An Investigation on the Synthesis of New Molecular Architectures from the Cyclotrimerisation of *exo*- and *endo*-Benzotricyclo[4.2.1.0^{2,5}]nonene

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Keywords: Arenes / Copper / Cyclotrimerisation / High-temperature bromination / Norbornene

We have performed an investigation on the cyclotrimerisation of molecules having *exo*- and *endo*-benzotricyclo[4.2.1.0^{2,5}]nonene skeletons (**3** and **4**) with the aim of producing their respective cyclotrimers **2** that feature unusual geometries and electronic properties. Activation towards the cyclotrimerisation reaction was performed using the *vic*-bromostannyl vinyl derivatives and was accomplished under copper-mediated or palladium-catalysed reaction conditions. While the *exo* isomer **3** proved to be quite reactive and afforded variable amounts of the *syn* and *anti* cyclotrimers, the *endo* isomer **4** turned out to be quite resistant to cyclotrimerisation because of steric hindrance. Only dimers and acyclic trimers were obtained from reactions using this substrate.

Introduction

The idea of constructing atom-by-atom nanoscale objects is described well as one of the contemporary approaches to structures that may exhibit unusual geometries and electronic properties for potential implementation in nanotechnology.[1] From this point of view, benzocyclotrimers of the general formula **1**[2] are molecules possessing a wealth of features that can be applied profitably in several instances. Their main peculiarity is that the two faces of the central aromatic ring are morphologically different and so the electronic distribution of the upper and lower surfaces is uneven, displaying higher electron density within the cavity.[3] For these reasons, such benzocyclotrimers can be examined as hosting agents, scaffolds for liquid-crystalline materials, for the synthesis of tripodal structures, and as starting materials for the synthesis of non-planar PAHs and fullerene substructures. Importantly, cyclotrimers of type **1** show an intrinsically unusual electronic feature: they possess alternation in the bond lengths of the central aromatic ring.[4] This feature, which makes the central ring resemble 1,3,5-cyclohexatriene more than benzene, is unique for such a system and legitimates further synthetic investigations of homologues and isosteres for future implementation. In this context, we were interested in preparing the benzocyclotrimers **2** containing a cyclobutene moiety directly attached to the required bicyclo[2.2.1] system, because many of the aforementioned features should be maximized (or at least altered) and, as a consequence, a clearer indication of the structure−behaviour relationship of the benzocyclotrimers is expected to emerge (Figure 1).

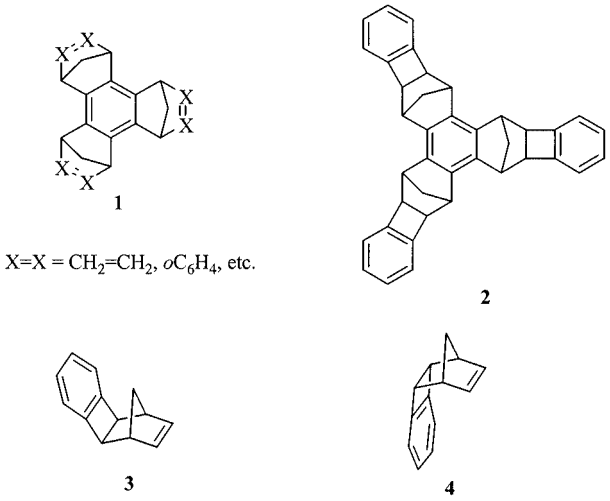

Figure 1. Starting and target molecules

The starting materials for the synthesis of the several diastereoisomers implicit in the general structure **2** are the known *exo*- and *endo*-benzotricyclo[4.2.1.0^{2,5}]nonenes **3**[5] and **4**,[6] which were submitted to bromination followed by dehydrobromination and metallation to obtain the direct

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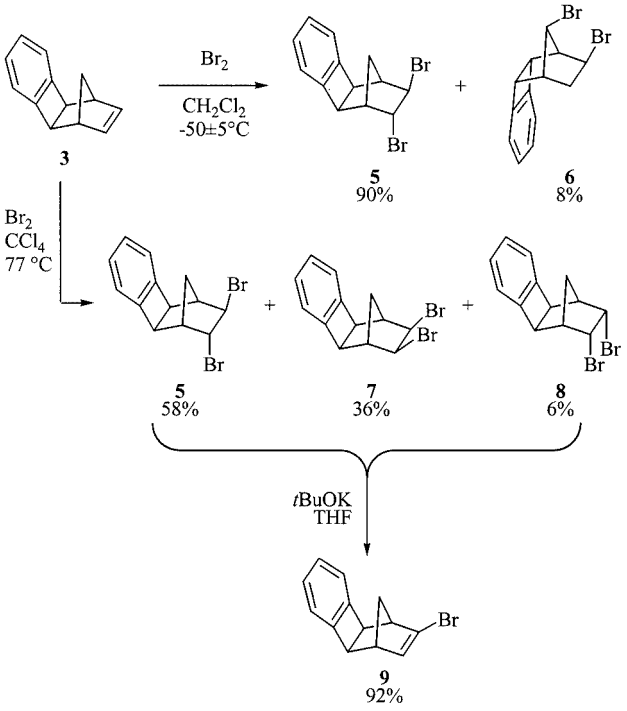
precursors for the cyclotrimerisation reaction (these compounds are described in the Results and Discussion). These operations were not trivial, because of the propensity of polycyclic systems to undergo rearrangements, and required an in-depth study of their behaviour. In this paper, we report in full our studies that led to the preparation of a number of functionalised derivatives of **3** and **4** and of the *syn* and *anti* cyclotrimers derived from the *exo* isomer **3**. The *endo* isomer **4** proved resistant to cyclotrimerisation under any of the reaction conditions known to lead to cyclotrimers of similar compounds. We believe that the reason for this failure rest upon steric hindrance that prevents the *endo* compound **4** from undergoing cyclotrimerisation and leads, instead, only to dimers and acyclic trimers that, in most instances, we isolated and characterized.

Results and Discussion

Synthesis of the Precursors of the Cyclotrimerisation Reaction

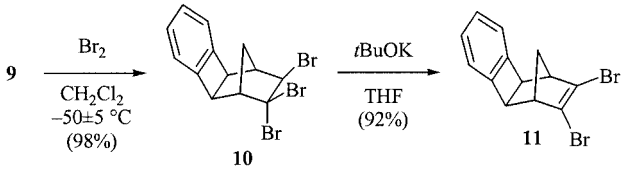
Prior to undertaking the present work, the starting vinylic monobromide **9** and dibromide **11** were unknown molecules. The electrophilic addition of bromine to *exo*-benzocyclobutenonorbornene **3**[5] was first reported by Nenitzescu et al.,[7] who described the formation of the *trans* dibromide **5**. In this reaction, beside to the reported non-rearranged product **5** (90%), we also observed formation of the rearranged dibromide **6** (8%). Its formation was not welcome because all the steps on the way to monobromide **9** were contaminated with this substance, which turned out to be inert under the reaction conditions and often had polarity too similar to the products to be easily separated. In the experiments that followed, aimed to minimize formation of **6**, we noticed that the reaction temperature has a dramatic influence on the product distribution and that increasing of the temperature favours the non-rearranged reaction products.[8] This factor encouraged us to raise the bromination temperature in the hope of obtaining only non-rearranged products. When a hot solution of bromine in CCl_4 was added directly to solution of **3** in CCl_4 under reflux, NMR spectroscopic analysis of the crude product indicated that the reaction mixture consisted of three products, which we separated by column chromatography and found to be consistent with *trans* dibromide **5** (58%), *exo-cis* dibromide **7** (36%) and *endo-cis* dibromide **8** (6%) (Scheme 1). In none of these compounds did any Wagner−Meerwein rearrangement occur and, thus, all of them were amenable to be subjected to dehydrobromination to **9**. Indeed, treatment of the mixture of dibromides **5**, **7** and **8** with potassium *tert*-butoxide furnished monobromide **9** in 92% yield.

Further bromination of **9** at −50 ± 5 °C in CH_2Cl_2 yielded only non-rearranged product **10** in nearly quantitative yields. In a manner similar to that of related compounds, this behavior indicates that stabilisation of the positive charge by the bromine atom makes it less prone to rearrange than the unsubstituted analogue. Elimination of



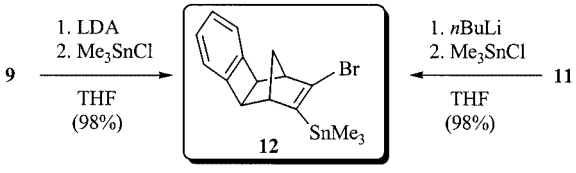
Scheme 1

HBr from tribromide **10**, using potassium *tert*-butoxide at room temperature, gave dibromide **11** in high yield (Scheme 2).



Scheme 2

Both **9** and **11** are the precursors of the required bromostannyl compound **12**. Deprotonation of **9** with LDA, followed by quenching with trimethyltin chloride, afforded **12** in quantitative yield and, likewise, in comparable yield, halogen−metal exchange of one of the bromine atoms in **11** with *n*BuLi, followed by quenching with trimethyltin chloride, also furnished the required bromostannyl compound **12** (Scheme 3).

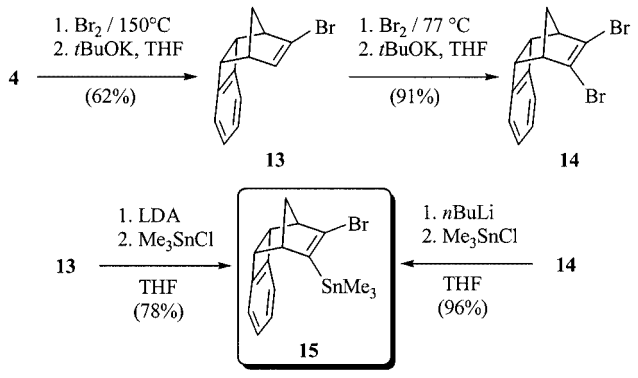


Scheme 3

As has been pointed out elsewhere,[9] compound **12** is not a trivial molecule because it represents an olefin bearing a metal and a leaving group at the two termini of the same

double bond. While in other occasions, a rapid elimination of Me_3SnBr to the triple bond would be expected, in this case compound **12** is stable because of the strain of the acetylene that would form.

The two *endo* starting materials **13** and **14** were synthesized by our procedure described in the literature (Scheme 4).[10]



Scheme 4

For the *exo* derivatives of **3**, compounds **13** and **14** were both transformed into the required bromostannyl derivative **15**. In these transformations, however, the *endo* structures derived from **4** exhibited a poorer reactivity with respect to the *exo* ones and, in many instances, we noticed the presence of side products. For example, deprotonation of **13** afforded **15** in 78% yield with the rest of the mass balance being composed of debrominated tin compound **16** and of olefin **4** in 4 and 14% yields, respectively (Figure 2).

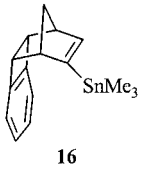


Figure 2. The debrominated tin compound

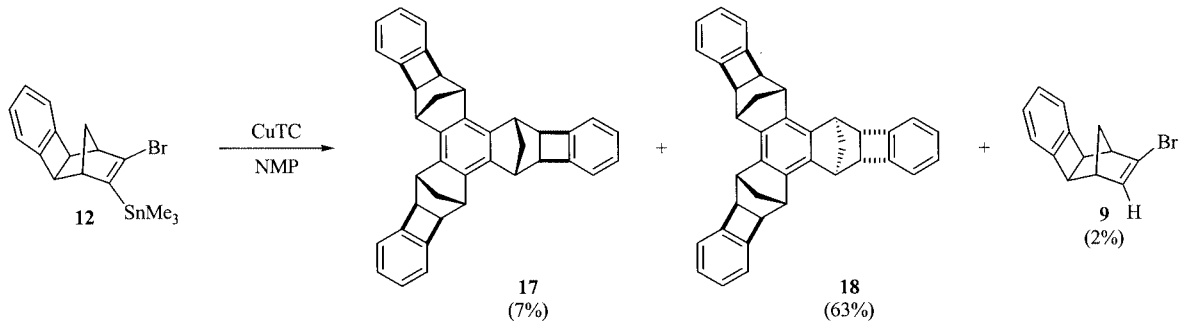
Cyclotrimerisation Reactions

Test runs of the cyclotrimerisation were performed on both the *exo* and *endo* structures under copper-mediated reactions on the bromostannyl compounds **12** and **15** and under palladium-catalysis with the dibromoolefins **11** and **14**.

Preliminary experiments were performed on the *exo*-substrate **12** under the reaction conditions known to give the best yields in cyclotrimers.[8e,8f] Presently, the highest yield in such a cyclotrimerisation reaction has been achieved using copper(I) 2-thiophenecarboxylate (CuTC) in *N*-methylpyrrolidone as solvent at 0 °C. Under these conditions, **12** afforded 70% yields of cyclotrimers in a 9:1 *anti*-to-*syn* ratio. A small amount of protodestannylated product **9** was also observed. No other products were observed in the crude reaction mixture even though the presence of dimers was carefully checked (Scheme 5).

We ascribe the formation of **9** to presence of adventitious water because no other proton sources are present in the reaction mixture. Supporting this hypothesis is the fact that when the reaction was performed with copper(I) nitrate trihydrate, a substantial quantity of the protodestannylated product **9** (39% yield) was observed in addition to the cyclotrimers **17** and **18** (4 and 23% yields, respectively). In this case, trace amounts of the dimers **19** and **20** were also produced. The presence of the dimers **19** and **20** bespeaks of a tin−tin coupling mechanism as has been observed in previous experiments performed to clear the mechanism of Cu^I-mediated cyclotrimerisation of polycyclic bromostannyl compounds.[11] The structures of the dimers were assigned so that comparisons could be made with samples obtained in higher yields and those formed in the experiments carried out under different conditions that are described hereafter.

Because it was known that neither CuTC nor $Cu(NO_3)_2$ is selective in affording only one of the *syn* or *anti* diastereomeric cyclotrimers, we carried out further experiments under the conditions known to afford either one of the stereoisomers selectively. For example, it is known that copper iodide in DMF, in the presence of lithium chloride, affords the *syn* cyclotrimer selectively in reactions with related substrates.[4f] In the present case, under comparable reaction conditions, cyclotrimers **17** and **18** were obtained in 5 and 3% yields, respectively. Although we observed a higher ratio of the *syn* cyclotrimer over the *anti* one, the poor yields suggest that this route is not a viable one for the selective synthesis of the *syn* cyclotrimer (Figure 3).



Scheme 5

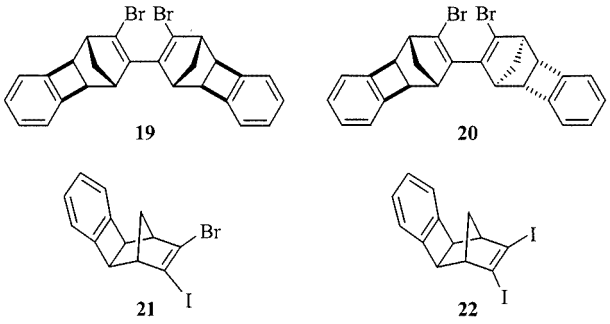


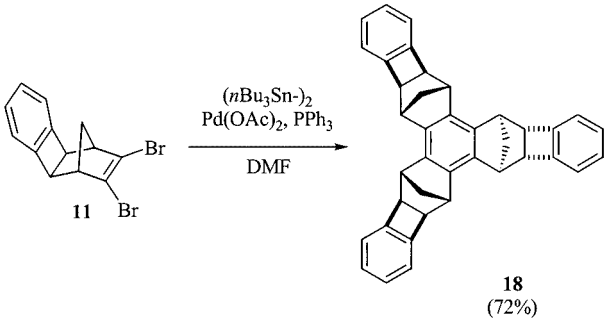
Figure 3. Byproducts from the reaction of **12** with CuI/LiCl

Beside the cyclotrimers, the mass balance of the reaction was composed of dimers **19** and **20** (total 7% yield) in a 4:3 ratio, and the "dihalide" products **21** (48% yield) and **22** (8% yield), together with a small amount of protodestannylated product **9** (5% yield). The structure of the dimers was assigned on the basis of their spectroscopic and spectrometric data. Presently, we are unable to determine which compound has the C_s structure and which has the C_2 one, although we suspect that the form that eventually will lead to the *syn* cyclotrimer (i.e., structure **19**) may predominate. The formation of **21** and **22** is the result of a metal−halogen exchange and it suggests the involvement of copper intermediates derived from both the tin and bromine substituents.

A final experiment with copper salts was performed with copper(II) 2-thiophenecarboxylate [$Cu(TC)_2$] to determine if Cu^{II} is also effective in promoting cyclotrimerisation of vicinal bromostannyl polycyclic olefins. In contrast with CuTC, which gave the best results in term of yields, $Cu(TC)_2$ afforded the cyclotrimers **17** and **18** in 20 and 15% yields, respectively. Importantly, we observed an increase in the ratio of the *syn* cyclotrimer and this method represents the highest-yielding route so far to the *syn* stereoisomer. Besides the cyclotrimers, we also observed dimers **19** and **20** (which did not form when using CuTC) and small amounts of dibromide **11** (9%) and monobromide **9** (4%).

A summary of the product distribution and yields obtained under the copper-mediated cyclotrimerisation reactions is reported in Table 1.

Finally, since the most-convenient procedure known for the preparation of only the *anti* cyclotrimer for related substrates is one that uses the dibromide and hexabutylditin in the presence of Pd^0, we applied these reaction conditions to **11**. Consistently, we obtained only the *anti* cyclotrimer **18** in 72% yield, together with several other products, which, because they were obtained in small amounts, were not investigated further (Scheme 6).



Scheme 6

The *endo* monomer **15** showed a strong reluctance to undergo cyclotrimerisation under the conditions that proved effective for its *exo* isomer, **12**. Scheme 1 reports the results obtained under the reaction conditions that we tested (Scheme 7).

While $Cu(TC)_2$ proved totally unreactive, side reactions leading to the protodestannylated compound **13** (95%) and the substitution product **23** (92%) emerged in the reactions with $Cu(NO_3)_2{\cdot}3H_2O$ and CuI/LiCl, respectively; not even traces of cyclotrimers could be detected. $Cu^{I}TC$ afforded a complex reaction mixture that we checked carefully for the presence of trimers, but with no success. Instead, we observed a number of acyclic trimers (**24**, **25**, **26**) and a dimer (**27**), together with a small amount of dibromide **14**. The presence of such a complex reaction mixture is indicative of the several paths that this reaction can follow, including tin−tin and tin−bromine coupling, in the absence of stereoelectronic limitations. At the present state of the art, we believe that the benzocyclotrimers do not form in the *endo* case because of steric hindrance, even though analysis of molecular models predicts that there is a fair possibility that the *anti* cyclotrimer could exist.

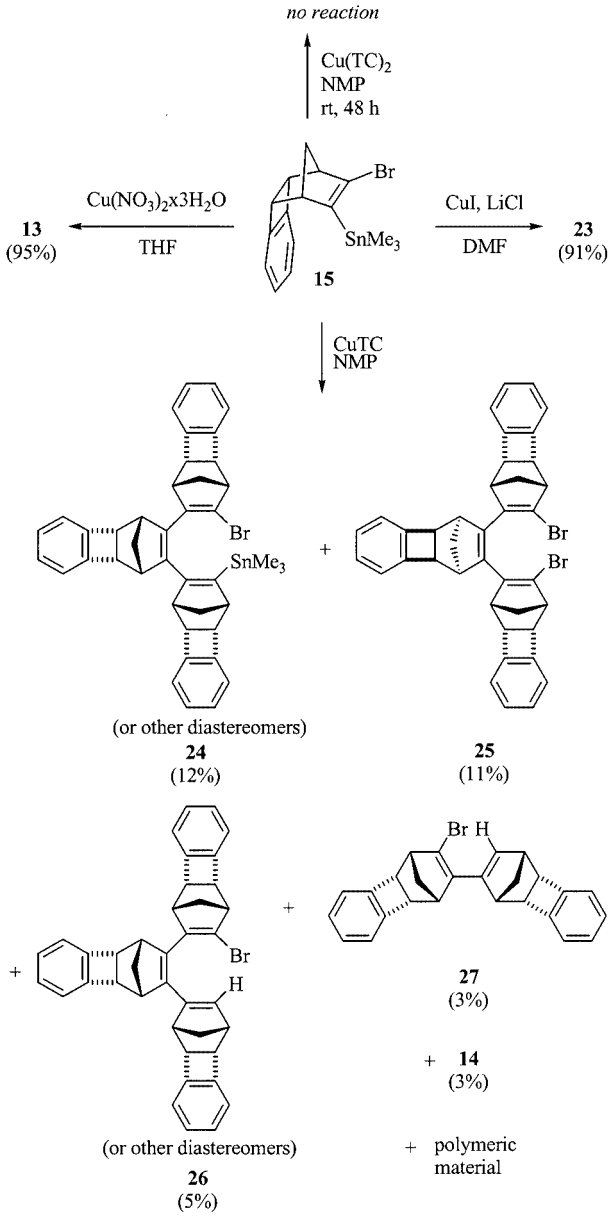
NMR Spectral Studies and Configuration Assignments

The structures of the compounds reported in this work have been elucidated on the basis of ^1H and ^{13}C NMR spectroscopic data and extensive double-resonance experiments.

Structural analysis of the compounds having norbornane skeletons was achieved with the help of the coupling constants. The configuration of the benzocyclobutene ring was determined by measuring the coupling constants between the protons H^1 (H^{10}) and H^2 (H^9). In the case of dibromides

Table 1. Product distribution and yields of the cyclotrimerisation of **12** promoted by copper salts

Copper reagent	*syn* Cyclotrimer **17**	*anti* Cyclotrimer **18**	Dimers **19** and **20**	Other products
CuTC	6%	63%	−	**9** (2%)
$Cu(NO_3)_2{\cdot}3H_2O$	4%	23%	traces	**9** (39%)
CuI/LiCl	5%	3%	7% (4:3 ratio)	**21** (48%), **22** (8%), **9** (5%)
$Cu(TC)_2$	20%	15%	13% (8:5 ratio)	**11** (9%), **9** (4%)



Scheme 7

6 (B-type), the coupling constants (J = 5.5 Hz) between protons H^1 (H^{10}) and H^2 (H^9) indicate the *endo* orientation of the benzocyclobutene ring, whereas, in the cases of monobromide **9**, dibromides **5**, **7**, and **8**, and tribromide **10** (A-type), the absence of this coupling constant between related protons confirms the *exo* orientation of the benzocyclobutene ring. In addition to this characteristic, for the B-type products there is no measurable coupling constant between the H_2 (H_9) and $H^{13}{}_{anti}$ protons. The existence, however, of long-range coupling constants (M or W orientation) between related protons in the A-type compounds indicate *exo* orientations of the benzocyclobutene ring. Similarly, the configuration of the bromine atoms at the C^{11}, C^{12} and C^{13} carbon atoms can be determined by measuring the coupling constants between the protons $H^{11}(H^{12})$ and $H^{10}(H^1)$ and the protons $H^{11}(H^{12})$ and $H^{13}{}_{syn}$. Dibromides **7** and **8** exhibit an AA′BB′ system for the aromatic protons, which supports the symmetrical structure and *syn*-addition of bromine to the double bond. Furthermore, a seven-line ^{13}C NMR spectrum also agrees with the proposed structure. The existence of a coupling between the CHBr protons and the bridgehead proton $H^{13}{}_{syn}$ (W or M arrangement of the coupled protons) and the lack of a coupling between the CHBr protons and H_1 (H^{10}) support the *exo* stereochemical arrangement of the bromine atoms in dibromide **7**. The structures of the other molecules were ascribed on the basis of their NMR spectra and similar considerations (Figure 4).

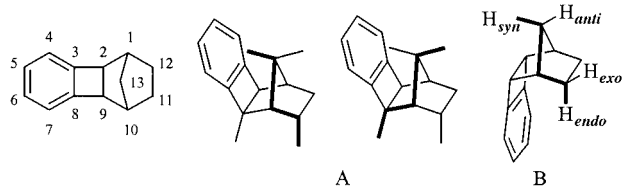


Figure 4. Long-range coupling for structural analyses

The structures of cyclotrimers **17** and **18** were assigned on the basis of both ^1H and ^{13}C NMR spectroscopic data. The *syn* cyclotrimer **17** exhibits an AA′BB′ system for the aromatic protons, which supports the symmetrical structure and all-*syn* orientation of the benzo units. Furthermore, a seven-line ^{13}C NMR spectrum is also in agreement with the proposed structure. The *anti* cyclotrimer **18** also exhibits an AA′BB′ system arising from the symmetric benzene ring and an ABCD system arising from the two non-symmetric benzene units. Furthermore, the ^{13}C NMR spectrum composed of twenty lines is also in agreement with the proposed structure.

The structure of dimer **27a** was assigned on the basis of NOESY experiments where we observed a vectorial interaction between vinyl proton $H^{12'}$, resonating at δ = 3.69 ppm, and the bridgehead proton H^{10}, resonating at δ = 2.55 ppm. The two possible structures of dimer **27** were minimized at the PM3 semi-empirical level[12] into the conformers **27a** and **27b**, shown below, which display distances between the two atoms of 2.675 and 4.810 Å, respectively (Figure 5).

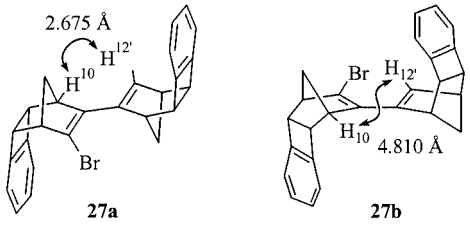


Figure 5. Distances between H^{10} and $H^{12'}$ protons in compounds **27a** and **27b**

The structure of trimeric dibromide **25** was assigned on the basis of symmetry considerations, which prompted us to exclude the non-symmetrical structure **25c** and its con-

formers, and with the aid of molecular modelling calculations performed at the PM3 semi-empirical level.[12] In fact, the calculated heat of formation of structure **25b** was calculated to be 41.38 kcal/mol lower than the other symmetric trimer **25a**, in which the sterically congesting aromatic rings collide dramatically (Figure 6).

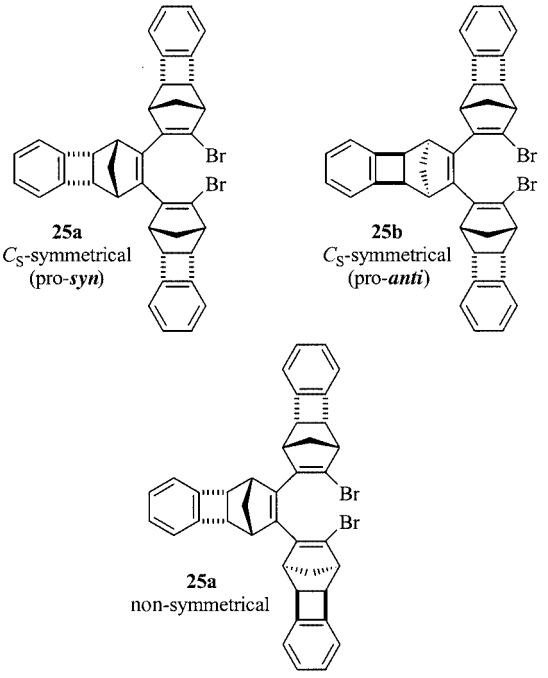


Figure 6. Possible symmetrical and non-symmetrical cyclotrimers

Experimental Section

General: Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1-mm cells or as KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 400 (Varian), 300 (Bruker) and 200 MHz (Varian and Bruker) spectrometers. Apparent splitting is given in all cases. All reactions were carried out under Ar atmospheres. All solvents were dried and distilled over CaH_2 (iPr_2NH, CCl_4, DME, DMF) or Na/benzophenone (THF). The progress of each reaction was monitored by TLC and/or ^{1}H NMR spectroscopy. Column chromatography (CC) was performed on silica gel (60-mesh, Merck). Flash chromatography (FC) was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F_{254} analytical aluminium plates. All substances reported in this paper are in their racemic form.

Caution: It has been reported[13] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders that contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. There is no report in the literature about the toxicological effects of the dibromide derived from benzonorbornadiene. We recommend, however, that these compounds must be handled only under extreme caution. In addition to this hazard, tin compounds also have toxical effects.[14]

Bromination of [1*S*(*R*),2*R*(*S*),9*S*(*R*),10*R*(*S*)]-Tetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (3) at −50 ± 5 °C: A solution of bromine (5.23 g, 32.68 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min to a magnetically stirred solution of **3**[5] (5.0 g, 29.72 mmol) in dry CH_2Cl_2 (60 mL) at −50 ± 5 °C. The bromine colour disappeared immediately. The solvent was evaporated and the crude product was recrystallised from *n*-hexane/CH_2Cl_2 (4:1) and *trans* dibromide **5** (8.5 g) was obtained. The residue from the mother liquor was chromatographed on silica gel (100 g) eluting with *n*-hexane.

The first fraction was [1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*),11*R*(*S*),12*R*(*S*)]-11,12-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene (**5**, 270 mg, 90% overall yield). Colourless crystals from CH_2Cl_2/*n*-hexane (1:4). M.p. 96−97 °C (lit.[7] m.p. 84 °C). $C_{13}H_{12}Br_2$ (328.0): calcd. C 47.60, H 3.69; found C 47.42, H 3.71. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.31−7.01 (m, 4 H, Aryl-H), 4.57 (dd, $J_{10,11}$ = 4.3, $J_{11,12}$ = 3.3 Hz, 1 H, 11-H), 3.96 (d, A-part of AX system, $J_{2,9}$ = 3.7 Hz, 1 H, 9-H), 3.90 (dd, $J_{11,12}$ = 3.3, $J_{12,13syn}$ = 2.9 Hz, 1 H, 12-H), 3.39 (d, X-part of AX system, $J_{2,9}$ = 3.7 Hz, 1 H, 2-H), 2.62 (m, 2 H, 1-H and 10-H), 1.78 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 11.4 Hz, 1 H, 13*anti*-H), 1.12 (br. d, X-part of AX system, $J_{13syn,13anti}$ = 11.4 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.8, 145.8, 130.2, 130.0, 124.4, 124.2, 62.9, 60.2, 50.1, 49.6, 47.0, 46.8, 31.9 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 3029, 2968, 2893, 1451, 1274, 1181, 927, 738 cm^{-1}.

The second fraction was [1*R*(*S*),2*R*(*S*),9*S*(*R*),10*R*(*S*),11*S*(*R*),13*R*(*S*)]-11,13-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene (**6**; 0.77 g, 8%). Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 115 °C. $C_{13}H_{12}Br_2$ (328.0): calcd. C 47.60, H 3.69, found C 47.37, H 3.72. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.30−7.07 (m, 4 H, Aryl-H), 4.17 (m, 1 H, H-13), 3.75 (t, $J_{2,9}$= $J_{9,10}$ = 5.5 Hz, 1 H, 9-H), 3.69−3.64 (m, 2 H, 2-H and 11-H), 3.07 (br. d, $J_{9,10}$ = 5.5 Hz, 1 H, 10-H), 2.80 (dd, $J_{1,2}$ = 5.5, $J_{1,12exo}$ = 4.5 Hz, 1 H, 1-H), 2.51 (dt, A-part of AB system, $J_{12endo,12exo}$ = 14.0, $J_{11,12exo}$ = $J_{1,12exo}$ = 4.5 Hz, 1 H, 12*exo*-H), 1.90 (ddd, B-part of AB system, $J_{12endo,12exo}$ = 14.0, $J_{11,12endo}$ = 8.0, $J_{12endo,13}$ = 1.3 Hz, 1 H, 12*endo*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.4, 147.1, 130.1, 130.0, 126.6, 126.2, 56.1, 54.6, 50.4, 49.9, 48.1, 47.3, 40.4 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2971, 2941, 1447, 1316, 1285, 1247, 1189, 977, 919, 842, 773 cm^{-1}.

Bromination of [1*S*(*R*),2*R*(*S*),9*S*(*R*),10*R*(*S*)]-Tetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (3) at 77 °C: A hot solution of bromine (0.57 g, 3.56 mmol) in CCl_4 (2 mL) was added dropwise over 5 min to a magnetically stirred solution of **3** (0.5 g, 2.97 mmol) in CCl_4. The resulting reaction mixture was heated for 1 min under reflux. After being cooled to room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (100 g) eluting with *n*-hexane.

The first fraction was [1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*),11*R*(*S*),12*R*(*S*)]-11,12-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene (**5**; 565 mg 58%).

The second fraction was [1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*),11*R*(*S*),12*S*(*R*)]-11,12-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene (**8**; 58 mg, 6%). Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 135−136 °C. $C_{13}H_{12}Br_2$ (328.0): calcd. C 47.60, H 3.69; found C 47.52, H 3.68. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.27−7.21 (AA′ part of AA′BB′ system, 2 H, Aryl-H), 7.08−7.02 (BB′ part of AA′BB′ system, 2 H, Aryl-H), 4.69 (AA′ part of AA′XX′ system, 2 H, 11-H and 12-H), 3.90 (m, 2 H, 2-H and 9-H), 2.61 (XX′-part of AA′XX system, 2 H, 1-H and 10-H), 1.31 (br. d, A-part of AB system, $J_{13syn,13anti}$ = 11.6 Hz, 1 H, 13*anti*-H), 1.18 (br. d, B-part of AB system, $J_{13syn,13anti}$ = 11.6 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.0, 129.9, 124.2, 57.4, 46.9, 46.1,

33.9 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 3010, 2968, 2883, 1458, 1277, 1208, 1112, 919, 892, 754, 734 cm^{-1}.

The third fraction was [1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*),11*S*(*R*),12*S*(*R*)]-11,12-dibromotetracyclo[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7-triene (**7**; 350 mg 36%). Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 163−164 °C. $C_{13}H_{12}Br_2$ (328.0): calcd. C 47.60, H 3.69; found C 47.49, H 3.66. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.28−7.24 (AA′ part of AA′BB′ system, 2 H, Aryl-H), 7.05−7.01 (BB′ part of AA′BB′ system, 2 H, Aryl-H), 4.16 (d, $J_{11,13syn} = J_{12,13syn}$ = 2.0 Hz, 2 H, 11-H and 12-H), 3.32 (m, 2 H, 2-H and 9-H), 2.73 (m, 2 H, 1-H and 10-H), 2.00 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 11.5 Hz, 1 H, 13*anti*-H), 1.02 (br. d, X-part of AX system, $J_{13syn,13anti}$ = 11.5 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.0, 130.2, 124.3, 57.5, 50.9, 49.9, 29.5 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2952, 2883, 1451, 1312, 1258, 1197, 1150, 1004, 900, 746 cm^{-1}.

Elimination of Dibromides 5, 7, and 8: A solution of potassium *tert*-butoxide (1.71 g, 15.24 mmol) in dry THF (5 mL) was added to a stirred solution of a mixture of dibromides **5**, **7**, and **8** (0.50 g, 1.52 mmol) in dry THF (20 mL). The resulting reaction mixture was stirred overnight at room temp. The solvent was evaporated, the mixture was diluted with water and the aqueous solution was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated. The residue was filtered through a short column of silica gel (10 g) eluting with *n*-hexane to give **9** as the sole product (349 mg, 92%).

[1*S*(*R*),2*R*(*S*),9*R*(*S*),10*R*(*S*)]-11-Bromotetracyclo[8.2.1.$0^{2,9}$.$0^{3,8}$]-trideca-3,5,7,11-tetraene (9): Colourless liquid. $C_{13}H_{11}Br$ (247.1): calcd. C 63.18, H 4.49 found C 63.28, H 4.51. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.27−7.08 (m, 4 H, Aryl-H), 6.31 (d, $J_{1,12}$ = 3.3 Hz, 1 H, 12-H), 3.45 (br. d, A-part of AB system, $J_{2,9}$ = 4.0 Hz, 1 H, 2-H or 9-H), 3.42 (br. d, B-part of AB system, $J_{2,9}$ = 4.0 Hz, 1 H, 2-H or 9-H), 2.92 (m, 1 H, 10-H), 2.85 (m, 1 H, 1-H), 1.64 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 9.2 Hz, 1 H, 13*anti*-H), 1.02 (br. d, X-part of AX system, $J_{13syn,13anti}$ = 9.2 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.5, 146.6, 137.6, 130.3, 129.5(2C), 124.1, 123.9, 52.5, 51.0, 49.5, 45.6, 43.4 ppm. IR (KBr): $\tilde{\nu}$ = 3068, 2968, 2852, 1582, 1458, 1351, 1293, 1189, 1162, 1042, 746 cm^{-1}.

Bromination of [1*S*(*R*),2*R*(*S*),9*R*(*S*),10*R*(*S*)]-11-Bromotetracyclo-[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7,11-tetraene (9) at −50 ± 5 °C: A solution of bromine (3.56 g, 22.25 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min to a magnetically stirred solution of **9** (5.00 g, 20.23 mmol) in dry CH_2Cl_2 (50 mL) at −50 ± 5 °C. The bromine colour disappeared immediately. The solvent was evaporated and the crude product was recrystallized from *n*-hexane/CH_2Cl_2 (3:1) to afford tribromide **10** (8.07 g, 98%).

[1*S*(*R*),2*S*(*R*),9*R*(*S*),10*R*(*S*),12*S*(*R*)]-11,11,12-Tribromotetracyclo-[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7-triene (10): Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 120 °C. $C_{13}H_{11}Br_3$ (406.9): calcd. C 38.37, H 2.72 found C 38.94, H 2.71. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.29−7.01 (m, 4 H, Aryl-H), 4.43 (d, $J_{12,13syn}$ = 2.8 Hz, 1 H, 12-H), 4.07 (br. d, A-part of AX system, $J_{2,9}$ = 3.7 Hz, 1 H, 9-H), 3.46 (br. d, X-part of AX system, $J_{2,9}$ = 3.7 Hz, 1 H, 2-H), 3.19 (m, 1 H, 10-H), 2.60 (m, 1 H, 1-H), 2.18 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 11.9 Hz, 1 H, 13*anti*-H), 1.04 (br. d, X-part of AX system, $J_{13syn,13anti}$ = 11.9 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.3, 145.3, 130.4 (2C), 124.5, 124.4, 75.5, 68.2, 60.0, 52.2, 49.9, 49.5, 30.9 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2968, 2894, 1458, 1297, 1274, 1189, 1139, 969, 927, 900, 773, 738 cm^{-1}.

Elimination of [1*S*(*R*),2*S*(*R*),9*R*(*S*),10*R*(*S*),12*S*(*R*)]-11,11,12-Tribromotetracyclo[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7-triene (10): The reaction was carried out as described above by using tribromide **10** (1.00 g, 2.46 mmol) and potassium *tert*-butoxide (0.83 g, 7.40 mmol) in dry THF (20 mL). The resulting reaction mixture was stirred overnight at room temp. After completion of the reaction, dibromide **11** was obtained as the sole product (0.72 g, 92% yield).

[1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*)]-11,12-Dibromotetracyclo-[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7,11-tetraene (11): Colourless crystals from CH_2Cl_2/*n*-hexane (1:1). M.p. 81−82 °C. $C_{13}H_{10}Br_2$ (326.0): calcd. C 47.89, H 3.09 found C 47.91, H 3.16. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.26−7.19 (AA′ part of AA′BB′ system, 2 H, Aryl-H), 7.13−7.06 (BB′ part of AA′BB′ system, 2 H, Aryl-H), 3.55 (m, 2 H, 2-H and 9-H), 2.98 (m, 2 H, 1-H and 10-H), 1.80 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 9.5 Hz, 1 H, 13*anti*-H), 1.09 (dt, X-part of AX system, $J_{13syn,13anti}$ = 9.5, $J_{1,13syn} = J_{10,13syn}$ = 1.6 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.2, 129.8, 129.6, 124.1, 53.2, 50.7, 42.7 ppm. IR (KBr): $\tilde{\nu}$ = 3068, 2979, 2941, 2875, 1582, 1451, 1277, 1158, 1054, 912, 823, 746 cm^{-1}. MS (EI, 70 eV): *m*/*z* = 324/326/328 (32) [M+], 245/247 (3), 166, (93), 139 (8), 102 (100), 82 (13%).

Synthesis of [(1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*)]-12-Bromotetracyclo-[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7,11-tetraene-11-yl]trimethylstannane (12) Starting from Monobromide 9: A solution of *n*BuLi in *n*-hexane (2.5 M, 25 mL, 62.5 mmol) was added dropwise to a solution of diisopropylamine (8.6 mL, 62.5 mmol) in dry THF (20 mL) at 0 °C and the resulting mixture was stirred 15 min. A solution of monobromide **9** (5.8 g, 23.5 mmol) in dry THF (40 mL) was then added dropwise and stirred for 30 min. Finally, trimethyltin chloride (4.7 g, 23.5 mmol) was added portionwise and the mixture was left to warm to room temp. overnight. The crude product was quenched with water (50 mL), extracted with Et_2O (3 × 30 mL) and the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by FC to obtain the bromo-stannyl olefin **12** (9.43 g, 98% yield).

[(1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*)]-12-Bromotetracyclo[8.2.1.$0^{2,9}$.$0^{3,8}$]-trideca-3,5,7,11-tetraene-11-yl]trimethylstannane (12): Colourless liquid. $C_{16}H_{19}BrSn$ (409.9): calcd. C 46.88, H 4.67; found C 46.89, H 4.68. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.24−7.07 (m, 4 H, Aryl-H), 3.36 (br. d, A-part of AX system, $J_{2,9}$ = 3.9 Hz, 1 H, 2-H or 9-H), 3.18 (br. d, X-part of AX system, $J_{2,9}$ = 3.9 Hz, 1 H, 2-H or 9-H), 2.92 (m, 1 H, 1-H or 10-H), 2.87 (m, 1 H, 1-H or 10-H), 1.55 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 9.2 Hz, 1 H, 13*anti*-H), 0.90 (dt, X-part of AX system, $J_{13syn,13anti}$ = 9.2, $J_{1,13syn,} = J_{10,13syn}$ = 1.5 Hz 1 H, 13*syn*-H), 0.32 (s, 9H-methyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 145.8, 144.7, 139.6, 127.32, 127.30, 122.1, 121.8, 52.1, 48.6, 48.4, 47.3, 41.1, −9.1 ppm.

Synthesis of [(1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*)]-12-Bromotetracyclo-[8.2.1.$0^{2,9}$.$0^{3,8}$]trideca-3,5,7,11-tetraene-11-yl]trimethylstannane (12) Starting from Dibromide 11: A solution of *n*BuLi in *n*-hexane (2.5 M, 0.25 mL, 0.63 mmol) was added dropwise to a solution of dibromide **11** (200 mg, 0.61 mmol) in dry THF (3 mL) at −78 °C and the resulting mixture was stirred for 1 h. Trimethyltin chloride (125 mg, 0.63 mmol) was added portionwise and the mixture was stirred 2 h at the same temperature and then left to warm to room temp. overnight at room temperature. The crude product was washed with water (50 mL) and extracted with Et_2O (3 × 30 mL) and then the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by FC and the bromo-stannyl olefin **12** was obtained (247 mg, 98% yield).

Cyclotrimerisation Reactions

Reaction of (Bromostannyl)alkene 12 with CuTC: Copper(I) thiophenecarboxylate (CuTC; 1.43 g, 7.50 mmol) was introduced into a 50-mL, two-necked, round-bottomed flask fitted with an argon inlet. The flask was purged with argon, capped with a septum and cooled to −20 °C. Dry *N*-methylpyrolidinone (25 mL) and bromostannyl-olefin **12** (2.05 g, 5.0 mmol) were added consecutively via syringe. The reaction was monitored by NMR spectroscopy. After 30 min, a 10% solution of aqueous NH_3 (20 mL) was added and the mixture was stirred until the brown solid disappeared. The mixture was extracted with Et_2O (3 × 20 mL) and the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. The mixture was purified by FC (*n*-hexane/CH_2Cl_2, 95:5). The **first fraction** was monobromide **9** (61 mg, 2%). The **second fraction** was the *anti*-cyclotrimer **18**: (524 mg, 63%). Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 277 °C. $C_{39}H_{30}$ (498.7): calcd. C 93.94, H 6.06; found C 93.92, H 6.03. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30−7.14 (m, 12 H, Aryl-H), 3.45 (m, 4 H), 3.42 (m, 2 H), 3.35 (br. d, *J* = 3.1 Hz, 2 H), 3.33 (m, 2 H), 3.31 (br. d, *J* = 3.1 Hz, 2 H), 1.66 (m, 3 H), 1.34 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.72, 145.69, 145.6, 137.2, 137.1, 136.8, 127.5(3C), 122.02, 121.98 (2C), 49.92, 49.89, 49.8, 41.7, 41.6(2C), 41.4, 41.3 ppm. IR (KBr): ṽ = 3056, 2948, 2875, 1451, 1381, 1343, 1277, 1189, 1004, 950, 931, 823, 765, 738 cm^{-1}. The **third fraction** was the *syn*-cyclotrimer **17**: (58 mg, 7%). Colourless crystals from CH_2Cl_2/*n*-hexane (1:2). M.p. 292 °C. $C_{39}H_{30}$ (498.7): calcd. C 93.94, H 6.06; found C 93.95, H 6.05. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24−7.21 (AA′ part of AA′BB′ system, 6 H, H-aryl), 7.06−7.03 (BB′ part of AA′BB′ system, 6 H, H-aryl), 3.39 (s, 6 H), 2.86 (s, 6 H), 1.10 (br. d, A-part of AB system, *J* = 9.9 Hz, 3 H), 0.90 (br. d, B-part of AB system, *J* = 9.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.2, 138.0, 127.6, 122.1, 47.7, 45.4, 27.3 ppm. IR (KBr): ṽ = 3064, 2941, 2864, 1451, 1335, 1266, 1189, 1100, 939, 908, 738 cm^{-1}.

Reaction of 12 with CuI/LiCl: A 25-mL, two-necked, flame-dried flask, equipped with magnetic stirring bar, was charged with LiCl (2.54 g, 60 mmol) and further dried (110 °C, vacuum/argon) for 30 min. After cooling to room temperature, dry DME (10 mL), DMF (40 mL) and CuI (9.52 g, 50 mmol) were added sequentially. After 15 min, the mixture was treated with a solution of **12** (4.10 g, 10 mmol) in dry DMF (20 mL) and stirred under argon at room temperature. The reaction mixture was monitored by means of NMR spectroscopy. After 40 h, the crude material was diluted with diethyl ether (100 mL) and washed several times with 5% aqueous NH_3 (30 mL each time) until the blue colour disappeared. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by FC using *n*-hexane as eluent. The monobromide **9** (124 mg, 5%), bromoiodide **21** (1.8 g, 48%), diiodide **22** (336 mg, 8%), dibromo dimers **19/20** (98 mg and 74 mg, 4% and 3%), *anti*-cyclotrimer **18** (50 mg, 3%), and *syn*-cyclotrimer **17** (83 mg, 5%) were eluted in that order.

[1*S*(*R*),2*S*(*R*),9*R*(*S*),10*R*(*S*)]-11-Bromo-12-iodotetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (21): Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 85 °C. $C_{13}H_{10}BrI$ (373.0): calcd. C 41.86, H 2.70; found C 41.85, H 2.72. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25−7.23 (m, 2 H, aryl-H), 7.10−7.07 (m, 2 H, aryl-H), 3.50 (br. d, A-part of AB system, $J_{2,9}$ = 4.2 Hz, 1 H, 2-H or 9-H), 3.45 (br. d, B-part of AB system, $J_{2,9}$ = 4.2 Hz, 1 H, 2-H or 9-H), 3.01 (m, 1 H, 1-H or 10-H), 2.96 (m, 1 H, 1-H or 10-H), 1.83 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 9.6 Hz, 1 H, 13*anti*-H), 1.05 (dt, X-part of AX system, $J_{13syn,13anti}$ = 9.6, $J_{1,13syn}$ = $J_{10,13syn}$ = 1.7 Hz 1 H, 13*syn*-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 143.9, 136.5, 127.8(2C), 122.20, 122.15, 101.2, 54.1, 51.4, 48.5, 48.4, 41.4 ppm. IR (KBr): ṽ = 3056, 2941, 2871, 1551, 1455, 1343, 1274, 1189, 1150, 1100, 1046, 1004, 900, 831, 771, 746 ppm. MS (EI, 70 eV): *m*/*z* = 372/374 (32) [M+], 293 (5), 245/247, (5), 166 (100), 139 (50), 115 (55), 102 (68), 82 (62%).

[1*R*(*S*),2*R*(*S*),9*S*(*R*),10*S*(*R*)]-11,12-Diiodotetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (22): Colourless crystals from CH_2Cl_2/*n*-hexane (1:1). M.p. 87 °C. $C_{13}H_{10}I_2$ (420.0): calcd. C 37.17, H 2.40; found C 37.15, H 2.39. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.26−7.07 (AA′BB′ system, 4 H, Aryl-H), 3.40 (m, 2 H, 2-H and 9-H), 2.98 (m, 2 H, 1-H and 10-H), 1.83 (br. d, A-part of AX system, $J_{13syn,13anti}$ = 9.6 Hz, 1 H, 13*anti*-H), 0.95 (dt, X-part of AX system, $J_{13syn,13anti}$ = 9.6 $J_{1,13syn}$ = $J_{10,13syn}$ = 1.6 Hz 1 H, 13*syn*-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.9, 127.7, 122.2, 111.6, 54.8, 48.2, 41.88 ppm. IR (KBr): ṽ = 3064, 2933, 2871, 1547, 1451, 1343, 1266, 1177, 1150, 1042, 1004, 900, 831, 777, 746 cm^{-1}. MS (EI, 70 eV): *m*/*z* = 420 (8) [M+], 254 (9), 191 (27), 166 (100), 139 (46), 115 (54), 102 (70), 82 (58%).

Bromo Dimer 19 or 20: Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 170 °C. $C_{26}H_{21}Br$ (413.4): calcd. C 75.55, H 5.12; found C 75.57, H 5.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27−7.09 (m, 8 H, Aryl-H), 3.70 (d, A-part of AX system, $J_{2(2'),9(9')}$ = 3.9 Hz, 2 H, 2(2′)-H or 9(9′)-H; 3.53 (d, X-part of AX system, $J_{2(2'),9(9')}$ = 3.9 Hz, 2 H, 2(2′)-H or 9(9′)-H), 3.52 (m, 2 H, 1-H and 1′-H), 2.98 (m, 2 H, 10-H and 10′-H), 1.66 (br. d, A-part of AX system, $J_{13syn,13anti}$ ($J_{13'syn,13'anti}$) = 9.3 Hz, 2 H, 13*anti*-H and 13′*anti*-H), 1.03 (dt, X-part of AX system, $J_{13syn,13anti}$($J_{13'syn,13'anti}$) = 9.3, $J_{13syn,1}$($J_{13'syn,1'}$) = $J_{13syn,10}$ ($J_{13'syn,10'}$) = 1.5 Hz, 2 H, 13*syn*-H and 13′*syn*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 144.5, 141.0, 127.5(2C), 124.0, 122.0(2C), 52.3, 49.2, 47.2, 45.6, 40.0 ppm. IR (KBr): ṽ = 3056, 2952, 2871, 1451, 1343, 1277, 1189, 1162, 1054, 912, 831, 738 cm^{-1}. MS (EI, 70 eV): *m*/*z* = 490/492/494 (4) [M+], 411/413 (3), 331 (6), 229 (13), 202 (13), 165 (15), 115 (20), 102 (100%).

Bromo Dimer 19 or 20: Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 201 °C. $C_{26}H_{21}Br$ (413.4): calcd. C 75.55, H 5.12; found C 75.52, H 5.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23−7.08 (m, 8 H, Aryl-H), 3.56 (d, $J_{2(2'),9(9')}$ = 3.0 Hz, 2 H, 2(2′)-H or 9(9′)-H), 3.51 (m, 4 H, 1-H, 1-H′ and 2(2′)-H or 9(9′)-H), 2.96 (m, 2 H, 10-H and 10′-H), 1.67 (br. d, A-part of AX system, $J_{13syn,13anti}$ ($J_{13'syn,13'anti}$) = 9.3 Hz, 2 H, 13*anti*-H and 13′*anti*-H), 1.01 (br. d, X-part of AX system, $J_{13syn,13anti}$ ($J_{13'syn,13'anti}$) = 9.3 Hz, 2 H, 13*syn*-H and 13′*syn*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 145.0, 140.6, 127.9(2C), 125.8, 122.42, 122.41, 52.6, 49.6, 48.1, 46.1, 40.3 ppm. MS (EI, 70 eV): *m*/*z* = 490/492/494 (5) [M+], 411/413 (2), 331 (4), 229 (14), 202 (13), 165 (18), 115 (29), 102 (100%).

Reaction of 12 with Cu(NO$_3$)$_2$·3H$_2$O: Copper(II)nitrate trihydrate (619 mg, 2.56 mmol) was added portionwise to a solution of **12** (1.05 g, 2.56 mmol) in THF (10 mL). The blue solution turned brown within 30 min. The crude reaction mixture was diluted with diethyl ether (100 mL) and washed several times with 5% aqueous NH_3 (30 mL each time) until the blue colour disappeared. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The mixture was purified by FC using a gradient of *n*-hexane/CH_2Cl_2 as eluent. The monobromide **9** (247 mg, 39%), dibromo dimers **19/20** (trace), *anti*-cyclotrimer **18** (98 mg, 23%), and *syn*-cyclotrimer **17** (17 mg, 4%) were eluted in that order.

Reaction of (Bromostannyl)alkene 12 with Cu(TC)$_2$: Copper(II) thiophenecarboxylate (1.16 g, 3.65 mmol) was introduced into a 50-mL, two-necked, round-bottomed flask fitted with an argon inlet.

The flask was purged with argon, capped with a septum and cooled to −20 °C. Dry *N*-methylpyrolidinone (25 mL) and bromostannyl-olefin **12** (1.0 g, 2.44 mmol) were added consecutively via syringe. The reaction was monitored by NMR spectroscopy. The reaction mixture was stirred for 24 h at room temperature. The crude reaction mixture was diluted with diethyl ether (100 mL) and washed with 5% aqueous NH_3. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The mixture was purified by FC using gradient of *n*-hexane/CH_2Cl_2 as eluent. The monobromide **9** (24 mg, 4%), dibromide **11** (72 mg, 9%), dibromo dimers **19/20** (30 mg and 48 mg, 5% and 8%, respectively), *anti*-cyclotrimer **18** (61 mg, 15%), and *syn*-cyclotrimer **17** (81 mg, 20%) were eluted in that order.

Reaction of Dibromide 11 with $Pd(OAc)_2$/$nBu_3SnSnnBu_3$: A mixture of dibromide **11** (111 mg, 0.34 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol) and hexabutylditin (296 mg, 0.51 mmol) in dry toluene (3 mL) was placed in a screw-capped pyrex test tube that was purged with argon, sealed and then heated under reflux for 24 h. After cooling to room temp., water (20 mL) was added and the mixture was extracted with diethyl ether (3 × 30 mL). The combined ethereal extracts were washed with brine, dried $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography through a short silica gel column eluting with an *n*-hexane/CH_2Cl_2 gradient. From the first fractions, products of ligand coupling were obtained. The last fractions gave the *anti*-cyclotrimer **18** (41 mg, 72%).

Reaction of Monobromide 13 with LDA and Me_3SnCl: This reaction was carried out following the procedure described above by using *n*BuLi (2.5 M in *n*-hexane, 25 mL, 62.5 mmol), diisopropylamine (8.6 mL, 62.5 mmol), dry THF (60 mL), monobromide **13**[10] (5.8 g, 23.5 mmol) and trimethyltin chloride (4.7 g, 23.5 mmol). After the usual workup and purification (flash chromatograph, *n*-hexane as eluent), stannyl olefin **16** (311 mg, 4%), (bromostannyl)alkene **15** (7.5 g, 78%), and alkene **4**[6] (552 mg, 14%), were obtained in that order.

[(1*S*(*R*),2*S*(*R*),9*S*(*R*),10*R*(*S*)]-(Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene-11-yl)trimethylstannane (16): Colourless liquid. $C_{16}H_{20}Sn$ (331.0): calcd. C 58.05, H 6.09; found C 58.08, H 6.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10−6.85 (m, 4 H, Aryl-H), 5.86 (d, $J_{1,12}$ = 2.7 Hz, 1 H, 12-H), 3.71 (m, 1 H, 2-H or 9-H), 3.69 (m, 1 H, 2-H or 9-H), 3.13 (m, 1 H, 1-H or 10-H), 3.05 (m, 1 H, 1-H or 10-H), 1.92 (br. d, A-part of AB system, $J_{13syn,13anti}$ = 8.4 Hz, 1 H, 13*anti*-H), 1.70 (br. d, B-part of AB system, $J_{13syn,13anti}$ = 8.4 Hz, 1 H, 13*syn*-H), −0.06 (s, 9H−H-methyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 148.3, 146.2, 143.5, 126.8, 126.7, 123.0, 122.7, 54.6, 49.0, 46.3, 46.2, 46.1, −9.0 ppm.

[(1*R*(*S*),2*S*(*R*),9*R*(*S*),10*S*(*R*)]-(12-Bromotetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene-11-yl)trimethylstannane (15): Colourless liquid. $C_{16}H_{19}BrSn$ (409.9): calcd. C 46.88, H 4.67; found C 46.91, H 4.71. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13−6.86 (m, 4 H, Aryl-H), 3.84 [t, $J_{2,9}$=$J_{1,2}$ (or $J_{9,10}$) = 4.7 Hz, 1 H, 2-H or 9-H], 3.68 [t, $J_{2,9}$=$J_{1,2}$ (or $J_{9,10}$) = 4.7 Hz, 1 H, 2-H or 9-H], 3.12 (m, 2 H, 1-H and 10-H), 2.19 (dt, A-part of AX system, $J_{13syn,13anti}$ = 8.5, $J_{13anti,1}$ = $J_{13anti,10}$ = 1.5 Hz, 1 H, 13*anti*-H), 1.68 (dt, X-part of AX system, $J_{13syn,13anti}$ = 8.5, $J_{1,13syn}$ = $J_{10,13syn}$ = 1.5 Hz, 1 H, 13*syn*-H), 0.00 (s, 9H-H-methyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.5, 147.4, 145.7, 134.3, 127.5, 127.0, 124.1, 122.7, 54.9, 54.7, 50.2, 47.3, 46.4, −8.9 ppm.

Synthesis of [(1*R*(*S*),2*S*(*R*),9*R*(*S*),10*S*(*R*)]-[12-Bromotetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene-11-yl]trimethylstannane (15) Starting from Dibromide 14:[10] The reaction was carried out by the procedure described above using *n*BuLi (2.5 M in *n*-hexane, 0.25 mL, 0.63 mmol), dibromide **14**[10] (200 mg, 0.61 mmol), THF (3 mL), and trimethyltin chloride (125 mg, 0.63 mmol). After the usual workup and purification, the (bromostannyl)alkene **15** (241 mg, 96%) was obtained as the sole product.

Reaction of 15 with CuI/LiCl: The reaction was carried out by the procedure described above using LiCl (254 mg, 6 mmol), DME (1 mL), DMF (6 mL), CuI (0.95 g, 5 mmol) and (bromostannyl)alkene **15** (410 mg, 1 mmol). The reaction mixture was monitored by means of NMR spectroscopy. After 3 d, the reaction was complete. After the usual workup, bromo-iodide **23** (340 mg, 91%) was obtained as the sole product.

[1*S*(*R*),2*R*(*S*),9*S*(*R*),10*R*(*S*)]-11-Bromo-12-iodotetracyclo-[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (23): Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 77 °C. $C_{13}H_{10}BrI$ (373.0): calcd. C 41.86, H 2.70; found C 41.89, H 2.68. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18−7.15 (m, 4 H, Aryl-H), 3.90 [t, $J_{2,9}$ = $J_{1,2}$ (or $J_{9,10}$) = 4.5 Hz, 1 H, 2-H or 9-H], 3.81 [t, $J_{2,9}$ = $J_{1,2}$ (or $J_{9,10}$) = 4.5 Hz, 1 H, 2-H or 9-H], 3.23 (m, 1 H, 1-H or 10-H), 3.19 (m, 1 H, 1-H or 10-H), 2.41 (dt, A-part of AX system, $J_{13syn,13anti}$ = 9.0, $J_{13anti,1}$ = $J_{13anti,10}$ = 1.5 Hz, 1 H, 13*anti*-H), 1.73 (dt, X-part of AX system, $J_{13syn,13anti}$ = 9.0, $J_{1,13syn}$ = $J_{10,13syn}$ = 1.8 Hz 1 H, 13*syn*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.7, 145.1, 131.8, 127.0, 126.8, 124.4, 123.5, 96.6, 54.6, 54.0, 53.0, 47.1, 46.9 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2979, 2941, 2864, 1574, 1451, 1343, 1285, 1181, 1123, 1054, 1004, 927, 811, 765, 734 cm^{-1}. MS (EI, 70 eV): *m*/*z* = 372/374 (24) [M+], 293 (7), 165 (86), 139 (60), 115 (70), 102 (100), 82 (72%).

Reaction of 15 with $Cu(NO_3)_2$·$3H_2O$: The reaction was carried by the procedure described above using copper nitrate trihydrate (619 mg, 2.56 mmol), (bromostannyl)alkene **15** (1.05 g, 2.56 mmol) and THF (10 mL). The reaction mixture was monitored by means of NMR spectroscopy. After 2 h, the reaction was complete. After the usual workup, the monobromide **13** (600 mg, 95%) was obtained as the sole product.

Reaction of (Bromostannyl)alkene 15 with CuTC: The reaction was carried out by the procedure described above using copper(I) thiophenecarboxylate (CuTC; 1.43 g, 7.5 mmol), dry *N*-methylpyrolidinone (25 mL) and bromostannyl-olefin **15** (2.05 g, 5 mmol) for 60 h. After the usual workup, the mixture was purified by FC using *n*-hexane as eluent. Five products were isolated in the following order: dibromide **14** (50 mg, 3%), monobromo dimer **27** (31 mg, 3%), bromo-tin-trimer **24** (144 mg, 12%), monobromo trimer **26** (52 mg, 5%), dibromo-trimer **25** (123 mg, 11%).

Monobromo Dimer 27: Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 215 °C. $C_{26}H_{21}Br$ (413.4): calcd. C 75.55, H 5.12; found C 75.56, H 5.14. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11−6.76 (m, 8 H, Aryl-H), 5.58 (d, $J_{1',12'}$ = 3.3 Hz, 1 H, 12′-H), 3.86 (t, $J_{2,9}$ = $J_{1,2}$ = 4.8 Hz, 1 H, 2-H), 3.72 (t, $J_{2',9'}$ = $J_{1',2'}$ = 4.8 Hz, 1 H, 2′-H), 3.69 (t, $J_{2',9'}$ = $J_{9',10'}$ = 4.8 Hz, 1 H, 9′-H), 3.61 (t, $J_{2,9}$ = $J_{9,10}$ = 4.8 Hz, 1 H, 9-H), 3.42 (br. d, $J_{9',10'}$ = 4.8 Hz, 1 H, 10′-H), 2.99 (br. d, $J_{1,2}$ = 4.8 Hz, 1 H, 1-H), 2.92 (m, 1 H, 1′-H), 2.55 (br. d, $J_{9,10}$ = 4.8 Hz, 1 H, 10-H), 1.80 (dt, A-part of AB system, $J_{13syn,13anti}$ = 8.4, $J_{13anti,1}$ = $J_{13anti,10}$ = 1.7 Hz, 1 H, 13*anti*-H), 1.72 (dt, A-part of AB system, $J_{13'syn,13'anti}$ = 8.6, $J_{13'anti,1'}$ = $J_{13'anti,10'}$ = 1.7 Hz, 1 H, 13′*anti*-H), 1.55 (dt, B-part of AB system, $J_{13'syn,13'anti}$ = 8.6, $J_{13'syn,1'}$ = $J_{13'syn,10'}$ = 1.7 Hz, 1 H, 13′*syn*-H), 1.47 (dt, B-part of AB system, $J_{13syn,13anti}$ = 8.4, $J_{13syn,1}$ = $J_{13syn,10}$ = 1.7 Hz, 1 H, 13*syn*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 147.4, 146.8, 140.8, 138.0, 131.0, 126.8, 126.7, 126.61, 126.56, 123.8, 123.6, 123.5, 123.2, 122.4, 115.9, 54.1, 54.0,

51.9, 48.9, 47.5, 47.3, 47.2, 46.3, 43.9, 43.6 ppm. MS (EI, 70 eV): *m/z* = 412/414 (9) [M+], 333 (15), 303 (12), 205 (37), 165 (100), 141 (80), 129 (47), 115 (46%).

Bromo-Tin Trimer 24: Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 210 °C. $C_{29}H_{29}BrSn$ (576.1): calcd. C 60.45, H 5.07; found C 60.43, H 5.08. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46−6.46 (m, 12 H, aryl-H), 3.79 (t, *J* = 4.6 Hz, 1 H), 3.66 (t, *J* = 4.6 Hz, 1 H), 3.65−3.59 (m, 2 H), 3.58 (t, *J* = 4.6 Hz, 1 H), 3.54 (t, *J* = 4.9 Hz, 1 H), 3.08 (br. d, *J* = 4.6 Hz, 1 H), 2.98 (br. dd, *J* = 4.6 Hz, 1 H), 2.46 (br. dd, *J* = 4.6, 1.5 Hz, 1 H), 1.92 (br. dd, *J* = 4.6, 1.5 Hz, 1 H), 1.84−1.78 (m, 2 H), 1.54 (br. d, *J* = 8.7 Hz, 1 H), 1.46−1.43 (m, 3 H), 1.40 (dt, *J* = 8.2, 1.5 Hz, 1 H), 1.31 (dt, *J* = 8.2, 1.5 Hz), 0.04 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 149.2, 148.8, 148.4, 147.5, 147.3, 146.7, 144.0, 139.9, 138.7, 137.3, 126.92, 126.86, 126.4, 126.3, 126.2, 126.0, 124.8, 123.8, 123.7, 123.3, 122.8, 122.6, 115.1, 54.3, 53.6, 53.5, 53.4, 52.2, 50.6, 49.3, 47.9, 47.4, 47.2, 47.11, 47.05, 46.7, 46.4, 46.0, −8.6 ppm.

Monobromo Trimer 26: Colourless crystals from CH_2Cl_2/*n*-hexane (1:3). M.p. 217−219 °C. $C_{39}H_{31}Br$ (579.6): calcd. C 80.82, H 5.39; found C 80.81, H 5.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18−6.61 (m, 12 H), 5.10 (d, *J* = 3.4 Hz, 1 H), 3.82 (t, *J* = 4.9 Hz, 1 H), 3.76 (t, *J* = 4.6 Hz, 1 H), 3.72 (t, *J* = 4.6 Hz, 1 H), 3.56 (t, *J* = 4.9 Hz, 1 H), 3.22 (m, 3 H), 2.88 (m, 2 H), 2.38 (m, 1 H), 1.90 (br. d, A-part of AB system, *J* = 8.3 Hz, 1 H), 1.77 (m, 1 H), 1.67 (m, 2 H), 1.61 (br. d, A-part of AB system, *J* = 8.3 Hz, 1 H), 1.40 (dt, B-part of AB system, *J* = 8.3, 1.5 Hz, 1 H), 1.22 (dt, B-part of AB system, *J* = 8.3, *J* = 1.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 147.7, 147.5, 147.3, 146.5, 140.2, 138.8, 136.6, 134.9, 131.0 (2C), 127.0, 126.8, 126.28, 126.25, 126.17, 125.6, 124.5, 123.7, 122.71, 122.70, 122.6, 122.4, 116.1, 54.6, 53.2, 52.0, 50.5, 48.3, 48.1, 47.2, 47.1, 46.9, 46.9, 46.8, 46.3, 46.3, 45.0, 44.9 ppm.

Dibromo Trimer 25: Waxy solid. $C_{39}H_{30}Br_2$ (658.5): calcd. C 71.14, H 4.59; found C 71.14, H 4.59. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82−6.62 (m, 12 H), 3.87−3.81 (m, 6 H), 3.24 (m, 4 H), 3.15 (m, 2 H), 1.87 (br. dt, A part of AB, *J* = 8.3, *J* = 1.5, 2 H), 1.84 (br. dt, A part of AB, *J* = 8.6, 1.5, 1 H), 1.64 (br. dt, B part of AB, *J* = 8.6, 1.5, 1 H), 1.45 (br. dt, B part of AB, *J* = 8.3, 1.5, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 147.3, 146.0, 135.8, 134.9, 134.1, 126.6, 125.7(2C), 123.7, 122.0, 121.2, 56.6, 52.8, 48.4, 48.3, 48.0, 43.6, 43.3, 42.8 ppm.

Acknowledgments

The authors are indebted to National Research Center (CNR project no 4633) and Scientific and Technical Research Council of Turkey [TÜBITAK project no TBAG-U/18 (101T105)] for financial support of a leave of absence of A.D. in Venice. This work also has been supported by the Turkish Academy of Sciences in the framework of the Young Scientist Award Program. (AD/TÜBA-GEBIP/2001-1-3). The work that was carried out in Italy was supported by MURST COFIN "Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni".

[1] V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 5524−5532.
[2] [2a] S. Cossu, O. De Lucchi, V. Lucchini, G. Valle, M. Balci, A. Dastan, B. Demirci, *Tetrahedron Lett.* **1997**, *38*, 5319−5322. [2b] R. Durr, S. Cossu, V. Lucchini, O. De Lucchi, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2805−2807. [2c] S. Cossu, O. De Lucchi, A. Paulon, P. Peluso, C. Zonta, *Tetrahedron Lett.* **2001**, *42*, 3515−3518. [2d] F. Fabris, L. Bellotto, O. De Lucchi, *Tetrahedron Lett.* **2003**, *44*, 1211−1213. [2e] G. Borsato, O. De Lucchi, F. Fabris, V. Lucchini, M. Pasqualotti, A. Zambon, *Tetrahedron Lett.* **2003**, *44*, 561−563. [2f] G. Borsato, O. De Lucchi, F. Fabris, L. Groppo, V. Lucchini, A. Zambon, *J. Org. Chem.* **2002**, *67*, 7894−7897.
[3] C. Zonta, S. Cossu, O. De Lucchi, *Eur. J. Org. Chem.* **2000**, 1965−1971.
[4] A. Matsuura, K. Komatsu, *J. Am. Chem. Soc.* **2001**, *123*, 1768−1769 and references cited therein.
[5] M. N. Paddon-Row, R. Hartcher, *J. Am. Chem. Soc.* **1980**, *102*, 662−670.
[6] M. P. Cava, M. J. Mitchell, *J. Am. Chem. Soc.* **1959**, *81*, 5409−5413.
[7] [7a] M. Avram, I. Pogany, F. Badea, C. D. Nenitzescu, *Tetrahedron* **1969**, *44*, 3851−3854. [7b] M. Avram, I. Pogany, I. G. Dinulescu, F. Chiraleu, C. D. Nenitzescu, *Rev. Roumaine Chim.* **1970**, *15*, 1207−1218.
[8] [8a] A. Tutar, M. Balci, *Tetrahedron* **2002**, *58*, 8979−8984. [8b] A. Dastan, M. Balci, T. Hökelek, D. Ülkü, O. Büyükgüngör, *Tetrahedron* **1994**, *50*, 10555−10578. [8c] A. Dastan, Ü. Demir, M. Balci, *J. Org. Chem.* **1994**, *59*, 6534−6538. [8d] A. Dastan, Y. Taskesenligil, F. Tümer, M. Balci, *Tetrahedron* **1996**, *52*, 14005−14020. [8e] A. Altundas, A. Dastan, M. M. McKee, M. Balci, *Tetrahedron* **2000**, *56*, 6115−6120. [8f] A. Dastan, *J. Chem. Res. (S)* **2001**, 463−464. [8g] A. Dastan, *Turk. J. Chem.* **2002**, *26*, 535−546.
[9] C. Zonta, S. Cossu, P. Peluso, O. De Lucchi, *Tetrahedron Lett.* **1999**, *40*, 8185−8188.
[10] A. Dastan, E. Uzundumlu, M. Balci, *Helv. Chim. Acta* **2002**, *81*, 2729−2739.
[11] [11a] S. Cossu, C. Cimenti, P. Peluso, A. Paulon, O. De Lucchi, *Angew. Chem. Int. Ed.* **2001**, *40*, 4086−4089. [11b] P. Peluso, O. De Lucchi, S. Cossu, *Eur. J. Org. Chem.* **2002**, 4032−4036.
[12] MacSpartan Plus package, Wavefunction Inc., 18401 Karman Ave., # 370, Irvine, CA 92715, USA.
[13] S. Winstein, *J. Am. Chem. Soc.* **1961**, *83*, 1516−1517.
[14] P. Patnaik, Van N. Reinhold in *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., New York, **1997**.

Received July 30, 2003

