Overcrowded 5,10,15-Trisubstituted Derivatives: Synthesis of 5,10,15-Tri(fluorenylidene)truxene

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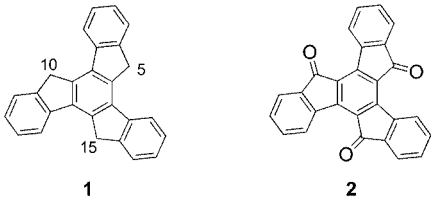
Sterically crowded 5,10,15-triarylated truxenes are obtained by reaction of truxenetrione with aryllithium compounds (aryl = 1-naphthyl, 2-naphthyl, 9-phenanthryl, 9-anthracenyl), followed by reduction of the tertiary alcohols with Et_3SiH and BF_3. Base-catalyzed isomerization of the *anti* derivatives provides *syn*-5,10,15-triarylated derivatives, with the exception of the 9-anthracenyl that could not be isomerized. Overcrowded 5,10,15-tri(fluorenylidene)truxene was also synthesized starting form the addition of fluorenyllithium to truxenetrione.

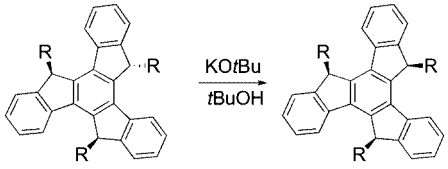
Introduction

Truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene) (**1**) and the triketone truxenetrione (diindeno[1,2-*a*;1′,2′-*c*]fluoren-5,10,15-trione) (**2**) (Figure 1) have received attention as potential starting materials for the construction of larger polyarenes[1−5] and for the synthesis of new materials.[6−9] For the synthesis of polyarenes with the topology of the fullerenes[10−12] we developed a synthesis of derivatives **3b** by the reaction of the trianion of **1** with a variety of alkylating agents, followed by isomerization with KO*t*Bu in *t*BuOH (Scheme 1).[13,14]



1 **2**

Figure 1. Truxene (**1**) and truxenetrione (**2**)



3a **3b**

Scheme 1

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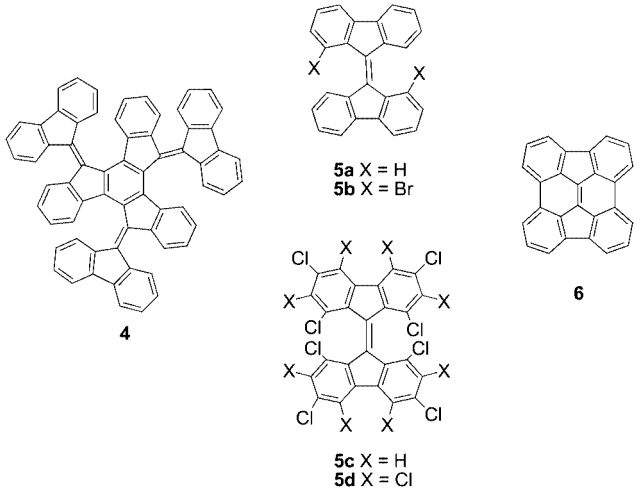
We also found that two *anti*-5,10,15-triaryltruxenes **3a** (R = Ph, *p*-Tol) could be cleanly equilibrated to give their *syn* isomers **3b**.[15] With the aim at developing related systems as platforms for the construction of molecular receptors, we wished to determine if this isomerization is general and, in particular, if *syn* derivatives **3b** with large aryl groups could be synthesized by this method.

Additionally, we decided to attempt the synthesis of **4**, a crowded analogue of bifluorenylidene [9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene] (**5a**) (Figure 2), which has received attention as precursor of fullerene fragments.[16,17] Thus, 1,1-dibromobifluorenylidene (**5b**) has been converted into the non-planar polyarene diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**6**) by FVP at 1000−1050 °C.[18] The twists around the central double bond of **5a** and **5b** are 31.9°[19] and 40°,[18] respectively. For disubstituted bifluorenylidenes,



4

Figure 2. Tri(fluorenylidene)truxene **4**, bifluorenylidenes **5a**−**d**, and diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**6**)

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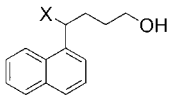
the $\Delta G^{\ddagger}$ for their conformational interconversions ranges from 12 to 22 kcal·mol^{-1}.[19,20] Chlorinated derivatives 1,1′,3,3′,6,6′,8,8′-octachloro-9,9′-bifluorenylidene (**5c**) and perchloro-9,9′-bifluorenylidene (**5d**) are very twisted molecules with a dihedral angle of 55° and 60°, respectively.[21] Twisted C=C bonds have also been observed for other alkenylidenefluorenes.[22,23] Chiral, twisted olefins have received much attention in the context of the construction of molecular motors and switches.[24]



7a X = OH
7b X = H

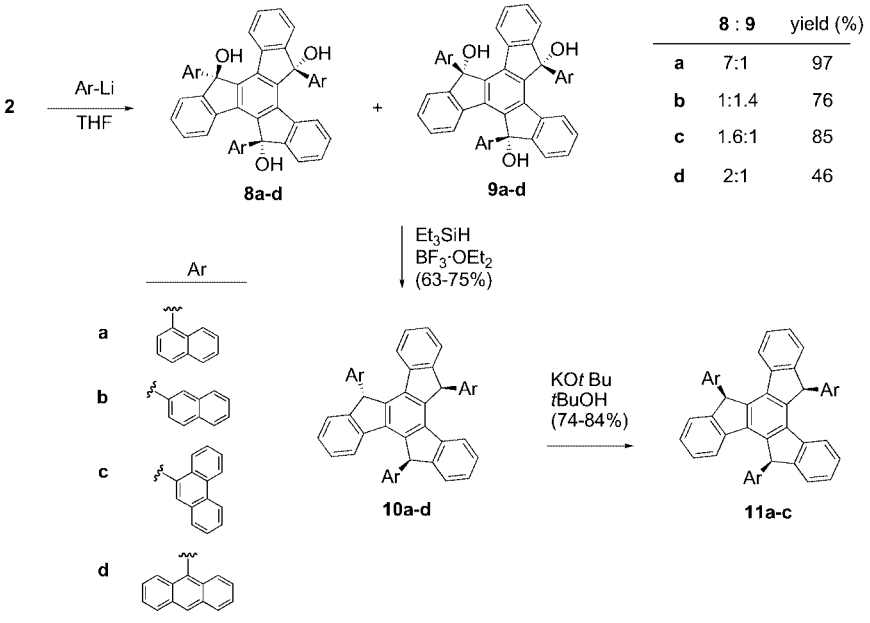
Figure 3. Byproducts of the reaction of 1-naphthylmagnesium bromide or dilithium naphthalene with THF

Results and Discussion

Synthesis of 5,10,15-Triaryltruxenes and Their Isomerization

Although the reaction of truxenetrione (**2**) with phenyl or tolylmagnesium bromide furnished the corresponding triaryltruxenetriols,[15] 1-naphthylmagnesium bromide failed to react with **2** in THF. Surprisingly, the diol **7a** was isolated in 6% yield (Figure 3). The alcohol **7b**, among other products, is also formed in the decomposition of dilithium naphthalene in THF.[25]

In contrast with the results with Grignard reagents, aryllithium compounds react cleanly with **2** to give mixtures of the triols **8** and **9** (Scheme 2 and Table 1). The *syn*-triols **9** show simple NMR spectra corresponding to their C_3 symmetry, while those of the *anti* isomers **8** are more complex. In the case of **8a**, the ^{1}H NMR spectra corresponds to a 4:1 mixture of isomers. Isomers **8** are more soluble than the *syn* derivatives **9**, which self-associate more efficiently.[13,15] Peaks at m/z = 720 in the EI-MS spectra of **8a**, **9a**, **8b,** and **9b** may correspond to the corresponding hydrocarbons, formed by an in probe reduction of the triols.



Scheme 2

Table 1. Experimental and literature values for the reduction have been converted into normal potential vs. Fc^+/Fc[34] and correspond to reversible processes

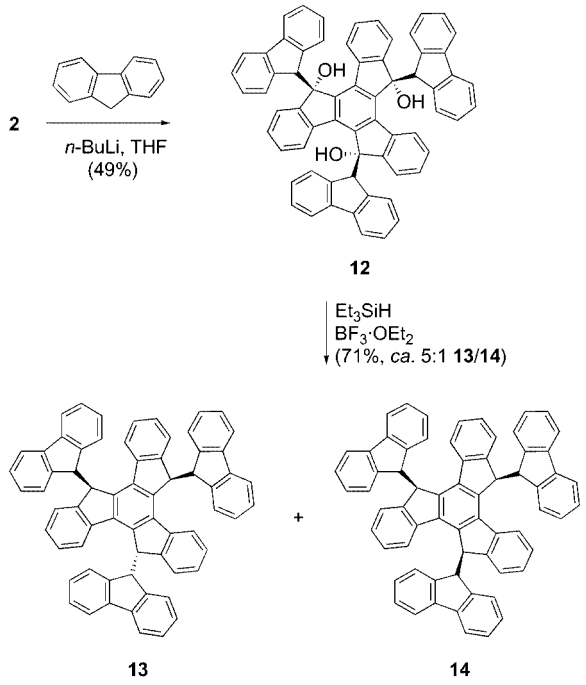
Compound [solvent, supporting electrolyte]	$E_I°$ (V)	$E_{II}°$ (V)	$E_{III}°$ (V)	$E_{IV}°$ (V)	Ref.
4 [CH_2Cl_2, $TBAPF_6$]	−1.40	−1.64	−1.88		
15 [CH_2Cl_2, $TBAPF_6$]	−1.31	−1.54[a]	−1.67		
2 [C_6H_5CN, $TBABF_4$]	−0.86	−1.01	−1.21		[7]
5a [MeCN, $NaClO_4$]	−1.51	−1.90			[30]
19 [MeCN, $TBABF_4$]	−0.19	−0.59	−0.81	−1.23	[7]
20 [DMF, $TBAClO_4$]	−0.73	−1.21			[31]

[a] Irreversible processes, the value of E_{pc} is given.

Reduction of mixtures of triols **8a** and **9a** with Et_3SiH and $BF_3{\cdot}OEt_2$ at 0 °C in CH_2Cl_2 [26] afforded a 7:1 mixture of **10a** and its *syn* isomer **11a** in 97% yield. For **8c−d/9c−d**, *anti* derivatives **10c−d** were isolated as exclusive compounds in good yields. The isomerization of the *anti*-**10a−c** with KO*t*Bu in *t*BuOH under reflux[13,15] gave *syn* **10a−c** in 74−84% yield. However, the isomerization of **10d** failed to proceed under these conditions. Clearly, the resulting truxene cannot be formed by this method as a result of the high bulkiness introduced by three bulky *syn* 9-anthracenyl substituents on the truxene surface.

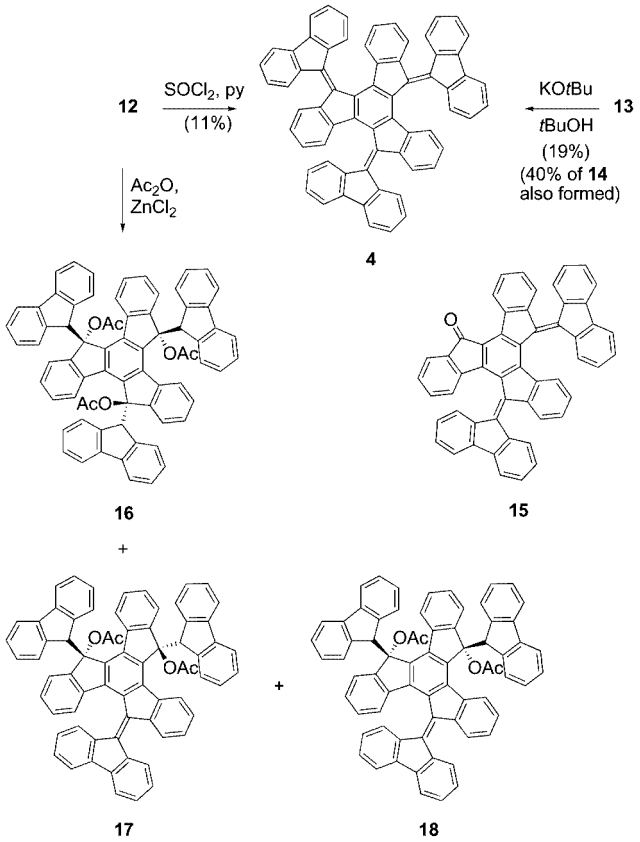
5,10,15-Tri(fluorenyl)truxenes

Reaction of 9-fluorenyllithium with **2** afforded the *syn*-triol **12** in 49% yield (Scheme 3). Small amounts of the *anti* isomer could be detected in the crude reaction mixtures, along with mono- and bis-addition products. Removal of the hydroxy groups of **12** gave a 5:1 mixture of *anti* **13** and *syn* **14** (71%).



Scheme 3

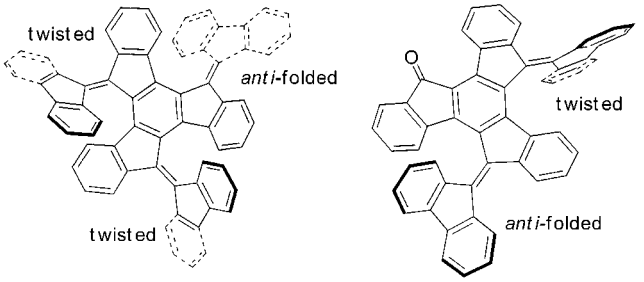
At the outset, we feared that the isomerization of *anti*-**13** under the basic conditions could be problematic due to the presence of the three additional acidic fluorene hydrogens. However, heating *anti*-**13** with KO*t*Bu in *t*BuOH gave *syn*-**14** in 40% yield. In this reaction, 5,10,15-tri(fluorenylidene)-truxene (**4**) was also isolated in 19% yield (Scheme 4). Dehydration of the triol **12** under more standard conditions by using thionyl chloride and pyridine (65 °C, 17 h) also afforded **4**, which could be isolated in 11% yield. Under more forcing conditions (75 °C, 24 h) a hexachloro derivative of formula $C_{66}H_{30}Cl_6$ was formed in 9% yield. Although the structure of this derivative could not be assigned with confidence, presumably it corresponds to the product of dichlorination at each of the fluorene substituents.[27] When the reaction with thionyl chloride was carried out with the crude product obtained in the reaction of fluorenyllithium to **2**, di(fluorenylidene)truxenone (**15**) could also be isolated. Dehydration of **12** could not be effected under acidic conditions (TsOH or P_2O_5 in toluene or benzene). Similar negative results were obtained upon treatment of **12** with methanesulfonyl chloride and triethylamine. Acetylation of the sterically hindered hydroxy groups of **12** could not be achieved under standard conditions. However, heating **12** with Ac_2O and $ZnCl_2$ at 120 °C for 4 h gave the *anti* triacetate **16** (27%). In this reaction, a 2.3:1 mixture of fluorenylidene derivatives **17** and **18** was also obtained in 7% yield. However, thermal elimination of acetic acid from **16** failed to give **4**.



Scheme 4

Tri(fluorenylidene)truxene (**4**) is purple in solution, with a maximum absorption at 500 nm in the UV/Vis spectrum (chlorobenzene). Bifluorenylidene (**5a**) is also purple and shows a maximum at 450 nm.[19e] This color is characteristic of twisted conformations in this type of compounds.[19e] In the solid-state **4** gives reddish crystals, which despite repeated efforts were not suitable for X-ray diffraction. Ketone **15** is dark red in solution, and shows a maximum at 524 nm (chlorobenzene).

^{1}H NMR spectroscopy has been used to distinguish qualitatively among twisted, *anti*-folded, and *syn*-folded conformations of difluorenylidenes **5** in solution.[28] In the twisted conformation, the signals of the inner hydrogen atoms (H-1, H-8, H-1′, H-8′) of **5** appear at δ = 8.39 ppm,[29] while in an *anti*-folded conformation, these hydrogen signals appear at higher field (δ = 6.8−7.2 ppm) as a result of shielding effect of diamagnetic ring currents of the opposing aromatic rings. The ^{1}H NMR spectrum of **4** at room temperature is rather complex, which is not consistent with a C_3 symmetrical structure with twisted fluorenylidenes. At low field (δ = 8.4−8.6 ppm) six doublets were observed, which correspond with two twisted fluorenylidenes (corresponding to two hydrogens of the fluorene and one of the truxene units). According to semiempirical PM3 calculations, the third fluorenylidene group could be *anti*-folded in the lowest energy conformation of **4** (Figure 4). In contrast to hydrocarbon **4**, the ketone **15** is red in solution. This ketone shows two downfield doublets at δ = 9.58 and 9.24 ppm, which correspond to H-4 and H-6 flanking the carbonyl group. Additionally, two hydrogen atoms resonate at δ = 8.66 and 8.47 ppm. This might indicate that one of the fluorenylidene is twisted in this molecule. In accordance, semiempirical PM3 calculations show a minimum conformation with one of the fluorenylidene *anti*-folded and another one twisted.



4 **15**

Figure 4. Minimum conformations of tri(fluorenylidene)truxene **4** and ketone **15**

Cyclic voltammetry of **4** shows three reversible reduction waves at −0.94, −1.18, and −1.45 V (vs. SCE) (Figure 5). On the other hand, the presence of a carbonyl group in **15** results in its easier reduction (Table 1). Data for **2**,[7] **5a**,[30] acceptor **19**,[7] and radialene **20**[31] (Figure 6) are also summarized in Table 1. In the case of **5a** and **20**, two reversible one-electron reductions lead to the corresponding dianion (Table 1). As expected, the first two reductions of **4** occur at lower potential that those of bifluorenylidene (**5a**) as a result of the more extended electron delocalization in the former. However, the delocalization in the dianion of **4** is not as effective as that of radialene **20**.[31]

Conclusion

The base-catalyzed isomerization of 5,10,15-triaryltruxenes with KO*t*Bu in *t*BuOH under reflux is a fairly general process and allows the synthesis of *syn* derivatives with substituents as large as 9-phenanthryl. *anti*-Tri(9-anthracenyl)-truxene could not be isomerized under the standard conditions. However, *syn*-tri(9-fluorenyl)truxene could be prepared in two steps from truxenetrione and 9-fluorenyllithium by the general method. The new overcrowded fluorenylidene derivative 5,10,15-tri(fluorenylidene)truxene was synthesized by dehydration of the corresponding triol or from *anti*-tri(9-fluorenyl)truxene. In solution, this derivative displays two twisted fluorenylidenes, while the third one is *anti*-folded.

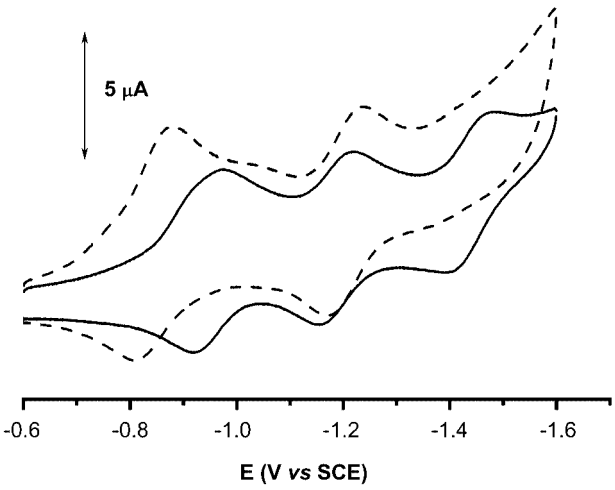
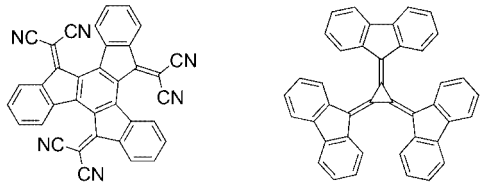


Figure 5. Cyclic voltammogram of compounds **4** and **15**. CV experiments were performed at room temperature in CH_2Cl_2 solutions containing 0.1 M $TBAPF_6$ as a supporting electrolyte; the scan rate was 100 mV/s



19 **20**

Figure 6. Truxene **19** and radialene **20**, analogues of tri(fluorenylidene)truxene **4**

Experimental Section

General Remarks: The NMR determinations were carried out at 23 °C, unless otherwise stated. Only the most significant IR frequencies and MS fragmentations are given. The FAB-MS spectra were obtained by using *m*-nitrobenzyl alcohol as the matrix. R_f were determined on TLC aluminum sheets coated with 0.2 mm GF_{254} silica gel. Elemental analyses were performed at the SIdI (UAM).

All reactions were carried out under Ar. Solvents were purified and dried by standard methods. The saturated aqueous NH_4Cl solution was buffered with NH_4OH (pH = 8). Chromatographic purifications were carried out with flash grade silica gel. "Usual workup" means pouring the crude reaction mixture into saturated aqueous

NH_4Cl solution, followed by extraction with the stated solvent, drying ($MgSO_4$), and evaporation of the solvent.

Truxene (**1**) and truxenetrione (**2**)[32] were prepared according to the described procedure.[33]

1-(1-Naphthyl)butane-1,4-diol (7): 1-Bromonaphthalene (1.81 mL, 13.0 mmol) and Mg turnings (316 mg, 13 mmol) in THF (80 mL) was sonicated for 2 h to give a yellow solution. After being cooled to 0 °C, a suspension of **2** (125 mg, 0.32 mmoles) in THF (5 mL) was added. The mixture was stirred at 23 °C for 17 h. After the usual workup and trituration with hexane, the crude product was chromatographed (EtOAc) to give **7** (166 mg, 6%). **7:** White solid; m.p. 100−102 °C; R_f = 0.40 (EtOAc). IR (KBr): $\tilde{\nu}_{max.}$ = 3300, 3186, 1043, 998, 804, 776 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.83−1.73 (m, 2 H), 2.00−1.89 (m, 1 H), 2.15−2.04 (m, 1 H), 3.78−3.65 (m, 2 H), 5.50 (dd, *J* = 8.3, 3.4 Hz, 1 H), 7.52−7.44 (m, 3 H), 7.64 (d, *J* = 6.9 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H), 7.89−7.85 (m, 1 H), 8.10−8.04 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.47, 35.44, 62.91, 71.03, 122.74, 122.99, 125.42, 125.50, 126.00, 127.87, 128.90, 130.25, 133.75, 140.28 ppm. EI-MS: *m*/*z* (%) = 216 (23) [M^+], 198 (8), 157 (100), 129 (82).

***anti*-5,10,15-Tri(1-naphthyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (8a) and *syn*-5,10,15-Tri(1-naphthyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (9a):** To a solution of 1-bromonaphthalene (3.24 mL, 23.43 mmol) in Et_2O (12 mL) was added *n*BuLi (9.37 mL, 23.43 mmol, 2.5 M in hexane) at −78 °C and the mixture was slowly warmed up to 23 °C. A suspension of **2** (900 mg, 2.34 mmol) in THF (80 mL) was added and the resulting mixture was stirred at 23 °C for 3 h. After the usual workup (Et_2O), the crude product was triturated with hexane to give a ca. 7:1 mixture of **8a** and **9a** (1.650 g, 91%) as a white solid. The mixture was separated by column chromatography (CH_2Cl_2/EtOAc, 10:1). **8a:** White solid; m.p. 272−274 °C; R_f = 0.89 (CH_2Cl_2/EtOAc, 10:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3554, 3514, 1467, 1048, 792, 772, 754, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.61 (s, 1 H), 2.79 (s, 1 H), 2.80 (s, 1 H), 6.03 (t, *J* = 7.6 Hz, 1 H), 8.04−6.93 (several m, 26 H), 9.02−8.83 (m, 5 H), 9.99−9.92 (m, 1 H) ppm, (minor signals were also observed, probably corresponding to a minor conformer). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 83.04, 83.29, 123.91, 124.16, 124.86, 124.91, 124.95, 125.00, 125.08, 125.40, 125.71, 125.79, 125.84, 126.06, 126.68, 126.75, 126.79, 128.39, 128.45, 128.59, 128.75, 128.85, 128.93, 128.98, 129.13, 129.18, 129.29, 129.54, 129.61, 134.12, 134.31, 134.38, 135.56, 135.58, 136.82, 136.92, 137.04, 137.12, 137.27, 137.35, 137.44, 139.74, 146.10, 146.17, 146.29, 146.42, 150.42, 150.56, 150.92 ppm (10 signals were not observed due to overlapping). EI-MS: *m*/*z* (%) = 768 (30) [M^+], 720 (100), 641 (20), 592 (74), 513 (6), 465 (26). HRMS ($C_{57}H_{36}O_3$): calcd. 768.2664; found 768.2645. **9a:** White solid; m.p. 278−280 °C; R_f = 0.20 (CH_2Cl_2/EtOAc, 10:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3535, 1467, 1050, 792, 774, 754, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.82 (s, 3 H), 5.99 (dt, *J* = 8.5, 1.2 Hz, 3 H), 7.04−6.90 (m, 9 H), 7.12 (t, *J* = 7.0 Hz, 3 H), 7.71−7.63 (m, 9 H), 7.77 (d, *J* = 7.7 Hz, 3 H), 7.96 (d, *J* = 7.7 Hz, 3 H), 8.83 (dd, *J* = 7.3, 1.6 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 82.97, 123.60, 124.10, 124.58, 124.74, 125.36, 126.11, 126.78, 128.62, 128.76, 128.82, 129.18, 129.40, 134.11, 136.46, 136.71, 139.72, 145.91, 150.84 ppm. EI-MS: *m*/*z* (%) = 768 (11) [M^+], 720 (100), 641 (7), 592 (70), 465 (24). HRMS ($C_{57}H_{36}O_3$): calcd. 768.2664; found 768.2673.

***anti*-5,10,15-Tri(naphthalen-2-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (8b) and *syn*-5,10,15-Tri(naphthalen-2-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (9b):** The same procedure described for the synthesis of **8a** and **9a** using 2-bromonaphthalene to give a ca. 1:1.4 mixture of **8b** and **9b** (76%) as a white solid. The mixture can be separated by column chromatography (CH_2Cl_2/EtOAc, 10:1). **8b:** White solid; m.p. 282−284 °C; R_f = 0.91 (CH_2Cl_2/EtOAc, 10:1). IR: $\tilde{\nu}$ = 3521, 1594, 738 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.85 (s, 1 H), 2.91 (s, 1 H), 2.92 (s, 1 H), 7.09−7.01 (m, 6 H), 7.39−7.30 (m, 4 H), 7.49−7.41 (m, 7 H), 7.55 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.67 (d, *J* = 8.5 Hz, 2 H), 7.78−7.72 (m, 4 H), 7.90−7.87 (m, 3 H), 8.06−7.98 (m, 3 H), 8.31 (s, 1 H), 8.34 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 83.88, 84.03, 84.25, 123.35, 123.43, 123.63, 123.71, 123.91, 124.02, 125.69, 126.00, 126.06, 126.28, 126.39, 126.56, 127.54, 128.07, 128.12, 128.34, 128.54, 128.62, 128.73, 128.79, 131.69, 132.57, 132.67, 132.75, 133.36, 135.57, 135.87, 135.95, 136.04, 139.55, 139.69, 139.88, 139.97, 140.02, 140.32, 143.42, 143.63, 143.79, 151.02, 151.32, 151.63 ppm (13 signals were not observed due to overlapping). EI-MS: *m*/*z* (%) = 768 (39) [M^+], 720 (100), 641 (18), 592 (57), 465 (48). HRMS ($C_{57}H_{36}O_3$): calcd. 768.2664; found 768.2673. **9b:** White solid; m.p. 276−278 °C; R_f = 0.38 (CH_2Cl_2/EtOAc, 10:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3528, 1598, 750, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.00 (s, 3 H) 7.02−6.99 (m, 6 H), 7.26−7.21 (m, 6 H), 7.45 (dt, *J* = 8.9, 1.2 Hz, 3 H), 7.38 (dt, *J* = 8.9, 1.2 Hz, 3 H), 7.64 (d, *J* = 8.9 Hz, 3 H), 7.70 (d, *J* = 8.1 Hz, 3 H), 7.83 (d, *J* = 8.5 Hz, 3 H), 8.00−7.98 (m, 3 H), 8.24 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 83.69 123.15, 123.35, 123.67, 125.66, 126.00, 126.33, 127.51, 127.98, 128.15, 128.48, 128.70, 132.50, 133.22, 135.68, 139.36, 139.55, 143.90, 151.09 ppm. EI-MS: *m*/*z* (%) = 768 (11) [M^+], 720 (100), 592 (60), 465 (51). HRMS ($C_{57}H_{36}O_3$): calcd. 768.2664; found 768.2669.

***anti*-5,10,15-Tri(phenanthren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (8c) and *syn*-5,10,15-Tri(phenanthren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (9c):** To a solution of 9-bromophenanthrene (4.380 g, 16.38 mmol) in Et_2O (30 mL) was added *n*BuLi (6.55 mL, 16.38 mmol, 2.5 M in hexane) at −78 °C and the mixture was slowly warmed up to −10 °C. A suspension of **2** (900 mg, 2.34 mmol) in THF (100 mL) was added and the resulting mixture was stirred at 23 °C for 17 h. After the usual workup (Et_2O), the crude product was triturated with hexane to give a ca. 1.6:1 mixture of **8c** and **9c** (1.826 g, 85%) as a yellow solid. The mixture was separated by column chromatography (CH_2Cl_2/EtOAc, 15:1). **8c:** White solid; m.p. 296−298 °C; R_f = 0.81 (CH_2Cl_2/EtOAc, 15:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3556, 3506, 1466, 1054, 744, 718 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.81 (s, 1 H) 2.94 (s, 1 H), 3.00 (s, 1 H), 5.97 (t, *J* = 7.5 Hz, 1 H), 7.02−6.88 (m, 6 H), 7.24−7.05 (m, 6 H), 7.42−7.37 (m, 2 H), 7.57−7.52 (m, 3 H), 7.72−7.66 (m, 6 H), 8.14−8.10 (m, 2 H), 8.23−8.17 (m, 3 H), 8.29 (d, *J* = 7.3 Hz, 1 H), 8.72−8.50 (m, 6 H), 9.20 (d, *J* = 2.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 83.05 83.36, 122.43, 122.55, 122.81, 123.18, 123.43, 123.76, 123.88, 124.11, 124.82, 124.98, 125.15, 125.57, 125.65, 125.76, 126.31, 126.43, 126.57, 126.77, 126.88, 126.95, 127.07, 127.16, 128.64, 128.83, 129.18, 129.35, 130.64, 130.95, 131.25, 131.30, 131.45, 135.54, 135.69, 135.95, 137.15, 137.35, 137.45, 139.85, 140.05, 140.15, 150.08, 150.22, 150.51 ppm (24 signals were not observed due to overlapping). FAB-MS: *m*/*z* (%) = 918 (49) [M^+], 901 (100), 884 (12), 741 (14), 723 (10). HRMS ($C_{69}H_{42}O_3$) calcd. 918.3134; found 918.3129. **9c:** White solid; m.p. > 300 °C; R_f = 0.13 (CH_2Cl_2/EtOAc, 15:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3535, 1466, 1054, 742, 720 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.87 (s, 3 H), 6.05 (t, *J* = 6.9 Hz, 3 H), 7.02−6.91 (m, 6 H), 7.11−7.09 (m, 3 H), 7.25−7.19 (m, 3 H), 7.36−7.31 (m, 3 H), 7.71−7.65 (m, 6 H), 6.20 (d, *J* = 6.9 Hz, 3 H), 8.28 (d, *J* = 6.9 Hz, 3 H), 8.62−8.57 (m, 6 H), 9.19 (s, 3 H) ppm. FAB-MS: *m*/*z* (%) =

918 (35) [M$^+$], 901 (82), 884 (6), 741 (14), 723 (7). HRMS ($C_{69}H_{42}O_3$): calcd. 918.3134; found 918.3101.

***anti*-5,10,15-Tri(anthracen-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (8d) and *syn*-5,10,15-Tri(anthracen-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (9d):** To a solution of 9-bromoanthracene (1.410 g, 5.70 mmol) in THF (15 mL) was added *n*BuLi (2.18 mL, 5.47 mmol, 2.5 M in hexane) at −78 °C, to give an orange suspension. A suspension of **2** (300 mg, 0.78 mmol) in THF (50 mL) was added and the resulting mixture was stirred at 23 °C for 17 h. In the aqueous workup (Et_2O), solid **9d** (180 mg, 19%) precipitated. The residue of the extraction was triturated with CH_2Cl_2 and hexane to give crude product, which was chromatographed (hexane/CH_2Cl_2, 1:10) to give **8d** (250 mg, 37%). **8d:** Pale yellow solid; m.p. > 300 °C. R_f = 0.38 (hexane/CH_2Cl_2, 1:10). IR (KBr): $\tilde{\nu}_{max.}$ = 3514, 3436, 1698, 1596, 1466, 1308, 1034, 880, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.47 (s, 1 H), 2.89 (s, 1 H), 2.96 (s, 1 H), 6.15 (d, *J* = 7.7 Hz, 1 H), 6.10 (d, *J* = 7.8 Hz, 1 H), 6.48−6.37 (m, 2 H), 6.52 (dt, *J* = 8.0, 1.1 Hz, 2 H), 6.74−6.69 (m, 1 H), 6.86−6.79 (m, 3 H), 6.90 (tt, *J* = 7.6, 1.1 Hz, 2 H), 7.10−7.04 (m, 2 H), 7.21−7.13 (m, 1 H), 7.26−7.20 (m, 2 H), 7.48 (d, *J* = 7.7 Hz, 1 H), 7.62−7.52 (m, 6 H), 7.75−7.64 (m, 4 H), 7.85−7.80 (m, 2 H), 8.14−8.07 (m, 3 H), 8.40 (s, 1 H), 8.45 (s, 1 H), 8.48 (s, 1 H), 9.86−9.81 (m, 3 H) ppm. FAB-MS: *m*/*z* (%) = 918 (39) [M$^+$], 901 (59) [M$^+$ − OH], 884 (7) [M$^+$ − 2OH], 741 (11) [M$^+$ − $C_{14}H_9$], 723 (13) [M$^+$ − OH − $C_{14}H_9$]. HRMS ($C_{69}H_{32}O_3$): calcd. 918.3134; found 918.3127. **9d:** White solid; m.p. > 300 °C; R_f = 0.12 (hexane/CH_2Cl_2, 1:10). IR (KBr): $\tilde{\nu}_{max.}$ = 3514, 1723, 1614, 1463, 1151, 1040, 886, 730 cm^{-1}. ^{1}H NMR (1,1,2,2-[D_2]tetrachloroethane, 300 MHz, 120 °C): δ = 8.49−6.55 (br. m) 10.00−9.50 (br. m) ppm. MALDI-TOF MS (dithranol): *m*/*z* = 918 [M$^+$], 901 (100) [M$^+$ − OH], 884 [M$^+$ −2OH].

General Procedure for the Reduction of the 5,10,15-Triaryl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triols: To a solution of *anti*- and *syn*-triols **8/9** (0.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added Et_3SiH (12.5 mmol) and BF_3·OEt_2 (7.5 mmol) and the mixture was stirred at this temperature for 45 min. After the usual workup, crude **10a**−**d** was obtained.

***anti*-5,10,15-Tri(1-naphthyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (10a) and *syn*-5,10,15-Tri(1-naphthyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (11a):** The mixture of **8a/9a** was reduced to give a ca. 7:1 mixture **10a** and **11a** as a white solid (97%). The mixture can be separated by chromatography (hexane/CH_2Cl_2, 2:3). **10a:** White solid; m.p. > 300 °C; R_f = 0.56 (hexane/CH_2Cl_2, 2:3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.63 (s, 2 H) 6.66 (s, 1 H), 7.20−6.71 (m, 12 H), 7.40−7.32 (m, 3 H), 7.73−7.64 (m, 9 H), 7.84 (dt, *J* = 8.5, 1.6 Hz, 3 H), 8.02−7.97 (m, 3 H), 8.93 (t, *J* = 7.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 48.36, 48.47 122.40, 122.54, 122.85, 122.91, 123.38, 123.46, 123.69, 123.85, 125.03, 125.33, 125.44, 125.97, 126.06, 126.36, 126.67, 126.78, 127.12, 127.62, 129.23, 132.05, 134.28, 136.93, 136.99, 138.30, 139.17, 139.33, 139.95, 148.70, 148.81 ppm, (26 signals were not observed due to overlapping). EI-MS: *m*/*z* (%) = 720 (100) [M$^+$], 592 (67), 465 (24). HRMS ($C_{57}H_{36}$): calcd. 720.2817; found 720.2808. **11a:** White solid; m.p. > 300 °C; R_f = 0.38 (hexane/CH_2Cl_2, 2:3). ^{1}H NMR (1,1,2,2-[D_2]tetrachloroethane, 300 MHz, 60 °C): δ = 5.13 (s, 3 H), 6.74 (d, *J* = 6.7 Hz, 3 H), 6.87−6.80 (m, 3 H), 7.19−6.94 (m, 9 H), 7.24 (d, *J* = 7.6 Hz, 3 H), 7.70−7.46 (m, 12 H), 7.87 (d, *J* = 8.3 Hz, 3 H), 8.46−8.43 (m, 3 H) ppm. EI-MS: *m*/*z* (%) = 720 (100) [M$^+$], 592 (67), 465 (24). HRMS ($C_{57}H_{36}$): calcd. 720.2817; found 720.2797.

Isomerization of *anti*-10a to *syn*-11a: A suspension of **10a** (46 mg, 0.107 mmol) and KO*t*Bu (14 mg, 0.12 mmol) was heated in *t*BuOH (20 mL) under refluxing conditions for 20 h. After the usual workup (CH_2Cl_2), and trituration with hexane, **11a** (47 mg, 84%) was obtained.

***anti*-5,10,15-Tri(naphthalen-2-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (10b):** The mixture of **8b/9b** was reduced to a mixture of **10b**−**11b**. Trituration with hexane gave **10b** as a white solid (75%). **10b:** White solid; m.p. 238−240 °C; R_f = 0.59 (hexane/CH_2Cl_2, 3:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.85 (s, 1 H), 5.87 (s, 1 H), 5.84 (s, 1 H), 7.10−7.01 (m, 6 H), 7.16 (t, *J* = 2.02 Hz, 1 H), 7.19 (t, *J* = 2.0 Hz, 1 H), 7.29 (d, *J* = 1.6 Hz, 1 H), 7.48−7.35 (m, 9 H), 7.74−7.62 (m, 10 H), 7.83−7.80 (m, 2 H), 7.87 (d, *J* = 1.2 Hz, 1 H), 7.93 (d, *J* = 1.2 Hz, 1 H), 7.95 (d, *J* = 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 54.10 54.21, 123.46, 123.57, 124.69, 124.89, 124.94, 125.31, 125.42, 125.55, 125.89, 125.97, 126.14, 126.25, 126.84, 126.92, 127.00, 127.49, 127.54, 128.87, 128.93, 132.50, 133.78, 138.72, 138.95, 139.05, 139.55, 139.61, 148.73, 148.87 ppm, (27 signals were not observed due to overlapping). EI-MS: *m*/*z* (%) = 720 (100) [M$^+$], 592 (47), 465 (39). HRMS ($C_{57}H_{36}$): calcd. 720.2817; found 720.2834.

Isomerization of *anti*-10b to *syn*-11b: Following the procedure described for the isomerization of *anti*-**10a**, **11b** (75%) was obtained. **11b:** Pale yellow solid; m.p. > 300 °C; R_f = 0.53 (hexane/CH_2Cl_2, 3:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.88 (s, 3 H), 7.81 (d, *J* = 7.9 Hz, 3 H), 7.74−7.67 (m, 6 H), 7.59−7.57 (m, 3 H), 7.48−7.36 (m, 9 H), 7.17−7.08 (m, 9 H), 5.43 (s, 3 H) ppm. EI-MS: *m*/*z* (%) = 720 (100) [M$^+$], 592 (61), 465 (50). HRMS ($C_{57}H_{36}$): calcd.720.2817; found 720.2803.

***anti*-5,10,15-Tri(phenanthren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (10c):** The mixture of **8c/9c** was reduced to a mixture of **10c/11c**. Trituration with hexane gave **10c** (71%). **10c**: White solid; m.p. 300−302 °C; R_f = 0.67 (1:1 hexane/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.78−6.70 (m, 4 H), 6.89−6.81 (m, 3 H), 7.10 (s, 1 H), 7.25−7.22 (m, 6 H), 7.41−7.35 (m, 6 H), 7.58−7.46 (m, 5 H), 7.69−7.64 (m, 2 H), 7.89−7.83 (m, 3 H) 8.01−7.95 (m, 3 H), 8.68−8.57 (m, 3 H), 8.91−8.86 (m, 3 H), 9.09−9.03 (m, 3 H) ppm. MALDI-TOF MS (dithranol): *m*/*z* = 870 [M$^+$]. FAB-MS: *m*/*z* (%) = 870 (30) [M$^+$], 693 (34).

Isomerization of *anti*-10c to *syn*-11c: Following the procedure described for the isomerization of **10a**, **11c** (74%) was obtained. **11c:** Pale brownish solid; m.p. 298−300 °C; R_f = 0.54 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.04 (t, *J* = 7.3 Hz, 3 H) 6.99−6.91 (m, 6 H), 7.10 (d, *J* = 7.3 Hz, 3 H), 7.21 (t, *J* = 7.7 Hz, 3 H), 7.33 (t, *J* = 7.5 Hz, 3 H), 7.68−7.64 (m, 9 H), 8.20 (d, *J* = 9.7 Hz, 3 H), 8.27 (d, *J* = 7.3 Hz, 3 H), 9.18 (s, 3 H), 8.60−8.57 (m, 6 H) ppm. FAB-MS: *m*/*z* (%) = 870 (20) [M$^+$], 693 (26).

***anti*-5,10,15-Tri(anthracen-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-(10d):** The mixture of **8d/9d** was reduced give crude **10d**. Trituration with hexane gave **10d** (63%). **10d:** Pale yellow solid; m.p. > 300 °C; R_f = 0.54 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.53−6.43 (m, 3 H), 6.62−6.56 (m, 1 H), 6.82−6.71 (m, 8 H), 6.92−6.89 (m, 2 H), 7.18−6.97 (m, 9 H), 7.32−7.25 (m, 2 H), 7.63 (t, *J* = 7.5 Hz, 3 H), 7.78−7.71 (m, 3 H), 7.81 (d, *J* = 8.9 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 1 H, 2 H), 8.19 (d, *J* = 8.5 Hz, 3 H), 8.44 (s, 2 H), 8.46 (s, 1 H), 9.04−8.91 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 49.26, 123.20, 123.28, 123.34, 123.94, 124.99, 124.08, 124.22, 124.65, 124.70, 124.79, 124.84, 124.90, 125.29, 125.33, 125.51, 126.39, 126.45, 126.48, 126.75, 126.91, 126.95, 127.84, 127.95, 128.75, 128.87, 129.29, 129.70, 129.82, 129.97, 131.58, 131.77, 131.83, 131.87, 132.93,

132.00, 132.16, 132.19, 132.59, 137.81, 138.02, 138.05, 138.70, 138.76, 138.96, 142.54, 143.26, 143.31, 147.92, 148.09, 148.26 ppm (17 signals were not observed due to overlapping). MALDI-TOF MS (dithranol): *m*/*z* = 870 [M^+], 693 [$M^+ - C_{14}H_9$]. FAB-MS: *m*/*z* (%) = 870 (9) [M^+], 693 (7) [$M^+ - C_{14}H_9$]. HRMS ($C_{69}H_{42}$) calcd. 870.3286; found 870.3271.

***syn*-5,10,15-Tri(4*aH*-fluoren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-triol (12):** To a solution of fluorene (3.636 g, 21.88 mmol) in Et_2O (30 mL) was added *n*BuLi (8.75 mL, 21.88 mmol, 2.5 M in hexane) at −78 °C and the mixture was slowly warmed up to 5 °C. A suspension of **2** (1.200 g, 3.13 mmol) in THF (120 mL) was added and the mixture was slowly warmed up to 23 °C and stirred at this temperature for 3 h. After the usual workup (Et_2O), the solid was triturated with hexane to give a mixture of **12,** and mono- and bis-addition products (2.300 mg). Traces of the *anti* isomer were also observed by ^{1}H NMR of the crude mixture. Pure *syn* **12** was obtained by column chromatography (1.350 mg, 49%). **12:** Pale yellow solid; m.p. > 300 °C; R_f = 0.44 (hexane/EtOAc, 3:1). IR (KBr): $\tilde{\nu}_{max.}$ = 3535, 3500, 1442, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.61 (s, 3 H). 5.43 (s, 3 H), 6.23 (d, *J* = 7.3 Hz, 3 H), 6.50 (t, *J* = 7.5 Hz, 3 H), 6.77 (t, *J* = 7.4 Hz, 3 H), 6.93 (t, *J* = 7.3 Hz, 3 H), 7.17 (t, *J* = 7.5 Hz, 3 H), 7.34 (d, *J* = 8.1 Hz, 3 H), 7.57−7.47 (m, 9 H), 7.80−7.76 (m, 3 H), 8.52−8.48 (m, 3 H), 8.79 (d, *J* = 8.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 50.90, 84.56, 119.44, 119.60 122.32, 123.50, 125.81, 126.18, 126.76, 127.35, 127.84, 127.95, 128.69, 129.01, 137.23, 139.76, 141.37, 142.51, 142.89, 143.39, 143.73, 147.06 ppm. MALDI-TOF MS (dithranol+NaI): *m*/*z* = 1788 [$2M^+$ + Na], 905 [M^+ + Na], 865, 848, 740, 700, 683, 627, 598, 535 (100). FAB-MS: *m*/*z* (%) = 865 (100) [M^+ − OH], 848 (12) [M^+ − 2OH], 829 (9), 717 (62), 700 (30), 663 (74). EI-MS: *m*/*z* (%) = 551 (100) [$M^+ - 2C_{13}H_9$], 535 (75) [$M^+ - 2C_{13}H_9$, − OH], 519 (46). $C_{66}H_{42}O_3 \cdot H_2O$: calcd.C 87.97, H 4.89; found C 87.72, H 5.10.

***anti*-5,10,15-Tri(4*aH*-fluoren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (13) and *syn*-5,10,15-Tri(4*aH*-fluoren-9-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (14):** To a suspension **12** (720 mg, 0.82 mmol) in CH_2Cl_2 (50 mL) was added Et_3SiH (2 mL) and $BF_3 \cdot OEt_2$ (1 mL) at 0 °C. The mixture was slowly warmed up to 23 °C for 17 h. After the usual workup (CH_2Cl_2), the residue was triturated (EtOAc) to give a ca. 5:1 mixture of **13** and **14** (486 mg, 71%). The mixture was separated by chromatography (hexane/EtOAc, 10:1). **13:** White solid; m.p. > 300 °C; R_f = 0.40 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.18 (br. s, 1 H), 5.32 (d, *J* = 3.2 Hz, 1 H), 5.34 (d, *J* = 2.4 Hz, 1 H), 5.53 (d, *J* = 2.4 Hz, 1 H), 5.64 (d, *J* = 2.0 Hz, 1 H), 5.72 (d, *J* = 2.8 Hz, 1 H), 5.76 (d, *J* = 7.7 Hz, 1 H), 6.11 (dt, *J* = 7.5, 0.8 Hz, 1 H), 6.19 (d, *J* = 7.3 Hz, 1 H), 6.23 (d, *J* = 7.3 Hz, 1 H), 6.30 (d, *J* = 7.7 Hz, 1 H), 6.47 (d, *J* = 6.5 Hz, 1 H), 6.61 (t, *J* = 7.7 Hz, 2 H), 6.87−6.74 (m, 5 H), 6.99 (t, *J* = 7.5 Hz, 1 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.30−7.23 (m, 3 H), 7.40 (d, *J* = 7.7 Hz 1 H), 7.46 (d, *J* = 7.3 Hz, 1 H), 7.65−7.53 (m, 7 H), 7.77 (d, *J* = 7.3 Hz, 2 H), 7.86 (d, *J* = 8.5 Hz, 1 H), 8.32−8.20 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 47.21, 47.41, 47.46, 49.08, 49.72, 50.09, 119.14, 119.22, 119.42, 120.06, 120.12, 122.15, 122.46, 123.44, 123.55, 123.74, 123.83, 123.96, 124.13, 124.24, 125.69, 125.89, 126.08, 126.14, 126.28, 126.45, 126.64, 126.81, 126.89, 127.23, 127.40, 127.51, 127.67, 138.30, 138.47, 138.55, 139.56, 139.81, 140.00, 140.28, 140.39, 140.62, 140.67, 140.81, 140.92, 142.15, 142.40, 142.79, 143.66, 144.35, 144.46, 145.08, 145.97, 146.05, 146.19 ppm (11 signals were not observed due to overlapping). FAB-MS: *m*/*z* (%) = 835 (6) [M^+ +1], 669 (100), 505 (70). EI-MS: *m*/*z* (%) = 834 (0.3) [M^+], 669 (57), 504 (22), 339 (100), 165 (45). HRMS ($C_{69}H_{42}$) calcd. 834.3287; found 834.3286. **14:** Pale yellow solid; m.p. > 300 °C; R_f = 0.22 (hexane/EtOAc, 10:1). ^{1}H NMR ([D_8]toluene, 300 MHz): δ = 4.47 (s, 3 H) 5.08 (s, 3 H), 6.30 (d, *J* = 7.3 Hz, 3 H), 6.43 (t, *J* = 7.1 Hz, 3 H), 6.62 (t, *J* = 7.8 Hz, 3 H), 6.85 (t, *J* = 8.1 Hz, 3 H), 7.27 (d, *J* = 7.7 Hz, 3 H), 7.40−7.33 (m, 6 H), 7.58 (d, *J* = 8.1 Hz, 3 H), 7.63 (d, *J* = 7.7 Hz, 3 H), 7.84 (d, *J* = 6.9 Hz, 3 H) ppm, (other aryl hydrogens are overlapping with the signals of the solvent). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.32 (s, 3 H), 4.84 (s, 3 H), 6.06 (d, *J* = 7.9 Hz, 3 H), 6.19 (t, *J* = 7.5 Hz, 3 H), 6.65 (d, *J* = 7.9 Hz, 3 H), 6.79 (t, *J* = 7.5 Hz, 3 H), 6.99 (t, *J* = 7.4 Hz, 3 H), 7.33 (t, *J* = 7.8 Hz, 3 H), 7.42 (d, *J* = 7.3 Hz, 3 H), 7.51−7.48 (m, 6 H), 7.64−7.60 (m, 3 H), 7.74−7.71 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 46.79, 48.52, 119.31, 119.78, 122.74, 123.21, 123.83, 124.55, 125.58, 126.20, 126.67, 126.92, 127.15, 127.51, 137.29, 139.81, 140.31, 140.70, 141.98, 143.32, 144.91, 145.91 ppm. MALDI-TOF MS (dithranol): *m*/*z* = 834 [M^+], 669 (100). FAB-MS: *m*/*z* (%) = 835 (8) [M^+ +1]. EI-MS: *m*/*z* (%) = 834 (0.5) [M^+], 669 (71), 504 (33), 339 (100), 165 (59). HRMS ($C_{69}H_{42}$): calcd. 834.3286; found 834.3267.

5,10,15-Tri(fluoren-9-ylidene)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4). Method a: To a suspension of *anti*-**13** (110 mg, 0.13 mmol) in *t*BuOH (6 mL) was added K-*t*BuO (20 mg, 0.18 mmol) and the mixture was heated under refluxing conditions for 20 h. After the usual workup and chromatography (hexane/CH_2Cl_2, 3:1), **4** (20 mg, 19%) and *syn*-**14** (44 mg, 40%) were obtained. **Method b:** To a solution of thionyl chloride (0.2 mL, 2.74 mmol) in CH_2Cl_2 (4 mL) at 0 °C, was added **12** (200 mg, 0.23 mmol) in pyridine (20 mL). The mixture was stirred at 23° for 2 h and at 65 °C for 17 h. The mixture was partitioned between 10% HCl and CH_2Cl_2. After the usual workup and chromatography (hexane/CH_2Cl_2, 3:2) **4** (20 mg, 11%) was obtained. **4:** Dark purple solid; m.p. > 300 °C; R_f = 0.63 (hexane/CH_2Cl_2, 3:2). IR (KBr): $\tilde{\nu}_{max.}$ = 3050, 2914, 2842, 1440, 1342, 1094, 776, 754, 722 cm^{-1}. UV/Vis (chlorobenzene): $\lambda_{max.}$(log ε) = 296 (4.53), 373 (4.16), 500 (4.49), 550 nm (sh). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.55 (t, *J* = 7.5 Hz, 1 H), 6.69−6.62 (m, 2 H), 6.74 (t, *J* = 7.5 Hz, 1 H), 6.82 (t, *J* = 7.5 Hz, 1 H), 6.90 (t, *J* = 7.6 Hz, 1 H), 7.05−6.95 (m, 4 H), 7.17−7.11 (m, 2 H), 7.33−7.23 (m, 3 H), 7.45−7.37 (m, 5 H), 7.52−7.49 (m, 2 H), 7.55 (d, *J* = 7.4 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.75−7.72 (m, 2 H), 7.80−7.77 (m, 2 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 8.43 (d, *J* = 8.0 Hz, 1 H), 8.47 (d, *J* = 7.7 Hz, 1 H), 8.49 (d, *J* = 8.1 Hz, 1 H), 8.55 (d, *J* = 7.7 Hz, 1 H), 8.56 (d, *J* = 10.8 Hz, 1 H), 8.58 (d, *J* = 8.1 Hz, 1 H) ppm. MALDI-TOF MS: *m*/*z* = 828 [M^+]. FAB-MS: *m*/*z* (%) = 829 (100) [M^+ + H$^+$], 663 (83). HRMS ($C_{66}H_{36}$): calcd. 828.2817; found 828.2808.

10,15-Bi(fluoren-9-ylidene)-10,15-dihydro-diindene[1,2-*a*;1′,2′-*c*]fluoren-5-one (15): When the method b used for the preparation of **4** ($SOCl_2$, pyridine, 65 °C) was carried out with the crude product of addition of fluorenyllithium to **2** (containing mono- and bis-addition products), ketone **15** could be isolated. **15**: Red solid; m.p. 298−300 °C; R_f = 0.33 (hexane/CH_2Cl_2, 3:2). IR (KBr): $\tilde{\nu}_{max.}$ = 3048, 2914, 2844, 1701, 1595, 1564, 730 cm^{-1}. UV/Vis [(chlorobenzene): $\lambda_{max.}$(log ε) = 290 (4.18), 340 (4.51), 384 (4.06), 438 (3.93), 524 nm (4.19). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.75 (dt, *J* = 7.7, 1.2 Hz, 1 H), 6.93 (dt, *J* = 7.7, 1.2 Hz, 1 H), 7.09 (t, *J* = 7.5 Hz, 3 H), 7.18 (t, *J* = 7.1 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.44−7.39 (m, 4 H), 7.52−7.46 (m, 4 H), 7.58 (d, *J* = 7.3 Hz, 2 H), 7.75−7.66 (m, 4 H), 7.82 (d, *J* = 7.3 Hz, 2 H), 8.47 (d, *J* = 7.3 Hz, 1 H), 8.66 (d, *J* = 7.7 Hz, 1 H), 9.24 (d, *J* = 7.7 Hz, 1 H), 9.58 (d, *J* = 6.9 Hz, 1 H) ppm. MALDI-TOF MS (dithranol): *m*/*z* = 681 [M^+ +1]. FAB-MS: *m*/*z* (%) = 680 (8) [M^+].

Acetylation of 12: To a suspension of **12** (400 mg, 0.45 mmol) in Ac_2O (25 mL) was added $ZnCl_2$ (12 mg, 0.09 mmol). The mixture was heated at 120 °C for 4 h. After the usual workup (CH_2Cl_2) chromatography (hexane/CH_2Cl_2, 4:1), triacetate **16** (120 mg, 27%) and a 2:1 mixture of *anti-syn* mixture of diacetates **17** and **18** was obtained (30 mg, 7%). **16**: Dark red solid; m.p. > 270−272 °C; R_f = 0.22 (hexane/CH_2Cl_2, 1:4). IR (KBr): $\tilde{\nu}_{max.}$ = 3050, 2918, 2846, 1748, 1442, 1362, 1218, 1022, 758 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.97 (s, 3 H), 2.12 (s, 3 H), 2.29 (s, 3 H), 5.29 (s, 1 H), 5.59 (s, 1 H), 5.67 (s, 1 H), 6.07 (d, *J* = 7.5 Hz, 1 H), 6.17 (d, *J* = 7.3 Hz, 1 H), 6.24 (d, *J* = 7.5 Hz, 1 H), 6.44−6.35 (m, 2 H), 6.85−6.73 (m, 5 H), 7.03−6.94 (m, 3 H), 7.08 (d, *J* = 7.5 Hz, 1 H), 7.35−7.15 (m, 6 H), 7.57−7.48 (m, 7 H), 7.69−7.65 (m, 2 H), 7.79 (dd, *J* = 8.5, 2.0 Hz, 1 H), 8.48−8.38 (m, 3 H), 8.62−8.56 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.99, 21.05, 21.35, 49.86, 50.14, 50.71, 88.63, 89.66, 89.90, 118.35, 118.78, 118.85, 119.50, 119.57, 119.73, 121.15, 122.12, 122.18, 123.81, 123.92, 123.97, 125.60, 125.81, 126.17, 126.25, 126.41, 126.64, 126.75, 127.10, 127.23, 127.35, 127.42, 127.58, 127.63, 128.04, 128.11, 128.22, 128.50, 128.69, 137.87, 138.02, 138.33, 138.70, 138.80, 139.00, 139.58, 139.85, 140.10, 140.21, 140.81, 141.16, 141.37, 142.39, 142.94, 143.10, 143.18, 143.53, 143.64, 144.13, 166.68, 167.53 ppm (11 signals were not observed due to overlapping). MALDI-TOF MS (dithranol): *m/z* = 949 (100) [M^+ − AcO], 890 [M^+ − 2AcO]. MALDI-TOF MS: *m/z* (dithranol + NaI) = 890 [M^+ − 2AcO], 949 (100) [M^+ − AcO], 1031 [M^+ + Na].

17/18 (2:1): Dark red solid;. R_f = 0.15 (hexane/CH_2Cl_2, 1:2). IR: $\tilde{\nu}$ = 3050, 2914, 2842, 1744, 1440, 1356, 1214, 1020, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.94 (s, 6 H), 2.14 (s, 3 H), 2.28 (s, 6 H), 2.37 (s, 3 H), 5.46 (s, 1 H), 5.52 (s, 1 H), 5.69 (s, 2 H), 5.81 (s, 2 H), 5.90−5.84 (m, 2 H), 6.15 (dd, *J* = 7.7, 4.2 Hz, 1 H), 6.21 (d, *J* = 7.5 Hz, 2 H), 6.27 (d, *J* = 7.5 Hz, 4 H), 6.35−6.31 (m, 4 H), 6.43 (t, *J* = 7.7 Hz, 2 H), 6.59 (t, *J* = 7.3 Hz, 2 H), 7.05−6.66 (m, 22 H), 7.18−7.12 (m, 3 H), 7.45−7.27 (m, 15 H), 7.62−7.48 (m, 24 H), 7.77−7.67 (m, 10 H), 8.35−8.32 (m, 1 H), 8.41 (d, *J* = 8.3 Hz, 2 H), 8.47 (d, *J* = 7.5 Hz, 2 H), 8.58−8.51 (m, 6 H), 8.76 (d, *J* = 8.1 Hz, 2 H), 8.84 (d, *J* = 8.1 Hz, 1 H), 9.07 (d, *J* = 7.9 Hz, 1 H), 9.13 (d, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.22, 21.28, 21.35, 21.42, 22.66, 50.00, 50.31, 50.89, 51.35, 89.03, 89.22, 89.40, 89.79, 118.44, 118.67, 118.92, 119.02, 119.34, 119.43, 119.61, 119.96, 120.01, 120.09, 120.13, 120.65, 121.76, 121.82, 122.18, 123.88, 123.97, 124.05, 124.11, 124.27, 124.43, 125.12, 125.37, 125.49, 125.78, 125.86, 125.93, 126.22, 126.43, 126.56, 126.59, 126.63, 126.75, 126.80, 126.87, 126.98, 127.10, 127.30, 127.33, 127.37, 127.41, 127.59, 127.65, 127.77, 127.88, 127.95, 128.08, 128.18, 128.36, 128.55, 128.72, 128.79, 129.35, 129.49, 132.11, 137.35, 137.55, 137.70, 137.86, 137.92, 138.08, 138.34, 138.45, 138.58, 138.86, 139.23, 139.47, 139.77, 139.88, 139.95, 140.02, 140.12, 140.31, 140.35, 140.39, 140.46, 140.74, 141.02, 141.24, 141.44, 141.93, 141.98, 142.25, 142.32, 142.47, 142.75, 142.79, 142.82, 142.90, 142.95, 143.01, 143.13, 143.36, 143.49, 143.53, 143.64, 143.78, 166.73, 167.11, 167.20 ppm (37 signals were not observed due to overlapping). MALDI-TOF MS (dithranol): *m/z* = 949 [M^+], 905, 889 (100) [M^+ − AcOH], 845, 830 [M^+ − 2AcOH], 741, 697, 681.

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