Synthesis of Benzotri(benzonorbornadienes) (BTBNDs): Rigid, Cup-Shaped Molecules with High Electron Density within the Cavity

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Cyclotrimerisation of benzo-polycyclic bromostannylalkenes **8a–d** with $Cu(NO_3)_2{\cdot}3H_2O$ in THF affords benzotri(benzonorbornadienes) **3a–d** as a mixture of the *syn* and *anti* isomers. The ratio of *syn* to *anti* is close to the 1:3 statistical value in most cases (i.e. in cyclotrimers **3a,b,d**), but highly in favour of the *anti* isomer in **3c**, where steric hindrance by the methoxy groups plays an important role in the stereochemistry of the cyclotrimerisation. The substrates for the cyclotrimerisation, i.e. the bromostannyl alkenes **8a–d**, were prepared from bromoalkenes **7a–d** by treatment with base (LDA) and quenching with trimethyltin chloride. In turn, bromoalkenes **7a–d** were prepared from alkenes **5a–d** by radical bromination-elimination. The reaction conditions used were designed to minimise Wagner-Meerwein rearrangements that would lead to unwanted bromo isomers. The cup-shaped *syn* cyclotrimers **3a–d** exhibit high electron density within the cavity as determined by AM1 semiempirical calculations of their electrostatic potential surfaces and are valuable substrates for supramolecular chemistry. As an example, it is shown that fullerene C_{60} is drawn into solution in acetonitrile by complexation with both the *syn* and *anti* trimer of benzonorbornadiene **3a**.

Introduction

The design and synthesis of new molecular architectures is essential to broaden the scope of molecular recognition in supramolecular chemistry.[1] In general, the affinity between the host and the guest structures is a function of the complementarity of their shapes and of electronic features among the host−guest pairs. If we take the ability to complex fullerene C_{60} as one example, molecules such as the calixarenes **1**[2] and cycloveratrol **2**[3] exhibit a strong affinity for the curved fullerene structure, because of the concurrent presence of appropriate shape and electronic features; mostly due in these two cases to the oxygen-substituted aromatic rings. The architecture of cup-shaped molecules such as **3** is also inherently shaped for accommodating fullerenes or other guest molecules in the cavity. Unlike **1** and **2**, benzocyclotrimers **3** exhibit a rigid geometry which may play an important role in determining selectivity. From another point of view, structures **3** represent an evolution of the molecular tweezers **4** recently reported by Klärner et al..[4] As apparent from the drawings below, beside the shape and the associated electronic features, structures **3c** and **3d** share with **1** and **2** the presence of the benzo rings and the oxygen substituents, while **3a** and **3b** share with **4** the [2.2.1] bridges and the rigid curved shapes. The option of obtaining either pure hydrocarbonic structures such as **3a** and **3b** or the oxygen substituted derivatives **3c** and **3d** offers opportunities for comparative study; in particular of how complexing properties are influenced by pure π interactions due to the benzo rings and by the oxygen substituents (Figure 1).

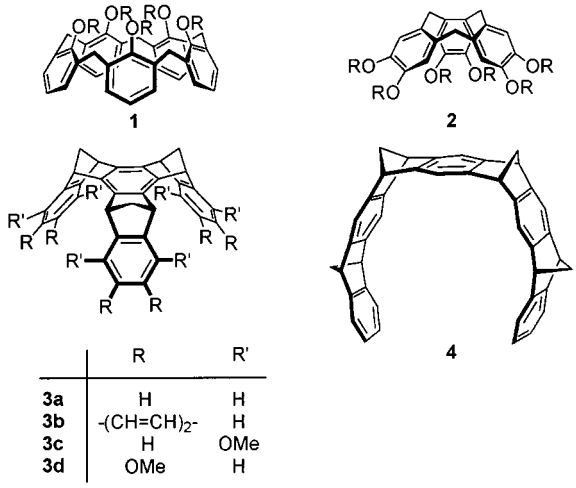

Figure 1. Structures of host molecules

Here we report on: (i) the synthesis, by cyclotrimerisation of bromo-trimethylstannyl alkenes,[5] of a number of cup-shaped aromatic hydrocarbons with general skeleton **3,** with or without substituents on the external aromatic rings; (ii) the semiempirical (AM1) determination of electronic distribution (electrostatic potential surfaces) as an estimate of the complexing potentialities of **3a−d**, and (iii) preliminary observations on their complexing abilities.

Results and Discussion

Synthesis of Benzotribenzonorbornadienes (BTBNDs)

The overall procedure for the preparation of the trimers of benzonorbornadiene **5a**,[6] naphthonorbornadiene **5b**,

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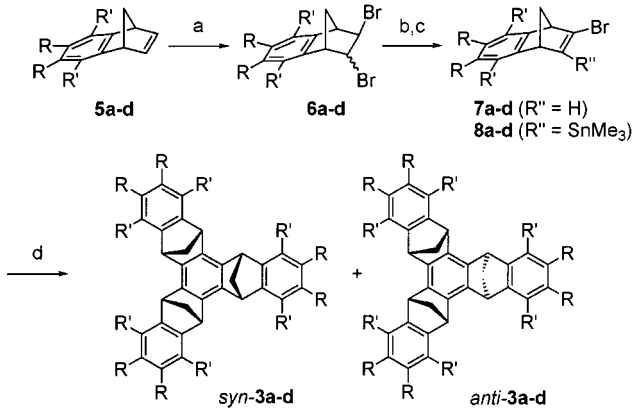
5,8-dimethoxybenzonorbornadiene **5c**, and 6,7-dimethoxybenzonorbornadiene **5d** is reported in Scheme 1.



Scheme 1. a: $C_2Br_2Cl_4$, CCl_4, hv; b: *t*BuOK, THF, reflux; c: 1. LDA, 2. Me_3SnCl, THF, −78° C; d: $Cu(NO_3)_2{\cdot}3\ H_2O$, THF

The preparation of the monomers **5a−d** was accomplished as described in the literature[7−10] (see Experimental Section). Under standard reaction conditions, addition of bromine to the double bond of any of the olefins **5a−d** occurs with complete rearrangement of the polycyclic skeleton, because of Wagner-Meerwein rearrangement of the intermediate carbocation.[11] To suppress such rearrangement the reaction was performed under radical-promoting conditions, employing 1,2-dibromotetrachloroethylene as the source of bromine and visible light to initiate the radical reaction.[12] An alternative procedure is the high temperature bromination developed by Balci et al.,[13] that avoids the use of photochemical apparatus. Under these conditions a mixture of *cis* and *trans* isomers **6** is obtained in high yield (Table 1). Dehydrobromination of the crude isomeric mixtures **6a−d** occurs swiftly upon treatment with *t*BuOK in refluxing THF, leading to the 2-bromobenzonorbornadienes **7a−d**.

Trimethylstannylation of the bromoalkenes **7a−d** was performed by generation of the vinyl anion with LDA, followed by quenching with trimethyltin chloride. In the [2.2.1] system of the molecules studied here, the bromoalkenyl anion is sufficiently stable under the reaction conditions to allow reaction with trimethyltin chloride. In other cases (e.g. in [2.2.2] polycyclic systems)[14] the anion spontaneously eliminates to afford the unstable alkyne, and stannylation is not generally possible. An alternative preparation of the β-bromostannylalkene is by halogen-metal exchange from the dibromo derivative (R" = Br in structure **7**). These dibromides are effectively prepared from **7** by bromination-dehydrobromination.[6]

The cyclotrimerisation reaction is performed at room temperature in THF with $Cu(NO_3)_2{\cdot}3H_2O$. The reaction is almost instantaneous and affords trimers **3** as a mixture of *syn* and *anti* isomers. Yields and diastereomeric ratios for trimers **3** are reported in Table 1. In the case of the 5,8-dimethoxy derivative, the ratio between the trimers is strongly in favour of the *anti* isomer (9:1). This value, anomalous with respect to the ratios observed with the other substrates, can be explained by the high steric hindrance of the methoxy groups in the *syn* structure **3c**.

As well as the trimers **3a−c**, variable amounts of dimers *syn*- and *anti*-**11** and some protodestannylated monomer **7** were also formed (Figure 2, Table 1). The dimers were isolated in a few instances (e.g. in the case of **11a**), but in all other cases they were only detected in the NMR spectrum and their isolation was not attempted. As was recently proposed,[15] dimers *syn* and *anti*-**11** are possible intermediates in the generation of the trimers **3**. The C_2-symmetric dimer *anti*-**11** (composed of two homochiral monomers) is the precursor of the *anti* trimer **3**, while symmetric (meso) dimer *syn*-**11** (composed of two heterochiral monomers) is that of the *syn* trimer **3**. Dimer formation is close to 1:1 in the case of **11a**, while in the 1:3 ratio for trimers **3a,b,d**. The 1:3 diastereomeric ratio in favour of the *anti* structure in the cyclotrimers **3** is the statistical value as each dimer reacts in two modes with the monomer. Hence dimer *RR* (or *SS*) reacts either with monomer *R* or *S*, and dimer *RS* (=*SR*) with monomer *R* or *S*. Three of these give the *anti* trimer and only one the *syn* one.

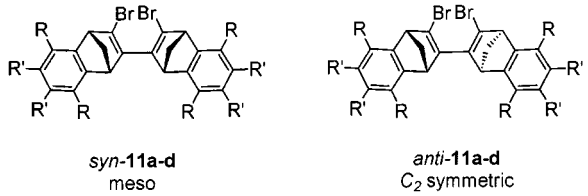


Figure 2. Structure of the dimers

The assignment of the structure of the dimers **11** is based on the MS and NMR spectroscopic data, but the designation of which isomer is the C_2-symmetric and which is the *meso* one is difficult. In this study the structures of the two isomers have been assigned on the basis of similarities of the NMR spectra with the respective dichloro derivatives.[6]

The electronic structures of the trimers were investigated in the light of Klärner's findings[16] that reported a correla-

Table 1. Yields and *syn-anti* diastereomeric ratio in the preparation of cyclotrimers **3a−d**

	R	R′	**6**[a] (%)	**7** (%)	**8** (%)	**3** (%)[b][c]	**11** (%)[b]	**7** (%)[b]	*dr* **3**[d]
a	H	H	quant.	quant.	quant.	70	15	15	1:3
b	-$(CH)_4$-	H	60	quant.	40	40	traces	40	1:3
c	H	OMe	quant.	quant.	45	15	10	65	1:9
d	OMe	H	92	95	20	47	traces	35	1:3

[a] Mixture of *trans* and *exo-cis* isomers in a ca. 1:10 ratio. − [b] Yields in the cyclotrimerisation reaction with $Cu(NO_3)_2{\cdot}3H_2O$. − [c] Mixture of *syn* plus *anti* isomers. − [d] *syn* versus *anti* isomers.

tion between the complexing ability of the concave side of non planar, aromatic hydrocarbons and the electrostatic potential surfaces (EPSs) calculated using the semiempirical AM1 method.[17] It was found that the concave sides of such molecules exhibit highly negative EPS values, while, on the outer surface, the values are comparable with those of polyalkylated benzenes. It is possible to predict the complexing ability of these hydrocarbons, taking account of EPS values and the complementarity of the geometries of the host-guest structure. The calculated (AM1) electrostatic potential surfaces, together with a perspective view of molecules **3a**−**d**, are reported in Figure 3.

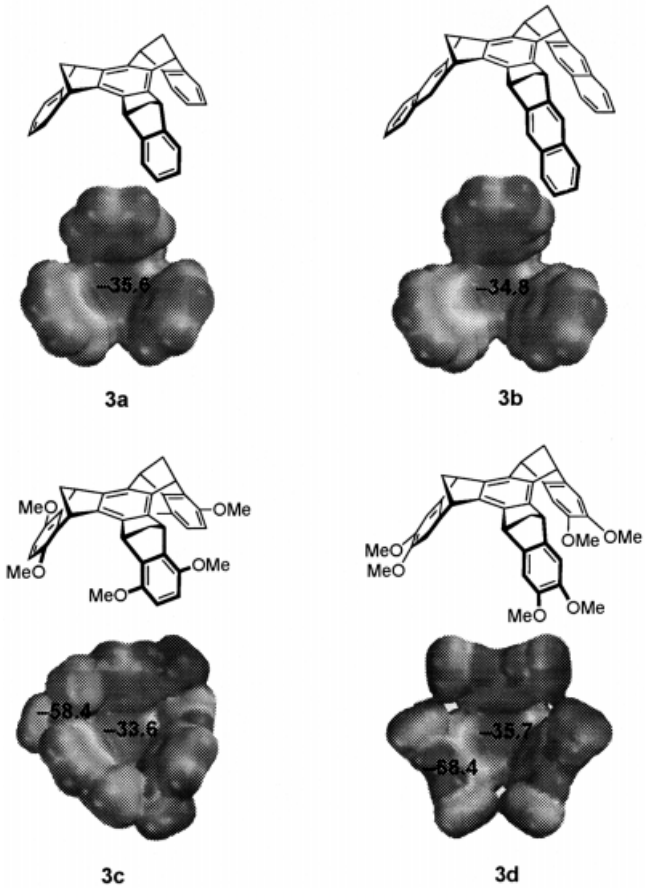


Figure 3. Semiempirically calculated EPSs (AM1) of the *syn*-cyclotrimers **3a**−**d**. The EPSs range from −68 to 22 kcal/mol

In agreement with the observations of Klärner, the molecules synthesised in the course of this study exhibit strongly negative EPS values in the concave side of the central aromatic rings. Remarkably, within the class of purely hydrocarbonic molecules, structure **3a** shows the lowest value so far reported in the literature. This fact suggests high complexing potentiality with molecules of higher EPS values, such as electron deficient systems. In this respect it is useful to remember that the molecules reported here display complementary behaviour with other cup-shaped PAHs. Indeed, while the region of higher electron density in **3** is within the cavity, cup-shaped PAHs, which are subunits of fullerenes, present unselective or inverse electron density between the inner and the outer surface of the molecule.[18]

Although complexation studies are in progress and will be reported in due time, it was noticed that *syn* trimer **3a** is able to draw fullerene C_{60} into solution in acetonitrile, a solvent unable to solubilise fullerenes.[19] This behaviour is suggestive of complex formation between **3a** and C_{60} in the same vein as found for calixarenes **1** and cycloveratrole **2**.[2,3] Figure 4 shows the UV spectrum of the cyclotrimer **3a** and that of an acetonitrile solution of **3a** after addition of C_{60}. Since UV absorption of C_{60} in acetonitrile is completely absent because of its practical insolubility, and since pure **3a** also does not absorb in this region, the observed curve can only be due to complex formation between C_{60} and cyclotrimer *syn*-**3a**.[20] The same behaviour is also observed with all other trimers **3** including their *anti* isomers, but in other cases the relative absorbances are superimposed. Several attempts to isolate the complex corresponding to that observed with this substrate have, however, so far failed.[1−3]

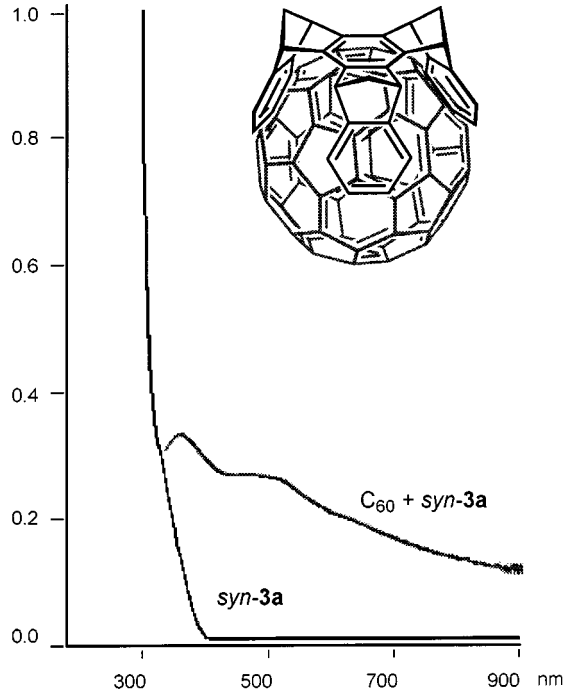


Figure 4. UV spectra of an acetonitrile solution of *syn*-**3a** (10^{-3} M) and of the same solution with C_{60} (excess) added

In conclusion, we have reported here on the synthesis of host compounds of type **3** which, because of variety of substitution and of associated electronic properties, may play an important role in supramolecular chemistry.[21] We are currently studying their complexing properties and, in view of their C_{3v} molecular symmetry, trying to prepare chiral derivatives of this class of compounds. To approach this chemistry more effectively, however, it is important to gain more information about the mechanism of the cyclotrimerisation reaction and to find methods leading stereoselectively to the *syn* structure. We are now pursuing these goals.

Experimental Section

General: Melting points are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 and Varian Unity 400 spectrometers. Commercial high purity reagents and solvents were employed without further purification. Microanalyses were performed on a Perkin Elmer 2400 CHN Elemental Analyser. For new compounds satisfactory determinations were obtained: C ± 0.3, H ± 0.27.

1,4-Dihydro-1,4-methanonaphthalene (Benzonorbornadiene) (5a): This compound was prepared according to the reported procedure[7] in 40% yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.25−6.91 (m, 4 H, H-6 and H-7), 6.80 (t, *J* = 1.8 Hz, 2 H, H-2 and H-3), 3.89 (t, *J* = 1.8 Hz, 2 H, H-1 and H-4), 2.32 (dt, *J* = 7.0 and 1.8 Hz, 1 H, H-9a), 2.31 (dt, *J* = 7.0 and 1.8 Hz, 1 H, H-9s). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 152.2, 143.5, 124.8, 122.1, 70.7, 50.9.

1,4-Dihydro-1,4-methanoanthracene (Naphthonorbornadiene) (5b): This compound was prepared according to the reported procedure[8] in 58% yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.67−7.62 (m, 2 H, Ar), 7.57 (s, 2 H, Ar), 7.40−7.35 (m, 2 H, Ar), 6.74 (t, *J* = 1.7 Hz, 2 H, H-2 and H-3), 3.98 (t, *J* = 1.7 Hz, 2 H, H-1 and H-4), 2.36 (dt, *J* = 7.5 and 1.7 Hz, 1 H, H-9a), 2.23 (dt, *J* = 7.5 and 1.7 Hz, 1 H, H-9s). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 148.5, 142.0, 132.0, 127.6, 125.1, 119.3, 66.5, 49.5.

1,4-Dihydro-5,8-dimethoxy-1,4-methanonaphthalene (5c): This compound was prepared according to the reported procedure[9] in 90% yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.82 (t, *J* = 1.8 Hz, 2 H, H-2 and H-3), 6.50 (s, 2 H, H-6 and H-7), 4.16 (q, *J* = 1.8 Hz, 2 H, H-1 and H-4), 3.79 (s, 6 H), 2.26−2.15 (m, 2 H, H-9). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 143.0, 130.1, 109.5, 70.1, 56.3, 50.0.

1,4-Dihydro-6,7-dimethoxy-1,4-methanonaphthalene (5d): This compound was prepared according to the reported procedure[10] in 40% yield. − m.p. 82−83 °C (sublimation). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.94 (s, 2 H, H-5 and H-8), 6.82 (t, *J* = 1.7 Hz, 2 H, H-2 and H-3), 3.88−3.82 (br. s, 2 H, H-1 and H-4), 3.84 (s, 6 H, OCH_3), 2.30 (dt, *J* = 7.0 and 1.2 Hz, 1/2 AB system, 1 H, H-9a or H-9s), 2.22 (d, *J* = 7.0 Hz, 1/2 AB system, 1 H, H-9a or H-9s). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 145.3, 144.0, 143.2, 107.7, 70.7, 56.6, 50.4.

General Procedure for the Bromination Reaction of 5a−d: A CCl_4 solution of polycyclic olefin **5a−d** and $CBrCl_2CBrCl_2$ (1.5 equivalents) was irradiated with a 250 W halogen lamp at reflux temperature, while stirring. The solvent was removed at reduced pressure and the residue was purified by flash-chromatography [eluent *n*-hexane (**6a,b**) or *n*-hexane/ethyl acetate 10:1 (**6c,d**)]. Starting materials and reaction times are indicated below.

2-*exo*,3-*endo*-Dibromo-1,4-methano-1,2,3,4-tetrahydronaphthalene (6a): Starting from **5a** (7.7 g, 54 mmol) and $CBrCl_2CBrCl_2$ (26.3 g, 81 mmol) in CCl_4 (100 mL); 6 h at reflux. − Pale yellow oil, 16.2 g, quantitative yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.33−7.22 (m, 4 H, Ar), 4.67 (dd, *J* = 2.7 and 1.2 Hz, 1 H, H-2), 3.81(t, *J* = 2.9 Hz, 1 H, H-3), 3.55 (br. s, 2 H, H-1 and H-4), 2.43 (dt, *J* = 10.1 and 1.5 Hz, 1 H, H-9s), 2.35 (dtd, *J* = 10.1, 2.6 and 1.8 Hz, 1H, H-9a).

2-*exo*,3-*endo*-Dibromo-1,4-methano-1,4-tetrahydroanthracene (6b): Starting from **5b** (3.63 g, 19 mmol) and $CBrCl_2CBrCl_2$ (9.2 g, 28.2 mmol) in CCl_4 (50 mL); 12 h at reflux. Pale yellow oil, 4 g, 60% yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.93−7.78 (m, 2 H, H-6 and H-9), 7.73 (s, 1 H, H-5 or H-10), 7.69 (s, 1 H, H-5 or H-10), 7.56−7.46 (m, 2 H, H-7 and H-8), 4.79 (dd, *J* = 4.0 and 2.7 Hz,1 H, H-3), 3.97 (t, *J* = 2.7 Hz, 1 H, H-2), 3.73 (br. s, 1 H, H-1), 3.65 (dd, *J* = 4.0 and 1.4 Hz, 1 H, H-4), 2.55 (dt, *J* = 10.2 Hz and 1.4 Hz, 1/2 AB system, 1 H), 2.25 (dt, *J* = 10.2 and 2.7 Hz, 1/2 AB system, H-1). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.6, 140.5, 134.0, 132.7, 128.0, 127.8, 125.7, 125.6, 122.6, 120.1, 57.4, 57.0, 53.2, 51.7, 45.4.

2-*exo*,3-*endo*-Dibromo-1,4-dihydro-1,4-methano-5,8-dimethoxynaphthalene (6c): Starting from **5c** (8.6 g, 42 mmol) and $CBrCl_2$ $CBrCl_2$ (24.6 g, 75 mmol) in CCl_4 (300 mL); 3 h at reflux. Yellow oil, 15 g, quantitative yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.68−6.63 (m, 2 H, H-6 and H-7), 4.62 (dd, *J* = 2.5 and 1.0 Hz, 1 H), 3.82 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.87−3.76 (m, 3 H), 2.37 (dt, *J* = 10.0 and 1.3 Hz, 1/2 AB system, 1 H, H-9a), 2.10 (d, *J* = 10.0 Hz, 1/2 AB system, 1 H, H-9s). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 149.8, 148.0, 132.8, 132.0, 111.0, 110.5, 57.1, 56.5, 56.2, 55.7, 49.9, 48.9, 46.3.

2-*exo*,3-*endo*-Dibromo-1,4-dihydro-6,7-dimethoxy-1,4-methanonaphthalene (6d): Starting from **5d** (7.0 g, 35 mmol) and $CBrCl_2$ $CBrCl_2$ (16.9 g, 52 mmol) in CCl_4 (200 mL); 3 h at reflux. Colourless oil, 12 g, 92% yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.87 (s, 1 H, H-5 or H-8), 6.84 (s, 1 H, H-5 or H-8), 4.65 (t, *J* = 3.2 Hz, 1 H, H-2), 3.87 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.75 (t, *J* = 2.6 Hz, 1 H, H-3), 3.49 (br. s, 1 H, H-1 or H-4), 3.45 (br. s, 1 H, H-1 or H-4), 2.38 (dt, *J* = 9.9 and 1.4 Hz, 1/2 AB system, 1 H, H-9a), 2.14 (dtd, *J* = 10.2, 2.7 and 1.8 Hz, 1/2 AB system, 1 H, H-9s). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 148.2, 147.9, 135.5, 135.4, 108.8, 105.8, 57.9, 57.1, 56.1, 56.0, 53.6, 52.0, 46.6.

General Procedure for the Dehydrobromination Reaction of 6a−d: A solution of *t*BuOK (1.5 equivalents) in dry THF was added dropwise to a solution of **6a−d** in dry THF and the resulting suspension was stirred at reflux temperature for 3 h. After cooling to room temp., the crude reaction mixture was diluted with diethyl ether (100 mL), washed with water (3 × 50 mL), dried ($MgSO_4$), concentrated at reduced pressure and purified.

2-Bromo-1,4-dihydro-1,4-methanonaphthalene (7a): Starting from **6a** (16.2 g, 53 mmol) and *t*BuOK (9.5 g, 8.5 mmol) in dry THF (200 mL), a pale yellow oil was obtained after bulb to bulb distillation (100 °C, 5 Torr): 11.6 g, quantitative yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.40−6.95 (m, 4 H, Ar), 6.72 (dt, *J* = 3.3 and 0.9 Hz, 1 H, H-3), 3.91 (br. s, 1 H, H-4), 3.80 (s, 1 H, H-1), 2.58 (dt, *J* = 7.3 and 1.7 Hz, 1/2 AB system, 1 H, H-9s), 2.35 (dtd, *J* = 7.3, 1.7 and 0.9 Hz, 1/2 AB system, 1 H, H-9a). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 149.9, 149.5, 140.4, 136.3, 125.6, 125.3, 122.2, 121.7, 69.1, 58.4, 51.8.

2-Bromo-1,4-dihydro-1,4-methanoanthracene (7b): Starting from **6b** (4.0 g, 11 mmol) and *t*BuOK (1.9 g, 17 mmol) in dry THF (60 mL), a colourless solid was collected after flash chromatography (eluent: *n*-hexane): 2.9 g, quantitative yield. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.79−7.67 (m, 2 H, H-6 and H-9), 7.71 (s, 1H, H-5 or H-10), 7.58 (s, 1H, H-5 or H-10), 7.46−7.37 (m, 2H, H-7 and H-8), 6.69 (d, *J* = 3.3 Hz, 1 H, H-3), 4.01 (br. s, 1 H, H-4), 3.91 (br. s, 1 H, H-1), 2.63 (dt, *J* = 7.6 and 1.5 Hz, 1/2 AB system, 1 H, H-11), 2.29 (d, *J* = 7.6 Hz, 1/2 AB system, 1 H, H-11). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 146.3 (C-10a or C-4a), 145.9 (C-10a or C-4a), 139.7 (C-3), 135.0 (C-2), 132.4 (C-5a or C-9a), 131.9 (C-5a or C-9a), 127.8 (C-6 or C-7), 127.7 (C-6 or C-7), 125.6 (C-9 or C-6), 125.5 (C-9 or C-6), 120.3 (C-10 or C-5), 119.7 (C-10 or C-5), 65.5 (C-11), 57.6 (C-1), 51.0 (C-4).

2-Bromo-1,4-dihydro-5,8-dimethoxy-1,4-methanonaphthalene (7c): Starting from **6c** (15 g, 41 mmol) in dry THF (100 mL) and *t*BuOK

(7.0 g, 62 mmol) in dry THF (100 mL), a yellow oil was obtained which was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 95:5): 11.3 g, quantitative yield. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.75 (d, *J* = 3.3 Hz, 1 H, H-3), 6.56 (s, 2 H, H-6 and H-7), 4.16 (br. s, 1 H, H-4), 4.12 (br. s, 1 H, H-1), 3.83 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 2.50 (dt, *J* = 7.1 and 1.6 Hz, 1/2 AB system, 1 H, H-9s), 2.25 (dtd, *J* = 7.1, 1.8 and 0.5 Hz, 1/2 AB system, 1 H, H-9a). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 149.2, 148.6, 140.0, 138.6, 138.2, 135.9, 110.8, 110.4, 69.0, 57.0, 55.0, 56.1.

2-Bromo-1,4-dihydro-6,7-dimethoxy-1,4-methanonaphthalene (7d): Starting from a solution of **6d** (12 g, 33 mmol) and *t*BuOK (5.6 g, 50 mmol) in dry THF (150 mL), a pale yellow oil was collected after flash chromatography (eluent: *n*-hexane/ethyl acetate 95:5): 8.6 g, 95% yield. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.03 (s, 1 H), 6.91 (s, 1 H), 6.74 (d, *J* = 3.2 Hz, 1 H), 3.88–3.84 (m, 1 H), 3.87 (s, 3 H), 3.76 (br. s, 1 H), 2.57 (dt, *J* = 8.7 and 1.4 Hz, 1 H), 2.29 (br. s, 1 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 146.0, 145.5, 142.2, 141.6, 140.4, 136.6, 108.0, 107.5, 69.53, 56.3, 56.3, 51.7.

General Procedure for the Trimethylstannylation Reaction of 7a–d: The procedure for the preparation of **8a** starting from **7a** is representative. A solution of *n*BuLi (4.7 mL of a 2.5 M solution in hexanes, 11.8 mmol) was added by syringe to a solution of freshly distilled diisopropylamine (1.7 mL, 11.8 mmol) in dry THF (20 mL) while stirring under argon at 0° C. After 15 min, the resulting solution was cooled at −78° C and a solution of 2-bromobenzonorbornadiene **7a** (1 g, 4.5 mmol) in THF (5 mL) was slowly added. The resulting mixture was stirred at −78° C for an additional hour, and treated at this temperature with trimethyltin chloride (0.9 g, 4.53 mmol), stirred at room temp. overnight, concentrated at reduced pressure, diluted with diethyl ether (70 mL), and washed with water (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated at reduced pressure.

2-Bromo-1,4-dihydro-1,4-methano-3-trimethylstannylnaphthalene (8a): After flash chromatography (eluent: *n*-hexane) a colourless oil was obtained (1.6 g, quantitative yield). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.31–7.14 (m, 2 H, Ar), 7.10–6.96 (m, 2 H, Ar), 4.00 (m, 1 H, H-1 or H-4), 3.84 (m, 1 H, H-4 or H-1), 2.52 (dt, $J_{10a-8} = J_{10a-1}$= 1.6 Hz, 1/2 AB system, H-10a or H-10b, 1 H), 2.25 (dt, J_{10b-4} = 1.5, $J_{10a-10b}$ = 7.3 Hz, 1/2 AB system, 1 H, H-10a o H-10b), 0.21 (s with side band, $J_{H-^{117}Sn}$ = 54.8 Hz, $J_{H-^{119}Sn}$ = 57.2 Hz, 9 H, Me). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.1 ($J_{C-^{117}Sn}$ = 396.1 Hz, $J_{C-^{119}Sn}$ = 414.6 Hz, C-3), 149.9 (J_{C-Sn} = 3.7 Hz, C-4a), 149.6 (J_{C-Sn} = 7.9 Hz, C 8a), 147.7 (J_{C-Sn} = 9.2 Hz, C-2), 125.0, 124.3, 121.9, 121.2 (C-5, C-6, C-7, C-8), 68.2 (J_{C-Sn} = 16.8 Hz, C 9), 60.3 (J_{C-Sn} = 31.0 Hz, C-1 or C-4), 57.0 (J_{C-Sn} = 33.0 Hz, C-4 or C-1), −9.3 ($J_{C-^{117}Sn}$ = 349.9 Hz, $J_{C-^{119}Sn}$ = 365.8 Hz, CH_3). – IR (neat) $\tilde{\nu}_{max}$ = 2973 cm^{-1}, 2934, 1550, 1455, 1264, 1019, 1011, 773, 752.

2-Bromo-1,4-dihydro-1,4-methano-3-trimethylstannylanthracene (8b): The general procedure reported above was employed, starting from **7b** (0.95 g, 3.5 mmol), LDA (9.1 mmol), dry THF (10 mL) and trimethyltin chloride (0.7 g, 3.5 mmol). A colourless oil was collected after flash chromatography (eluent: *n*-hexane): 0.6 g, 40% yield. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.82–7.72 (m, 2 H, H-6 and H-9), 7.63 (s, 1 H, H-5 or H-10), 7.56 (s, 1 H, H-5 or H-10), 7.51–7.42 (m, 2 H, H-7 and H-8), 4.14 (s, 1 H, H-1 o H-4), 3.98 (s, 1 H, H-1 o H-4), 2.62 (dd, *J* = 7.7 and 0.9 Hz, 1/2 AB system, 1 H, H-11s), 2.31 (dd, *J* = 7.7 and 0.9 Hz, 1/2 AB system, 1 H, H-11a), 0.29 (s with side band, 9 H, $J_{H-^{117}Sn}$ = 54.6 Hz, $J_{H-^{119}Sn}$ = 57.2 Hz, CH_3 bonded to Sn). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 152.1, 149.9, 149.6, 147.7, 125.0, 124.3, 121.9, 121.2, 68.2, 60.3, 57.0, −9.3 ($J_{C-^{117}Sn}$ = 347.8 Hz, $J_{C-^{119}Sn}$ = 365.4 Hz, CH_3).

2-Bromo-1,4-dihydro-5,8-dimethoxy-1,4-methano-3-trimethylstannylnaphthalene (8c): The general procedure reported above was employed, starting from **7c** (7.9 g, 28 mmol) in dry THF (20 mL), LDA (72 mmol) in dry THF (280 mL) and trimethyltin chloride (14.5 g, 72 mmol). The crude product was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 95:5), affording a yellow oil: 5.3 g, 45% yield. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.54 (s, 2 H, H-7 and H-6), 4.26 (dd, *J* = 1.9 and 1.7 Hz, 1 H, H-4), 4.14 (dd, *J* = 1.9 and 1.6 Hz, 1 H, H-1), 3.83 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 2.41 (dt, *J* = 7.1 and 1.6 Hz, 1/2 AB system, 1 H, H-9a), 2.18 (dt, *J* = 7.1 and 1.6 Hz, 1/2 AB system, 1 H, H-9s), 0.21 (s with side band, $J_{H-^{117}Sn}$ = 54.6 Hz, $J_{H-^{119}Sn}$ = 57.2 Hz, 9 H, CH_3 bonded to Sn). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.2 ($J_{C-^{117}Sn}$ = 396.6 Hz, $J_{C-^{119}Sn}$ = 417.3 Hz, C-3), 149.1, 148.7, 148.0 (J_{C-Sn} = 9.6 Hz), 138.9 (J_{C-Sn} = 3.8 Hz), 138.3 (J_{C-Sn} = 7.5 Hz), 109.9, 110.6, 68.1 (J_{C-Sn} = 16.6 Hz), 57.1, 57.0 (J_{C-Sn} = 30.7 Hz), 56.0, 53.6 (J_{C-Sn} = 34.8 Hz), −9.4 ($J_{C-^{117}Sn}$ = 347.6 Hz, $J_{C-^{119}Sn}$ = 367.3 Hz, CH_3 bonded to Sn).

3-Bromo-1,4-dihydro-6,7-dimethoxy-1,4-methano-2-trimethylstannylnaphthalene (8d): The general procedure reported above was employed, starting from a solution of **7d** (4 g, 14.3 mmol) LDA (37 mmol) in THF (50 mL), and trimethyltin chloride (7.4 g, 37 mmol). The crude product was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 95:5), giving a colourless oil: 1.2 g, 20% yield. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.00 (s, 1 H, H-5 or H-8), 6.81 (s, 1 H, H-5 or H-8), 3.94 (dt, *J* = 1.6 and 1.5 Hz, 1 H, H-1 or H-4), 3.86 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.77 (dt, *J* = 2.2 and 1.5 Hz, 1 H, H-1 or H-4), 2.48 (dt, *J* = 7.0 and 1.6 Hz, 1/2 AB system, 1 H, H-9a), 2.21 (dt, *J* = 2.2 and 1.6 Hz, 1/2 AB system, 1 H, H-9s), 0.20 (s with side band, $J_{H-^{117}Sn}$ = 54.6 Hz, $J_{H-^{119}Sn}$ = 57.2 Hz, 9H, CH_3 bonded to Sn). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 152.2 (C-3 $J_{C-^{117}Sn}$ = 398.0 Hz, $J_{C-^{119}Sn}$ = 416.3 Hz), 143.0 (J_{C-Sn} = 9.8 Hz), 145.9, 145.3, 142.3 (J_{C-Sn} = 4.1 Hz), 141.8 (J_{C-Sn} = 8.1 Hz), 107.8, 107.2, 68.7 (J_{C-Sn} = 16.8 Hz), 60.4 (J_{C-Sn} = 31.6 Hz), 57.1 (J_{C-Sn} = 33.5 Hz), 56.4, 56.2, −9.3 ($J_{C-^{117}Sn}$ = 348.8 Hz, $J_{C-^{119}Sn}$ = 368.7 Hz, CH_3 bonded to Sn).

General Procedure for the Cyclotrimerisation Reaction of 8a–d: The reaction of **8a** is representative. A stirred THF (12 mL) solution of **8a** (1.2 g, 3.1 mmol), was treated with $Cu(NO_3)_2 \cdot 3\ H_2O$ (0.75 g, 3.1 mmol) at room temp., monitoring by TLC (eluent: *n*-hexane). After 1 h, the crude reaction mixture was diluted with ethyl acetate (100 mL) and washed several times with 5% aqueous NH-3 (30 mL each time) until any blue colour disappeared. The organic phase was dried (Na_2SO_4), filtered, and concentrated at reduced pressure. The residue, consisting of of *syn*-**3a**: *anti*-**3a** in the ratio reported in Table 1, was recrystallised from THF/diethyl ether, affording colourless rhombic crystals (exclusively isomer *syn*-**3**) which were collected by filtration. Yields of dimers and protodestannylated compound are reported in Table 1.

***syn*-3a and *anti*-3a:** The crude reaction mixture was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 95:5).

***syn*-3a:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11–7.05 (m, 6 H, H-1, H-4, H-7, H-10, H-13 and H-16), 6.79–6.74 (m, 6 H, H-2, H-3, H-8, H-9, H-14 and H-15), 4.34 (t, *J* = 1.5 Hz, 6 H, H-5, H-6, H-11, H-12, H-17 and H-18), 2.48 (dt, *J* = 7.8 and 1.6 Hz, 3 H, H-19s, H-20s and H-21s), 2.44 (dt, *J* = 7.8 and 1.6 Hz, 3 H, H-19a, H-20a, H-21a). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.8 (C-4a, C-6a, C-10a, C-12a, C-16a and C-18a), 137.9 (C-5a, C-5b, C-11a,

C-11b, C-17a and C-17b), 124.9 (C-2, C-3, C-8, C-9, C-14 and C-15), 121.1 (C-1, C-4, C-7, C-10, C-13 and C-16), 65.6 (C-19, C-20 and C-21), 48.9 (C-5, C-6, C-11, C-12, C-17 and C-18).

***anti*-3a:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.31 (m, 2 H), 7.22 (m, 2 H), 7.18 (m, 2 H), 6.98 (m, 2 H), 6.88 (m, 4 H), 4.31 (4 H, s), 4.28 (t, *J* = 1.5 Hz, 2 H), 2.43 (dt, *J* = 7.8 and 2.4 Hz, 2 H), 2.37 (dt, *J* = 7.8 and 1.6 Hz, 1 H), 2.30 (dt, *J* = 7.8 and 1.6 Hz, 2 H), 2.19 (dt, *J* = 7.9 and 1.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.6 (C-4a and C-18a), 150.3 and 150.2 (C-6a, C-10a, C-12a and C-16a), 138.1, 138.0, 137.9, 125.0, 124.8, 124.7 and 121.4 (C-1 and C-4), 121.30 and 121.28 (C-7, C-10, C-13 and C-16), 65.4 (C-20 and C-21), 45.2 (C-19), 48.92, 48.90, 48.83.

11a: (mixture of isomers in 55:45 ratio), ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58−7.53, 7.41−7.37, 7.20−7.13 (series of m, 16 H, Ar, both isomers), 4.69 (br. s, 2 H, major isom.), 4.46 (br. s, 2H, minor isom.), 3.86 (br. s, 4 H, both isom.), 2.57 (dt, *J* = 7.7 and 1.7 Hz, 1/2 AB system, 1 H, major isom.), 2.45 (dt, *J* = 7.7 and 1.7 Hz, 1/2 AB system, 1 H, minor isom.), 2.26 (dt, *J* = 7.7 and 1.7 Hz, 1/2 AB system, 1 H, minor isom.), 2.19 (dt, *J* = 7.7 and 1.7 Hz, 1/2 AB system, 1 H, major isom.). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = (both isomers) 149.4, 149.2, 149.0, 148.7, 145.2, 144.1, 132.3, 131.1, 125.2, 125.1, 124.8, 124.5, 122.8, 122.2, 121.8, 121.7; (major isom.): 65.8, 60.1, 52.7; (minor isom.): 66.7, 59.7, 53.0. − MS (70 eV): *m*/*z* = 442, 440, 438, 281, 280 (base peak), 279, 278, 277, 276, 265, 165, 139, 115.

***syn*-3b and *anti*-3b:** The general procedure described above was employed, starting from **8b**. The crude reaction mixture was purified by crystallisation from THF/diethyl ether (40% yield).

***syn*-3b:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56−7.47 (m, 6H, H-2, H-5, H-10, H-13, H-18 and H-21), 7.46 (s, 6H, H-1, H-6, H-9, H-14, H-18 and H-21), 7.20−7.11 (m, 2H, H-3, H-4, H-11, H-12, H-19 and H-20), 4.51 (s, 6H, H-7, H-8, H-15, H-16, H-23 and H-24), 2.57 (dt, *J* = 8.1 and 1.4 Hz, 3H, H-25s, H-26s and H-27s), 2.50 (dt, *J* = 8.1 and 1.5 Hz, 3H, H-25a, H-26a and H-27a). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.5 (C-6a, C-24a, C-8a, C-14a, C-17a and C-22a), 137.6 (C-7a, C-7b, C-15a, C-15b, C-23a and C-23b), 132.2 (C-1a, C-5a, C-9a, C-13a, C-17a and C-21a), 127.5 (C-2, C-5, C-10, C-13, C-18 and C-21), 124.7 (C-3, C-4, C-11, C-12, C-19 and C-20), 119.0 (C-1, C-6, C-8, C-15, C-17 and C-22), 63.5 (C-25, C-26 and C-27), 48.5 (C-7, C-8, C-15, C-16, C-23 and C-24).

***anti*-3b:** ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.77−7.59 (m, 6 H, H-3, H-4, H-11, H-12, H-19 and H-20), 7.71 (s, 2H, H-2 and H-5), 7.58 (s, 4 H, H-9, H-14, H-17 and H-22), 7.43−7.25 (m, 6 H, H-2, H-5, H-10, H-13, H-18 and H-21), 4.48 (t, *J* = 1.5 Hz, 4 H, H-8, H-15, H-16 and H-23), 4.46 (t, *J* = 1.6 Hz, 2 H, H-7 and H-24), 2.53−2.36 (m, 4 H, H-26 and H-27), 2.41−2.18 (m, 2H, H-25). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.6 (C-6a and C-24a), 147.2 and 146.9 (C-8a, C-14a, C-17a and C-22a), 138.15, 138.05 and 137.8 (C-7a, C-7b, C-15a, C-15b, C-23a and C-23b), 132.2 and 132.1 (C-1a, C-5a, C-9a, C-13a, C-17a and C-21a), 127.62, 127.58 and 127.4 (C-2, C-5, C-10, C-13, C-18 and C-21), 125.2, 124.98 and 124.96 (C-2, C-3, C-10, C-11, C-18 and C-19), 119.2 and 119.1 (C-1, C-6, C-8, C-15, C-17 and C-22), 62.9 (C-26 and C-27), 62.7 (C-25), 48.5, 48.42 and 49.40 (C-7, C-8, C-15, C-16, C-23 and C-24).

***syn*-3c *and anti*-3c:** The general procedure described above was employed, starting from **8c**. Recrystallisation from THF/diethyl ether gives dimers **11c** (10% yield). The mother liquors were concentrated and recrystallisation from methanol/THF afforded *anti*-**3c**. The mother liquors were purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 80:20), affording *syn*-**3c**.

***syn*-3c:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.36 (s, 6 H, H-2, H-3, H-8, H-9, H-14 and H-15), 4.62 (t, *J* = 1.5 Hz, 6 H, H-5, H-6, H-11, H-12, H-17 and H-18), 3.75 (s, 18 H, OCH_3), 2.43 (dt, *J* = 7.6 and 1.5 Hz, 3 H, H-19a, H-20a and H-21a), 2.31 (dt, *J* = 7.6 and 1.5 Hz, 3 H, H-19s, H-20s and H-21s). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.3 (C-1, C-4, C-7, C-10, C-13 and C-16), 142.3 (C-4a, C-6a, C-10a, C-12a, C-16a and C-18a), 138.7 (C-5a, C-5b, C-11a, C-11b, C-17a and C-17b), 109.7 (C-2, C-3, C-8, C-9, C-14 and C-15), 66.8 and 56.4 (C-19, C-20 and C-21), 45.6 (C-5, C-6, C-11, C-12, C-17 and C-18).

***anti*-3c:** ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.54 (s, 2 H, H-2 and H-3), 6.44 (AA′BB′ system, *J* = 7.9 Hz, 4 H, H-8, H-9, H-14 and H-15), 4.63 (dt, *J* = 1.5 and 0.9 Hz, 2 H), 4.60 (t, *J* = 1.5 Hz, 2 H, H-5, H-18), 4.59 (dt, *J* = 1.5 and 1.1 Hz, 2 H,), 3.83 (s, 6 H, OCH_3), 3.79 (s, 6 H, OCH_3), 3.78 (s, 6 H, OCH_3), 2.36 (dt, *J* = 7.8 and 1.5 Hz, 2 H, H-20a and H-21a), 2.33 (dt, *J* = 7.9 and 1.5 Hz, 1 H, H-19a), 2.18 (dt, *J* = 7.8 and 1.5 Hz, 2 H, H-20s and H-21s), 2.13 (dt, *J* = 7.8 and 1.5 Hz, 1 H, H-19s). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.75, 148.71, 148.4 (C-1, C-4, C-7, C-10, C-13 and C-16), 139.8 (C-4a and C-18a), 139.5, 138.9 (C-6a, C-10a, C-16a and C-18a), 138.1 (C-5b, C-11a, C-11b and C-17a), 138.0 (C-5a and C-17b), 110.3 and 109.7 (C-8, C-9, C-14 and C-15) 110.2 (C-2 and C-3), 65.8, 56.7 and 56.4 (C-19 and C-20), 64.5 (C-21), 45.6, 45.3 and 45.2 (C-5, C-6, C-11, C-12, C-17 and C-18).

11c: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.61 (s, 4 H, Ar), 4.43 (br. s, 2 H), 4.14 (br. s, 2H), 3.85 (s, 6H, OMe), 3.79 (s, 6H, OMe), 2.37 (dt, *J* = 8.0 and 2.0 Hz, 1/2 AB system, 2 H), 2.16 (dt, *J* = 8.0 and 2.0 Hz, 1/2 AB system, 2 H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 149.2, 148.7, 148.4, 145.8, 138.4, 132.0, 111.3, 111.0, 65.5, 57.2, 57.1, 56.7, 50.2.

***syn*-3d and *anti*-3d:** The general procedure described above was employed, starting from **8d**. The crude reaction mixture was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate 80:20), 47% yield.

***syn*-3d**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.76 (s, 6 H, H-1, H-4, H-7, H-10, H-13 and H-16), 4.26 (t, *J* = 2.0 Hz, 6 H, H-5, H-6, H-11, H-12, H-17 and H-18), 3.71 (s, 18 H, OCH_3), 2.48 (dt, *J* = 7.6 and 1.5 Hz, 1/2 AB system, 3 H, H-19, H-20 and H-21), 2.43 (dt, *J* = 7.6 and 1.5 Hz, 1/2 AB system, 3 H, H-19, H-20 and H-21). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.8 (C-2, C-3, C-8, C-9, C-14 and C-15), 142.3 (C-4a, C-6a, C-10a, C-12a, C-16a and C-18a), 137.7 (C-5a, C-5b, C-11a, C-11b, C-17a and C-17b), 106.7 (C-1, C-4, C-7, C-10, C-13 and C-16), 65.5 and 56.0 (C-19, C-20 and C-21), 48.1 (C-5, C-6, C-11, C-12, C-17 and C-18).

***anti*-3d**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.97 (s, 2 H), 6.88 (s, 2 H), 6.85 (s, 2 H), 4.28−4.22 (m, 6 H), 3.87 (s, 6 H), 3.81 (s, 6H), 3.78 (s, 6 H), 2.47−2.18 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.8, 142.7, 142.6 (C-4a, C-6a, C-10a, C-12a, C-16a and C-18a), 138.06, 137.98, 137.89 (C-5a, C-5b, C-11a, C-11b, C-17a and C-17b), 146.0, 145.9 (C-2, C-3, C-8, C-9, C-14 and C-15), 107.1, 106.8 (C-1, C-4, C-7, C-10, C-13 and C-16), 56.32, 56.28, 56.25, 65.39, 65.28 (C-19, C-20 and C-21), 48.85, 48.81 (C-5, C-6, C-11, C-12, C-17 and C-18).

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