Synthesis and Self-Association of *syn*-5,10,15-Trialkylated Truxenes

Óscar de Frutos,[a,b] Thierry Granier,[a,c] Berta Gómez-Lor,[d] Jesús Jiménez-Barbero,[e] Ángeles Monge,[d] Enrique Gutiérrez-Puebla,[d] and Antonio M. Echavarren*[a]

Abstract: *syn*-Trialkylated truxenes have been synthesized by alkylation of the truxene trianion followed by base-catalyzed isomerization of the *anti* isomers. ^{1}H NMR studies, including a determination of diffusion coefficients, as well as molecular mechanics calculations, demonstrate that these derivatives self-associate in solution through arene – arene interactions. The benzyl derivatives show the strongest associations, which are a result of both benzyl – benzyl and truxene – truxene interactions.

Keywords: cross-coupling · cyclophanes · hydrocarbons · palladium · stacking interactions

Introduction

Association through arene – arene interactions (π stacking) is a subject of great importance in contemporary chemistry.[1] The stacking interactions of aromatic hydrocarbons in water are usually attributed to the hydrophobic effect,[2] although attractive electrostatic interactions play an important role in the aromatic stacking interactions of heterocycles.[3] In this regard, it is of great interest that remarkably high degrees of self-association have been observed for some planar aromatics[4] and porphyrins[5] in nonpolar solvents.

The heptacyclic polyarene truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene) (**1**)[6] has been recognized as a potential starting material for the construction of larger polyarenes and bowl-shaped fragments of the fullerenes.[7–12] Although planar C_3-symmetric substituted truxenes have received much attention in the field of liquid crystals, in the case of 2,3,7,8,12,13-hexahydroxytruxenes only the hexaesters and hexaethers have been studied.[13–18] A further potential use of **1** would be as a starting material for the synthesis of C_3 tripods by *syn* trialkylation.[19]

We have recently found that some *syn*-trialkylated derivatives **3** self-associate tightly in $CDCl_3$ solution.[20, 21] This high degree of self-association was quite unexpected for these nonplanar derivatives. We describe herein the synthesis of trialkylated truxenes by alkylation of the trianion of **1**, as well as a study of the self-association of trialkylated truxenes **3** through arene – arene interactions in $CDCl_3$, which sheds light on the ordering of aromatic molecules through π-stacking interactions.

Results and Discussion

Synthesis of alkylated truxenes: Alkylation of the anions of the lithium, sodium, and potassium salts of **1** gives rise to mixtures of *anti* (**2**) and *syn* (**3**) derivatives (Scheme 1). Interestingly, and contrary to intuition, *anti* **2** could be isomerized to the *syn*-trialkylated truxenes **3**. Thus, simple heating of the *anti* derivatives with KO*t*Bu in refluxing *t*BuOH led cleanly to the *syn* isomers **3**. In most cases, the crude alkylated derivatives of the trilithium trianion of **1** were directly isomerized to the *syn* isomers in good to excellent yields. Thus, **3a – c**, **3f – j**, and **3r – u** were obtained in yields of 59 – 85 %. On the other hand, derivatives **3k** and **3l** were obtained by alkylation of the trianion of the tripotassium salt of **1**, followed by recrystallization, and were recovered in yields of 58 and 30 %, respectively. Silylation of the lithium anion of **1** with chlorotrimethylsilane in THF at – 20 °C gave a mixture of products, from which the *syn*-derivative **3d** was obtained in 43 % yield following the addition of hexane. In this case, attempted isomerization of the *anti* isomer by refluxing with KO*t*Bu in *t*BuOH led only to decomposition.

[a] Prof. Dr. A. M. Echavarren, Dr. Ó. de Frutos, Dr. T. Granier
Departamento de Química Orgánica
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)

[b] Dr. Ó. de Frutos
Present address: Lilly, S.A.
Alcobendas, 28018 Madrid (Spain)

[c] Dr. T. Granier
Present address: Givaudan
Überlandstrasse 138, 8006 Dübendorf (Switzerland)

[d] Dr. B. Gómez-Lor, Dr. Á. Monge, Prof. Dr. E. Gutiérrez-Puebla
Instituto de Ciencia de Materiales de Madrid, CSIC
Cantoblanco, 28049 Madrid (Spain)

[e] Prof. Dr. J. Jiménez-Barbero
Instituto de Química Orgánica, CSIC
Juan de la Cierva 3, 28006 Madrid (Spain)

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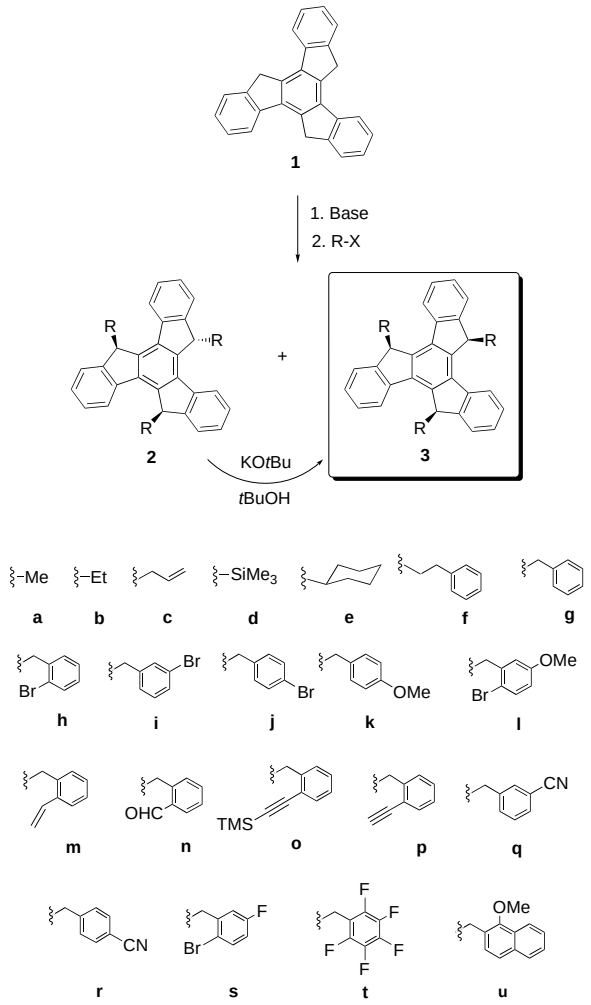


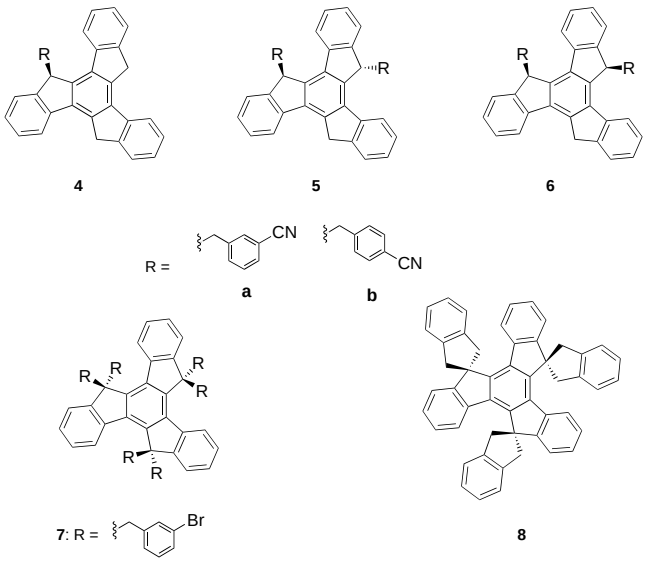
Scheme 1. Synthesis of trialkylated truxenes **3**.

Substitution with a secondary halide also proved possible. Thus, reaction of the truxene trianion with cyclohexyl iodide afforded **3e** in 33% yield.

Stille coupling of **3h** with vinyltributylstannane afforded **3m** (72%), which was converted into trialdehyde **3n** (98%) by ozonolysis followed by treatment with PPh_3. Alternatively, palladium-catalyzed coupling of **3h** with (trimethylsilylethynyl)tributylstannane[22] gave trialkyne **3o** (55%), which could be converted to **3p** (80%) by treatment with K_2CO_3 in MeOH/THF.

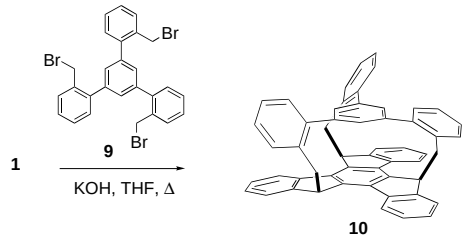
Treatment of **1** with *n*BuLi (1.1 equivalents) followed by the addition of *m*-(bromomethyl)benzonitrile (1.1 equivalents) furnished a mixture of mono- (**4a**), *anti*-dialkylated (**5a**), *syn*-dialkylated (**6a**), *anti*-trialkylated (**2q**), and *syn*-trialkylated (**3q**) truxenes. Similarly, a mixture of **4b**, **5b**, **6b**, **2r**, and **3r** was obtained by using *p*-(bromomethyl)benzonitrile as the alkylating agent (Scheme 2).

Further alkylation of **3i** with *m*-bromobenzyl bromide in THF using KOH as the base furnished the hexabenzyl derivative **7** (54%). This compound was also synthesized in 84% yield by treating **1** with KOH in THF and then adding *m*-bromobenzyl bromide. A similar alkylation of **1** with α,α'-dibromo-*o*-xylene quantitatively afforded the trispiro derivative **8**.



Scheme 2. Different alkylated truxenes.

Reaction of the truxene trianion with a tris(benzyl bromide) such as **9**[7c] can afford the corresponding cyclophane derivative.[23] Compound **9** could be readily synthesized in two steps by a Suzuki coupling of 1,3,5-tribromobenzene with 2-methylphenylboronic acid in toluene/EtOH/H_2O in the presence of Na_2CO_3 as the base and $[Pd(PPh_3)_4]$ as the catalyst (72% yield), followed by standard benzylic bromination with *N*-bromosuccinimide (91% yield). In the event, alkylation of **1** with **9** with KOH in THF gave truxenephane **10** in 66% yield (Scheme 3). This compound could also be prepared by Co^I-mediated [2+2+2] reaction of the alkyne derivatives of truxene **3p**, albeit in lower yield.[24]



Scheme 3. Synthesis of truxenephane **10**.

Stability of *syn*-trialkylated truxenes: The facile isomerization of derivatives **2** to **3** under basic conditions suggests that *syn*-trialkylated truxenes are more stable than the *anti* isomers, although this conclusion is at first glance quite surprising since it seems to contradict the general belief that greater steric congestion corresponds to lower stability.[25] However, there are examples in which the most hindered conformers are indeed the most stable.[26, 27] A remarkable example of this phenomenon is seen with 1,3,5-trineopentylbenzene, the most stable conformation of which has three *syn tert*-butyl groups.[26a] In such cases, the attractive van der Waals forces between the alkyl chains are responsible for the greater stability of the *syn* conformers, whereas the repulsive, purely

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steric interactions, are not very different in the *syn* and *anti* conformers.

The greater stability of *syn* trialkylated truxenes **3** is in accord with semiempirical calculations[28] (Table 1). It might be a consequence of the attractive van der Waals interactions between the side chains.[29] Indeed, MM2 calculations[30] reveal that most of the energy difference between *syn*- and *anti*-*tert*-butyltruxenes can be ascribed to these interactions.[31]

Table 1. PM3 energies [kcal mol^{-1}] of selected 5,10,15-trisubstituted truxenes.

	R	H°_{anti}	H°_{syn}	$H^\circ_{anti} - H^\circ_{syn}$
1	Me (**3a**)	86.7	86.4	0.3
2	allyl (**3c**)	147.6	146.5	1.1
3	2-Br-benzyl (**3g**)	201.3	200.9	0.4
4	Cy (**3e**)	36.7	36.2	0.5
5	*t*Bu	60.3	56.2	4.1
6	Ph	193.5	193.2	0.3
7		149.9	147.4	2.5

NMR studies: Truxenes **3** show NMR data consistent with C_3 symmetry. In the ^{1}H NMR spectra of derivatives **3g**–**u**, the benzylic hydrogens appear as AMX systems with coupling constants $J_{AM} = 3-4$ Hz, $J_{AX} = 9-10$ Hz, and $J_{MX} = 13-14$ Hz, which indicates that these substituents adopt a rather rigid preferred conformation. This is in contrast to what is seen for 9-benzylfluorenes, the benzylic hydrogens of which give rise to AX_2 systems with coupling constants $J_{AX} = 7-8$ Hz,[32] indicative of freely rotating benzyl groups. Truxenephane **10** shows $J_{AX} = 10.6$ Hz and $J_{MX} = 14.2$ Hz, while $J_{AM} \approx 0$ Hz, which corresponds to a dihedral angle of about 90° between the truxene benzylic hydrogen and one of the methylene hydrogens.

In order to determine the preferred conformation of derivatives **3**, a more detailed study was carried out on truxene **3h**. The hydrogens of the truxene scaffold are labeled Ht, those of the aryl group Ha, and the geminal methylene hydrogens Hb_1 and Hb_2 (Figure 1a). In the benzyl derivatives **3f**–**u**, the more shielded methylene hydrogen is Hb_2, which couples with Ht_5 with $^3J = 8.3-11.7$ Hz. In the case of **3h**, the side chain benzylic hydrogens show $J(Hb_1,Ht_5) = 4.8$ Hz and $J(Hb_2,Ht_5) = 10.1$ Hz. The higher intensity NOE interactions for **3h** are summarized in Figure 1b. As expected, at a **3h** concentration of about 3 mM, only positive NOEs are seen in the NOESY experiment at room temperature. The more significant result is the absence of any observable NOEs between the benzylic hydrogen Hb_2 and the hydrogens in the vicinity of Hb_1. This result supports the hypothesis that the side chains of truxenes **3g**–**t** adopt an almost rigid conformation.

Interestingly, the ^{1}H NMR chemical shifts in $CDCl_3$ proved to be concentration dependent. The most notable chemical shift changes related to the signals of the hydrogens labeled Ht_1 (truxene aryl) and Ht_5 (truxene benzyl) (see Figure 1a), which showed significant high-field shielding on increasing the concentration. The other aryl and side-chain hydrogens showed less pronounced concentration-dependent shifts.

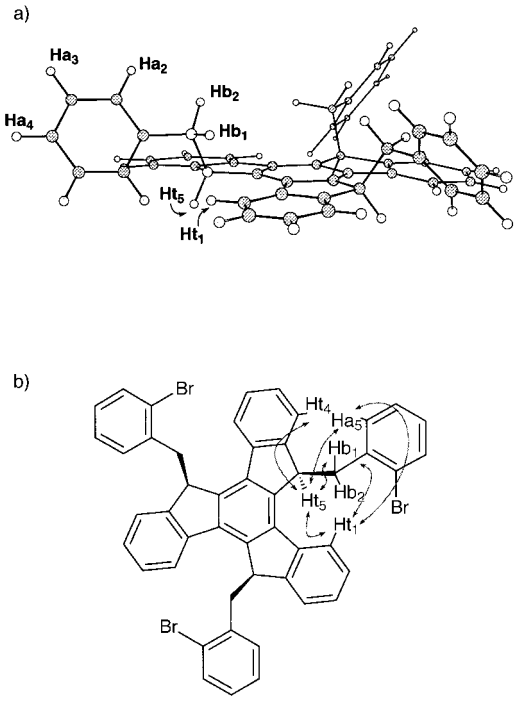


Figure 1. a) Labeling of the hydrogens of 5,10,15-tribenzylated truxenes. b) Selected NOEs for **3h** ($CDCl_3$ solution, 23 °C).

Values of K_{assoc} were determined assuming that the predominant association is due to a monomer–dimer equilibrium (see Table 2).[33, 34] The highest K_{assoc} values were obtained for tribenzyl truxenes **3g**–**t**, while **3a**–**d** and **3f** associate weakly. In fact, **3i** was found to show the highest K_{assoc} value determined for a self-association in nonpolar solution that does not involve hydrogen bonds.[4, 5] A van't Hoff analysis of **3g** led to $\Delta H = -5.9 \pm 0.2$ kcal mol^{-1} and $\Delta S = -8.4 \pm 0.9$ cal mol^{-1} K^{-1}, which indicates that the association is an enthalpy driven process. Association was also observed in [D_6]benzene, although the K_{assoc} values obtained by monitoring the shifts of Ht_1 and Ht_5 were in some cases substantially different, which suggests that a more complex association takes place in this solvent.

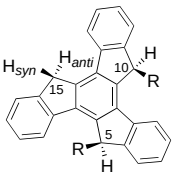
Table 2. Association constants in $CDCl_3$ at 25 °C.[a]

Truxene	K_{assoc} [M^{-1}]	Truxene	K_{assoc} [M^{-1}]
3a	9	**3q**	470
3b	8	**3r**	330
3c	10	**3s**	205
3d	2	**3t**	170
3f	11	**4a**	15
3g	270 (135)	**4b**	100
3h	102 (125)	**5a**	< 2
3i	580 (530)	**5b**	< 2
3j	390	**6a**	110
3k	200	**6b**	50
3l	62	**7**	< 1
3m	180	**8**	< 1
3n	200	**10**	< 1
3o	85	**11**	90
3p	90		

[a] Values in parentheses were determined in [D_6]benzene.

The association behavior of mono- and dibenzylated derivatives **4**–**6** was most revealing. Thus, while **4a**, **4b**, **6a**, and **6b** self-associate in $CDCl_3$ solution, no association was observed for *anti*-dibenzylated derivatives **5a** and **5b** (Table 2). The largest upfield shifts (0.9–1.1 ppm) were observed for the truxene benzylic hydrogens of **6a** and **6b** that are *anti* to the benzylic chains (Table 3), which show similar shifts to those observed for the related *syn*-tribenzylated derivatives **2p** and **2q**. The *syn* H15 also showed significant shieldings (of the order of 0.5 ppm).

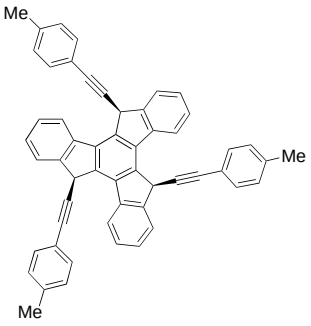
Table 3. $\Delta\delta$ for truxene benzylic hydrogens of **6a** and **6b** ($CDCl_3$ at 25 °C).



	$\Delta\delta$	
	6a[a]	**6b**[b]
H-5	1.05	0.91
H-10	1.07	0.93
H-15*syn*	0.55	0.47
H-15*anti*[c]	1.07	0.87

[a] 0.34–43.1 mM; [b] 0.44–55.9 mM; [c] as references, shifts of δ 1.13 (0.37–47.3 mM) and 1.15 (0.09–23.3 mM) were observed for **2p** and **2q**, respectively.

The *anti* isomers **2** do not associate in $CDCl_3$. Interestingly, the ^{1}H NMR spectrum of **10** in $CDCl_3$ does not change with concentration ($0.6-35\times10^{-3}$ M), which indicates that the association observed for derivatives **3**, **4**, and **6** in solution is not a result of a simple truxene–truxene interaction. Similarly, derivatives **7** and **8** do not show a concentration dependence of their ^{1}H NMR spectra, which implies that an interaction of their side chains is not sufficient for association. On the other hand, derivative **11**[21] with rigid arylethynyl side chains at C-5, C-10, and C-15 shows a moderate degree of association in solution (Table 2).



11

In terms of chemical shift variations, a similar behavior to that observed on increasing the concentration was observed in the case of **3i** upon lowering the temperature, both in $CDCl_3$ and CD_2Cl_2 solution. In fact, the resonance of Ht_1 was shifted upfield by about 1 ppm when the solution was cooled from +30 to −90 °C. The other aryl hydrogens of the core showed smaller changes, although they showed a notable linewidth increase on cooling below −20 °C. The aryl hydrogens of the *meta*-bromophenyl moiety were found to behave differently. Indeed, these hydrogens did not show chemical shift changes, and their signals were only broadened at much lower temperatures, starting at −60 °C. Regarding the aliphatic hydrogens, the chemical shift of the most downfield methylene hydrogen resonance (Hb_1) did not vary much with temperature, while the other methylene hydrogen resonances (Hb_2) and that of Ht_5 were shifted upfield (by about 0.4 and 0.9 ppm, respectively). These data indicate that in the associated state these aliphatic hydrogens, as well as Ht_1 of the truxene scaffold, are affected by the ring currents of some of the aromatic moieties. This behavior parallels that observed for **3i** upon increasing the concentration.

NOESY experiments were also performed on **3i** in both [D_6]benzene and $CDCl_3$ solutions at low and higher concentrations and at low temperatures. In contrast to the experiment performed on a 3 mM solution of **3i**, which showed only a positive NOE as expected for the molecular weight of this molecule, NOESY cross-peaks observed for a 20 mM solution were negative, indicating the existence of relatively long H/H correlation times (longer than 300 ps), which is rather unusual for a molecule of this size. This fact is indicative of the presence of species other than the discrete monomer in a solution of this concentration. A similar effect was observed in [D_6]benzene solution. Moreover, the small and large coupling constants for the benzylic hydrogens Hb_1 and Hb_2, respectively, were shown to be independent of the concentration. The observation of cross-peaks between the methylene hydrogens Hb_1 and Hb_2 and both *ortho* hydrogens is indicative of rotation about the CH_2–Ar linkage in both the 3 mM and 20 mM solutions. However, besides the trivial cross-peaks, new NOESY cross-peaks appeared upon increasing the concentration (20 mM) or on lowering the temperature to 0 °C. These peaks were assigned to Ht_3/Ha_2, Ht_3/Hb_2, Ht_1/Hb_2, Ht_3/Ht_5, Ht_2/Hb_1, and Ht_6/Ht_5. Additionally, a symmetry-related Ha_5/Ha_5 cross-peak was also observable in the ^{13}C-decoupled HSQC-NOESY spectrum. Thus, the presence of species higher than monomeric was unequivocally demonstrated.

The presence of oligomeric species was tested for by carrying out NMR diffusion measurements in order to estimate the average molecular weight. In order to compare the measured diffusion coefficients at different concentrations, compounds **7** and **10**, which do not associate in $CDCl_3$ solution (Table 2), were also tested as model compounds. Indeed, the diffusion coefficients (D) of these molecules hardly varied with concentration (1–10 mM). For **7**, D was calculated to be $5.1\pm0.1\times10^{-6}$ cm^{2}s^{-1}, while the value for **10** was $6.3\pm0.1\times10^{-6}$ cm^{2}s^{-1}. On the other hand, with both **3h** and **3i**, notable variations in D were observed with increasing concentration. Specifically, D for **3h** increased monotonically from 4.6×10^{-6} to 5.1×10^{-6} cm^{2}s^{-1}, while that for **3i** increased from 4.7×10^{-6} to 5.2×10^{-6} cm^{2}s^{-1} when the concentration was decreased from 20 to 1 mM. These values, when compared to those of **7** and **10**, qualitatively illustrate that **3h** and **3i** show some dimeric nature, especially at the higher concentrations in $CDCl_3$ solution. Although, in principle, the

  0947-6539/02/0813-2882 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 13

presence of higher oligomers cannot be ruled out by this method, the values of the diffusion coefficients indicate that the average molecular weight is close to that expected for a dimer and hence that the concentration of trimers or higher oligomers must be small in this concentration range.

Molecular mechanics calculations: MM2* calculations on the association of **3i** were performed for both the unsolvated system and with the GB/SA solvent model for chloroform. To simplify the calculations, pairs of enantiomers of **3i** were considered in each case. Twenty different geometries of a putative dimer were built and submitted to energy minimizations under both dielectric conditions. Some of the more stable conformers of **3i** are depicted in Figure 2. In the most stable association (model A, Figure 2) [MM2* relative energy (GB/SA solvation model for chloroform) 0 kcal mol^{-1}], the side chains of the two molecules are facing each other, and the aromatic cores are mutually disposed in an almost parallel arrangement. The cores are about 6 Å apart, while the shortest distance between one side chain and the core of the second molecule is about 4 Å. Notably, the distance between the centroids of two benzene rings interacting in a T-shaped arrangement through van der Waals forces is around 4.90 Å.[35, 36] A second, less stable association model (B) shows the truxene cores interacting with each other, with the side chains pointing out of the cluster towards the solvent. The energy difference between the two forms amounts to just 2.5 kcal mol^{-1} (in vacuo) and 1.5 kcal mol^{-1} (solvent). Since the molecular mechanics energy values should only be considered as approximate, both forms could, in principle, be involved in the association process.

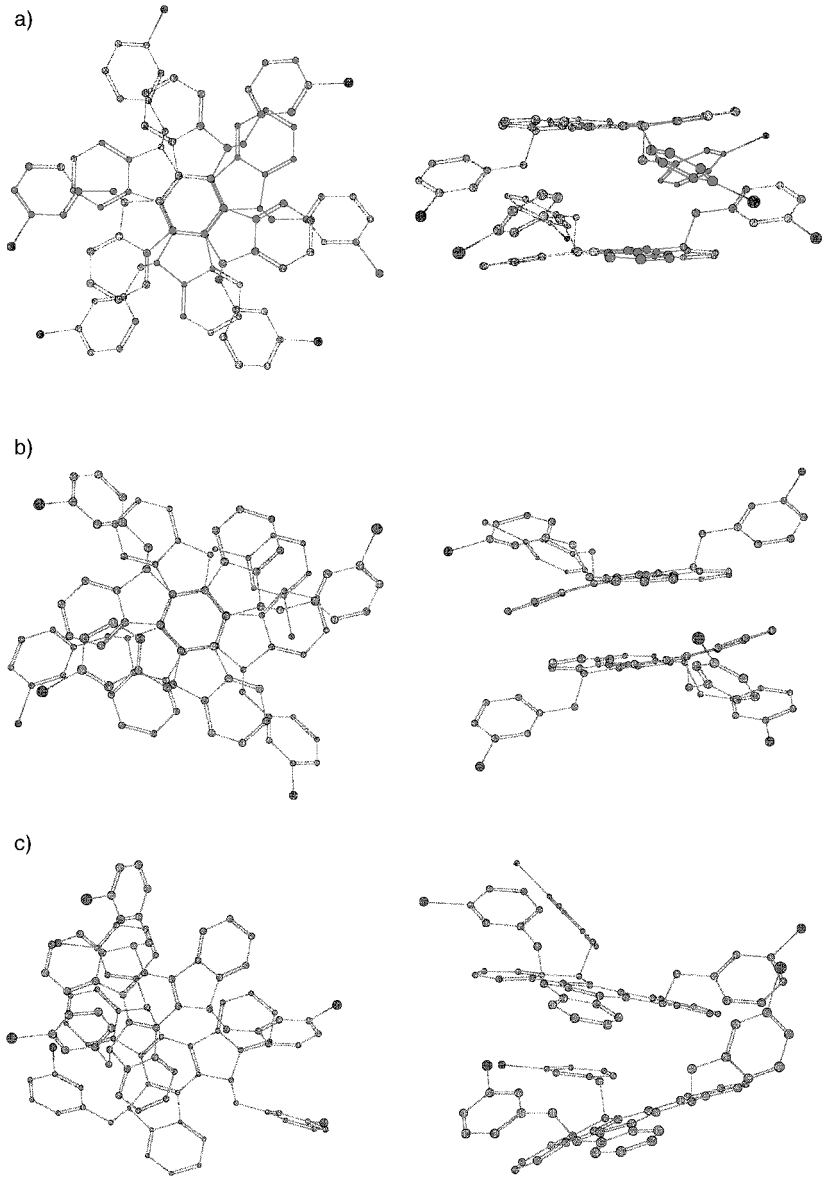
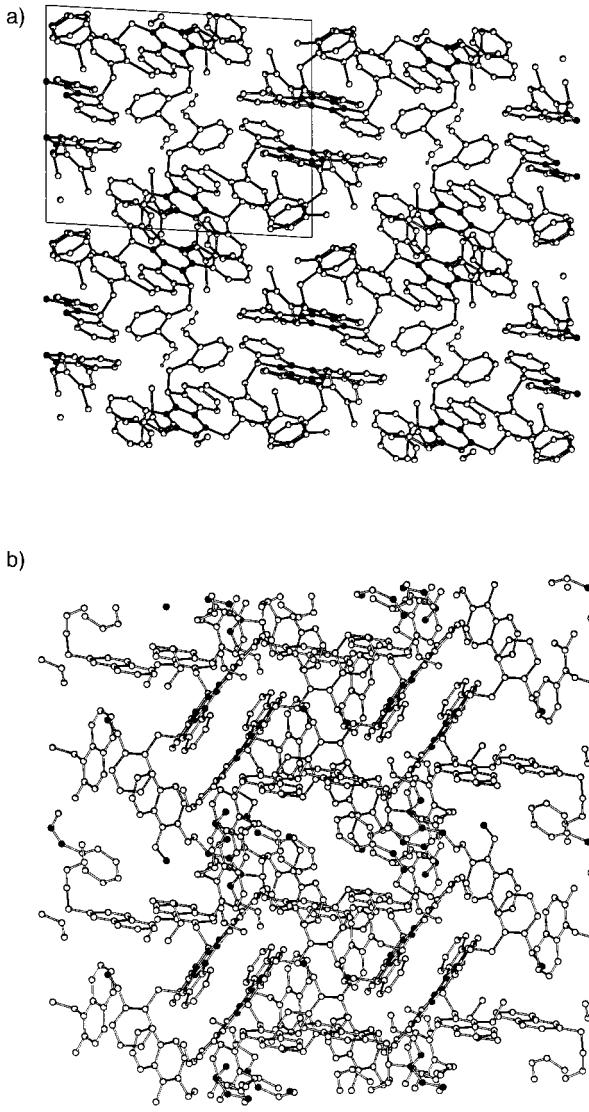


Figure 2. Two different perspectives of one of the possible self-association modes of compound **3i**. a) The side chains of the two molecules are facing each other, and the cores are mutually disposed in a quasi-parallel manner. b) The aromatic cores are facing each other, and the side chains are pointing outwards into the solvent in an non-symmetric manner. c) The side chains of the two molecules are facing each other in a non-symmetric manner.

There is a third form (C, Figure 2), in which the side chains of one molecule are interacting with the core of the second molecule. However, this alternative dimer is destabilized by more than 6 kcal mol^{-1} in chloroform and by more than 10 kcal mol^{-1} in vacuo.

Packing in the solid state: In the solid state, *syn*-tribenzylated truxenes **3h**[37] and **3u** pack with a staggered face-to-face arrangement of their truxene moieties (interplanar distance 3.6–3.7 Å) (Figure 3). Truxenephane **10** shows a similar packing, the truxene moieties facing each other with a distance between their centroids of 3.70 Å.[20] The crystal data and structures for **3h**, **3u**, and **10** are summarized in Table 4 and Figure 4. Interestingly, the face-to-face interaction occurs between pairs of enantiomers.

Association model: Upon increasing the concentration or lowering the temperature, the largest shieldings for **3** are observed on hydrogens Ht_1 and Ht_5, which demonstrates that the truxene scaffold is involved in the association. This type of association (model B, Figure 2) is supported by the observation of a greater upfield shift of the truxene methylene hydrogen resonances *anti* to the benzylic chains in **6a**,**b**.



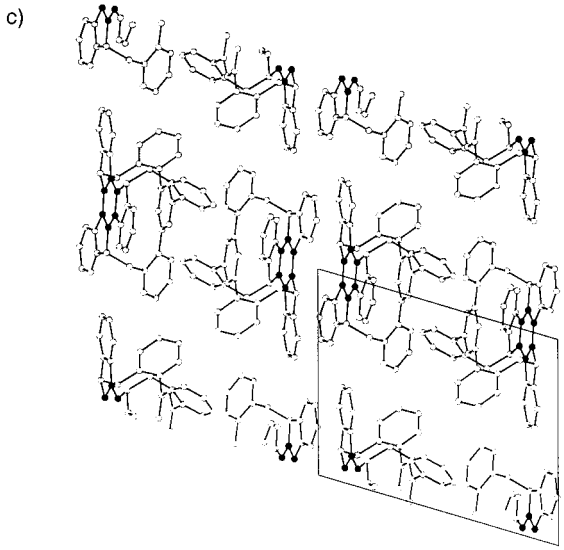


Figure 3. a) Crystallographic packing of **3h** along the (1,0,0) direction. b) Crystallographic packing of **3u** along the (1,0,0) direction. c) Crystallographic packing of **10** along the (1,0,0) direction.

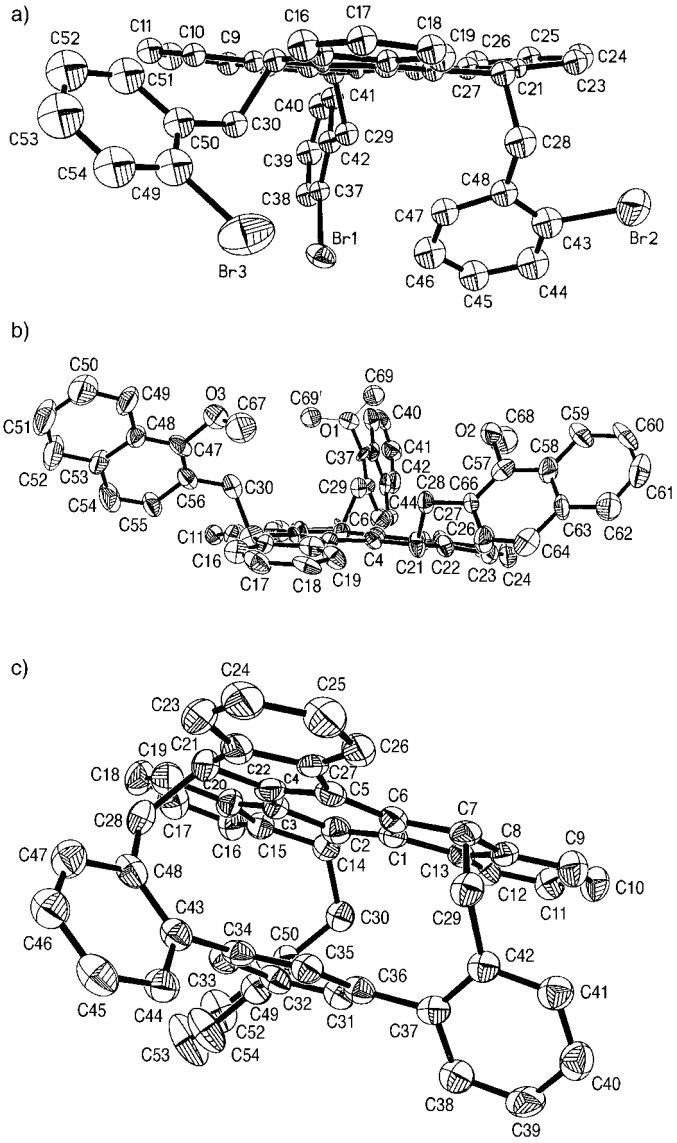


Figure 4. ORTEP diagrams for a) **3h**, b) **3u**, and c) **10**.

However, cyclophane **10**, with a free truxene face, does not self-associate in $CDCl_3$, which indicates that truxene–truxene interactions alone are not sufficient for binding. Indeed, the lower association constants of **3a–d** and **3f** as compared with those displayed by **3g–t** (Table 2) highlight the important role played by the benzyl side chains of these *syn*-trisubstituted derivatives. Moreover, the fact that the Hb_1 of **3i** show significant shieldings indicates that the benzyl side chains are also involved in the association, presumably through an interlocking of the side chains of the two molecules (model A, Figure 2). This type of association is supported by the observation of a significant shielding of *syn*-H15 of **6a**, **b** with increasing concentration. However, the lack of association observed with **7** indicates that side chain–side chain interactions alone are insufficient to warrant self-association in molecules of this type.

All the above data, taken together, indicate that the relatively strong association shown by **3g–t** in solution is a consequence of both truxene–truxene and benzyl–benzyl interactions. Although NOESY experiments favor benzyl–

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benzyl interactions (model A, Figure 2), the participation of truxene–truxene interactions (model B) cannot be neglected, since this form is basically invisible to NOE analysis. Interestingly, in the solid state, **3h**, **3u**, and **10** stack by an interlocking of their side chains and a face-to-face arrangement of their truxene scaffolds. However, it is important to note that in solution the behavior is probably more complex, since, in addition to interactions between pairs of enantiomers, self-association between pairs of truxenes of the same chirality might also be feasible.

Although interpretation of the effect of substituents on the association is complex, it is interesting to note that *meta*-substituted derivatives **3i** and **3q** show the highest association constants. The pentafluorophenylmethyl derivative **3t** shows a lower association constant than the parent benzyl derivative **3g** (Table 2).

Conclusion

A variety of *syn*-trialkylated truxenes **3** can be readily synthesized in gram amounts from **1** by alkylation reactions followed by base-catalyzed isomerization. Palladium-catalyzed cross-coupling reactions permit the introduction of alkenyl or alkynyl side chains without any isomerization to the *anti* isomers.

Some of the *syn*-trialkylated truxenes **3** self-associate strongly in solution. In particular, relatively strong associations have been found for the benzyl derivatives. ^{1}H NMR experiments and molecular mechanics calculations indicate that these derivatives associate in solution through both interlocking of their side chains and face-to-face interactions of the truxene scaffolds.

Experimental Section

General: NMR spectra were recorded at 23 °C, unless otherwise stated. All ^{13}C spectra were proton-decoupled. Only the most significant MS fragmentations are given. R_f values were determined by TLC on aluminium-backed sheets coated with 0.2 mm GF_{254} silica gel. Elemental analyses were performed at the SIdI (UAM). Solvents were purified and dried using standard procedures. Chromatographic purifications were carried out on flash grade silica gel using distilled solvents. Trituration means stirring with the stated solvent, filtering off, and washing with the same solvent. Saturated aqueous NH_4Cl solution was buffered by the addition of NH_4OH (final pH 8). All reactions were carried out under Ar.

Synthesis of alkylated truxenes: 10,15-Dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (truxene, **1**) was prepared by the trimerization of indanone according to the known method.[6]

Alkylation of truxene (1) (General procedure)

a) *anti*-Alkylated truxenes: A mixture of **1** (1.5 mmol) and NaH (3.1 equiv, 60% in mineral oil) in DMF (25 mL) was sonicated for 45 min at 4 °C to give a bright-red mixture. On addition of a solution of the alkylating agent (3.5 equiv) in DMF (10 mL), the red color faded almost immediately. After 10 min, the mixture was diluted with EtOAc, washed with 10% aqueous HCl and saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. The residue was either treated with hexane or purified by flash column chromatography to give *anti*-trialkylated truxenes **2**.

b) *syn*-Alkylated truxenes (3)

Method 1: A mixture of truxene (3 mmol) and KH (3.1 equiv, 35% in mineral oil) in THF (35 mL) was sonicated at 4 °C for about 15–30 min or until an almost transparent bright-red solution had been formed. A solution of the alkylating agent (3.5 equiv) in THF (15 mL) was then added, whereupon the red color faded almost immediately. After 10 min, the mixture was diluted with EtOAc, washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and filtered. The filtrate was concentrated and treated with EtOAc to give the *syn*-trialkylated truxenes **3** as a solid.

Method 2: *n*BuLi (3.1 equiv) was added to a suspension of **1** (1.5 mmol) in THF (50 mL) at −78 °C and the mixture was slowly warmed to −10 °C over a period of 4 h. A solution of the alkylating agent (3.5 equiv) in THF (10 mL) was then added to the red solution. After 30 min, the mixture was diluted with EtOAc, washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. The residue was treated with hexane affording a 3:1 *anti*/*syn* mixture of trialkylated truxenes as a pale-yellow solid. The crude solid was then heated under reflux with KO*t*Bu (1 equiv) in *t*BuOH (30 mL) for 12 h. After cooling, the solvent was partially evaporated, the concentrated solution was filtered, and the filtrate was concentrated to dryness. The residue was treated with hexane to give **3**. Further recrystallization from ethanol or toluene yielded pure compounds.

Method 3: As Method 2, with the exceptions that 2 mol equiv *n*BuLi (0.96 mmol) were used, that the mixture was slowly warmed to −20 °C for 3 h, and that 2.4 mol equiv alkylating agent were used. Extractive work-up and chromatography gave a mixture of mono-, di-, and trialkylated derivatives, which was separated by column chromatography.

***anti*-5,10,15-Tris(2-bromophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (2h)**: 60–66% (Method 2). Pale-yellow solid: m.p. 204–205 °C; R_f = 0.23 (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, J = 7.0 Hz, 1H), 8.38 (d, J = 6.9 Hz, 1H), 8.24 (d, J = 6.9 Hz, 1H), 7.58 (dd, J = 7.7, 1.4 Hz, 2H), 7.52 (dd, J = 7.7, 1.6 Hz, 1H), 7.48–7.37 (m, 3H), 7.21 (tt, J = 7.4, 1.6 Hz, 2H), 7.15–7.02 (m, 9H), 6.92 (dd, J = 7.3, 2.0 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 5.17 (dd, J = 10.6, 4.9 Hz, 1H), 5.11 (dd, J = 10.4, 5.1 Hz, 1H), 5.10 (dd, J = 9.4, 4.9 Hz, 1H), 4.11 (dd, J = 14.0, 5.0 Hz, 1H), 4.10 (dd, J = 14.2, 4.8 Hz, 1H), 3.98 (dd, J = 14.3, 5.2 Hz, 1H), 2.88 (dd, J = 10.4, 9.6 Hz, 1H), 2.67 (dd, J = 14.3, 10.4 Hz, 1H), 2.47 (dd, J = 14.3, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.69, 146.61, 146.47, 141.43, 140.53, 140.39, 140.19, 139.83, 139.69, 139.14 (2C), 138.60, 136.93, 136.76, 136.68, 132.83 (2C), 132.73, 132.02, 132.00, 131.81, 128.08 (2C), 127.24, 127.11, 126.83, 126.02, 125.89, 125.81, 125.69, 125.54 (2C), 125.39, 125.29, 125.20, 122.96, 122.88, 122.59, 46.70, 46.35, 46.26, 38.93, 38.88, 38.80 (four carbons are not observed); EI-MS: m/z (%): 848, 846 (7) $[M]^+$, 679 (70), 599 (11), 508 (22), 429 (20), 339 (100); elemental analysis calcd for $C_{48}H_{33}Br_3$: C 68.08, H 3.93; found C 68.09, H 4.17.

***anti*-5,10,15-Tris(3-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (2q)**: Pale-yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.05 (d, J = 7.7 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.56–7.46 (m, 3H), 7.40 (td, J = 1.6, 7.7 Hz, 1H), 7.38–7.23 (m, 6H), 7.21–7.05 (m, 7H), 7.02 (t, J = 7.9 Hz, 1H), 6.98 (td, J = 1.6, 7.7 Hz, 1H), 6.92 (t, J = 1.6 Hz, 1H), 6.81 (td, J = 1.6, 8.1 Hz, 1H), 4.94 (dd, J = 3.6, 6.9 Hz, 1H), 4.88 (dd, J = 4.0, 8.7 Hz, 1H), 4.78 (dd, J = 3.6, 7.7 Hz, 1H), 3.77 (dd, J = 3.6, 13.8 Hz, 1H), 3.69 (dd, J = 4.0, 13.8 Hz, 1H), 3.09 (dd, J = 7.7, 13.7 Hz, 1H), 3.54 (dd, J = 3.6, 13.7 Hz, 1H), 3.02 (dd, J = 8.1, 13.7 Hz, 1H), 2.74 (dd, J = 8.9, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.64 (2C), 146.59, 140.00, 139.89, 139.78, 139.72, 139.42, 139.17, 139.00, 138.92, 136.96, 136.88, 134.09, 133.67, 132.81, 130.07, 129.91, 128.54, 128.40, 128.23, 127.82, 126.78, 126.70, 125.22, 125.17, 122.71, 122.52, 122.43, 118.78, 118.72 (2C), 111.78, 111.58, 111.42, 47.49, 47.38, 47.24, 38.21, 37.48 (2C).

***anti*-5,10,15-Tris(4-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (2r)**: Pale-yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (d, J = 7.7 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.43–7.54 (m, 5H), 7.38–7.18 (m, 9H), 7.04 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 8.3 Hz, 2H), 6.70 (d, J = 8.3 Hz, 2H), 4.98 (dd, J = 3.9 Hz, 7.1, 1H), 4.87 (dd, J = 4.6, 9.2 Hz, 1H), 4.82 (dd, J = 3.8, 7.6 Hz, 1H), 3.75 (dd, J = 3.8, 7.2 Hz, 1H), 3.71 (dd, J = 4.0, 7.7 Hz, 1H), 3.53 (dd, J = 3.7, 13.9 Hz, 1H), 3.18 (dd, J = 7.5, 8.9 Hz, 1H), 3.14 (dd, J = 7.8, 8.4 Hz, 1H), 2.45 (dd, J = 9.3, 14.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.66, 146.44, 144.68, 144.35, 143.65, 140.33, 140.17, 139.41, 138.99, 136.60, 135.79, 135.70, 135.09, 131.72, 131.07, 129.99, 129.85, 127.34, 126.86, 126.58, 126.17,

126.03, 125.52, 125.11, 124.71, 122.46, 122.40, 122.18, 118.92, 118.75, 110.13, 109.80, 46.80, 46.49, 38.32, 37.98, 36.06.

***syn*-5,10,15-Trimethyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3a)**: 79% (Method 2); pale-yellow solid; m.p. 228 °C (decomp); $R_f = 0.37$ (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 41.6 mM): $\delta = 7.95$ (d, $J = 7.5$ Hz, 3H), 7.61 (d, $J = 7.3$ Hz, 3H), 7.46 (td, $J = 7.3$, 1.0 Hz, 3H), 7.38 (td, $J = 7.3$, 1.0 Hz, 3H), 4.39 (q, $J = 7.1$ Hz, 3H), 1.69 (d, $J = 7.2$ Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 41.6 mM): $\delta = 150.37$, 142.59, 139.66, 135.73, 126.89, 126.39, 124.07, 122.75, 41.97, 18.77; HR-MS: *m*/*z*: calcd for $C_{30}H_{24}$: 384.18780; found: 384.18872.

***syn*-5,10,15-Triethyl-10,15-dihydro-5*H*-diindeno[1,2-a;1′,2′-*c*]fluorene (3b)**: 24% (Method 1); 76% (Method 2); pale-yellow solid; m.p. 229–230 °C; $R_f = 0.30$ (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 88 mM): $\delta = 7.80$ (d, $J = 7.5$ Hz, 3H), 7.58 (d, $J = 7.2$ Hz, 3H), 7.45 (td, $J = 7.5$, 1.1 Hz, 3H), 7.36 (td, $J = 7.4$, 1.0 Hz, 3H), 4.19 (dd, $J = 6.5$, 3.4 Hz, 3H), 2.33–2.23 (m, 3H), 2.17–2.03 (m, 3H), 0.55 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 88 mM): $\delta = 148.36$, 141.03, 140.74, 136.12, 126.75, 126.03, 124.41, 122.50, 47.49, 24.85, 9.17; EI-MS: *m*/*z* (%): 426 (45) $[M]^+$, 397 (100), 369 (27), 339 (57); HR-MS: *m*/*z*: calcd for $C_{48}H_{36}$: 426.23475; found: 426.23520.

***syn*-5,10,15-Tris(1-prop-2-enyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (3c)**: 21% (Method 1); 73% (Method 2); pale-yellow solid; m.p. 200–201 °C; $R_f = 0.33$ (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 110 mM): $\delta = 7.66$ (d, $J = 7.3$ Hz, 3H), 7.56 (d, $J = 7.2$ Hz, 3H), 7.46 (td, $J = 7.4$, 2.5 Hz, 3H), 7.36 (td, $J = 7.4$, 1.4 Hz, 3H), 5.62–5.41 (m, 3H), 4.80–4.76 (m, 6H), 4.17 (dd, $J = 9.1$, 3.9 Hz, 3H), 3.20–3.01 (m, 3H), 2.61–2.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 110 mM): $\delta = 148.09$, 140.44, 140.39, 135.84, 134.85, 126.92, 126.05, 124.86, 122.54, 116.88, 46.09, 36.42; EI-MS: *m*/*z* (%): 462 (18) $[M]^+$, 421 (100), 380 (34), 339 (93); elemental analysis calcd for $C_{36}H_{30}$: C 93.46, H 6.54; found: C 93.29, H 6.79.

***syn*-5,10,15-Tris(trimethylsilyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (3d)**: 43% (Method 1); white solid; m.p. 287 °C (decomp); $R_f = 0.32$ (hexane/EtOAc 100:1); ^{1}H NMR (200 MHz, $CDCl_3$, 110 mM): $\delta = 7.97$ (d, $J = 7.4$ Hz, 3H), 7.59 (d, $J = 7.2$ Hz, 3H), 7.41 (t, $J = 7.3$ Hz, 3H), 7.32 (t, $J = 7.3$ Hz, 3H), 4.47 (s, 3H), −0.08 (s, 27H); ^{13}C NMR (50 MHz, $CDCl_3$, 110 mM): $\delta = 147.0$, 140.7, 140.5, 133.1, 124.8, 124.4, 123.5, 122.9, 43.2, −1.4; EI-MS: *m*/*z* (%): 558 (52) $[M]^+$, 485 (20), 382 (58), 339 (18); elemental analysis calcd for $C_{36}H_{42}Si_3$: C 77.38, H 7.58; found: C 77.29, H 7.87.

***syn*-5,10,15-Tricyclohexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3e)**: 33% (Method 2; after trituration of the crude residue with hexane); white solid; m.p. > 300 °C; $R_f = 0.40$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 6.8 mM): $\delta = 7.81$ (d, $J = 7.6$ Hz, 3H), 7.63 (d, $J = 7.4$ Hz, 3H), 7.45 (dd, $J = 7.3$, 7.1 Hz, 3H), 7.32 (ddd, $J = 7.6$, 7.5, 0.8 Hz, 3H), 4.36 (d, $J = 2.3$ Hz, 3H), 2.46 (ddd, $J = 12.4$, 11.9, 2.7 Hz, 3H), 2.25 (br d, $J = 11.6$ Hz, 3H), 1.87–1.79 (m, 6H), 1.51 (dd, $J = 16.2$, 3.3 Hz, 3H), 1.40–1.30 (m, 6H), 0.98 (qt, $J = 13.1$, 3.4 Hz, 3H), 0.80 (qt, $J = 13.0$, 3.5 Hz, 3H), 0.63 (br d, $J = 12.7$ Hz, 3H), 0.32 (qd, $J = 12.6$, 3.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 6.8 mM): $\delta = 146.55$, 141.79, 141.31, 135.87, 126.81, 125.54 (2C), 122.15, 52.77, 40.44, 33.35, 27.20, 26.44, 26.18, 25.71; EI-MS: *m*/*z* (%): 588 (46) $[M]^+$, 422 (28), 339 (93).

***syn*-5,10,15-Tris(2-phenylethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3f)**: 67% (Method 2); white solid; m.p. > 300 °C; $R_f = 0.35$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 61.0 mM): $\delta = 7.69–7.66$ (m, 3H), 7.63–7.59 (m, 3H), 7.45–7.39 (m, 6H), 7.21–7.08 (m, 9H), 6.98 (dd, $J = 8.1$, 1.6 Hz, 6H), 4.16 (dd, $J = 7.3$, 3.1 Hz, 3H), 2.59–2.44 (m, 3H), 2.41–2.31 (m, 6H), 2.23–2.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 61.0 mM): $\delta = 148.22$, 142.01, 140.95, 140.61, 135.86, 128.53, 128.45, 128.20, 128.13, 127.00, 126.22, 125.69, 124.57, 122.79, 46.21, 34.35, 31.73; EI-MS: *m*/*z*: 654 (63) $[M]^+$, 549 (100), 445 (23), 339 (55); HR-MS: *m*/*z*: calcd for $C_{51}H_{42}$: 654.32865; found: 654.32855.

***syn*-5,10,15-Tris(phenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3g)**: 69% (Method 2); beige solid; m.p. > 300 °C (softens at 205 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 32.6 mM): $\delta = 7.65$ (d, $J = 7.6$ Hz, 3H), 7.49–7.44 (m, 3H), 7.28–7.22 (m, 3H), 7.21–7.16 (m, 9H), 6.87–6.84 (m, 6H), 6.68 (d, $J = 7.4$ Hz, 3H), 3.72 (dd, $J = 10.2$, 3.5 Hz, 3H), 3.54 (dd, $J = 14.0$, 3.5 Hz, 3H), 2.21 (dd, $J = 14.0$, 10.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 32.6 mM): $\delta = 147.78$, 140.70, 140.14, 139.27, 135.15, 129.36, 127.79, 126.82, 126.05, 125.61, 125.46, 122.82, 47.14, 38.29; EI-MS: *m*/*z* (%): 612 (17) $[M]^+$, 521 (100), 431 (41), 339 (99), 91 (15); HR-MS: *m*/*z*: calcd for $C_{48}H_{36}$: 612.28170; found: 612.28009.

***syn*-5,10,15-Tris(2-bromophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3h)**: 32% (Method 2), obtained along with the *anti* isomer (35%); 68% (Method 2); Pale-yellow solid; m.p. 230–231 °C; $R_f = 0.23$ (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 21 mM): $\delta = 7.80$ (d, $J = 7.6$ Hz, 3H), 7.49 (dd, $J = 7.8$, 1.4 Hz, 3H), 7.40 (td, $J = 7.5$, 0.6 Hz, 3H), 7.17 (td, $J = 7.6$, 0.9 Hz, 3H), 7.14 (td, $J = 7.4$, 1.5 Hz, 3H), 7.04 (ddd, $J = 7.7$, 7.5, 1.8 Hz, 3H), 6.82 (dd, $J = 7.5$, 1.8 Hz, 3H), 6.61 (d, $J = 7.4$ Hz, 3H), 4.08 (dd, $J = 10.1$, 4.8 Hz, 3H), 3.65 (dd, $J = 14.3$, 4.9 Hz, 3H), 2.62 (dd, $J = 14.3$, 10.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 21 mM): $\delta = 146.86$, 140.61, 140.00, 138.94, 135.70, 132.61, 131.58, 127.84, 126.97, 126.81, 125.72, 125.49, 125.34, 122.80, 45.85, 38.56; EI-MS: *m*/*z* (%): 849 (3) $[M]^+$, 679 (70), 599 (12), 508 (16), 429 (18), 339 (100); elemental analysis calcd for $C_{48}H_{33}Br_3$: C 68.08, H 3.93; found: C 67.73, H 4.15.

***syn*-5,10,15-Tris(3-bromophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3i)**: 75% (Method 2); slightly brown solid; m.p. 225 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (t, $J = 7.3$ Hz, 3H), 7.46 (d, $J = 7.6$ Hz, 3H), 7.38 (t, $J = 7.3$, 1.2 Hz, 3H), 7.27 (d, $J = 7.6$ Hz, 3H), 7.02–6.96 (m, 6H), 6.62 (d, $J = 6.5$ Hz, 6H), 3.32 (br d, $J = 12.3$ Hz, 3H), 3.17 (br d, $J = 8.8$ Hz, 3H), 2.08 (dd, $J = 12.9$, 11.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.60$, 141.64, 140.35, 139.96, 135.03, 132.10, 129.37, 128.22, 127.11, 126.27, 125.77, 123.04, 122.00, 46.71, 37.98; EI-MS: *m*/*z* (%): 849 (2) $[M]^+$, 679 (59), 599 (4), 508 (17), 429 (1), 339 (100); HR-MS: *m*/*z*: calcd for $C_{48}H_{33}{}^{81}Br_2{}^{79}Br$: 850.00914; found: 850.01105.

***syn*-5,10,15-Tris(4-bromophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3j)**: 61% (Method 2); pale-yellow solid; m.p. 246–247 °C; $R_f = 0.23$ (hexanes/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 17.7 mM): $\delta = 7.54$ (d, $J = 7.6$ Hz, 3H), 7.46 (t, $J = 7.3$ Hz, 3H), 7.29 (t, $J = 7.5$ Hz, 3H), 7.24–7.19 (m, 6H), 6.81 (d, $J = 7.4$ Hz, 3H), 6.59–6.55 (m, 6H), 3.70 (dd, $J = 9.5$, 3.7 Hz, 3H), 3.34 (dd, $J = 13.9$, 3.6 Hz, 3H), 2.25 (dd, $J = 13.9$, 9.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 17.7 mM): $\delta = 147.44$, 140.20, 140.00, 137.71, 135.19, 130.91 (2C), 130.74 (2C), 127.04, 125.94, 125.35, 122.74, 119.97, 46.77, 37.62; EI-MS: *m*/*z* (%): 849 (2) $[M]^+$, 679 (29), 510 (14), 339 (100); elemental analysis calcd for $C_{48}H_{33}Br_3 \cdot 0.5\,C_7H_8$: C 69.07, H 4.16; found: C 69.27, H 4.44.

***syn*-5,10,15-Tris(4-methoxyphenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3k)**: 58% (Method 1); pale-yellow solid; m.p. 198–200 °C (softens at 110 °C); ^{1}H NMR (300 MHz, 34 mM, $CDCl_3$): $\delta = 7.61$ (d, $J = 7.6$ Hz, 3H), 7.45 (t, $J = 7.4$, 3H), 7.26–7.21 (m, 3H), 6.76–6.69 (m, 15H), 3.76 (s, 9H), 3.64 (dd, $J = 10.0$, 3.2 Hz, 3H), 3.45 (dd, $J = 13.9$, 3.5 Hz, 3H), 2.14 (dd, $J = 14.0$, 10.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 157.85$, 147.95, 140.70, 140.11, 134.89, 131.44, 130.15, 126.64, 125.47, 122.88, 113.14, 55.16, 47.19, 37.37; EI-MS: *m*/*z* (%): 702 (9) $[M]^+$, 581 (100), 460 (30), 339 (83), 121 (34); HR-MS: *m*/*z*: calcd for $C_{51}H_{42}O_3$: 702.31340; found: 702.31576.

***syn*-5,10,15-Tris(2-bromo-5-methoxyphenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3l)**: 30% (Method 1); white solid; m.p. 138–139 °C; $R_f = 0.23$ (hexane/EtOAc 100:1); ^{1}H NMR (300 MHz, $CDCl_3$, 21 mM): $\delta = 7.94–7.88$ (m, 3H), 7.43 (t, $J = 7.4$ Hz, 3H), 7.37 (d, $J = 8.8$ Hz, 3H), 7.20 (t, $J = 7.5$ Hz, 3H), 6.74 (br d, $J = 7.5$ Hz, 3H), 6.62 (dd, $J = 8.8$, 3.0 Hz, 3H), 6.61 (br s, 3H), 4.21–4.12 (m, 3H), 3.72–3.62 (m, 3H), 3.65 (s, 9H), 2.70–2.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 21 mM): $\delta = 158.29$, 146.64, 140.60, 139.97, 139.75, 135.94, 133.00, 127.05, 125.91, 125.69, 122.79, 117.41, 115.82, 113.56, 55.36, 46.02, 38.82; EI-MS: *m*/*z* (%): 940, 938 (12) $[M]^+$, 739 (80), 659 (14), 540 (20), 459 (21), 339 (100); elemental analysis calcd for $C_{51}H_{39}Br_3O_3$: C 65.20, H 4.18; found: C 65.23, H 4.37.

***syn*-5,10,15-Tris(2-ethenylphenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3m)**: A mixture of **3h** (460 mg, 0.54 mmol), vinyltributylstannane (6.18 mg, 1.94 mmol), $[Pd(PPh_3)_4]$ (60 mg, 0.05 mmol), and 1,4-hydroquinone (ca. 5 mg) in toluene (10 mL) was heated under reflux for 16 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate was concentrated. The residue was treated with hexane to give **3m** (270 mg, 72%) as a pale-yellow solid. M.p. 205–206 °C; $R_f = 0.23$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 38 mM): $\delta = 7.72$ (d, $J = 7.6$ Hz, 3H), 7.44–7.37 (m, 6H), 7.25–7.21 (m, 6H), 7.15 (dd, $J = 7.5$, 7.3 Hz, 3H), 7.11–7.07 (m, 3H), 6.59 (d, $J = 7.4$ Hz, 3H), 6.52 (dd, $J = 17.4$, 11.0 Hz, 3H), 5.38 (dd, $J = 17.4$, 1.5 Hz, 3H), 5.03 (dd, $J = 11.0$, 1.5 Hz, 3H), 3.94 (dd, $J = 10.6$, 4.0 Hz, 3H), 3.58 (dd, $J = 14.4$, 4.1 Hz, 3H), 2.45 (dd, $J = 14.4$, 10.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 6.8 mM): $\delta = 147.36$, 141.11, 139.91, 138.07, 137.04, 135.40, 135.23, 129.87, 127.31, 126.87, 126.45, 126.11, 125.77, 125.58, 122.65, 115.63, 46.98, 35.20; EI-MS:

0947-6539/02/0813-2886 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 13

m/z (%): 690 (15) $[M]^+$, 573 (99), 456 (35), 339 (100); HR-MS: *m/z*: calcd for $C_{54}H_{42}$: 690.32865; found: 690.32739.

***syn*-5,10,15-Tris(2-formylphenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (3n)**: Ozone was bubbled through a solution of **3m** (607 mg, 0.88 mmol) in CH_2Cl_2 (40 mL) at −78 °C. After 5 min, TLC analysis showed that the starting material had been consumed. PPh_3 (691 mg, 2.64 mmol) was then added and the solution was warmed to 23 °C for 1 h. The solvent was subsequently evaporated and the residue was treated with EtOAc to give **3n** as a white solid (600 mg, 98 %). M.p. 235–236 °C; $R_f = 0.28$ (hexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$, 29 mM): $\delta = 9.78$ (s, 3H), 7.71–7.64 (m, 6H), 7.42 (t, $J = 7.5$ Hz, 3H), 7.33 (td, $J = 7.3$, 1.6 Hz, 3H), 7.25–7.16 (m, 6H), 6.82 (d, $J = 7.6$ Hz, 3H), 6.76 (d, $J = 7.4$ Hz, 3H), 3.97 (dd, $J = 8.4$, 4.9 Hz, 3H), 3.67 (dd, $J = 13.8$, 4.9 Hz, 3H), 3.16 (dd, $J = 13.8$, 8.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 29 mM): $\delta = 191.12$, 146.42, 141.20, 139.88, 139.72, 135.45, 134.59, 132.86, 131.45, 129.18, 127.13, 126.61, 125.88, 125.57, 122.65, 46.80, 32.65; EI-MS: *m/z* (%): 696 (13) $[M]^+$, 577 (93), 459 (36), 339 (100); elemental analysis calcd for $C_{51}H_{36}O_3 \cdot 0.3\,H_2O$: C 87.15, H 5.26; found: C 87.06, H 5.59 (the presence of water was confirmed by ^{1}H NMR).

***syn*-5,10,15-Tris[2-(trimethylsilylethynyl)phenylmethyl]-10,15-dihydro-5*H*-diindeno[1,2-a;1′,2′-*c*]fluorene (3o)**: A solution of **3h** (245 mg, 0.29 mmol), (trimethylsilylethynyl)tributylstannane (410 mg, 1.06 mmol), and $[Pd(PPh_3)_4]$ (30 mg, 0.03 mmol) in toluene (6 mL) was heated under reflux for 39 h. The mixture was then filtered through Celite, the filtrate was concentrated, and the residue was purified by chromatography (hexane → hexane/EtOAc 100:1) to give **3o** as a yellow solid (145 mg, 55 %). M.p. 216 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 0.08 mM): $\delta = 7.68$ (d, $J = 7.3$ Hz, 3H), 7.43 (t, $J = 7.5$ Hz, 3H), 7.34 (dd, $J = 7.7$, 1.2 Hz, 3H), 7.21 (t, $J = 7.3$ Hz, 3H), 7.19 (t, $J = 7.5$ Hz, 3H), 7.12 (t, $J = 7.3$ Hz, 3H), 6.99 (d, $J = 7.1$ Hz, 3H), 6.63 (d, $J = 7.7$ Hz, 3H), 3.78 (dd, $J = 9.7$, 4.0 Hz, 3H), 3.64 (dd, $J = 13.7$, 4.0 Hz, 3H), 2.73 (dd, $J = 13.7$, 9.7 Hz, 3H), −0.06 (s, 27H); ^{13}C NMR (50 MHz, $CDCl_3$, 0.08 mM): $\delta = 147.29$, 141.99, 140.97, 139.90, 135.67, 132.23, 128.95, 128.16, 126.70, 125.91, 125.74, 125.57, 123.93, 122.75, 104.30, 97.70, 47.27, 35.93, −0.11; EI-MS: *m/z* (%): 900 (6) $[M]^+$, 713 (100), 526 (28), 339 (85); HR-MS: *m/z*: calcd for $C_{63}H_{60}Si_3$: 900.40026; found: 900.40029.

***syn*-5,10,15-Tris(2-ethynylphenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (3p)**: A mixture of **3o** (850 mg, 0.94 mmol) and K_2CO_3 (130 mg, 0.94 mmol) in THF/MeOH (1:1; 50 mL) was stirred at 23 °C for 12 h. After standard extractive work-up (CH_2Cl_2), the crude residue was treated with hexane to give **3p** (525 mg, 81 %) as a white solid. M.p. 194–195 °C; $R_f = 0.33$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 50 mM): $\delta = 7.70$ (d, $J = 7.7$ Hz, 3H), 7.43–7.41 (m, 3H), 7.36 (t, $J = 7.5$ Hz, 3H), 7.17–7.10 (m, 9H), 6.82–6.79 (m, 3H), 6.70 (d, $J = 7.7$ Hz, 3H), 4.45 (dd, $J = 9.9$, 4.5 Hz, 3H), 3.84 (dd, $J = 14.1$, 4.4 Hz, 3H), 3.05 (s, 3H), 2.80 (dd, $J = 14.1$, 9.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 50 mM): $\delta = 147.28$, 142.15, 141.02, 140.51, 136.11, 133.06, 130.02, 128.44, 126.92, 126.30, 125.79, 125.62, 122.97, 122.68, 83.20, 81.17, 46.64, 36.94; EI-MS: *m/z* (%): 684 (2) $[M]^+$, 569 (15), 462 (12), 421 (91), 339 (100); HR-MS: *m/z*: calcd for $C_{54}H_{36}$: 684.28168; found: 684.28101.

***syn*-5,10,15-Tris(3-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (3q)**: Yellow solid: m.p. 225–226 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 24 mM): $\delta = 7.58$ (t, $J = 7.3$ Hz, 3H), 7.45 (d, $J = 7.3$ Hz, 3H), 7.36–7.43 (m, 6H), 7.18 (t, $J = 8.1$ Hz, 3H), 6.97 (t, $J = 1.0$ Hz, 3H), 6.86 (dt, $J = 1.0$, 8.1 Hz, 3H), 6.70 (d, $J = 7.3$ Hz, 3H), 3.40 (dd, $J = 3.0$, 9.0 Hz, 3H), 3.32 (dd, $J = 3.0$, 13.0 Hz, 3H), 2.31 (dd, $J = 9.0$, 13.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 94 mM): $\delta = 146.97$, 139.95, 139.80, 139.58, 135.09, 133.84, 132.27, 129.93, 128.51, 127.34, 126.50, 125.39, 122.82, 118.75, 111.72, 46.33, 37.57; EI-MS: *m/z* (%): 687 (9) $[M]^+$, 571 (100), 455 (29), 339 (99), 116 (27); HR-MS: *m/z*: calcd for $C_{51}H_{33}N_3$: 687.26745; found: 687.26642.

***syn*-5,10,15-Tris(4-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (3r)**: 67 % (Method 2); pale-yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz, 5.8 mM): $\delta = 7.59$ (d, $J = 7.7$ Hz, 3H), 7.49 (t, $J = 7.5$ Hz, 3H), 7.40 (d, $J = 8.1$ Hz, 6H), 7.30 (t, $J = 7.1$ Hz, 3H), 6.83 (d, $J = 8.5$ Hz, 6H), 6.80 (d, $J = 7.7$ Hz, 3H), 3.89 (dd, $J = 3.4$, 9.2 Hz, 3H), 3.48 (dd, $J = 3.3$, 13.7 Hz, 3H), 2.40 (dd, $J = 9.3$, 13.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, 30 mM): $\delta = 146.90$, 144.07, 139.89, 139.73, 135.44, 131.54, 129.94, 127.49, 126.42, 125.35, 122.70, 118.75, 110.28, 46.65, 38.42; EI-MS: *m/z* (%): 687 (2) $[M]^+$, 571 (75), 470 (10), 456 (47), 369 (22), 356 (5), 354 (12), 339 (100), 116 (28); HR-MS: *m/z*: calcd for $C_{51}H_{33}N_3$: 687.26745; found: 687.26727.

***syn*-5,10,15-Tris(2-bromo-5-fluorophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3s)**: 59 % (Method 2); white solid; m.p. 254–255 °C; $R_f = 0.20$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 6.6 mM): $\delta = 7.56$ (d, $J = 7.7$ Hz, 3H), 7.47 (t, $J = 7.5$ Hz, 3H), 7.41 (d, $J = 8.8$ Hz, 3H; $J(^{19}F,^1H) = 5.5$ Hz), 7.27 (t, $J = 7.4$ Hz, 3H), 6.78 (dd, $J = 8.8$, 3.0 Hz, 3H; $J(^{19}F,^1H) = 9.1$ Hz), 6.64 (d, $J = 7.4$ Hz, 3H), 6.52 (d, $J = 3.0$ Hz, 3H; $J(^{19}F,^1H) = 9.6$ Hz), 3.56 (dd, $J = 10.1$, 4.8 Hz, 3H), 3.43 (dd, $J = 14.4$, 4.8 Hz, 3H), 2.52 (dd, $J = 14.4$, 10.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 6.6 mM): $\delta = 161.37$ (d, $^1J(^{13}C,^{19}F) = 246.3$ Hz), 146.55, 140.91 (d, $^3J(^{13}C,^{19}F) = 6.3$ Hz), 140.25, 139.78, 135.90, 133.65 (d, $^3J(^{13}C,^{19}F) = 6.3$ Hz), 127.23, 126.28, 125.39, 122.76, 119.42, 118.20 (d, $^2J(^{13}C,^{19}F) = 23.1$ Hz), 115.14 (d, $^2J(^{13}C,^{19}F) = 23.1$ Hz), 46.86, 36.01; EI-MS: *m/z* (%): 904, 902 (9) $[M]^+$, 715 (79), 635 (11), 527 (27), 339 (100); elemental analysis calcd for $C_{48}H_{30}Br_3F_3$: C 64.00, H 3.36; found: C 63.44, H 3.34.

***syn*-5,10,15-Tris(2,3,4,5,6-pentafluorophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3t)**: 59 % (Method 2); pale-yellow solid; m.p. > 300 °C; $R_f = 0.21$ (hexane/EtOAc 100:1); ^{1}H NMR ($CDCl_3$, 300 MHz, 27.2 mM): $\delta = 7.79$ (d, $J = 8.1$ Hz, 3H), 7.50 (t, $J = 7.5$ Hz, 3H), 7.26 (t, $J = 7.4$ Hz, 3H), 6.64 (d, $J = 7.3$ Hz, 3H), 3.79 (dd, $J = 10.7$, 4.2 Hz, 3H), 3.51 (dd, $J = 13.5$, 4.2 Hz, 3H), 2.49 (dd, $J = 13.5$, 10.7, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, 27.2 mM) (significant signals only): $\delta = 145.94$, 139.60, 139.41, 135.99, 127.82, 126.55, 124.58, 122.71, 45.13, 26.62; EI-MS: *m/z* (%): 882 (10) $[M]^+$, 701 (88), 520 (31), 339 (100), 181 (17); HR-MS: *m/z*: calcd for $C_{48}H_{21}F_{15}$: 882.14037; found: 882.14325.

***syn*-5,10,15-Tris(1-methoxynaphthalen-2-ylmethyl)-10,15–10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3u)**: 85 % (Method 2); pale-yellow solid; m.p. > 300 °C (softens at 175 °C); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.10–8.02$ (m, 6H), 7.92–7.88 (m, 3H), 7.63 (d, $J = 8.5$ Hz, 3H), 7.56–7.47 (m, 9H), 7.22 (d, $J = 8.5$ Hz, 3H), 7.12–7.07 (m, 3H), 6.35 (d, $J = 7.2$ Hz, 3H), 4.64 (dd, $J = 11.7$, 4.6 Hz, 3H), 3.64 (s, 9H), 3.85 (dd, $J = 14.1$, 4.1 Hz, 3H), 2.53 (dd, $J = 14.1$, 11.7 Hz, 3H); ^{13}C NMR (360 MHz, $CDCl_3$): $\delta = 154.34$, 147.64, 141.37, 140.17, 135.54, 134.06, 128.98, 128.37, 128.04, 127.95, 127.09, 125.83, 125.78, 125.58, 123.46, 122.90, 122.26, 62.00, 46.57, 33.05 (one C resonance was not observed); EI-MS: *m/z* (%): 852 (6) $[M]^+$, 681 (100), 510 (31), 339 (86), 171 (20).

5-(3-Cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4a): 82 % (Method 3); pale-yellow solid; m.p. 235–236 °C (softens at 179 °C); ^{1}H NMR ($CDCl_3$, 300 MHz, 20 mM): $\delta = 8.00$ (d, $J = 7.3$ Hz, 1H), 7.86 (d, $J = 7.3$ Hz, 1H), 7.67 (t, $J = 7.1$ Hz, 2H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.56 (td, $J = 1.0$, 7.3 Hz, 1H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.47–7.22 (m, 5H), 7.10 (t, $J = 7.7$ Hz, 1H), 7.08 (t, $J = 1.0$ Hz, 1H), 6.93 (td, $J \approx 1$, 7.7 Hz, 1H), 6.99 (d, $J = 7.3$ Hz, 1H), 4.54 (dd, $J = 3.8$, 8.3 Hz, 1H), 4.23 (d, $J = 21.8$ Hz, 1H), 4.03 (d, $J = 22.2$ Hz, 1H), 3.95 (d, $J = 22.2$ Hz, 1H), 3.86 (d, $J = 22.2$ Hz, 1H), 3.74 (dd, $J = 3.8$, 13.9 Hz, 1H), 2.88 (dd, $J = 8.5$, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz, 31 mM): $\delta = 146.16$, 144.24, 143.85, 141.31, 140.97, 140.74, 139.90, 138.66, 137.30, 136.57, 135.95, 135.78, 135.22, 133.86, 132.73, 129.86, 128.33, 127.49, 126.92, 126.42, 126.08, 125.46, 125.06, 124.72, 122.39, 121.96, 119.08, 118.86, 111.58, 47.22, 37.68, 36.38, 36.21; EI-MS: *m/z* (%): 457 (12) $[M]^+$, 341 (100); HR-MS: *m/z*: calcd for $C_{35}H_{23}N$: 457.18305; found: 457.18375.

5-(4-Cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4b): 77 % (Method 3); pale-yellow solid; m.p. 276–277 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 10 mM): $\delta = 8.11$ (d, $J = 7.1$ Hz, 1H), 7.95 (d, $J = 7.3$ Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.67 (d, $J = 7.3$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 8.1$ Hz, 2H), 4.80 (dd, $J = 4.4$, 8.1 Hz, 1H), 4.36 (d, $J = 22.1$ Hz, 1H), 4.18 (d, $J = 21.9$ Hz, 1H), 4.16 (d, $J = 21.8$ Hz, 1H), 4.07 (d, $J = 21.8$ Hz, 1H), 3.82 (dd, $J = 4.0$, 13.6 Hz, 1H), 3.10 (dd, $J = 8.4$, 14.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz, 10 mM): $\delta = 146.16$, 144.13, 143.85, 142.89, 141.42, 140.86, 136.34, 135.84, 135.33, 131.38, 130.14, 127.54, 126.98, 126.59, 126.30, 126.13, 125.57, 125.46, 125.18, 124.78, 122.41, 122.02, 119.03, 109.94, 47.44, 38.25, 36.61, 36.44; EI-MS: *m/z* (%): 457 (10) $[M]^+$, 341 (100); HR-MS: *m/z*: calcd for $C_{35}H_{23}N$: 457.18305; found: 457.18301.

***anti*-5,10-Bis(3-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (5a)**: 20 % (Method 3); yellow solid; m.p. 135–136 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 80 mM): $\delta = 8.19$ (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 7.3$ Hz, 1H), 7.75 (d, $J = 7.4$ Hz, 1H), 7.59

(td, $J = 1.2$, 7.7 Hz, 1H), 7.51 (td, $J = 1.2$, 7.3 Hz, 1H), 7.45 (td, $J = 1.2$, 7.3 Hz, 1H), 7.44 (td, $J = 1.2$, 7.5 Hz, 1H), 7.35 (td, $J = 1.2$, 7.3 Hz, 1H), 7.24–7.34 (m, 4H), 7.11 (d, $J = 6.9$ Hz, 1H), 7.09 (d, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 7.00 (dt, $J = 1.6$, 8.1 Hz, 2H), 6.91 (dt, $J = 1.6$, 7.7 Hz, 1H), 6.87 (dt, $J = 1.6$, 8.1 Hz, 1H), 5.01 (dd, $J = 4.0$, 7.7 Hz, 1H), 4.78 (dd, $J = 4.0$, 7.7 Hz, 1H), 4.31 (d, $J = 22.2$ Hz, 1H), 4.15 (d, $J = 22.2$ Hz, 1H), 3.78 (dd, $J = 4.0$, 13.7 Hz, 1H), 3.72 (dd, $J = 4.0$, 13.7 Hz, 1H), 3.17 (dd, $J = 7.7$, 13.7 Hz, 1H), 2.97 (dd, $J = 8.1$, 13.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, 75 mM): $\delta =$ 146.58, 146.19, 144.29, 140.75, 140.58, 140.19, 139.41, 139.25, 138.86, 138.74, 137.77, 137.07, 136.49, 135.95, 133.80, 133.76, 132.89, 129.91, 128.28, 127.78, 127.70, 127.17, 126.86, 126.58, 126.47, 125.58, 125.17, 124.77, 122.58, 122.45, 122.12, 118.79, 111.49, 111.44, 47.55, 47.41, 37.74, 37.55, 36.56; EI-MS: m/z (%): 572 (8) $[M]^+$, 456 (100), 340 (95); HR-MS: m/z: calcd for $C_{43}H_{28}N_2$: 572.22525; found: 572.22528.

***anti*-5,10-Bis(4-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (5b)**: 16% (Method 3); yellow solid; m.p. 200–201 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 27 mM): $\delta = 8.20$ (d, $J = 7.7$ Hz, 1H), 7.76 (d, $J = 7.3$ Hz, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 7.3$ Hz, 1H), 7.59 (d, $J = 7.3$ Hz, 1H), 7.57 (d, $J = 7.1$ Hz, 1H), 7.53–7.37 (m, 4H), 7.36–7.20 (m, 9H), 7.15 (d, $J = 7.3$ Hz, 1H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 8.1$ Hz, 2H), 5.05 (dd, $J = 4.0$, 7.3 Hz, 1H), 4.84 (dd, $J = 4.0$, 7.0 Hz, 1H), 4.33 (d, $J = 22.2$ Hz, 1H), 4.18 (d, $J = 22.2$ Hz, 1H), 3.80 (dd, $J = 4.1$, 13.7 Hz), 3.74 (dd, $J = 4.0$, 13.7 Hz, 1H), 3.29 (dd, $J = 7.3$, 13.3 Hz, 1H), 3.07 (dd, $J = 7.7$, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz, 100 mM): $\delta = 147.45$, 147.11, 145.18, 144.49, 144.28, 141.54, 141.38, 141.03, 139.67, 139.56, 138.59, 137.97, 137.34, 136.72, 133.09, 132.05, 130.86, 129.04, 128.41, 127.92, 127.63, 125.87, 125.53, 123.31, 123.21, 122.81, 119.63, 110.54, 47.74, 47.58, 38.33, 38.15, 36.74; EI-MS: m/z (%): 572 (8) $[M]^+$, 513 (3), 512 (8), 472 (8), 471 (6), 470 (13), 458 (10), 457 (48), 456 (100), 355 (12), 354 (14), 341 (39), 340 (98), 339 (41), 338 (4), 337 (11); HR-MS: m/z: calcd for $C_{43}H_{28}N_2$: 572.22525; found: 572.22675.

***syn*-5,10-Bis(3-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (6a)**: 7% (Method 3); yellow solid; m.p. 238–239 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 43 mM): $\delta = 7.71$ (d, $J = 7.7$ Hz, 1H), 7.63–7.23 (m, 11H), 7.19 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.07 (t, $J = 1.6$ Hz, 1H), 6.96 (t, $J = 1.6$ Hz, 1H), 6.90–6.84 (m, 2H), 6.83 (d, $J = 7.7$ Hz, 1H), 6.65 (d, $J = 7.7$ Hz, 1H), 3.78 (dd, $J = 3.6$, 8.9 Hz, 1H), 3.75 (d, $J = 22.2$ Hz, 1H), 3.66 (dd, $J = 3.4$, 9.5 Hz, 1H), 3.55 (dd, $J = 3.8$, 13.9 Hz, 1H), 3.33 (dd, $J = 3.4$, 13.9 Hz, 1H), 3.14 (d, $J = 22.2$ Hz, 1H), 2.62 (dd, $J = 8.7$, 13.9 Hz, 1H), 2.23 (dd, $J = 10.1$, 14.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, 43 mM): $\delta = 146.75$, 146.47, 144.41, 140.50, 140.33, 140.11, 139.83, 139.61, 138.94, 136.49, 135.82, 135.12, 134.04, 133.75, 132.55, 132.44, 130.00, 129.87, 128.57, 128.34, 127.41, 126.86, 126.67, 126.29, 126.16, 125.57, 125.24, 124.82, 122.54, 122.49, 122.26, 118.89, 118.80, 111.83, 111.58, 46.70 (2C), 37.81, 37.43, 36.99; EI-MS: m/z (%): 572 (9) $[M]^+$, 456 (98), 340 (100); HR-MS: m/z: calcd for $C_{43}H_{28}N_2$: 572.22525; found 572.22455.

***syn*-5,10-Bis(4-cyanophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (6b)**: 14% (Method 3); yellow solid; m.p. 130–131 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 70 mM): $\delta = 7.76$ (d, $J = 7.3$ Hz, 1H), 7.58 (d, $J = 7.3$ Hz, 1H), 7.56 (d, $J = 7.1$ Hz, 1H), 7.15–7.53 (m, 14H), 6.96 (d, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.64 (d, $J = 8.3$ Hz, 2H), 6.61 (d, $J = 8.3$ Hz, 2H), 3.93 (dd, $J = 3.5$, 8.2 Hz, 1H), 3.83 (d, $J = 22.2$ Hz, 1H), 3.78 (dd, $J = 3.5$, 10.5 Hz, 1H), 3.55 (dd, $J = 13.5$, 13.7 Hz, 1H), 3.32 (dd, $J = 3.4$, 14.1 Hz), 3.28 (d, $J = 22.1$ Hz, 1H), 2.78 (dd, $J = 8.3$, 13.6 Hz, 1H), 2.08 (dd, $J = 10.2$, 14.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, 70 mM): $\delta =$ 146.66, 146.44, 144.68, 144.35, 143.65, 140.33, 140.17, 139.41, 138.99, 136.60, 135.79, 135.70, 135.09, 131.72, 131.07, 129.99, 129.85, 127.34, 126.86, 126.58, 126.17, 126.03, 125.52, 125.11, 124.71, 122.46, 122.40, 122.18, 118.92, 118.75, 110.13, 109.80, 46.80, 46.49, 38.32, 37.98, 36.06; EI-MS: m/z (%): 573 (3) $[M+H]^+$, 572 (7) $[M]^+$, 512 (2), 472 (13), 471 (25), 470 (63), 457 (38), 456 (96), 355 (12), 369 (12), 356 (12), 355 (36), 354 (70), 342 (7), 341 (37), 340 (100), 339 (38), 338 (3), 337 (10), 207 (35), 116 (24); HR-MS: m/z: calcd for $C_{43}H_{28}N_2$: 572.22525; found: 572.22455.

5,5,10,10,15,15-Hexa(3-bromophenylmethyl)-10,15-dihydro-5*H*-diindeno-[1,2-*a*;1′,2′-*c*]fluorene (7)

Method a: A solution of **3i** (100 mg, 0.118 mmol) in THF (25 mL) was treated with KOH (59 mg, 1.05 mmol) and the resulting mixture was heated under reflux for 15 min. It was then treated with *m*-bromobenzyl bromide (265 mg, 1.06 mmol) and stirred for 24 h at this temperature. After standard extractive work-up (CH_2Cl_2), followed by chromatography (hexane/CH_2Cl_2 1:0 → 0:1), **7** (86 mg, 54%) was obtained.

Method b: A suspension of **1** (137 mg, 0.4 mmol) and KOH (224 mg, 4.0 mmol) in THF (60 mL) was heated to reflux for 30 min, treated with *m*-bromobenzyl bromide (900 mg, 3.6 mmol), and stirred for 24 h at this temperature. After standard extractive work-up (CH_2Cl_2), followed by chromatography (hexane/CH_2Cl_2 1:0 → 0:1), **7** (135 mg, 84%) was obtained as a yellow solid. M.p. 130–140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.42$ (d, $J = 7.7$ Hz, 3H), 7.24 (dd, $J = 1.2$, 7.3 Hz, 3H), 7.50 (td, $J = 1.0$, 7.5 Hz, 3H), 7.42 (t, $J = 7.1$ Hz, 3H), 7.06 (ddd, $J = 1.2$, 2.0, 8.1 Hz, 6H), 6.78 (t, $J = 1.6$ Hz, 6H), 6.64 (t, $J = 7.7$ Hz, 6H), 6.06 (dt, $J = 1.2$, 7.7 Hz, 6H), 3.83 (d, $J = 13.3$ Hz, 6H), 3.51 (d, $J = 13.3$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 149.45$, 144.29, 139.39, 139.02, 138.47, 133.25, 129.04, 128.90, 128.12, 127.37, 126.25, 125.89, 125.22, 121.09, 56.81, 40.47; EI-MS: m/z (%): 1360, 1358, 1356, 1354 (4) $[M]^+$, 1355 (3), 1328 (8), 1187 (100), 1031 (54), 1017 (61).

Tris-spirotruxene 8: A suspension of truxene (**1**; 137 mg, 0.4 mmol) in THF (60 mL) was heated under reflux for 30 min. The oil bath was then removed, and the mixture was treated with KOH (320 mg, 5.70 mmol). Argon was bubbled through the resulting mixture for 3 min. After heating under reflux for a further 30 min, α,α'-dibromo-*o*-xylene (320 mg, 1.21 mmol) was added and the reaction mixture was stirred for 15 h under reflux. After standard work-up, trituration of the crude mixture in hexane and filtration gave **8** (262 mg, >99%) as a light-brown solid. M.p. >300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.36–7.47$ (m, 15H), 6.99–7.13 (m, 9H), 4.36 (d, $J = 16.6$ Hz, 6H), 3.28 (d, $J = 17.0$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 157.62$, 145.07, 143.15, 136.87, 136.62, 127.53, 127.11, 126.95, 125.52, 123.46, 120.76, 55.39, 42.56; EI-MS: m/z (%): 648 (100) $[M]^+$; HR-MS: m/z: calcd for $C_{51}H_{36}$: 648.28170; found: 648.28070.

Truxenephane 10: KOH (224 mg, 4 mmol) was added to a refluxing solution of **1** (137 mg, 0.4 mmol) in THF (80 mL). After heating for 30 min, **9** (240 mg, 0.408 mmol) was added and the mixture was heated under reflux for a further 2 h. After standard extractive work-up, the residue was purified by chromatography (hexane/EtOAc 1:1) to give **10** (180 mg, 66%) as a white solid, which was recrystallized from EtOH or CH_3CN. M.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.83$ (d, $J = 7.8$ Hz, 3H), 7.42 (d, $J = 7.1$ Hz, 3H), 7.34 (d, $J = 7.8$ Hz, 3H), 7.27–7.24 (m, 3H), 7.12–7.08 (m, 6H), 6.95 (dt, $J = 7.5$, 1.3 Hz, 3H), 6.88 (s, 3H), 6.70 (dt, $J = 7.6$, 1.2 Hz, 3H), 5.05 (d, $J = 14.1$ Hz, 3H), 4.70 (d, $J = 10.5$ Hz, 3H), 3.74 (dd, $J = 14.2$, 10.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.60$, 142.92, 142.16, 141.50, 140.90, 137.34, 136.73, 134.41, 131.31, 128.73, 127.14, 126.88, 126.86, 126.69, 125.80, 122.34, 46.30, 33.87 (one C signal was not observed); EI-MS: m/z (%): 684 (53) $[M]^+$, 341 (100), 253 (10); elemental analysis calcd for $C_{54}H_{36} \cdot 0.5$ EtOH: C 93.32, H 5.55; found: C 93.41, H 5.47.

Determination of K_{assoc}: The chemical shifts of Ht_1 and HT_5 of compounds **3** in $CDCl_3$ solution were monitored at different concentrations. These solutions were obtained by dilution from a starting concentration as close as possible to the saturation point. The values of K_{assoc} given in Table 2 are an average of those determined from the chemical shifts of Ht_1 and HT_5 and are subject to an estimated maximum error of 10–15%. In the case of **3h**, K_{assoc} was determined with a ±20% error by monitoring the chemical shifts of the six hydrogens that show significant variations in their chemical shifts.

The method of Chen[33] was applied for the calculation of K_{assoc} from the variation of the chemical shifts assuming a monomer (A) to dimer (A_2) equilibrium.

Diffusion measurements: Experiments were performed on a Bruker DRX 500 MHz spectrometer at temperatures of 10–15 °C to avoid convection effects. Different concentrations (from 20 to 1 mM) were employed. Gradients were calibrated using a pure D_2O sample by following the residual HDO signal. The maximum strength of the gradient unit was deduced to be 56.5 G cm^{-1}. The common pulse sequence (LED)[38] was employed to avoid T_2 relaxation effects. Twelve different gradient strengths were employed and the experiments were repeated at least twice. Diffusion coefficients were calculated from the following relationship:

$$\ln (A_G/A_0) = -\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D$$

where A represents the signal intensity at zero and G gradient intensities, D is the diffusion coefficient, and Δ, δ are the delays in the STE pulse sequence.

  0947-6539/02/0813-2888 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 13

Qualitatively, average molecular weights may be estimated from diffusion coefficients using the Stokes–Einstein equation:

$$D = kT/6\pi\eta r$$

where η is the viscosity and r is the hydrodynamic radius of a spherical molecule.

Determination of the NOE values: NOESY experiments were carried out using the standard pulse sequence with mixing times between 150 and 500 ms. HSQC-NOESY experiments were also performed in order to detect intermolecular NOEs between symmetry-related protons. A mixing time of 300 ms was used and decoupling was set to "off" during acquisition.

X-ray structure determinations: Colorless crystals of **3h**, **3u**, and **10** showing well defined faces were mounted on a Bruker–Siemens Smart CCD diffractometer equipped with a low temperature device and a normal focus, 2.4 kW sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, $\lambda = 0.71067$ Å) operating at 50 kV and 20 mA. Data were collected over a hemisphere of the reciprocal space by a combination of two exposure sets. Each exposure of 10 s covered 0.3° in ω.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Br in compound **3h** were taken from the International Tables for X-ray Crystallography.[39] The structures were solved by the Multan and Fourier methods. Due to the instability, poor diffraction spectra, and existence of disordered solvent molecules in **3h** and **3u**, the final R values are quite high (**3h** was only isotropically refined). Compound **3u** also exhibited positional disorder around one methoxy group (C69 and C69′ positions). A summary of the fundamental crystal and refinement data is given in Table 4.

Most of the calculations were carried out with SMART[40] software for data collection and reduction, and SHELXTL[41] for structure solution and refinements.

CCDC-101806, -101807, and -173909 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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Table 4. Crystal data and structure refinement for compounds **3h**, **3u**, and **10**.

	3h	**3u**	**10**
formula	$C_{48}H_{33}Br_3 \cdot (H_2O)_{0.5}$	$C_{63}H_{48}O_3 \cdot C_7H_8 \cdot (CH_2Cl_2)_{0.5}$	$C_{56}H_{36} \cdot (CH_3CN)_{0.5}$
molecular weight	858.50	987.62	705.35
T [K]	193	153	223
λ	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	14.984(2)	16.308(3)	11.0374(10)
b [Å]	15.435(2)	15.192(3)	13.1540(12)
c [Å]	18.020(2)	21.937(3)	15.4398(14)
α [°]	80.914(3)	90	67.227(2)
β [°]	74.251(3)	95.911(4)	69.677(2)
γ [°]	66.706(2)	90	65.345(2)
V [Å^3]	3678.2(7)	5406(2)	1831.7(3)
Z	4	4	2
ρ_{calcd} [mg m^{-3}]	1.545	1.210	1.279
μ [mm^{-1}]	3.326	0.120	0.073
$F(000)$	1712	2072	742
crystal size [mm]	0.04 × 0.12 × 0.16	0.1 × 0.1 × 0.2	0.2 × 0.2 × 0.2
2θ range [°]	4–35	4–47	4–42
limiting indices	$-12 \le h \le 10$	$-16 \le h \le 9$	$-11 \le h \le 10$
	$-12 \le k \le 4$	$-4 \le k \le 15$	$-13 \le k \le 10$
	$-14 \le l \le 14$	$-16 \le l \le 21$	$-15 \le l \le 13$
reflections collected	4667	7155	5138
independent reflections	3406 ($R_{int} = 0.0480$)	4416 ($R_{int} = 0.0789$)	3219 ($R_{int} = 0.0390$)
absorption correction	none	none	none
refinement method	full-matrix least squares on F^2		
data/restraints/parameters	3404/0/422	5536/0/622	3219/0/510
GoF on F^2	1.013	1.022	1.200
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0923$	$R1 = 0.1110$	$R1 = 0.0826$
	$wR2 = 0.2196$	$wR2 = 0.2508$	$wR2 = 0.1806$
R indices (all data)	$R1 = 0.1316$	$R1 = 0.2208$	$R1 = 0.0945$
	$wR2 = 0.2465$	$wR2 = 0.3220$	$wR2 = 0.1887$
largest diff peak/hole [e Å^{-3}]	2.751/−0.608	0.497/−0.527	0.567/−0.460

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