Synthesis of New C_{3h} and C_{3v} Truxene Derivatives

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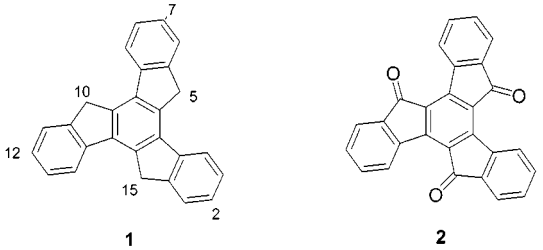
Palladium-catalyzed cross coupling of 2,7,12-tribromotruxene with organostannanes and boronic acids leads to 2,7,12-trisubstituted truxenes. 5,10,15-Triarylated and trialkynylated truxene derivatives are obtained by the reaction of truxenone with aryl Grignard reagents or an alkynyllithium, followed by reduction of the tertiary alcohols with Et_3SiH or BF_3. *syn*-5,10,15-Triarylated derivatives were obtained by the base-catalyzed isomerization of the *anti* derivatives.

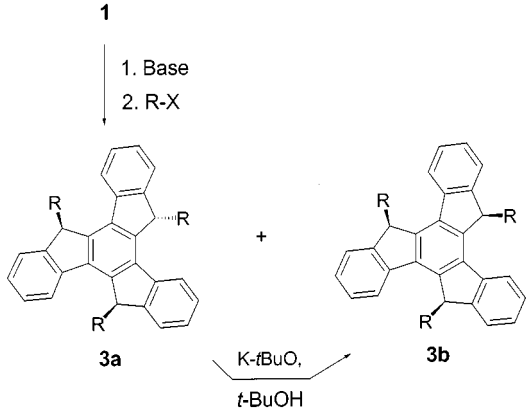
Introduction

The heptacyclic polyarene truxene (10,15-dihydro-*5H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene) (**1**) and the triketone truxenone (diinden[1,2-a;1′,2′-c]fluore-5,10,15-trione) (**2**) have received attention as potential starting materials for the construction of larger polyarenes.[1−4] As part of a program on the synthesis of polycyclic aromatic hydrocarbons related to fragments of the fullerenes,[5] we have recently developed a synthesis of truxene derivatives by the reaction of the trianion of **1** with a variety of alkylating agents (Scheme 1). This alkylation reaction furnishes mixtures of *anti*- (**3a**) and *syn*-5,10,15-trialkylated (**3b**) derivatives, from which the less soluble *syn*-trialkylated truxenes **3b** were separated selectively by crystallization. Interestingly, in most cases, the *anti* derivatives **3a** were cleanly isomerized with KO*t*Bu in *t*BuOH under refluxing conditions to their *syn* isomers **3b**.[6] Derivatives of type **3** with *o*-bromobenzyl or 1-bromonaphthyl-2-methyl side chains were used as starting materials for the synthesis of large polyarenes[6,7] with an intramolecular palladium-catalyzed arylation[8−10] as the key step.



1 **2**

Scheme 1



The derivatives **3b** were shown to self-associate in solution.[6] However, the accurate determination of the association constant in certain cases was hampered by the very low solubility of some of these derivatives. We therefore, decided to synthesize more soluble truxenes substituted on the aryl rings by using palladium-catalyzed cross-coupling reactions from 2,7,12-tribromotruxene (**5c**).[11] This derivative was synthesized by the electrophilic bromination of **1**. We have also examined a more classical approach based on the acid-catalyzed trimerization of substituted indanones.[12,13] It is important to note that, although planar C_3 substituted truxenes have received great attention as liquid crystals, only hexaesters or hexaethers of 2,3,7,8,12,13-hexahydroxytruxenes have been studied.[14−19] We also report the synthesis of 5,10,15-trisubstituted C_{3v} truxenes from truxenone (**2**), which may serve as templates for the construction of larger molecular arrays.

Results and Discussion

Synthesis of C_{3h} Truxenes by Acid-Catalyzed Trimerization of Indanones

Simple truxenes are commonly synthesized by the acid-catalyzed trimerization of 1-indanones.[12,13,20] Alternatively, 3-phenylpropionic acids could also be employed as

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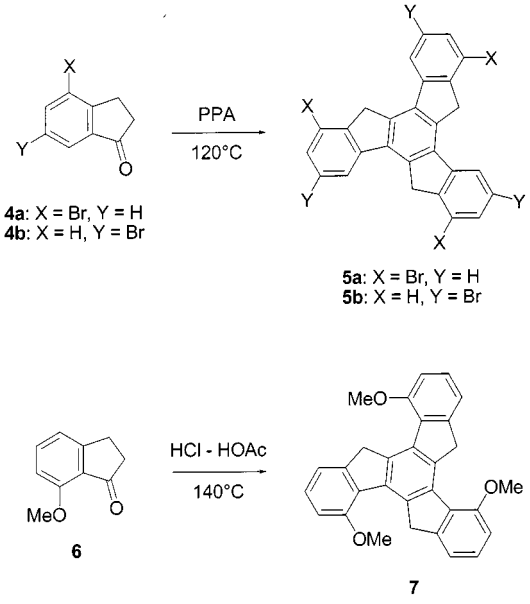
the starting materials since these compounds cyclize to 1-indanones under the acidic reaction conditions.[21] We therefore tried the trimerization of 4-bromo- (**4a**) and 6-bromo-1-indanone (**4b**), which were readily available by the bromination of 1-indanone with excess Br_2 and $AlCl_3$.[22,23] The best results were obtained by performing the condensation reactions in polyphosphoric acid at 120 °C. Nevertheless, the corresponding tribromotruxenes **5a** and **5b** were obtained in low yields (43 and 24%, respectively) as insoluble solids (Scheme 2). Due to the low solubility of **5a**−**b**, analytically pure samples could not be obtained by recrystallization or flash column chromatography.



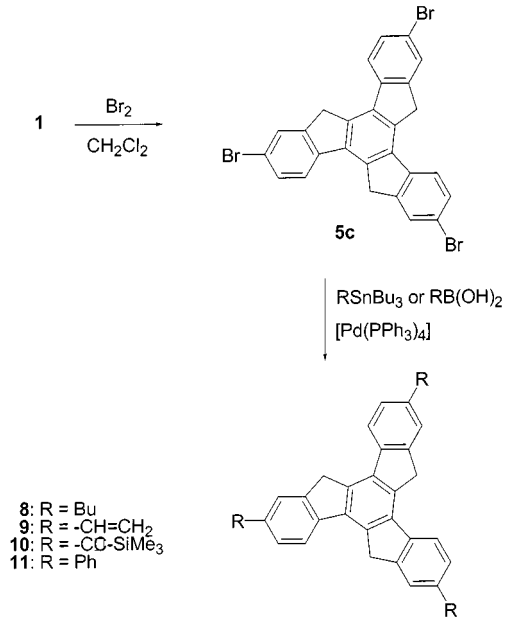
Scheme 2

We also tried to synthesize a truxene substituted at the more sterically hindered C-4, C-9, and C-13 positions. We expected that this steric hindrance would give rise to an increased solubility in common solvents. The trimerization of 7-methoxy-1-indanone (**6**)[24] was performed in a mixture of HOAc and HCl at 140 °C for 16 h, yielding 4,9,13-trimethoxytruxene **7** in 28% yield. The ^1H NMR spectrum of **7** in $CDCl_3$ at room temperature showed the methylene hydrogens as a broad singlet at $\delta = 4.58$, as a probable consequence of the slow *syn-anti* conformer interconversion. As expected, truxene **7** is more soluble than **5a** and **5b**.

Although the acid-catalyzed trimerization of 1-indanones allows for the straightforward synthesis of truxenes, the isolated yields were rather low. More importantly, the need for strongly acidic conditions in the trimerization is a serious limitation for the synthesis of truxenes bearing functional groups sensitive to acids.

Synthesis of C_{3h} Substituted Truxenes by Palladium-Catalyzed Coupling Reactions

The electrophilic bromination of truxene (**1**) was examined more than one hundred years ago.[21a] However, at that time the actual formula of **1** was under discussion and a dimeric $C_{18}H_{12}$ structure was actually preferred, and obviously the regiochemistry of the resulting derivative was not demonstrated. Based on simple orientation effects in the aromatic electrophilic substitution, the reaction of **1** with Br_2 was expected to furnish **5c** by reaction at C-2, C-7, and C-12, which are *para* to the central aromatic ring. In the event, the reaction of **1** with Br_2 (5 mol equiv.) in CH_2Cl_2 at 23 °C for 16 h in the dark afforded **5c** in 92% yield (Scheme 3). This truxene is also rather insoluble and the ^1H NMR spectrum had to be measured in $[D_2]$1,1,2,2-tetrachloroethane at 130 °C. Iodination with $[Ipy_2]BF_4$ [25] afforded a mixture of the triiodo and diiodo derivatives, which could not be separated due to their high insolubility.



Scheme 3

The Stille coupling[26] of tribromo **5c** with tetrabutyltin (6 mol equiv.) was performed in the presence of $Pd(PPh_3)_4$ (30 mol %) in toluene (15 mL) under refluxing conditions to furnish **8** in 42% yield. The alternative Suzuki coupling[27] of **5c** with 1-butylboronic acid and aqueous 2 M K_2CO_3 also proceeded with $Pd(PPh_3)_4$ (30 mol %) in toluene (reflux) to afford **8**, albeit in lower yield (30%) (Scheme 3). The NOE's summarized in Figure 1 fully confirm the assigned regiochemistry for the parent tribromotruxene **5c** and its derivatives.

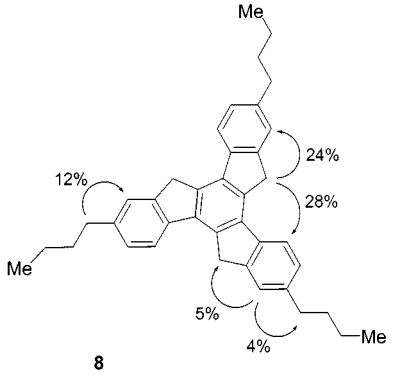


Figure 1. Significant NOE's observed on tributyltruxene **8**

The coupling of **5c** (100 mg, 0.17 mmol) with vinyltributyltin (6 mol equiv.) in the presence of $Pd(PPh_3)_4$ (30 mol %) in toluene under refluxing conditions[28] afforded 2,7,12-trivinyltruxene (**9**) in 39% yield. Surprisingly, the ^1H NMR spectrum ([D_2]1,1,2,2-tetrachloroethane, 26 °C) of **9**, in addition to the signals corresponding to the vinyl and aryl hydrogens, showed two broad singlets at $\delta = 4.23$ (s, 3 H) and 4.25 (s, 3 H) for the methylene hydrogens, which correlate with the methylene carbon at $\delta = 36.2$ in the HMQC experiment. This result is unlikely to be caused by hindered rotation of the vinyl groups, since low barriers (3.1 to 3.3 kcal·mol^{-1}) are associated with this rotation.[29] On the other hand, gelation[30] was clearly observed upon cooling a warm [D_2]1,1,2,2-tetrachloroethane solution to room temperature, which suggest that the unexpected splitting may be due to a self-association of **9**. Indeed, heating at 100 °C in [D_2]1,1,2,2-tetrachloroethane led to the expected singlet at $\delta = 4.24$ for the methylene hydrogens.

Similar couplings of **5c** with (trimethylsilylethynyl)tributyltin and phenyltributyltin furnished truxenes **10** (54%) and **11** (59%), respectively. 2,7,12-Triphenyltruxene (**11**) could also be obtained by the Suzuki coupling with phenylboronic acid in 60% yield.

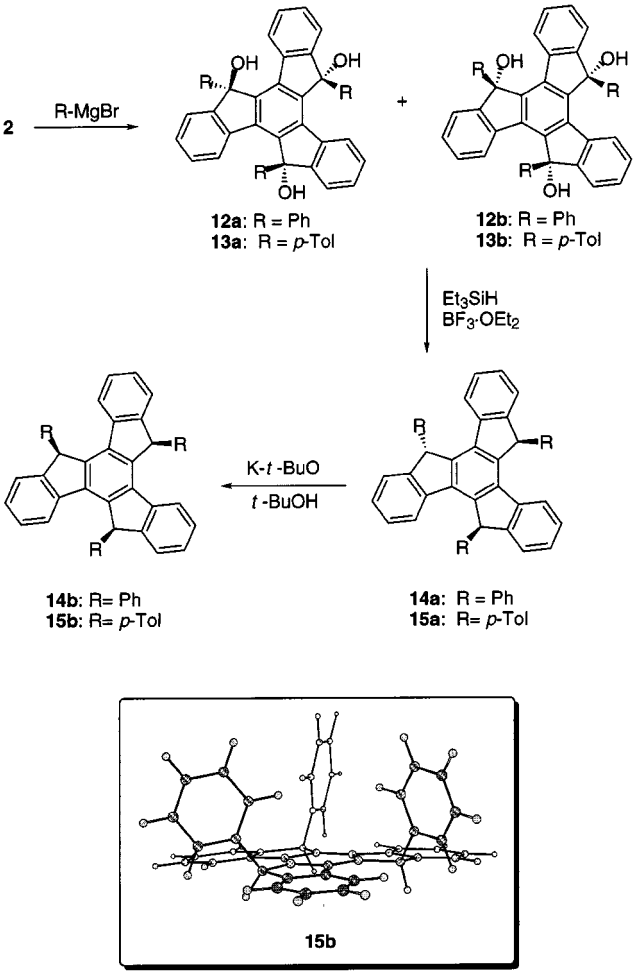
Synthesis of C_{3v} Truxenes from Truxenone

The reaction of truxenone (**2**) with organolithium reagents has been used for the synthesis of *syn*- and *anti* mixtures of the corresponding triols.[2,3,12] Accordingly, the reaction of **2** with phenylmagnesium bromide and *p*-tolylmagnesium bromide afforded **12** and **13** in 83 and 92% yields, respectively (Scheme 4). These derivatives were obtained as ca. 1.6:1 mixtures of *anti* (**12a** and **13a**) and *syn* (**12b** and **13b**) derivatives, which could be separated by chromatography.

Removal of the hydroxyl group was carried out by reduction of the benzylic carbocations with Et_3SiH.[31] Interestingly, reaction of the mixture of **12a** and **12b** with Et_3SiH and $BF_3{\cdot}OEt_2$ at 0 °C in CH_2Cl_2 afforded selectively *anti* **14a** in 73% yield. Analogously, a mixture **13a** and **13b** gave exclusively *anti* **15a** in 83% yield (Scheme 4). Interestingly, reduction was also observed upon treatment of the tertiary alcohols with $BF_3{\cdot}OEt_2$ in CH_2Cl_2, a result that has precedent in the chemistry of polycyclic aromatic hydrocarbons.[32]

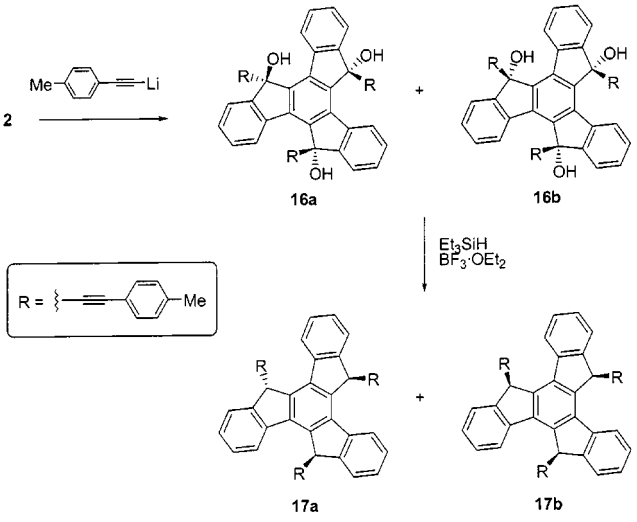
The isomerization of the *anti*-triaryl truxenes was performed with KO*t*Bu in *t*BuOH under reflux.[6] Under these conditions, the less soluble *syn*-triaryl derivatives **14b** and **15b** were obtained in 60% and 70% yields, respectively. The minimized structure for *syn*-5,10,15-triphenyltruxene (**14b**) (semiempirical, PM3 level)[33] shows, as expected, a C_{3h} symmetry with an almost flat truxene base. At this level of theory, the heat of formation of *syn*-5,10,15-triphenyltruxene (**14b**) is only 0.3 kcal·mol^{-1} lower than *anti* isomer **14a**.

This methodology was applied for the preparation of a 5,10,15-trialkynyl truxene derivative. Thus, reaction of **2** with lithium (*p*-tolyl)acetylide gave a mixture of *anti* (**16a**) and *syn* (**16b**) derivatives (ca. 1.5:1) in 84% yield (Scheme 5). In this case, treatment of this mixture with Et_3SiH and $BF_3{\cdot}OEt_2$ gave a mixture of *anti* (**17a**) and *syn*



Scheme 4

(**17b**) trialkynyl truxenes. Although flash chromatography allowed for the isolation of the pure isomers, the attempted isomerization of *anti* (**17a**) with KO*t*Bu in *t*BuOH led only to decomposition. This decomposition might be due to formation of the isomeric trisallene, which appears be unstable under these reaction conditions.[34] Indeed, in ana-



Scheme 5

logy with the behavior of 9-phenylethynylfluorene,[35] **17a** reacted immediately with Et_3N in $CDCl_3$ to give a new compound, which decomposed to give insoluble materials.

Conclusion

The electrophilic bromination of truxene gave 2,7,12-tribromotruxene (**5c**) in high yield. This tribromotruxene was used as the starting material for the preparation of 2,7,12-trisubstituted truxenes by the Stille or Suzuki coupling reaction with organostannanes or boronic acids. On the other hand, 5,10,15-triarylated and trialkynylated truxene derivatives were obtained by reduction of the tertiary alcohols with Et_3SiH promoted by BF_3. The base-catalyzed isomerization of the *anti*-triaryl derivatives afforded *syn*-5,10,15-triarylated truxenes. These readily available new truxenes could be used for the synthesis of more complex truxenes. In particular, 2,7,12-tributyltruxene (**8**) could be functionalized at C-5, C-10, and C-15 by alkylation to give soluble substituted truxenes. Additionally, *syn*-5,10,15-triarylated truxenes could be employed as scaffolds for the construction of large cavities based on truxenes. The Stille or Suzuki coupling of 2,7,12-tribromotruxene (**5c**) with long-chain organostannanes or boranes could also be used for the introduction of long chains on the truxene nucleus for the preparation of liquid crystals.

Further studies on the association of trivinyl truxene **9** and the synthesis of more complex truxenes based on the methodology described herein are underway.

Experimental Section

General: The NMR determinations were carried out at 23 °C, unless otherwise stated. Only the most significant IR frequencies and MS fragmentations are given. R_f values 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 an atmosphere of 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.

Truxene (**1**) and truxenone (**2**) were prepared according to the described procedure.[12] Purification of **1** was carried out by Soxhlet extraction with toluene. 7-Methoxy-1-indanone was prepared in four steps from 4-bromophenol according to the described procedure.[24] ^{13}C NMR spectra of compounds **5a**−**c**, **11**, **13a**−**b**, **14b**, and **15b** could not be obtained due to their high insolubility.

Synthesis of 4-Bromoindanone (4a) and 6-Bromoindanone (4b):[22] A homogeneous mixture of $AlCl_3$ (11.24 g, 84.3 mmol) and 1-indanone (4.00 g, 30.27 mmol) was heated at 110 °C for 0.5 h. Bromine (2.0 mL, 38.91 mmol) was added dropwise to the resulting black gum. After 45 min. the mixture was allowed to warm to room temperature, ice-water was added, and the mixture was poured into Et_2O. The organic layer was washed with water, saturated $NaHCO_3$ and saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated to give a dark red solid, which was purified by chromatography (9:1, hexane/EtOAc), affording a mixture of bromo-1-indanones as yellow solids. 4-Bromo-1-indanone (**4a**) was further purified from 5-bromo-1-indanone by crystallization (CH_2Cl_2/EtOH).

4-Bromo-1-indanone (4a): (3.03 g, 47%); m.p. 76−77 °C. − R_f = 0.65 (5:1, hexane/EtOAc). − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.74 (t, J = 8 Hz, 2 H), 3.09 (t, J = 8 Hz, 2 H), 7.27 (t, J = 7 Hz, 1 H), 7.71 (d, J = 7 Hz, 1 H), 7.76 (d, J = 7 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (CH_2-2), 37.4 (CH_2-3), 122.1 (C-4), 122.4 (CH-7), 129.2 (CH-6), 138.1 (CH-5). The structure was confirmed by HMBC and HMQC correlations.

6-Bromo-1-indanone (4b): (1.35 g, 21%); m.p. 96−98 °C (m.p. ref.[36] 109−110 °C). − R_f = 0.53 (5:1, hexane/EtOAc). − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.71 (t, J = 6.5 Hz, 2 H), 3.08 (t, J = 6.5 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 1 H), 7.67 (dd, J = 8.1, 2 Hz, 1 H), 7.86 (d, J = 2.0 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 25.5 (CH_2), 36.4 (CH_2), 121.4 (C), 126.5 (CH), 128.2 (CH), 137.2 (CH), 138.7 (C), 153.5 (C), 205.7 (CO). − EI-MS: *m*/*z* (%) = 210 (100) [M^+], 182 (52), 131 (9), 103 (79), 75 (35). − Minor compounds: 4,6-dibromo-1-indanone (88 mg, 1%); R_f = 0.74 (5:1, hexane/EtOAc). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.78 (m, 2 H), 3.05 (m, 2 H), 7.83 (d, J = 2.0 Hz, 1 H), 7.90 (d, J = 2.0 Hz, 1 H); 5-bromo-1-indanone (193 mg, 3%); R_f = 0.7 (5:1, hexane/EtOAc). − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.78 (m, 2 H), 2.98 (m, 2 H), 7.39 (d, J = 7.2 Hz, 1 H), 7.53 (d, J = 7.2 Hz, 1 H), 7.95 (s, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 121.8 (C), 122.3 (C), 133.6 (CH), 137.7 (CH), 140.2 (CH), 157.3 (C); 4,7-dibromo-1-indanone (180 mg, 2%); R_f = 0.38 (5:1, hexane/EtOAc). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.79 (m, 2 H), 3.09 (m, 2 H), 7.30 (d, J = 12 Hz, 1 H), 7.77 (d, J = 12 Hz, 1 H).

1,6,11-Tribromo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (5a): Polyphosphoric acid (10 mL) was heated at 120 °C. Then, 4-bromoindanone (**4a**; 1.810 g, 8.57 mmol) was added and the mixture was stirred for 12 h. The suspension was washed with water, extracted with CH_2Cl_2, filtered and the residue was washed with CH_2Cl_2, acetone and Et_2O to give **5a** as a yellow solid (712 mg, 43%). − IR: ṽ = 1558, 993, 738 cm^{-1}. − EI-MS: *m*/*z* (%) = 655.8 (19), 575.9 (34) [M^+], 497.0 (55), 417.1 (31), 339.1 (58). − HRMS ($C_{27}H_{15}Br_3$): calcd. 575.8725; found 575.8720.

3,8,13-Tribromo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (5b): This truxene was obtained by a similar procedure to that of **5a** from 6-bromoindanone (**4b**; 186 mg, 0.88 mmol) to give **5b** (41 mg, 24%) as a light brown solid. − IR: ṽ = 1594, 1460, 994, 866, 792 cm^{-1}. − ^1H NMR (300 MHz, [D_2]1,1,2,2-tetrachloroethane, 120 °C): δ = 7.53 (m, 9 H), 4.22 (s, 6 H). − EI-MS: *m*/*z* (%) = 577.9 (91) [M^+], 498.9 (78), 418.1 (46), 339.2 (85). − HRMS ($C_{27}H_{15}Br_3$): calcd. 575.8725; found 575.8741.

10,15-Dihydro-4,9,14-trimethoxy-5*H*-diindeno[1,2-a;1′,2′-c]fluorene (7): A solution of 7-methoxy-1-indanone (**6**; 2.100 g, 14.2 mmol) in HOAc (10 mL) and HCl 35% (5 mL) was heated at 140 °C for 16 h. The mixture was cooled to room temperature, filtered, and washed with water and acetone to give **7** (513 mg, 28%) as a white solid; m.p. > 300 °C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (s, 9 H), 4.58 (br s, 6 H), 6.91 (d, J = 7.6 Hz, 3 H), 7.27 (dd, J = 7.6 7.4 Hz, 3 H), 7.33 (d, J = 7.4 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 41.2, 54.9, 108.8, 117.3, 127.6, 130.1, 136.8, 136.9, 147.4, 154.5. − EI-MS: *m*/*z* = 432 (100) [M^+], 401 (28). − HRMS ($C_{30}H_{24}O_3$): calcd. 432.1725; found 432.1721.

2,7,12-Tribromo-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (5c): Bromine (0.38 mL, 7.31 mmol) was added dropwise to a suspension of truxene (**1**; 500 mg, 1.46 mmol) in CH_2Cl_2 (10 mL) at

23 °C in the dark. The mixture was stirred for 16 h, the excess of bromine was removed by bubbling N_2 through the solution and the solid was filtered, washed with CH_2Cl_2, acetone, and ethyl acetate to give **5c** (782 mg, 92%) as a yellow solid; m.p. > 300 °C. − ^{1}H NMR ([D$_2$]1,1,2,2-tetrachloroethane, 130 °C, 300 MHz): δ = 4.22 (s, 6 H), 7.60 (dd, *J* = 8.1, 1.9 Hz, 3 H), 7.74 (d, *J* = 8.1 Hz, 3 H), 7.80 (d, *J* = 1.9 Hz, 3 H). − EI-MS: *m*/*z* (%) = 576 (30) [M$^+$], 500.5 (100), 419.1 (46), 339.2 (66). − HRMS ($C_{27}H_{15}Br_3$): calcd. 575.8725; found 575.8729.

2,7,12-Tri-*n*-butyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (8). Method a: A mixture of **5c** (200 mg, 0.35 mmol), Pd(PPh$_3$)$_4$ (120 mg, 0.104 mmol) and tetra-*n*-butyltin (700 μL, 2.1 mmol) in toluene (15 mL) was heated under refluxing conditions for 72 h. The mixture was cooled to room temperature, partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed (hexane → 4:1 hexane/CH_2Cl_2) to give **8** as a white solid (75 mg, 42%).

Method b: A mixture of **5c** (200 mg, 0.35 mmol), Pd(PPh$_3$)$_4$ (120 mg, 0.104 mmol), aqueous 2 M K_2CO_3 (1.1 mL, 2.2 mmol) and 1-butylboronic acid (117 mg, 1.15 mmol) in toluene (15 mL) was heated under refluxing conditions for 20 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2, washed with H_2O, and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed (hexane → 4:1 hexane/CH_2Cl_2) to give **8** as a white solid (53 mg, 30%); m.p. 160−162 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (t, *J* = 7.3 Hz, 9 H), 1.39−1.51 (m, 6 H), 1.66−1.76 (m, 6 H), 2.76 (t, *J* = 7.7 Hz, 6 H), 4.16 (s, 6 H), 7.30 (d, *J* = 7.7 Hz, 3 H), 7.49 (s, 3 H), 7.84 (d, *J* = 7.7 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 22.5, 34.08, 35.9, 36.3, 121.5, 125.2, 127.1, 134.4, 139.9, 139.5, 141.2, 144.1. − EI-MS: *m*/*z* (%) = 510 (100) [M$^+$], 454 (48), 411 (12), 367 (14). − HRMS ($C_{39}H_{42}$): calcd. 510.3128; found 510.3286

2,7,12-Triethenyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (9): A mixture of **5c** (100 mg, 0.17 mmol), Pd(PPh$_3$)$_4$ (60 mg, 0.052 mmol), vinyltributyltin (323 mg, 1.02 mmol), and hydroquinone (5 mg) in chlorobenzene (8 mL) was heated under refluxing conditions for 20 h. The mixture was cooled to room temperature, partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed (CH_2Cl_2) and triturated with EtOH to give **9** as a white solid (28 mg, 39%); m.p. > 300 °C. − ^{1}H NMR ([D$_2$]1,1,2,2-tetrachloroethane, 26 °C, 500 MHz): δ = 4.23 (s, 3 H), 4.25 (s, 3 H), 5.27 (d, *J* = 10.9 Hz, 3 H), 5.82 (d, *J* = 17.5 Hz, 3 H), 6.81 (dd, *J* = 17.5, 10.8 Hz, 3 H), 7.50 (d, *J* = 7.7 Hz, 3 H), 7.70 (s, 3 H), 7.84 (d, *J* = 7.8 Hz, 3 H). − ^{1}H NMR ([D$_2$]1,1,2,2-tetrachloroethane, 100 °C, 500 MHz): δ = 4.24 (s, 6 H), 5.22 (d, *J* = 11 Hz, 3 H), 5.75 (d, *J* = 17.3 Hz, 3 H), 6.79 (dd, *J* = 17.4, 10.8 Hz, 3 H), 7.46 (d, *J* = 8.2 Hz, 3 H), 7.67 (s, 3 H), 7.86 (d, *J* = 8.0 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 36.2, 121.6, 122.5, 125.4, 135.3, 131.2, 135.7, 136.5, 137.2, 141.2, 144.1. − EI-MS: *m*/*z* (%) = 420 (58) [M$^+$], 394 (100), 368 (19). − HRMS ($C_{33}H_{24}$): calcd. 420.1878; found 420.1876.

10,15-Dihydro-2,7,12-tris(trimethylsilylethynyl)-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (10): A mixture of **5c** (200 mg, 0.35 mmol), Pd(PPh$_3$)$_4$ (120 mg, 0.104 mmol) and (trimethylsilylethynyl)tributyltin (526 mg, 1.36 mmol) in toluene (20 mL) was heated under refluxing conditions for 20 h. The black suspension was partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (hexane → 9:1 hexane/CH_2Cl_2) to give **10** as a yellow solid (115 mg, 54%); m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.34 (s, 27 H), 3.54 (s, 6 H), 7.35 (d, *J* = 9 Hz, 3 H), 7.43 (d, *J* = 9 Hz, 3 H), 7.48 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 0.2, 35.8, 94.3, 105.9, 120.7, 121.2, 128.2, 130.9, 135.7, 135.9, 141.1, 143.1. − EI-MS: *m*/*z* (%) = 630 (100) [M$^+$] , 534 (91). − HRMS ($C_{42}H_{42}Si_3$): calcd. 630.2594; found 630.2605.

10,15-Dihydro-2,7,12-triphenyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (11). Method a: A mixture of **5c** (100 mg, 0.172 mmol), Pd(PPh$_3$)$_4$ (60 mg, 0.052 mmol), and phenyltributylstannane (0.225 mL, 0.69 mmol) in toluene (10 mL) was heated under refluxing conditions for 20 h. The black suspension was partitioned between H_2O and Et_2O, and the organic layer was washed with a saturated aqueous solution of KF, filtered and washed with CH_2Cl_2 to give **11** as a pale brown solid (58 mg, 59%).

Method b: A mixture of **5c** (200 mg, 0.35 mmol), Pd(PPh$_3$)$_4$ (120 mg, 0.104 mmol), 2 M aqueous K_2CO_3 (1.1 mL, 2.2 mmol) and phenylboronic acid (140 mg, 1.15 mmol) in toluene (10 mL) was heated under refluxing conditions for 18 h. The mixture was cooled to room temperature, filtered, and washed with CH_2Cl_2, H_2O and acetone to give **11** as a brown solid (120 mg, 60%); m.p. > 300 °C. − ^{1}H NMR ([D$_2$]1,1,2,2-tetrachloroethane, 130 °C, 300 MHz): δ = 4.30 (s, 6 H), 7.34 (m, 6 H), 7.45 (t, *J* = 7.08, 6 H), 7.70 (m, 6 H), 7.88 (s, 3 H), 7.95 (d, *J* = 8.16, 3 H). − EI-MS: *m*/*z* (%) = 570 (100) [M$^+$], 494 (80), 415(8), 339 (2). − HRMS ($C_{45}H_{30}$): calcd. 570.2348; found 570.2344.

***anti*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-triphenyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (12a) and *syn*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-triphenyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (12b):** Phenylmagnesium bromide (25 mL of a 0.3 M solution in THF, 7.58 mmol) was slowly added to a suspension of truxenone (**2**; 287 mg, 0.74 mmol) in THF (25 mL) at 0 °C and the mixture was warmed to 23 °C for 4 h. The solution was then poured into saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2, and dried (Na_2SO_4). The solvent was evaporated and the residue was triturated with hexane to give **12** as a mixture (ca. 1.6:1) of *anti* (**12a**) and *syn* (**12b**) isomers (387 mg, 83%). The mixture of isomers was separated by flash column chromatography (CH_2Cl_2 → 4:1 CH_2Cl_2/Et_2O).

12a: white solid: m.p. > 300 °C. − H NMR ($CDCl_3$, 200 MHz): δ = 2.68 (s, 1 H), 2.70 (s, 1 H), 2.74 (s, 1 H), 7.34−7.06 (m, 18 H), 7.64−7.54 (m, 6 H), 7.82−7.76 (m, 3 H). − EI-MS: *m*/*z* (%) = 618 (100) [M$^+$], 570 (78), 541 (61), 415 (20), 105(20). − MALDI-TOF MS (**12a** as its own matrix): *m*/*z* (%) = 617 (100) [M$^+$ − H]. − HRMS ($C_{45}H_{30}O_3$): calcd. 618.2195; found 618.2194.

12b: white solid, m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.68 (s, 3 H), 7.08−7.34 (m, 18 H), 7.53 (d, *J* = 7.0, 6 H), 7.74 (d, *J* = 7.0, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 83.5, 123.6, 124.7, 126.3, 127.2, 128.5, 135.7, 139.7, 142.1, 142.1, 151.7. − EI-MS: *m*/*z* (%) = 618 (100) [M$^+$], 570 (11), 541 (92), 105(71). − FAB-MS: *m*/*z* = 619 (19) [M$^+$ + 1], 618 (42), 617 (20), 603 (13), 602 (49), 601 (100), 600 (9), 599 (5), 585 (6), 584 (9), 542 (13), 541 (29), 525 (9), 524 (6), 523 (7), 512 (7), 463 (7), 400 (6), 289 (12), 242 (18), 176 (17), 165 (13), 154 (61), 136 (57), 105 (69), 77 (59). − HRMS ($C_{45}H_{30}O_3$): calcd. 618.2195; found 618.2209.

***anti*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-tris-*p*-tolyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (13a) and *syn*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-tris-*p*-tolyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (13b):** *p*-Tolylmagnesium bromide (6.5 mL of a 1.0 M solution in Et_2O, 6.5 mmol) was added to a suspension of **2** (279 mg, 0.72 mmol) in 25 mL of THF cooled to 0 °C, and the mixture was warmed to 23 °C for 4 h. The solution was then poured into saturated aqueous NH_4Cl solution. The mixture was extracted with

CH_2Cl_2, dried (Na_2SO_4), the solvent was evaporated and the residue was triturated with hexane to yield **13** as a mixture (ca. 1.6:1) of *anti* (**13a**) and *syn* (**13b**) isomers (440 mg, 91%). The mixture of isomers was separated by flash column chromatography (10:1, CH_2Cl_2/Et_2O).

13a: pale yellow solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, 6 H), 2.26 (s, 3 H), 2.65 (s, 1 H), 2.68 (s, 1 H), 2.71 (s, 1 H), 7.02−7.15 (m, 12 H), 7.32 (d, *J* = 8.5 Hz, 3 H), 7.43 (d, *J* = 8.0 Hz, 4 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 7.80−7.85 (m, 3 H). − EI-MS: *m*/*z* (%) = 660 (100) [M^+], 612 (41), 569 (51), 119 (24). − MALDI-TOF MS: *m*/*z* (%) = 659 (100) [$M^+ - H$]. − HRMS ($C_{48}H_{36}O_3$): calcd. 660.2664; found 660.2664.

13b: pale yellow solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.22 (s, 9 H), 2.68 (s, 3 H), 6.97−7.14 (m, 9 H), 7.15−7.30 (m, 3 H), 7.38 (d, *J* = 8.1 Hz, 6 H), 7.76 (d, *J* = 6.5 Hz, 3 H). − EI-MS: *m*/*z* (%) = 660 (100) [M^+], 612 (38), 569(53), 119 (30). − MALDI-TOF MS: *m*/*z* (%) = 659 (100) [$M^+ - H$]. − HRMS ($C_{48}H_{36}O_3$): calcd. 660.2664; found 660.2666.

***anti*-10,15-Dihydro-5,10,15-Triphenyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (14a):** To a mixture of **12a** and **12b** (370 mg, 0.6 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added Et_3SiH (0.5 mL) and $BF_3{\cdot}OEt_2$ (0.25 mL). After being stirred at 0 °C for 30 min., the mixture was poured into saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2 and dried (Na_2SO_4). The solvent was evaporated and the residue was triturated with hexane to yield **14a** (252 mg, 73%) as a pale yellow solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.63 (s, 2 H), 5.65 (s, 1 H), 7.08−7.34 (m, 21 H), 7.37−7.42 (m, 3 H), 7.47−7.53 (m, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 54.0, 54.1, 123.4, 123.6, 124.5, 124.7, 126.8, 126.8, 127.4, 128.2, 129.0, 129.0, 138.7, 139.22, 139.3, 141.3, 148.9, 148.8, (several signals were not observed due to overlapping). − EI-MS: *m*/*z* (%) = 570 (100) [M^+], 493 (21), 415 (47), 339 (5), 285 (9), 246 (21), 207 (16). − FAB-MS: *m*/*z* = 571 (7) [$M^+ + 1$], 570 (12), 494 (6), 493 (7), 191 (6), 154 (13), 147 (14), 136 (13), 105 (10), 91 (18), 77 (9), 73 (13), 57 (100), 55 (25). − HRMS ($C_{45}H_{30}$): calcd. 570.2348; found 570.2344.

***syn*-10,15-Dihydro-5,10,15-triphenyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (14b):** To a suspension of **14a** in *t*BuOH (15 mL) was added KO*t*Bu (67 mg, 0.6 mmol) and the mixture was heated under refluxing conditions for 48 h. After cooling to room temp., the mixture was diluted with H_2O and the solid was separated by centrifugation and washed with water and acetone to give **14b** (205 mg, 60%) as a white solid; m.p. > 300 °C. − ^{1}H NMR ([D_2]1,1,2,2-tetrachloroethane, 130 °C, 300 MHz): δ = 5.44 (s, 3 H), 7.09−7.16 (m, 9 H), 7.44−7.47 (m, 3 H), 7.36−7.38 (m, 3 H), 7.23−7.24 (m, 12 H). − MALDI-TOF MS: *m*/*z* (%) = 570 (11) [M^+]. − HRMS ($C_{45}H_{30}$): calcd. 570.2348; found 570.2356.

***anti*-10,15-Dihydro-5,10,15-tris-*p*-tolyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (15a):** To a mixture of **13a** and **13b** (211 mg, 0.32 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added Et_3SiH (0.5 mL) and $BF_3{\cdot}OEt_2$ (0.25 mL). After being stirred at 0 °C for 30 min. the solution was poured into a saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2 and dried (Na_2SO_4). The solvent was evaporated and the residue was triturated with hexane to yield **15a** (162 mg, 83%) as a pale yellow solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, 9 H), 5.59 (s, 1 H), 5.60 (s, 1 H), 5.63 (s, 1 H), 7.04−7.16 (m, 18 H), 7.53−7.56 (m, 3 H), 7.34−7.40 (m, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.0, 53.7, 53.7, 123.5, 123.7, 124.4, 124.6, 126. 8, 127.1, 127.2, 129.7, 131.7, 136.2, 138.1, 138.3, 138.7, 139.2, 139.6, 149.2, 149.1, (several signals were not observed due to overlapping). − MALDI-TOF MS: *m*/*z* (%) = 612 (100) [M^+]. − HRMS ($C_{48}H_{36}$): calcd. 612.2817; found 612.2823.

***syn*-10,15-Dihydro-5,10,15-tris-*p*-tolyl-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (15b):** To a suspension of **15a** (80 mg, 0.13 mmol) in *t*BuOH (10 mL) was added KO*t*Bu (23 mg, 0.2 mmol) and the mixture was heated under refluxing conditions for 48 h. After cooling to room temp., the mixture was diluted with H_2O, the solid separated by centrifugation and washed with water and acetone to give **15b** (56 mg, 70%) as a white solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.23 (s, 9 H), 5.14 (s, 3 H), 7.08−7.11 (m, 12 H), 7.11−7.21 (m, 6 H), 7.34 (d, *J* = 7.3 Hz, 3 H), 7.41 (d, *J* = 6.4 Hz, 3 H). − EI-MS: *m*/*z* (%) = 612 (100) [M^+], 520 (26), 420 (37), 91 (10). − HRMS ($C_{48}H_{36}$): calcd. 612.2817; found 612.2817.

***anti*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-tris(*p*-tolylethynyl)-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (16a) and *syn*-10,15-Dihydro-5,10,15-trihydroxy-5,10,15-tris(*p*-tolylethynyl)-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (16b):** To a suspension of truxenone (**2**; 300 mg, 0.78 mmol) in THF (25 mL) at 0 °C was slowly added a solution of lithium (*p*-tolyl)acetylide [prepared from *p*-tolylacetylene (0.9 mL, 7.1 mmol) in 25 mL of THF and 2.5 mL of a solution 2.5 M of *n*BuLi in hexane]. The reaction mixture was warmed to 23 °C for 4 h. The solution was then poured into a saturated aqueous NH_4Cl solution and the mixture was extracted with CH_2Cl_2 and dried (Na_2SO_4). The solvent was evaporated and the residue was triturated with hexane to yield **16** as a mixture (ca. 1.5:1) of *anti* (**16a**) and *syn* (**16b**) isomers (480 mg, 84%). The mixture of isomers could be separated by flash column chromatography (CH_2Cl_2 → 10:1 CH_2Cl_2/Et_2O).

16a: pale brown solid; m.p. 174−175 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.31 (s, 9 H), 2.78 (br s, 3 H), 7.05 (d, *J* = 8.1 Hz, 6 H), 7.25−7.30 (m, 6 H), 7.49−7.60 (m, 6 H), 7.90−7.97 (m, 3 H), 8.88 (d, *J* = 8.1 Hz, 1 H), 8.93 (d, *J* = 7.7 Hz, 2 H). − ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.4, 75.0, 75.1, 75.2, 86.8, 86.9, 119.1, 123.8, 123.9, 123.9, 126.9, 128.9, 129.3, 129.5, 131.8, 131.8, 136.2, 138.4, 138.7, 140.2, 140.3, 148.6, (several signals were not observed due to overlapping). − FAB-MS: *m*/*z* (%) = 732 (14) [M^+], 715 (64). − HRMS ($C_{54}H_{36}O_3$): calcd. 732.2664; found 732.2649.

16b: pale brown solid; m.p. 259−260 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.26 (s, 9 H), 2.65 (br s, 3 H), 7.00 (d, *J* = 8.1 Hz, 6 H), 7.23 (d, *J* = 8.6 Hz, 6 H), 7.44−7.57 (m, 6 H), 7.86 (d, *J* = 7.5 Hz, 3 H), 8.80 (d, *J* = 8.6 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.7, 74.9, 84.2, 86.7, 119.2, 123.7, 126.8, 128.8, 129.2, 129.5, 131.9, 136.1, 138.1, 138.6, 140.2, 148.5. − EI-MS: *m*/*z* (%) = 732 (0.6) [M^+], 616 (8), 500(43), 384 (49). − HRMS ($C_{54}H_{36}O_3$): calcd. *m*/*z* = 732.2664; found 732.2649.

***anti*-10,15-Dihydro-5,10,15-tris(*p*-tolylethynyl)-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (17a) and *syn*-10,15-Dihydro-5,10,15-tris(*p*-tolylethynyl)-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (17b):** To a mixture of **16a** and **16b** (146 mg, 0.2 mmol) in CH_2Cl_2 (8 mL) at 0 °C were added Et_3SiH (0.5 mL) and $BF_3{\cdot}OEt_2$ (0.25 mL). After being stirred at 0 °C for 30 min. the mixture was poured into a saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), the solvent was evaporated and the residue was triturated with hexane to yield **17** as a mixture of *anti* (**17a**) and *syn* (**17b**) isomers (83 mg, 61%). The mixture of isomers could be separated by flash column chromatography (hexane → 1:1 hexane/CH_2Cl_2).

17a: white solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.27 (s, 9 H), 5.40 (s, 1 H), 5.44 (s, 1 H), 5.51 (s, 1 H), 7.01 (d, *J* = 7.5, 6 H), 7.18−7.24 (m, 6 H), 8.58−8.61 (m, 3 H), 7.45−7.57 (m, 6 H), 7.86−7.92 (m, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ =

21.4, 39.5, 83.4, 83.6, 85.3, 85.4, 85.5, 120.2, 124.4, 124.5, 124.6, 125.0, 125.0, 127.7, 127.8, 128.8, 131.5, 136.3, 136.4, 136.5, 137.9, 138.0, 139.0, 139.1, 139.2, 144.8, 144.97, 145.1, (several signals were not observed due to overlapping). − FAB-MS: *m/z* (%) = 684 (17) [M^+], 569 (25). − HRMS ($C_{54}H_{36}$): calcd. 684.2817; found 684.2822.

17b: white solid; m.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.26 (s, 9 H), 5.16 (s, 3 H), 7.00 (d, *J* = 8.1, 6 H), 7.23 (d, *J* = 8.6 Hz, 6 H), 7.44−7.57 (m, 6 H), 7.86 (d, *J* = 7.5 Hz, 3 H), 8.80 (d, *J* = 8.6 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4, 39.2, 83.4, 85.3, 120.2, 124.3, 125.0, 127.6, 127.8, 128.8, 131.6, 136.2, 137.9, 139.1, 144.8, (one signal was not observed due to overlapping). − FAB-MS: *m/z* (%) = 684 (14) [M^+], 569 (17). − HRMS ($C_{54}H_{36}$): calcd. 684.2817; found 684.2847.

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