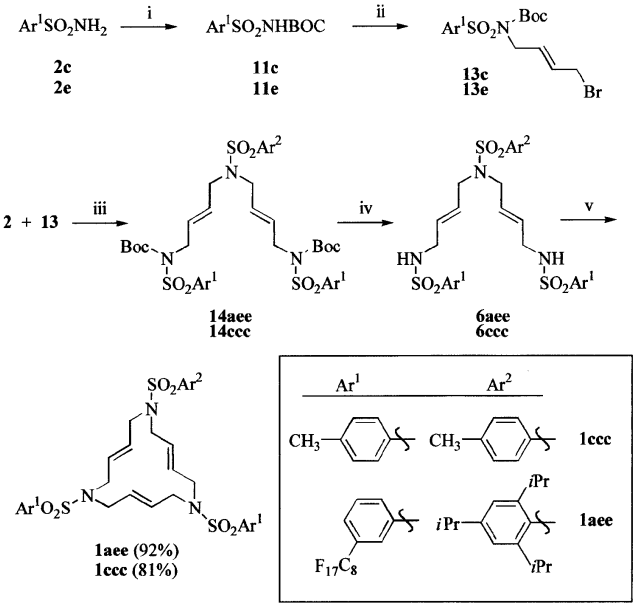
Scheme 3. Selective route to **3**; reagents and conditions: i. (*tert*-BuOCO)$_2$O, Et$_3$N, DMAP (0.1 equiv.), dichloromethane; ii. for **12aa** and **12cc**, K_2CO_3/CH_3CN, then **8** (0.5 equiv.), reflux; for **12dd**, K_2CO_3/DMF, **8** (0.5 equiv.), room temp.; iii. TFAA/dichloromethane, room temp.; iv. for **3aa** and **3cc**, K_2CO_3/CH_3CN, reflux, then **8** (8 equiv.); for **3dd**, NaH/DMF, **8** (8 equiv.), 80 °C

As anticipated, condensation of **3** with different sulfonamides **2** was straightforward and led to the formation of macrocycles **1aaf**, **1add**, and **1ccg**, featuring different aryl rings (Scheme 4).

Pathway c was also followed successfully (Scheme 5). Thus, Boc-protected sulfonamides **11c** and **e** were treated with dibromide **8** (4 equiv.) to afford bromosulfonamides **13c** and **e**. Condensation of **13** with **2** led to **14**, which gave trisulfonamides **6aee** and **6ccc** after deprotection. Final ring



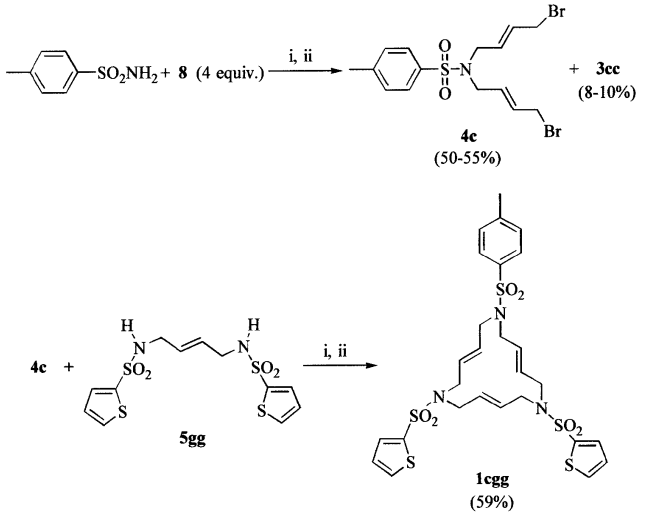
Scheme 4. Preparation of **1aaf**, **1add**, and **1ccg**: for **1aaf** and **1ccg**, K_2CO_3/CH_3CN, reflux; for **1add**, NaH/DMF on **2a**, then **3dd**, 90 °C



Scheme 5. Preparation of **1aee** and **1ccc** by pathway c; reagents and conditions: i. (*tert*-BuOCO)$_2$O, Et$_3$N, DMAP (0.1 equiv.), dichloromethane; ii. K_2CO_3/CH_3CN, **8** (4 equiv.), reflux; iii. K_2CO_3/CH_3CN, **13** (2 equiv.), reflux; iv. TFAA/dichloromethane, room temp.; v. K_2CO_3/CH_3CN, **8** (1 equiv.), reflux

closure was achieved by treatment of **6** with one equivalent of dibromide **8** to afford **1aee** and **1ccc**.

Pathway b depends on the availability of **4**. Although no selective preparation of **4** has yet been achieved, dibromosulfonamides **4** are the major products from the direct reaction between arenesulfonamides **2** and dibromobutene **8**. Therefore, they offer a valuable alternative means to the preparation of macrocycles **1**, as already remarked. A further application of pathway b is shown in Scheme 6. Thus, treatment of **2c** with **8** (4 equiv.) afforded a mixture of **4c** (50−55%) and **3cc** (8−10%), with the former consistently the major component of the mixture. Column chromatography was required in order to isolate pure **4c**. Treatment of pure **4c** with **5gg**, however, afforded macrocycle **1cgg** in 59% yield.



Scheme 6. Application of pathway b. Preparation of **1cgg**; reagents and conditions: i. K_2CO_3/CH_3CN, reflux; ii. column chromatography

X-ray Analysis of 1ccc

In order to establish fully the conformation of the **1ccc** compound, its crystal structure was determined by X-ray diffraction. A perspective view of the molecule (without hydrogen atoms) is shown in Figure 2. The C22 and C23 atoms are disordered between two conformations, although only one of these is depicted in the figure. The three double bonds occupy a central position in each macrocycle arm, in a disposition suitable for forming π-bonds with a metal. The flexibility of these arms promises eventual accommodation of metals of differing atomic radii.

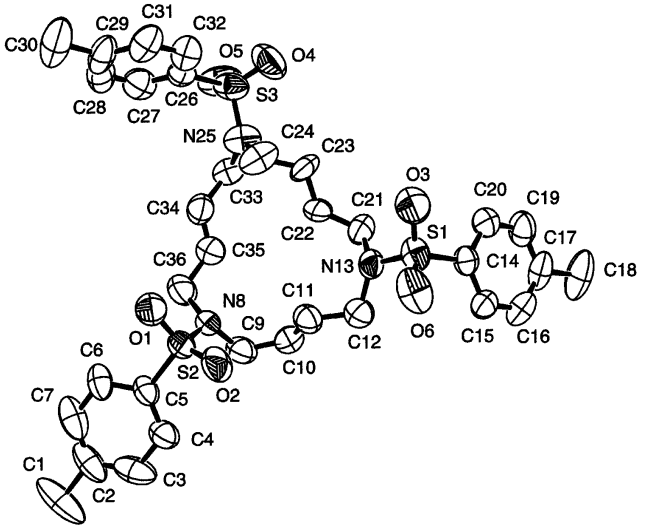


Figure 2. X-ray structure of **1ccc**. Perspective view

Conclusion

In summary, selective and efficient preparations of a new type of 15-membered macrocycles have been achieved. All three pathways, a, b, and c, are good. Pathways a and c produce intermediates selectively and final condensation steps are remarkably efficient. Pathway b is less selective, but the required intermediate **4** is the major product in the direct reaction between **2** and **8**. The final condensation step is also remarkably efficient. A summary of the different 15-membered macrocycles prepared by each pathway is given in Scheme 7.

SUMMARY

	Pathway a	Pathway b	Pathway c
1aaa	**2a** + **3aa** (79%)	**4a** + **5aa** (60%)	
1aab	**2b** + **3aa** (75%)		
1aaf	**2f** + **3aa** (73%)		
1add	**2a** + **3dd** (80%)		
1aee			**6aee** + **8** (92%)
1ccc			**6ccc** + **8** (81%)
1ccg	**2g** + **3cc** (58%)		
1cgg		**4c** + **5gg** (59%)	
1fff	**2f** + **3ff** (51%)		

Scheme 7. Macrocycles **1** and their synthetic pathways; yields refer to the last condensation step

At present we are studying the coordinating properties of macrocycles **1**.

Experimental Section

General: 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 AC250. ^{1}H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at δ = 7.26 and tetramethylsilane at δ = 0.00. Coupling constants are reported in Hz. ^{13}C NMR (62.5 MHz) chemical shifts are expressed relative to $CDCl_3$ at δ = 77.00 and tetramethylsilane at δ = 0.00. − 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 were prepared at 5 mg/mL in THF. Samples 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".

X-ray Analysis of 1ccc: A crystal of approximate dimensions 0.43 × 0.34 × 0.06 mm was used for the cell determination and data collection. The resulting crystal data were a = 23.413, b = 9.438, c = 15.502 Å, β = 91.26°, V = 3424.7 Å^3, Z = 4, ρ_C= 1.299 g/cm^3, monoclinic *Cc* space group, μ(Mo-K_α) = 0.263 mm^{-1}, T = 294(1) K. Data were recorded using the ω-2θ scan mode up to a 2θ of 60.8°. The 9262 collected intensities gave 4899 unique data (R_{int} = 0.0227), which were corrected for Lorentz, polarization, and absorption effects (empirical Psi scan, max. and min. transmission were 0.9105 and 0.8811, respectively). The structure was solved by direct methods, using SHELXS-97 and refined by full-matrix, least-squares methods on F^2 over the complete set of data, using SHELXL-97. The C22 and C23 atoms appeared in two half-occupancy disordered positions. Anisotropic thermal parameters were

refined for the non-hydrogen atoms and the hydrogen atoms were introduced in their calculated positions. The final *R* indices for reflections with [$I>2\sigma(I)$] were $R1 = 0.0470$, $wR2 = 0.1335$, and those for all data, $R1 = 0.0781$, $wR2 = 0.1437$. The Flack absolute structure parameter was 0.03(8). The largest difference peak and hole were 0.324 and −0.345 e/Å^3.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143209. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44−(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Arenesulfonamides 2: Compounds **2** and the corresponding sulfonyl chlorides are all commercially available, with the exceptions of **2d** and **e**. Both of these were prepared by chlorosulfonation (chlorosulfonic acid) followed by treatment of the arenesulfonyl chloride with concentrated ammonia. Chlorosulfonation of iodobenzene was performed at room temperature, but chlorosulfonation of (perfluorooctyl)benzene required 120 °C. (Perfluorooctyl)benzene was prepared by the general method of McLoughlin and Thrower.[13]

4-Iodophenylsulfonamide (2d): M.p. 191−193°C (ref.[14] m.p. 191−192°C.)

[3-(Perfluorooctyl)phenyl]sulfonamide (2e): M.p. 158−160°C. − IR (KBr): $\tilde{\nu}$ = 3347, 3267, 1341, 1223, 1147, 1113 cm^{-1}. − ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 6.86 (s, 2 H), 7.87 (t, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 8.18 (s, 1 H), 8.22 (d, *J* = 8.0 Hz, 1 H). − ^{13}C NMR (62.5 MHz, [D$_6$]acetone): δ = 105−120 (complex absorption), 125.6 (t, *J* = 6.4 Hz), 128.0, 130.2 (t, *J* = 23.9 Hz), 131.4 (t, *J* = 9.2 Hz), 131.4, 146.7. − MS; *m/z* (%): 575.1 [M$^+$] (1), 205.9 (100). − $C_{14}H_6F_{17}NO_2S$ (575.1): calcd. C 29.22, H 1.04, N 2.40; found C 28.96 and 29.12, H 0.98 and 0.95, N 2.40 and 2.42.

***N*-(*tert*-Butyloxycarbonyl)arenesulfonamides 11:** These were prepared according to the general method of ref.[12]

***N*-(*tert*-Butyloxycarbonyl)(2,4,6-triisopropylphenyl)sulfonamide (11a):** (7.50 g, 93%), m.p. 139−141 °C. − IR (KBr): $\tilde{\nu}$ = 3242, 2963, 1749, 1425, 1369, 1332, 1237, 1131 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.6 Hz, 6 H), 1.25 (d, *J* = 6.6 Hz, 12 H), 1.29 (s, 9 H), 2.89 (sept, *J* = 6.6 Hz, 1 H), 4.11 (sept, *J* = 6.6 Hz, 2 H), 7.15 (s, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.7, 27.9, 29.7, 34.2, 83.5, 123.7, 132.0, 149.4, 151.0, 153.6. − $C_{20}H_{33}NO_4S$ (383.5): calcd. C 62.63, H 8.67, N 3.65; found C 62.80 and 62.82, H 8.63 and 8.65, N 3.48 and 3.52.

***N*-(*tert*-Butyloxycarbonyl)(4-methylphenyl)sulfonamide (11c):** (6.70 g, 90%), m.p. 117−119 °C (ref.[12] m.p. 117−119 °C).

***N*-(*tert*-Butyloxycarbonyl)(4-iodophenyl)sulfonamide (11d):** (7.00 g, 90% after recrystallization), m.p. 134−136 °C (cyclohexane). − IR (KBr): $\tilde{\nu}$ = 3440 (br), 3233, 1742, 1435, 1344, 1173, 1150 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.41 (s, 9 H), 7.35 (s, 1 H, NH), 7.73 (d, *J* = 8.7 Hz, 2 H), 7.91 (d, *J* = 8.7 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.9, 84.5, 101.6, 129.6, 138.2, 138.6, 148.9. − $C_{11}H_{14}INO_4S$ (383.2): calcd. C 34.48, H 3.68, N 3.66; found C 34.75 and 34.67, H 3.45 and 3.42, N 3.31 and 3.27.

***N*-(*tert*-Butyloxycarbonyl)[3-(perfluorooctyl)phenyl]sulfonamide (11e):** (10.1 g, 89% after recrystallization), m.p. 106−110 °C (cyclohexane). − IR (KBr): $\tilde{\nu}$ = 3429 (br), 3234, 1747, 1446, 1357, 1241, 1219, 1209, 1150, 1113 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 9 H), 7.52 (s, 1 H, NH), 7.74 (t, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 8.26 (br absorption, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.7, 84.8, 100−120, 126.8 (t, *J* = 8.6), 129.8, 130.2 (t, *J* = 26.0), 131.7, 131.9 (t, *J* = 6.9 Hz), 140.2, 148.7. − $C_{19}H_{14}F_{17}NO_4S$ (675.4): calcd. C 33.79, H 2.09, N 2.07; found C 33.73 and 33.78, H 1.99 and 1.95, N 2.03 and 2.07.

***N*-(*tert*-Butyloxycarbonyl)(2-thienyl)sulfonamide (11g):** (9.84 g, 93%), m.p. 101−105°C. − IR (KBr): $\tilde{\nu}$ = 3281, 1745, 1413, 1338, 1230, 1141, 1089, 1021, 827, 775, 662 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (s, 9 H), 7.12 (dd, *J* = 5.0 and 3.8 Hz, 1 H), 7.69 (dd, *J* = 5.0 and 1.5 Hz, 1 H), 7.83 (dd, *J* = 3.8 and 1.5 Hz, 1 H), 7.85 (br s, 1 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.9, 84.4, 127.2, 133.5, 134.6, 139.3, 149.0. − $C_9H_{13}NO_4S_2$ (263.3): calcd. C 41.05, H 4.98, N 5.32; found C 41.25 and 41.24, H 5.04 and 4.98, N 5.53 and 5.40.

(*E*)-*N,N′*-Bis(arylsulfonyl)-*N,N′*-bis(*tert*-butyloxycarbonyl)-2-butene-1,4-diamines (12)

(*E*)-*N,N′*-Bis(*tert*-butyloxycarbonyl)-*N,N′*-bis[(2,4,6-triisopropylphenyl)sulfonyl]-2-butene-1,4-diamine (12aa). − General Method: A stirred mixture of **11a** (6.00 g, 15.8 mmol), potassium carbonate (6.48 g, 46.9 mmol) and acetonitrile (86 mL) was heated at 80 °C (bath temperature). Then, dibromobutene **8** (1.68 g, 7.8 mmol) was added. The reaction was monitored by tlc and heated until completion (6−14 h). The salts were filtered off and the filtrate was evaporated to afford **12aa** (6.36 g, 99%), m.p. 148−150 °C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 1727, 1370, 1338, 1288, 1255, 1168, 1150 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (s, 18 H), 1.25 (d, *J* = 6.6 Hz, 36 H), 2.90 (sept, *J* = 6.6 Hz, 2 H), 3.92 (sept, *J* = 6.6 Hz, 4 H), 4.42 (br s, 4 H), 6.01 (br s, 2 H), 7.73 (s, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.4, 27.7, 29.2, 46.3, 83.5, 123.4, 128.9, 134.0, 150.2, 150.8, 153.0. − $C_{44}H_{70}N_2O_8S_2$ (819.2): calcd. C 64.52, H 8.61, N 3.42, S 7.83; found C 63.87 and 64.06, H 8.32 and 8.39, N 3.38 and 3.39, S 7.53 and 7.47.

(*E*)-*N,N′*-Bis(*tert*-butyloxycarbonyl)-*N,N′*-bis[(4-methylphenyl)-sulfonyl]-2-butene-1,4-diamine (12cc): (7.20 g, 81%), m.p. 130−132 °C. − IR (KBr): $\tilde{\nu}$ = 1725, 1350, 1289, 1157 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (s, 18 H), 2.40 (s, 6 H), 4.47 (d, *J* = 4.4 Hz, 4 H), 5.91 (br s, 2 H), 7.28 (d, *J* = 7.3 Hz, 4 H), 7.80 (d, *J* = 8.8 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 27.8, 47.4, 84.2, 128.1, 129.1, 129.3, 137.1, 144.0 150.7. − $C_{28}H_{38}N_2O_8S_2$ (594.7): calcd. C 56.55, H 6.44, N 4.71; found C 56.25 and 56.45, H 6.50 and 6.48, N 4.67 and 4.68.

(*E*)-*N,N′*-Bis(*tert*-butyloxycarbonyl)-*N,N′*-bis[(4-iodophenyl)-sulfonyl]-2-butene-1,4-diamine (12dd): (1.42 g, 92%), m.p. 145−147 °C (cyclohexane). − IR (KBr): $\tilde{\nu}$ = 1716, 1362, 1301, 1158 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34 (s, 18 H), 4.46 (br s, 4 H), 5.91 (br s, 2 H), 7.62 (d, *J* = 8.0 Hz, 4 H), 7.84 (d, *J* = 8.7 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.9, 47.4, 84.9, 100.8, 129.1, 129.4, 138.0, 139.7, 149.2. − $C_{26}H_{32}I_2N_2O_8S_2$ (818.4): calcd. C 38.15, H 3.94, N 3.42; found C 38.19 and 38.25, H 3.94 and 3.98, N 3.15 and 3.30.

(*E*)-*N,N′*-Bis(*tert*-butyloxycarbonyl)-*N,N′*-bis[(2-thienyl)sulfonyl]-2-butene-1,4-diamine (12gg): (8.36 g, 96%), m.p. 130−131°C. − IR (KBr): $\tilde{\nu}$ = 1714, 1398, 1327, 1253, 1167, 1146, 778, 661 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.43 (s, 9 H), 4.40−4.42 (m, 4 H), 5.83−5.85 (m, 2 H), 7.07 (dd, *J* = 5.0 and 3.8 Hz, 2 H), 7.63 (dd, *J* = 5.0 and 1.3 Hz, 2 H), 7.75 (dd, *J* = 3.8 and 1.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.9, 48.1, 84.7, 126.9, 128.8, 129.8, 132.9, 134.3, 140.3, 150.5. − $C_{22}H_{30}N_2O_8S_4$ (578.7): calcd. C 45.66, H 5.22, N 4.84; found C 45.16 and 45.26, H 5.13 and 5.18, N 4.84 and 4.88.

(*E*)-*N,N′*-Bis(arylsulfonyl)-2-butene-1,4-diamines (5)

(*E*)-*N,N′*-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-2-butene-1,4-diamine (5aa): See ref.[9]

(*E*)-*N,N′*-Bis[(4-methylphenyl)sulfonyl]-2-butene-1,4-diamine (5cc). − General Method: A mixture of **12cc** (5.95 g, 10.0 mmol), trifluoroacetic acid (25 mL), and dichloromethane (25 mL) was stirred at room temperature for 2 h. The liquid was distilled off under vacuum and the residue was recrystallized from ethyl acetate or ethanol to afford **5cc** (3.79 g, 96%), m.p. 148−149 °C (ethanol). − IR (KBr): $\tilde{\nu}$ = 3277, 1430, 1326, 1157, 1090, 1039 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.46 (s, 6 H), 3.46 (br, *J* ca. 3 Hz, 4 H), 4.84 (br s, 2 H, NH), 5.48 (br s, 2 H), 7.30 (d, *J* = 8.0 Hz, 4 H), 7.71 (d, *J* = 8.0 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.0, 43.8, 126.6, 128.0, 129.3, 136.4, 143.2. − $C_{18}H_{22}N_2O_4S_2$ (394.5): calcd. C 54.80, H, 5.62, N 7.11; found C 54.63 and 54.79, H 5.57 and 5.55, N 7.14 and 7.14.

(*E*)-*N,N′*-Bis[(4-iodophenyl)sulfonyl]-2-butene-1,4-diamine (5dd): (3.30 g, 98%), m.p. 232−233 °C. − IR (KBr): $\tilde{\nu}$ = 3277, 1330, 1159 cm^{-1}. − ^1H NMR (250 MHz, [D_8]THF): δ = 2.9 (br s, 2 H, NH), 3.49 (br s, 4 H), 5.59 (br s, 2 H), 6.86 (bt, 2 H), 7.62 (d, *J* = 8.8 Hz, 2 H), 7.97 (d, *J* = 7.8 Hz, 2 H). − ^{13}C NMR (62.5 MHz, [D_8]THF): δ = 46.4, 101.1, 130.8, 140.5, 143.9. − $C_{16}H_{16}I_2N_2O_4S_2$ (618.2): calcd. C 31.08, H 2.61, N 4.53; found C 31.21 and 31.26, H 2.47 and 2.56, N 4.51 and 4.36.

(*E*)-*N,N′*-Bis[3-(perfluorooctyl)phenyl)sulfonyl]-2-butene-1,4-diamine (5ee): (8.00 g, 90%), m.p. 160−162 °C. − IR (KBr): $\tilde{\nu}$ = ca. 3440 (br), 3261, 1333, 1216, 1150 cm^{-1}. − NMR spectra were not recorded due to lack of solubility. − $C_{32}H_{16}F_{34}N_2O_4S_2$ (1202.6): calcd. C 31.96, H 1.34, N 2.33; found C 32.26 and 32.23, H 1.23 and 1.24, N 2.14 and 2.24.

(*E*)-*N,N′*-Bis[(2-thienyl)sulfonyl]-2-butene-1,4-diamine (5gg): (2.42 g, 77%), m.p. 150−151°C. − IR (KBr): $\tilde{\nu}$ = 3284, 1321, 1153 cm^{-1}. − ^1H NMR (250 MHz, [D_4]methanol): δ = 3.50 (br s, 4 H), 5.53 (br s, 2 H), 7.16 (dd, *J* = 5.0 and 3.9 Hz, 2 H), 7.60 (br dd, *J* = 3.9 and 1.1 Hz, 2 H), 7.78 (dd, *J* = 5.0 and 1.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz, [D_4]methanol): δ = 44.6, 127.6, 128.2, 132.0, 132.1, 141.9. − $C_{12}H_{14}N_2O_4S_4$ (378.5): calcd. C 38.08, H 3.73, N 7.40; found C 38.21 and 37.97, H 3.77 and 3.77, N 7.31 and 7.27.

(*E,E,E*)-*N,N′*-Bis(arylsulfonyl)-1,14-dibromo-5,10-diazatetradeca-2,7,12-trienes (3)

(*E,E,E*)-1,14-Dibromo-*N,N′*-bis[(2,4,6-triisopropylphenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene (3aa). − General Method: A stirred mixture of **5aa** (2.25 g, 4.0 mmol), dibromobutene **8** (6.35 g, 30 mmol), anhydrous potassium carbonate (1.94 g, 14 mmol), and acetonitrile (25 mL) was refluxed for 24 h and left stirring for 24 h more. The salts were filtered off, and the filtrate was evaporated. The residue was dissolved in THF (50 mL), and then water (200 mL) was added. The solvents and excess **8** were distilled in the rotary evaporator. The dry residue was digested in hexanes for 1 h at room temperature and the solid formed was filtered to afford **3aa** (1.85 g, 57%), m.p. 132−135 °C. See ref.[9] for spectral data.

(*E,E,E*)-1,14-Dibromo-*N,N′*-bis[(4-iodophenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene (3dd). − General Method: A stirred mixture of **5dd** (4.30 g, 7.0 mmol), dibromobutene **8** (11.90 g, 55.7 mmol), NaH (60% dispersion in mineral oil, 1.39 g, 34.8 mmol), and anhydrous DMF (50 mL) was heated at 80 °C for 17 h. After cooling to room temperature, water (100 mL) was added and the mixture was evaporated in a rotary evaporator. Addition of water and evaporation was repeated, and the residue was dried and recrystallized from cyclohexane to afford **3dd** (2.46 g, 40%), m.p. 163−166 °C. − IR (KBr): $\tilde{\nu}$ = 1343, 1160 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.73−3.78 (m, 8 H), 3.88 (d, *J* = 7.3 Hz, 4 H), 5.49−5.59 (m, 4 H), 5.72−5.85 (m, 2 H), 7.51 (d, *J* = 8.1 Hz, 4 H), 7.89 (d, *J* = 8.8 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 31.2, 48.3, 48.5, 100.1, 128.6, 129.1, 129.2, 130.9, 138.5, 139.6. − $C_{24}H_{26}Br_2I_2N_2O_4S_2$ (884.2): calcd. C 32.60, H 2.96, N 3.17; found C 31.95 and 31.78, H 2.83 and 2.76, N 3.31 and 3.42.

(*E,E,E*)-1,14-Dibromo-*N,N′*-bis[(4-methylphenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene (3cc): This was prepared using potassium carbonate in acetonitrile: 0.77 g (15%), m.p. 112 °C. − IR (KBr): $\tilde{\nu}$ = 1341, 1160 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 6 H), 3.72 (d, *J* ca. 6 Hz, 4 H), 3.75 (d, *J* = 6.5 Hz, 4 H), 3.88 (d, *J* = 6.8 Hz, 4 H), 5.45−5.49 (m, 2 H), 5.54 (dt, *J* = 15.0 and 6.4 Hz, 2 H), 5.78 (dt, *J* = 15.0 and 7.5 Hz, 2 H), 7.32 (d, *J* = 7.9 Hz, 4 H), 7.68 (d, *J* = 8.25 Hz, 4 H). − ^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 22.0, 31.9, 48.6, 48.9, 127.6, 129.6, 130.0, 130.3, 130.9, 137.2, 144.0. − $C_{26}H_{32}Br_2N_2O_4S_2$ (660.5): calcd. C 47.28, H 4.88, N, 4.24; found C, 47.17 and 47.18, H 4.91 and 4.90, N, 4.13 and 4.11.

(*E,E,E*)-1,14-Dibromo-*N,N′*-bis[(5-dimethylaminonaphth-1-yl)-sulfonyl]-5,10-diazatetradeca-2,7,12-triene (3ff) and *N,N*-Bis[(*E*)-4-bromo-2-butenyl][5-(dimethylamino)naphth-1-yl]sulfonamide (4f): A magnetically stirred mixture of 5-dimethylaminonaphth-1-ylsulfonamide (**2f**) (2.50 g, 10.0 mmol), dibromobutene **8** (8.57 g, 40.0 mmol), potassium carbonate (4.15 g, 30.0 mmol), and acetonitrile (60 mL) was refluxed for 20 h. The salts were filtered off and the filtrate was evaporated to afford an oily residue which was chromatographed through silica gel with mixtures of hexanes - ethyl acetate of increasing polarity. First compound eluted was **4f** (1.70 g, 33%), oil. − IR(film): $\tilde{\nu}$ = 1325, 1143, 793 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.89 (s, 6 H), 3.84 (d, *J* = 7.0 Hz, 4 H), 3.89 (d, *J* = 6.6 Hz, 4 H), 5.57 (dt, *J* = 15.0 and 6.6 Hz, 2 H), 5.79 (dt, *J* = 15.0 and 8.0 Hz, 2 H), 7.19 (d, *J* = 7.3 Hz, 1 H), 7.52 (apparent t, *J* = 7.3 Hz, 1 H), 7.57 (apparent t, *J* = 8.8 Hz, 1 H), 8.21 (d, *J* = 8.1 Hz, 1 H), 8.24 (d, *J* = 7.0 Hz, 1 H), 8.56 (d, *J* = 7.3 Hz, 1 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 31.3, 45.5, 47.4, 115.4, 119.4, 123.3, 128.2, 129.4, 129.6, 130.0, 130.4, 130.7, 131.0. − $C_{20}H_{24}Br_2N_2O_2S$ (516.3): calcd. C 46.53, H 4.69, N 5.43; found C 46.67 and 46.85, H 4.64 and 4.58, N 5.13 and 5.12. − Second compound eluted was **3ff** (0.85 g, 21%), m.p. 69−70 °C. − IR(KBr): $\tilde{\nu}$ = 1350, 1143, 793 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.85 (s, 12 H), 3.76 (apparent t, *J* = 8.05, 12 H), 5.38 (m, 2 H), 5.48 (dt, *J* = 15.3 and 5.8 Hz, 2 H), 5.62 (dt, *J* = 14.6 and 8.0, 2 H), 7.15 (d, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 8.0 Hz, 2 H), 8.19 (overlapped d, 4 H), 8.52 (d, *J* ca. 8 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 31.2, 45.4, 47.1, 47.3, 115.3, 119.4, 123.2, 128.1, 129.2, 129.4, 129.8, 130.2, 130.5, 130.8, 134.5, 151.3. − $C_{36}H_{42}Br_2N_4O_4S_2$ (818.7): calcd. C 52.82, H 5.17, N 6.84; found C 52.57 and 52.81, H 5.20 and 5.27, N 6.77 and 6.77.

(*E,E,E*)-1,14-Dibromo-*N,N′*-bis[(4-methylphenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene (3cc) and *N,N*-Bis[(*E*)-4-bromo-2-butenyl](4-methylphenyl)sulfonamide (4c): These were prepared from **2c** and **8** by the same procedure as **3ff** and **4f** (see preceding preparation). First compound eluted was **4c** (10.88 g, 50%), oil. − IR (film): $\tilde{\nu}$ = 1339, 1159 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.79 (d, *J* = 6.5 Hz, 4 H), 3.89 (d, *J* = 6.3 Hz, 4 H), 5.58 (dt, *J* = 15.2 and 6.4 Hz, 2 H), 5.80 (dt, *J* = 15.2 and ca. 6 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.68 (d, *J* = 8.5 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 22.0, 31.9, 48.7, 127.6, 130.0, 130.3, 131.2, 137.2, 144.0. − $C_{15}H_{19}Br_2NO_2S$ (437.2): calcd. C

41.21, H 4.38, N 3.20; found C 41.28 and 41.39, H 4.21 and 4.26, N, 3.47 and 3.41. Second compound eluted was **3cc** (1.37 g, 8%). See above for physical data.

_N_-[(_E_)-4-Bromo-2-butenyl]-_N_-(_tert_-butyloxycarbonyl)arenesulfonamides (13)

_N_-[(_E_)-4-Bromo-2-butenyl]-_N_-(_tert_-butyloxycarbonyl)(4-methylphenyl)sulfonamide (13c): A stirred mixture of **11c** (4.00 g, 14.8 mmol), dibromobutene **8** (12.7 g, 59.3 mmol), anhydrous potassium carbonate (10.2 g, 74.0 mmol), and acetonitrile (100 mL) was refluxed for 5 h. The salts were filtered off and the filtrate was evaporated. The oily residue was chromatographed through silica gel with hexanes/ethyl acetate (10:1) to afford **13c** (5.66 g, 95%), m.p. 64−66 °C. − IR (KBr): $\tilde{\nu}$ = 1721, 1355, 1152 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (s, 9 H), 2.44 (s, 3 H), 3.97 (d, J = 6.6 Hz, 2 H), 4.45 (d, J = 5.1 Hz, 2 H), 5.81−6.06 (m, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 27.8, 31.6, 47.1, 84.4, 128.1, 129.2, 130.1, 136.9, 144.2, 150.6. − $C_{16}H_{22}BrNO_4S$ (404.3): calcd. C, 47.53, H 5.48, N 3.46; found C 47.12 and 47.17, H 5.49 and 5.47, N 3.36 and 3.32.

_N_-[(_E_)-4-Bromo-2-butenyl]-_N_-(_tert_-butyloxycarbonyl)-[3-(perfluorooctyl)phenyl]sulfonamide (13e): This was obtained as for **13c**. Sulfonamide **13e** (1.77 g, 87%) was a solid, m.p. 55−57 °C. − IR(KBr): $\tilde{\nu}$ = 1729, 1370, 1296, 1240, 1205, 1176, 1150 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (s, 9 H), 3.96 (d, J = 7.3 Hz, 2 H), 4.47 (d, J = 6.0 Hz, 2 H), 5.80−6.08 (m, 2 H), 7.71 (t, J = 8.1 Hz, 1 H), 7.85 (d, J = 7.7 Hz, 1 H), 8.16−8.18 (m, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 27.7, 31.1, 47.4, 85.3, 126.7, 129.4, 129.5, 130.8, 131.6, 141.3, 150.2. − $C_{23}H_{19}BrF_{17}NO_4S$ (808.3): calcd. 34.18, H 2.37, N 1.73; found C 34.40 and 34.47, H 2.50 and 2.47, N 1.60 and 1.62.

(_E,E_)-1,6,11-Tris(arylsulfonyl)-1,11-bis(_tert_-butyloxycarbonyl)-1,6,11-triazaundeca-3,8-dienes (14)

(_E,E_)-1,11-Bis(_tert_-butyloxycarbonyl)-1,11-bis[[3-(perfluorooctyl)phenyl]sulfonyl]-6-[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (14aee): A stirred mixture of sulfonamide **2a** (0.291 g, 1.03 mmol), bromosulfonamide **13e** (1.65 g, 2.06 mmol), anhydrous potassium carbonate (0.86 g, 6.2 mmol), and acetonitrile (10 mL) was refluxed for 20 h. The salts were filtered off and the filtrate was evaporated. The residue was partitioned between water and ethyl acetate. The organic layer was dried and evaporated to afford **14aee** (1.70 g, 93%) as a white solid, m.p. 42−43 °C. − IR (KBr): $\tilde{\nu}$ = 1737, 1370, 1320, 1296, 1245, 1214, 1152 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (apparent t, J ca. 7 Hz, 18 H), 1.33 (s, 18 H), 2.91 (sept, J = 6.8 Hz, 1 H), 3.83 (d, J = 5.4 Hz, 4 H), 4.15 (sept, J = 5 Hz, 2 H), 4.43 (d, J = 4.9 Hz, 4 H), 5.7−6.0 (m, 4 H), 7.18 (s, 2 H), 7.71 (t, J = 7.8 Hz, 2 H), 7.82 (d, J = 7.7 Hz, 2 H), 8.12 (d, J = 7.7 Hz, 2 H), 8.17 (s, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 27.6, 29.2, 34.2, 46.4, 47.9, 85.1, 123.9, 126.6 (t), 128.7, 129.6 (t), 130.0, 130.9, 131.3, 141.4, 150.2, 151.5, 153.2. − $C_{61}H_{61}F_{34}N_3O_{10}S_3$ (1738.3): calcd. C 42.15, H 3.54, N 2.42; found C 42.35 and 42.23, H 3.35 and 3.46, N 2.16 and 2.22.

(_E,E_)-1,11-Bis(_tert_-butyloxycarbonyl)-1,6,11-tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (14ccc): This was obtained as for **14aee**, from **2c** and **13c**. Trisulfonamide **14ccc** (1.70 g, 96%) was a solid, m.p. 54−55 °C. − IR (KBr): $\tilde{\nu}$ = 1730, 1355, 1159 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.32 (s, 18 H), 2.43 (s, 9 H), 3.82 (d, J = 6.6 Hz, 4 H), 4.37 (d, J = 5.9 Hz, 4 H), 5.5−5.8 (m, 4 H), 7.31 (d, J ca. 8.0 Hz, 6 H), 7.70 (d, J = 8.8 Hz, 2 H), 7.76 (d, J = 8.8 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.4, 21.5, 27.8, 47.4, 47.9, 84.2, 127.1, 127.9, 128.1, 129.2, 129.7, 129.8, 137.1, 143.3, 144.1, 150.6. − $C_{39}H_{51}N_3O_{10}S_3$ (818.0): calcd. C 57.26, H 6.28, N 5.14; found C 57.22 and 57.27, H 6.30 and 6.47, N 5.00 and 5.00.

(_E,E_)-1,6,11-Tris(arylsulfonyl)-1,6,11-triazaundeca-3,8-dienes (6): Compounds **6** were prepared from the corresponding compounds **14** as for compounds **5**, by treatment with a 1:1 (v/v) mixture of trifluoroacetic acid and dichloromethane at room temperature.

(_E,E_)-1,11-Bis{[3-(perfluorooctyl)phenyl]sulfonyl}-6-[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (6aee): 1.22 g (95%), m.p. 121−124 °C. − IR (KBr): $\tilde{\nu}$ = 3297, 1366, 1329, 1301, 1242, 1209, 1152 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (apparent t, J = 7 Hz, 18 H), 2.91 (sept, J = 6.8 Hz, 1 H), 3.60 (br s, 4 H), 4.12 (br s, 4 H), 4.08 (sept, J = 6.8 Hz, 2 H), 5.39 (br, 2 H, NH), 5.66 (br s, 4 H), 7.17 (s, 2 H), 7.70 (t, J = 7.9 Hz, 2 H), 7.82 (d, J = 7.9 Hz, 2 H), 8.10−8.15 (br absorption, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.7, 34.1, 44.4, 47.3, 123.9, 125.6 (t), 128.6, 129.9, 130.5, 130.7, 131.0, 141.2, 151.4, 153.4. − $C_{51}H_{45}F_{34}N_3O_6S_3$ (1538.1): calcd. C 39.83, H 2.95, N 2.73; found C 39.58 and 39.70, H 2.71 and 2.66, N 2.49 and 2.49.

(_E,E_)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (6ccc): 1.22 g (95%), oil. − IR(film): $\tilde{\nu}$ = 3283, 1328, 1159 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 9 H), 3.46 (d, J = 4.8 Hz, 4 H), 3.62 (d, J = 5.3 Hz, 2 H), 5.14 (br s, 2 H), 5.35−5.60 (m, 4 H), 7.29 (d, J = 7.8 Hz, 6 H), 7.63 (d, J = 8.2 Hz, 2 H), 7.73 (d, J = 6.6 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 26.9, 44.3, 48.7, 127.0, 127.1, 127.9, 128.3, 129.6, 129.7, 136.6, 143.6. − HRMS; calcd. m/z for (M − $NHSO_2C_7H_7$) 447.1440; found 447.1412.

(_E,E,E_)-1,6,11-Tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes (1)

(_E,E,E_)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1aaa): A new preparation of **1aaa** (1.58 g, 60%) was performed using **4a** and **5aa**, according to ref.[9]

(_E,E,E_)-1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-11-[(4-vinylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1aab): See ref.[9] A new preparation afforded this product (0.77 g, 75%), with m.p. 152−154 °C.

(_E,E,E_)-11-[(5-Dimethylaminonaphthyl)sulfonyl]-1,6-bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1aaf): A stirred mixture of **2f** (0.029 g, 0.113 mmol), **3aa** (0.100 g, 0.113 mmol), anhydrous potassium carbonate (0.509 g, 3.68 mmol), and acetonitrile (12 mL) was refluxed for 24 h. The salts were filtered off and the filtrate was evaporated to give a residue, which was chromatographed through silica gel with mixtures of hexanes/ethyl acetate of increasing polarity to afford **1aaf** (80 mg, 73%), m.p. 196−198 °C. − IR (KBr): $\tilde{\nu}$ = 1364, 1149 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23 (d, J = 6.6 Hz, 24 H), 1.25 (d, J = 6.6 Hz, 12 H), 2.88 (s, 6 H), 2.88 (sept, J = 6.6 Hz, 2 H), 3.77 (br absorption, 8 H), 3.89 (br absorption, 4 H), 4.08 (sept, J = 6.6 Hz, 4 H), 5.79 (br absorption, 6 H), 7.15 (s, 4 H), 7.17 (d, J = 8.8 Hz, 1 H), 7.51 (apparent t, J = 8.8 Hz, 1 H), 7.54 (apparent t, J = 8.8 Hz, 1 H), 8.17 (d, J ca. 7 Hz, 1 H), 8.25 (d, J = 8.8 Hz, 1 H), 8.54 (d, J = 8.8 Hz, 1 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 29.2, 34.2, 45.4, 48.9, 49.1, 50.6, 115.3, 119.4, 123.1, 123.9, 128.2, 130.0, 130.1, 130.4, 130.5, 130.9, 134.5, 151.5, 153.1. − MALDI-TOF MS; m/z (%): 971 [M − 1], 973 [M + 1], 995 [M + Na], 1011 [M + K]. − $C_{54}H_{76}N_4O_6S_3$ (973.4): calcd. C 66.63, H

7.87, N 5.76; found C 66.28 and 66.47, H 7.91 and 7.95, N 5.29 and 5.36.

(*E,E,E*)-1,6-Bis[(4-iodophenyl)sulfonyl]-11-[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1add): Sulfonamide **2a** (0.033 g, 0.11 mmol) in anhydrous DMF (4 mL) was treated with sodium hydride (60% in mineral oil, 0.020 g, 0.5 mmol). This mixture was added to a solution of **3dd** (0.10 g, 0.11 mmol) in anhydrous DMF (13 mL). The mixture was heated at 90 °C with stirring for 17 h. Water (20 mL) was added and the solvents were evaporated under vacuum. The addition of water and subsequent evaporation was repeated. The dry residue was chromatographed through silica gel with hexanes - ethyl acetate (10:2) to afford **1add** as an oil which was recrystallized from cyclohexane (0.09 g, 80%), m.p. 82−84 °C. − IR (KBr): $\tilde{\nu}$ = 1342, 1160 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (apparent t, *J* = 7 Hz, 18 H), 2.90 (sept, *J* = 6.6 Hz, 1 H), 3.70−3.85 (br absorption, 12 H), 4.07 (sept, *J* = 6.6 Hz, 2 H), 5.50−5.85 (m, 6 H), 7.16 (s, 2 H), 7.50 (d, *J* = 8.8 Hz, 4 H), 7.89 (d, *J* = 8.8 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 29.2, 29.3, 34.1, 48.6, 50.6, 51.1, 100.0, 124.0, 127.3, 128.5, 129.7, 128.8, 130.6, 138.5, 139.2, 151.5, 153.3. − MALDI-TOF MS; *m/z* (%): 1027.7 [M + Na], 1043.7 [M + K]. − $C_{39}H_{49}I_2N_3O_6S_3$ (1005.8): calcd. C 46.57, H 4.91, N 4.18; found C 46.07 and 46.03, H 4.96 and 4.88, N 3.99 and 4.00.

(*E,E,E*)-1,6-Bis[(4-methylphenyl)sulfonyl]-11-[(2-thienyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1ccg): This was prepared as for **1aaf**, from **2g** and **3cc**. Macrocycle **1ccg** (0.24 g, 58%) was a solid, m.p. 189−191 °C. − IR (KBr): $\tilde{\nu}$ = 1338, 1160 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 6 H), 3.69 (br s, 12 H), 5.60 (br s, 6 H), 7.12 (dd, *J* = 5.1 and 3.6 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 4 H), 7.54 (d, *J* = 3.6 Hz, 1 H), 7.59 (d, *J* = 5.1 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 50.7, 51.0, 127.2, 127.5, 129.0, 129.5, 129.7, 129.8, 131.8, 132.0, 135.9, 143.6. − MALDI-TOF MS; *m/z* (%): 662.2 [M + 1], 684.2 [M + Na], 700.2 [M + K]. − $C_{30}H_{35}N_3O_6S_4$ (661.9): calcd. C 54.44, H 5.33, N 6.35; found C 54.41 and 54.32, H 5.19 and 5.19, N 6.23 and 6.16.

(*E,E,E*)-1,6,11-Tris-[(5-dimethylaminonaphthyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1fff): This was prepared as for **1aaf**, from **2f** and **3ff**. Macrocycle **1fff** (0.36 g, 51%) was a solid, m.p. 105−107 °C, IR (KBr): $\tilde{\nu}$ = 1325, 1144 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.86 (s, 18 H), 3.75 (br s, 12 H), 5.54 (br s, 6 H), 7.14 (d, *J* = 7.3 Hz, 3 H), 7.48 (apparent t, *J* = 7.3 Hz, 3 H), 7.50 (apparent t, *J* = 8.0 Hz, 3 H), 8.13 (d, *J* = 5.8 Hz, 3 H), 8.21 (d, *J* = 8.7 Hz, 3 H), 8.5 (d, *J* = 8.7 Hz, 3 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.4, 50.0, 115.3, 119.4, 123.1, 128.2, 129.9, 130.0, 130.5, 134.6, 151.8 − MALDI-TOF MS; *m/z* (%): 905.4 [M −1], 929.4 [M + Na], 945.4 [M + K]. − HRMS: calcd. for $C_{48}H_{54}N_6O_6S_3$: *m/z* 907.3345; found 907.3349.

(*E,E,E*)-1,6-Bis{[3-(perfluorooctyl)phenyl]sulfonyl}-11-[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1aee): A solution of **6aee** (1.54 g, 1.00 mmol) and dibromobutene **8** (0.214 g, 1.00 mmol) in acetonitrile (75 mL) was added dropwise over 2 h to a stirred suspension of anhydrous potassium carbonate (0.69 g, 5.00 mmol) in boiling acetonitrile (75 mL). Refluxing was continued for 17 h, the salts were filtered off, and the filtrate was evaporated. The residue was recrystallized from cyclohexane to afford **1aee** (1.46 g, 92%) as a solid, m.p 57−59 °C. − IR (KBr): $\tilde{\nu}$ = 1351, 1243, 1213, 1152, 1116 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26 (apparent t, *J* = 7 Hz, 18 H), 2.92 (sept, *J* = 6.8 Hz, 1 H), 3.65−3.90 (br absorption, 12 H), 4.09 (sept, *J* = 6.8 Hz, 2 H), 5.5−5.9 (m, 6 H), 7.18 (s, 2 H), 7.74 (t, *J* = 8.0 Hz, 2 H), 7.85 (d, *J* = 7.7 Hz, 2 H), 8.03 (br absorption, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.7, 29.2, 34.1, 48.7, 50.6, 51.0, 124.0, 125.6, 129.5, 129.6, 130.0, 130.2, 130.4, 130.5, 130.8, 130.9, 131.0, 140.7, 151.4, 151.5, 153.4 − MALDI-TOF MS; *m/z* (%): 1611.6 [M + Na], 1627.6 [M + K]. − $C_{55}H_{49}F_{34}N_3O_6S_3$ (1590.1): calcd. C 41.54, H 3.11, N 2.64; found C 41.29 and 41.40, H 2.93 and 3.07, N 2.55 and 2.47.

(*E,E,E*)-1,6,11-Tris-[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1ccc): This was prepared as for **1aee**. Macrocycle **1ccc** (1.29 g, 81%) was a solid, m.p. 198−200 °C. − IR (KBr): $\tilde{\nu}$ = 1337, 1160 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 9 H), 3.67 (br s, 12 H), 5.56 (br s, 6 H), 7.31 (d, *J* = 8.0 Hz, 6 H), 7.65 (d, *J* = 8.0 Hz, 6 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 22.2, 51.3, 127.8, 130.1, 130.5, 136.8, 144.2. − MALDI-TOF MS; *m/z* (%): 692.1 [M + Na], 708.1 [M + K]. − $C_{33}H_{39}N_3O_6S_3$ (669.9): calcd. C 59.17, H 5.87, N 6.27; found C 59.14 and 59.19, H 5.99 and 5.90, N 6.20 and 6.22.

(*E,E,E*)-11-[(4-Methylphenyl)sulfonyl]-1,6-bis[(2-thienyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (1cgg): A mixture of bissulfonamide **5gg** (0.943 g, 3.0 mmol) and anhydrous potassium carbonate (1.659 g, 12.0 mmol) was heated at 70°C in acetonitrile (160 mL) for 20 minutes. Then, dibromosulfonamide **4c** (1.31 g, 3.00 mmol) was added. The mixture was refluxed for 14 h. The salts were filtered off and the solvent was evaporated from the filtrate. The residue was chromatographed through silica gel with hexanes/ethyl acetate (7:3). First, **4c** was recovered (0.162 g, 12%). Then macrocycle **1cgg** was eluted (1.157 g, 59%), m.p. 58−60°C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 1342, 1157 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.73 (br s, 12 H), 5.64−5.68 (br s, 6 H), 7.15 (dd, *J* = 5.0 and 3.7 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.58 (dd, *J* = 3.9 and 1.3 Hz, 2 H), 7.63 (dd, *J* = 5.0 and 1.3, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.3, 50.5, 50.8, 127.0, 127.3, 128.8, 129.1, 129.6, 131.5, 131.7, 135.3, 139.0, 143.2. − MALDI-TOF MS; *m/z* (%): 654.1 [M + 1], 676.1 [M + Na], 692.0 [M + K]. − HRMS; Calcd. *m/z* for (M + 1) 654.0876, found 654.0895.

Acknowledgments

Financial support from the Spanish MEC (projects PB93-0896 and PB98-0902), and from the CIRIT-Generalitat de Catalunya [project 98SGR0056, predoctoral scholarships (to J.C., S.C., and J.T.) and a postdoctoral contract (to C.M.)] are gratefully acknowledged.

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Received May 5, 2000
[O002224]