Synthesis of C_3 Benzo[1,2-*e*:3,4-*e*′:5,6-*e*′′]tribenzo[*l*]acephenanthrylenes (Crushed Fullerene Derivatives) by Intramolecular Palladium-Catalyzed Arylation

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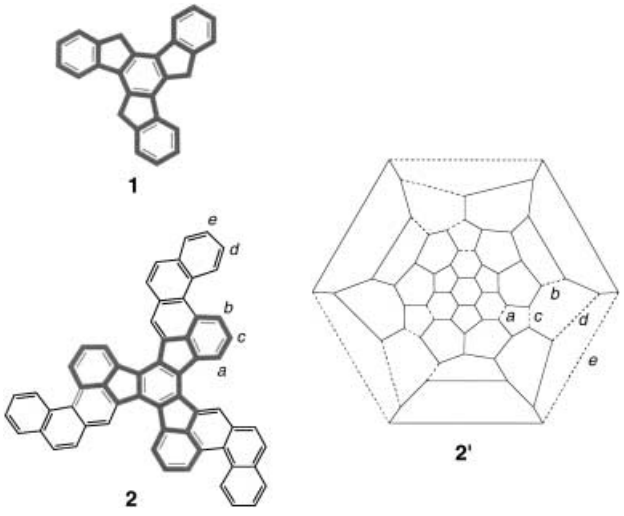
Abstract: The C_{60} polyarenes **4**, **5**, **18a**, and **18b** have been synthesized from truxene by triple alkylation at C5, C10, and C15 followed by a palladium-catalyzed intramolecular arylation. The synthesis of "crushed fullerene" $C_{60}H_{30}$ (**2**) is the most efficient reported to date and proceeds in 33% overall yield.

Keywords: arylation · fullerenes · palladium · polyarenes · truxenes

Introduction

The chemistry of bowl-shaped polyarenes[1] has attracted great interest due to their potential use as starting materials for the development of syntheses of fullerenes alternative to those based on the vaporization of graphite.[2] Progress towards the synthesis of large polyarenes is also of interest in the area of materials science.[3] Fullerenes have been formed pyrolytically in low yield from aromatic hydrocarbons such as naphthalene and corannulene.[4,5] Peaks attributable to $C_{60}^{+\cdot}$ have been found in the mass spectra of cyclic polyynes[6,7] and of products obtained by the glow discharge of $CHCl_3$ vapor.[8] Additionally, C_{60} has been identified in benzene/oxygen flames.[9]

We described in a preliminary communication a regiocontrolled approach for the synthesis of $C_{60}H_{30}$ (**2**), a polyarene with a decacyclene core fused with three naphthyl units that possesses the exact carbon atom topology of the C_{60} Schlegel diagram **2**′ (Scheme 1).[10] The synthesis of **2** was based on palladium-catalyzed intramolecular arylation[11,12] of a derivative of truxene **1**.[13,14] This heptacyclic polyarene has been recognized as a potential starting material for the construction of large polyarenes by several groups.[15,16,17,18] Two alternative preparations of **2** have been reported. The first, reported by Jennenskens et al.,[19] was based on the dehydrogenation of polyarenes in the presence of S_8, which gave predominantly the C_1 isomer of **2**. A second, more recent synthesis of **2**, reported by Scott et al., was based on the $TiCl_4$-catalyzed trimerization of 5*H*-benzo[*f*]acephenanthrylen-4-one.[20] This approach was later applied for the prepa-



Scheme 1.

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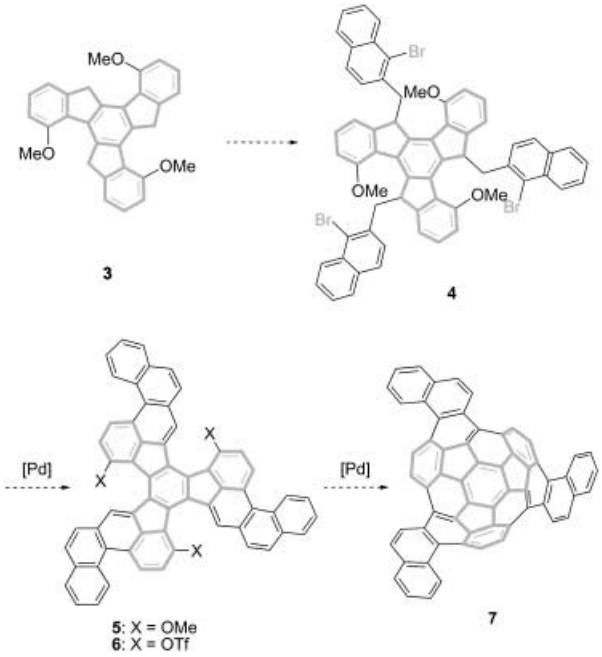
ration of a chlorinated derivative of **2** in 11 steps from 1-bromo-4-chlorobenzene, which afforded C_{60} in 0.1–1.0% yield upon flash vacuum pyrolysis at 1100°C.[21]

Our goal is to accomplish a stepwise synthesis of C_{60} based on the application of palladium-catalyzed arylation as the key tool (Scheme 2).[22] Thus, a triple alkylation of a tri-



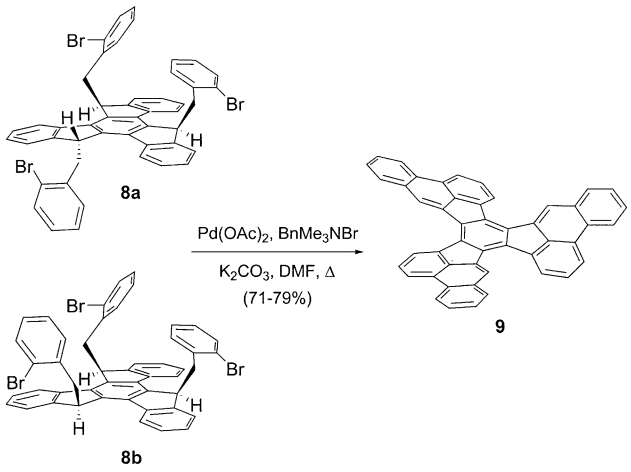
Scheme 2.

substituted truxene derivative **3**[23] would give **4**, which could provide **5** by palladium-catalyzed intramolecular arylation. Transformation of **5** into the tris(triflate) derivative **6** could then allow a second arylation to be carried out, furnishing bowl-shaped polyarene **7**. Polyarene **7** is a rather interesting synthetic target in its own right, besides being a potential precursor of C_{60} and of endohedral complexes of C_{60}.

Herein, we detail the synthesis of $C_{60}H_{30}$ (**2**), tributyl- and triaryl derivatives (**18a** and **18b**), trimethoxy derivative **5**, as well as two C_{48} derivatives (**9** and **11**), which document the versatility of our approach for the preparation of C_3 polyarenes based on triple arylation of a truxene core.

Results and Discussion

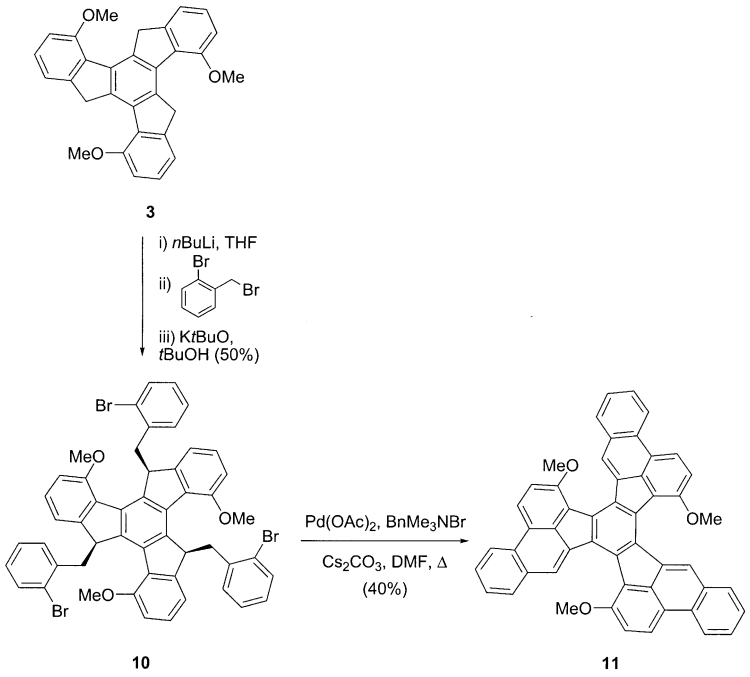
Synthesis of C_{48} polyarenes: As a prelude to the synthesis of $C_{60}H_{30}$ (**2**), we first investigated the palladium-catalyzed cyclization of **8a** and **8b** bearing three *ortho*-bromobenzyl groups. As expected, these derivatives, readily available by alkylation of the trianion of **1**,[14] were cyclized in the presence of $Pd(OAc)_2$ as a precatalyst to give C_{48} polyarene **9** (Scheme 3). Interestingly, derivative **8a**, with three benzyl groups in a *syn* relationship, was cy-



Scheme 3.

clized at 130°C in DMF as the solvent, while the cyclization of the *anti* isomer **8b** had to be carried out at 150–165°C in DMF or DMA to give **9** in good yield (71–79%).

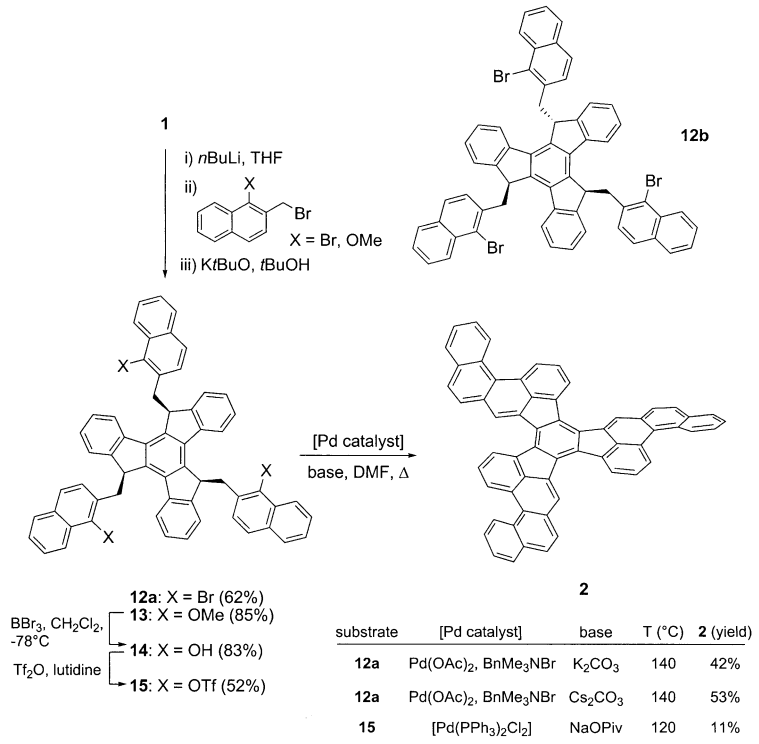
Compound **11**, a simpler analogue of the trimethoxy compound **5**, was similarly synthesized from 4,9,14-trimethoxytruxene (**3**).[23] Thus, triple alkylation of the trilithium trianion of **3** with *o*-bromobenzyl bromide gave a mixture of **10** and its *anti* isomer; the latter was isomerized under basic conditions to afford **10** in 50% overall yield (Scheme 4).



Scheme 4.

Palladium-catalyzed arylation of **10** was best carried out in the presence of the more soluble Cs_2CO_3 as the base, leading to **11** in 40% yield, which is considerably more soluble than the parent compound **9**.

Synthesis of $C_{60}H_{30}$ (2): For the synthesis of **2** we tried the cyclization of naphthalene analogues of **8a** and **8b**. Thus, alkylation of the trilithium trianion of **1** with 1-bromo-2-(bromomethyl)naphthalene[24] gave the *anti* derivative **12b** as the major compound, which was isomerized with KO*t*Bu in *t*BuOH under reflux conditions to give *syn*-5,10,15-tris[2-(1-bromo)naphthylmethyl]truxene (**12a**) in 62% overall yield (Scheme 5). Similarly, **13** was obtained by using 2-(bromomethyl)-1-methoxynaphthalene[25] as the electrophile in the alkylation reaction, followed by base-catalyzed isomerization (85% overall yield). Demethylation of **13** with BBr_3 in CH_2Cl_2 at −78°C afforded tris(naphthol) **14** in 83% yield. Trifluoromethanesulfonylation of **14** with Tf_2O and 2,6-lutidine in CH_2Cl_2 provided tris(triflate) **15** in 52% yield.



substrate	[Pd catalyst]	base	T (°C)	**2** (yield)
12a	$Pd(OAc)_2$, $BnMe_3NBr$	K_2CO_3	140	42%
12a	$Pd(OAc)_2$, $BnMe_3NBr$	Cs_2CO_3	140	53%
15	$[Pd(PPh_3)_2Cl_2]$	NaOPiv	120	11%

Scheme 5.

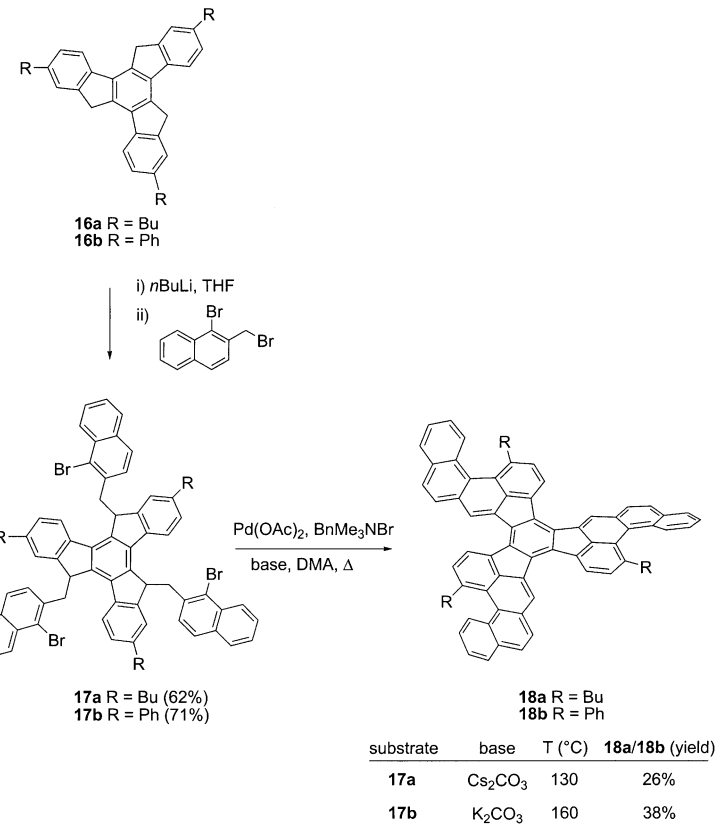
Treatment of **12a** with $Pd(OAc)_2$ (10–20 mol%) in the presence of $BnMe_3NBr$ and K_2CO_3 or with NaOAc in DMF or DMA at 110–160°C gave complex mixtures of insoluble materials. However, the use of higher amounts of $Pd(OAc)_2$ (100 mol%, 0.3 equiv) with K_2CO_3 as the base led to cleaner mixtures, from which **2** could be isolated in 42% yield (Scheme 5). The use of the more soluble Cs_2CO_3 as the base increased the yield of **2** to 53%. Tris(triflate) **15** could also be cyclized to give **2**, albeit in lower yield (11%), by using $[Pd(PPh_3)_2Cl_2]$ (150 mol%) and excess NaOPiv in DMA at 120°C.[26]

Synthesis of tributyl and triphenyl derivatives of 2: Polyarene **2** is a highly insoluble substance and its ^{1}H NMR spectrum could only be obtained in $[D_2]$-1,1,2,2-tetrachloroethane at 130°C. In an attempt to prepare a more soluble analogue, the synthesis of a tributylated derivative was undertaken. Thus, alkylation of 2,7,12-tributyltruxene (**16a**)[23] with 1-bromo-2-(bromomethyl)naphthalene gave a mixture of **17a** and its *anti* isomer in 62% yield (Scheme 6). Arylation of this mixture with $Pd(OAc)_2$, $BnMe_3NBr$, and Cs_2CO_3 in DMA at 130°C for 24 h afforded **18a**, which was isolated in 26% yield. Similarly, alkylation of 2,7,12-triphenyltruxene (**16b**)[26] gave **17b** as a 5.5:1 *anti*/*syn* mixture in 71% yield, which was treated with $Pd(OAc)_2$, $BnMe_3NBr$, and K_2CO_3 in DMA at 160°C to give **18b** in 38% yield.

Synthesis of trimethoxy derivative 5: Compound **5**, a derivative of **2** with three substituents at the strategic positions C3, C13, and C23, was synthesized from 4,9,14-trimethoxytruxene (**3**). Thus, triple alkylation of the trilithium trianion of **3** with 1-bromo-2-(bromomethyl)naphthalene gave a 1:3 *syn*/*anti* mixture (**4a,b**) in 90% yield. Attempted isomerization of **4b** to the *syn*-isomer **4a** under the standard conditions (heating with KO*t*Bu in *t*BuOH) was unsuccessful in this case. Treatment of the mixture of **4a,b** with $Pd(OAc)_2$ in the presence of Cs_2CO_3 as the base led to triple palladium-catalyzed intramolecular arylation, furnishing **5** as a soluble yellow solid in 66% yield (Scheme 7).

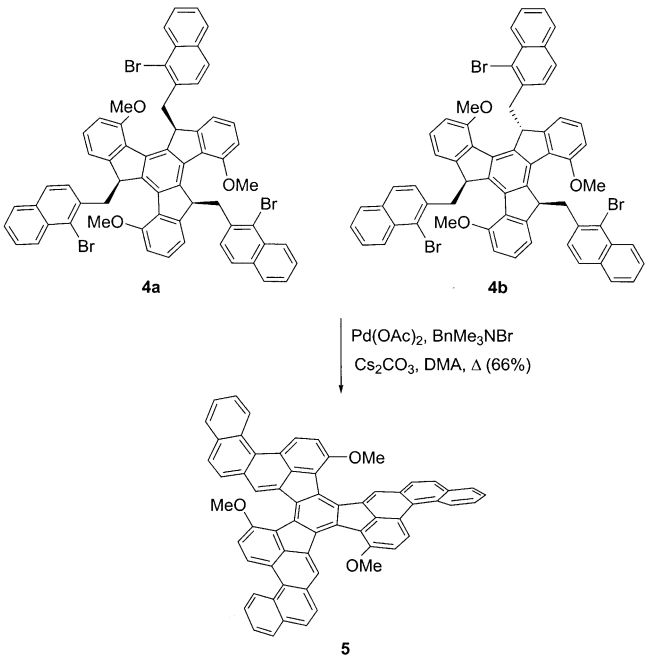
Structure of C_3 $C_{60}H_{30}$ derivatives: The ^{1}H NMR spectrum of **18a** in $CDCl_3$ at room temperature shows only broad resonances, which suggests a slow equilibration of different conformers at this temperature. However, the spectrum was found to be well-resolved in $[D_2]$-1,1,2,2-tetrachloroethane at 120°C (Figure 1). The ^{1}H assignments were made on the basis of COSY and NOESY experiments. The ^{13}C NMR spectrum of **18a** in $CDCl_3$ at room temperature showed the expected 20 C(sp^2) signals between $\delta = 141$ and 123 ppm. Although observation of the correct number of resonances for sp^2-type carbons suggests that **18a** possesses C_3 symmetry, ten C(sp^3) signals were observed for the butyl groups (range: $\delta = 35.6$–13.8 ppm) instead of the expected four, which indicates that the *n*-butyl chains adopt different conformations. The ^{1}H NMR spectrum of triphenylated **18b** featured only very broad resonances, even at 120°C.

Since the room temperature NMR data suggested the presence of several conformers in the case of **18a**, we performed DFT calculations at the B3LYP/6–31G(d)//AM1



substrate	base	T (°C)	**18a**/**18b** (yield)
17a	Cs_2CO_3	130	26%
17b	K_2CO_3	160	38%

Scheme 6.



Scheme 7.

level of theory to study the energy differences among the several possible isomers of the trimethyl analogue **18c**. The compound shows six axes of chirality: three are derived from the relative positions of the aromatic surfaces connected to the central benzene ring, and the other three are related to the positions of the methyl groups above and below the mean plane of the molecule. After exploring the different possibilities, it was established that conformers **18c** (C_3) and **18c** (C_1) (Scheme 8) are the most stable ones, being almost isoenergetic ($\Delta\Delta H_f$ (C_3–C_1) = 0.6 kcal mol^{-1}).

The ^{1}H NMR spectrum of **5** in $CDCl_3$ at room temperature was found to be well-resolved (Figure 2) and corresponded to an average C_3 symmetry. It is noteworthy that the signals of H-3 and H-4 are shifted downfield, whereas that of H-10 is shifted upfield due to the buttressing effect of the methoxy group.

Conclusion

Palladium-catalyzed intramolecular arylation constitutes a versatile method for the synthesis of large C_{48} polyarenes **9** and **11**, as well as of C_{60} polyarenes **4**, **5**, **18a**, and **18b**. The synthesis of $C_{60}H_{30}$ (**2**) is the most efficient reported to date and proceeds in just three steps from truxene (**1**) in 33% overall yield. Polyarene **5** has been similarly synthesized from trimethoxytruxene **3**

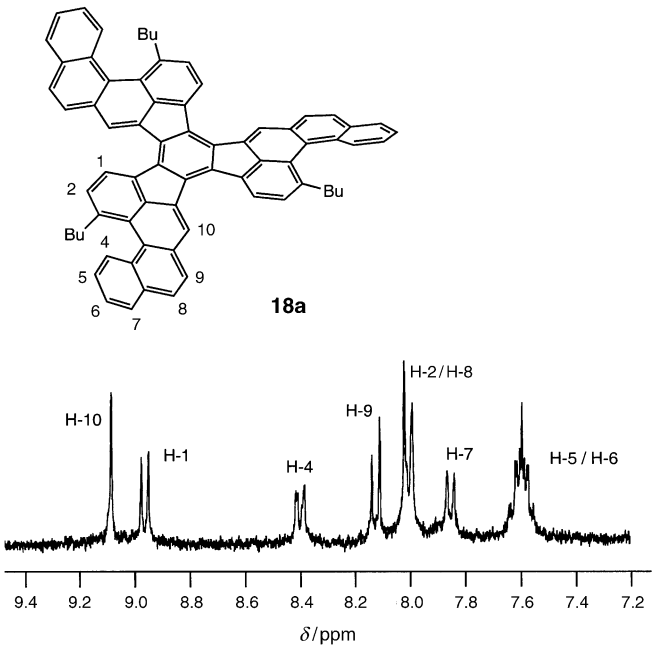
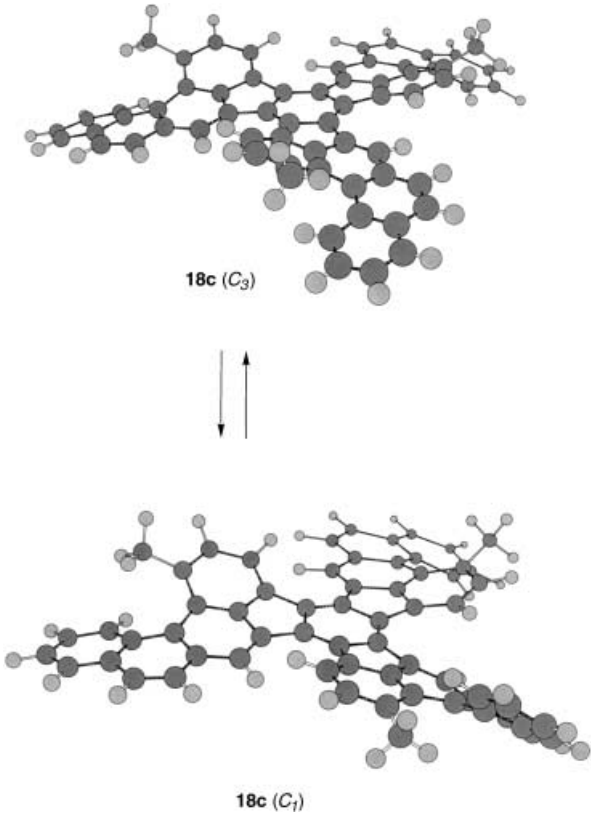


Figure 1. Aromatic region of the ^{1}H NMR spectrum of **18a** ([D_2]-1,1,2,2-tetrachloroethane, 300 MHz, 120°C). Assignments are based on a NOESY experiment.



Scheme 8. Minimum conformers for model **18c** (DFT calculations at the B3LYP/6–31G(d)//AM1 level).

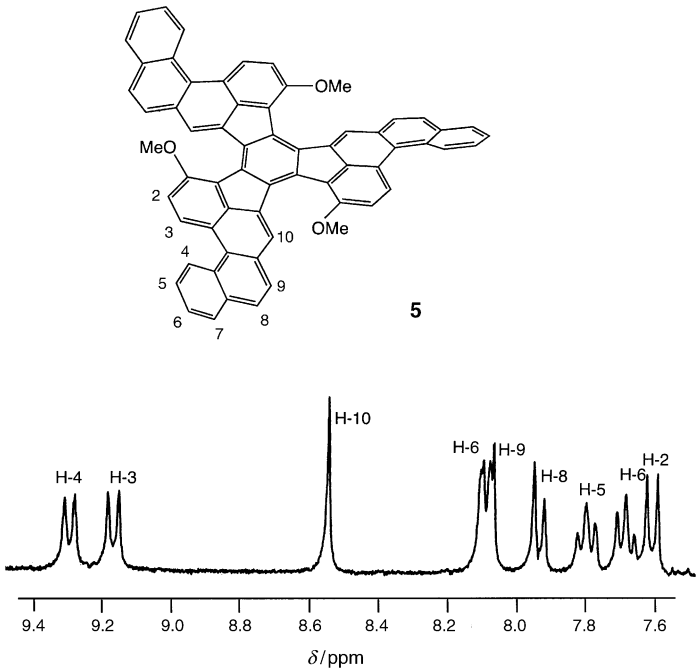


Figure 2. Aromatic region of the ^{1}H NMR spectrum of **5** ($CDCl_3$, 23 °C). Assignments are based on a NOESY experiment.

in two steps (59% yield) and represents a potential starting material for the preparation of **7** via tris(triflate) **6**. The synthesis of bowl-shaped **7** from **5** is now being pursued.

Experimental Section

Unless stated otherwise, NMR spectra were recorded at 23 °C. Solid-state high-resolution CP-MAS ^{13}C NMR spectra were recorded at 100.63 MHz on a Bruker MSL 400 spectrometer, with a pulse width of 6.5 μs and a contact time of 1 ms. EI mass spectra were obtained with a probe temperature of 300 °C, an ion source at 300 °C, and an electron energy of 70 eV. FAB mass spectra were obtained by using *m*-nitrobenzyl alcohol as the matrix. Elemental analyses were performed at the UAM (SIdI). The presence of solvents of crystallization was confirmed by ^{1}H NMR. Solvents were purified and dried according to standard procedures. Chromatographic purifications were carried out on flash grade silica gel eluting with distilled solvents. All reactions were carried out under argon.

Truxene (**1**), tribenzyl derivatives **8a** and **8b**,[21] 2,7,12-tri-*n*-butyltruxene (**16a**),[26] 2,7,12-triphenyltruxene (**16b**),[26] and 1-bromo-2-(bromomethyl)-naphthalene[26] were prepared according to known procedures. 1-Methoxy-2-(bromomethyl)naphthalene was prepared by a small modification of a known method.[26] The synthesis and X-ray structure of *syn*-5,10,15-tris(1-methoxy-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[3,2-*a*;3′,2′-*c*]fluorene **13** has been reported elsewhere.[21]4,9,14-Trimethoxytruxene (**3**) was prepared following an improvement of our previously reported procedure[26] that obviates the need for catalytic debromination of 4-bromo-7-hydroxy-1-indanone. Thus, 7-hydroxy-1-indanone was directly prepared from 4-bromophenyl propenoate in a one-pot process (30% overall yield) that involves a Fries rearrangement, closure to the indanone, and protiodebromination.[4] A mixture of 4-bromophenyl propenoate (11.70 g, 51.52 mmol), $AlCl_3$ (130 g, 0.97 mol), and NaCl (43.0 g, 0.79 mol) was heated at 160 °C for 5 h. The warm mixture was poured into ice, extracted with EtOAc, and the extract was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (hexane/EtOAc, 10:1) to give 7-hydroxy-1-indanone as a yellow solid (2.30 g, 32%); m.p. 116–117 °C. It was found that the yield of the final step (acid-catalyzed trimerization of 7-methoxy-1-indanone) could be increased to 53% by heating at a lower temperature (120 °C instead of 160 °C).

Benzo[*e*]diacephenanthrylene[4,5-*j*;4′,5′-*l*]fluoranthene (9): **Method a**: A mixture of **8a** (500 mg, 0.59 mmol), $Pd(OAc)_2$ (13 mg, 0.06 mmol), $BnMe_3NBr$ (135 mg, 0.59 mmol), and K_2CO_3 (831 mg, 5.9 mmol) in DMF (15 mL) was stirred at 150 °C for 24 h. The mixture was then cooled to 23 °C and diluted with water, and the solid produced was filtered off and washed with water and acetone to give **9** as a clear brown solid (252 mg, 71%). When the reaction was carried out in DMA at 165 °C, **9** was obtained in 79% yield.

Method b: A mixture of **8b** (150 mg, 0.18 mmol), $Pd(OAc)_2$ (4 mg, 0.02 mmol), $BnMe_3NBr$ (41 mg, 0.18 mmol), and K_2CO_3 (244 mg, 1.8 mmol) in DMF (5 mL) was stirred at 130 °C for 24 h. The mixture was then cooled to 23 °C and diluted with water, and the solid produced was filtered off and washed with water and acetone to give **9** as a clear brown solid (77 mg, 71%); m.p. >350 °C; ^{1}H NMR (300 MHz, [D_2]-1,1,2,2-tetrachloroethane, 130 °C): δ = 9.01 (s, 3H), 8.87 (d, J = 7.9 Hz, 3H), 8.66–8.64 (m, 3H), 8.52 (d, J = 7.8 Hz, 3H), 8.19 (d, J = 7.4 Hz, 3H), 7.87 (t, J = 7.9 Hz, 3H), 7.69–7.58 ppm (m, 6H); ^{13}C NMR (solid-state, 100.6 MHz): δ = 134.99, 131.48, 128.32, 124.56, 121.16 ppm; EI-MS: m/z (%): 600 ([M^+], 23), 528 (7).

***syn*-5,10,15-Tris(2-bromophenylmethyl)-4,9,14-trimethoxy-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (10)**: *n*BuLi (2.90 mL, 2.5 M in hexanes, 7.20 mmol) was added to **3** (1.000 g, 2.31 mmol) in THF (200 mL) at −78 °C. The red solution obtained was slowly allowed to warm to −10 °C over a period of 3 h, and then a solution of *o*-bromobenzyl bromide (2.010 g, 8.10 mmol) in THF (50 mL) was added. The resulting mixture was warmed to 23 °C and stirred at this temperature for 16 h. After standard extractive work-up (CH_2Cl_2, H_2O) and evaporation of the solvent, trituration with hexane gave a 3:1 mixture of *anti*- and *syn*-trialkylated derivatives as a yellow solid (1.190 g, 55%). This mixture was suspended together with KO*t*Bu (220 mg, 4.00 mmol) in *t*BuOH (200 mL) and heated under reflux conditions for 12 h. After the mixture had cooled, the solvent was evaporated and the residue was chromatographed (hexane/CH_2Cl_2, 4:1) to give *syn*-**10** as a pale brown solid (590 mg, 27%); m.p. 267–268 °C; R_f = 0.15 (hexane/CH_2Cl_2, 4:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (dd, J = 12.0, 1.6 Hz, 3H), 7.15 (t, J =

12.0 Hz, 3H), 7.07–6.78 (m, 15H), 5.32 (td, J = 8.8, 3.2 Hz, 3H), 4.04 (s, 9H), 3.43 (dd, J = 20.2, 8.1 Hz, 3H), 2.99 ppm (dd, J = 20.9, 12.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.23, 149.51, 142.22, 139.26, 135.53, 132.32, 130.97, 129.57, 127.55, 127.49, 126.73, 126.09, 118.01, 109.70, 55.59, 50.70, 39.79 ppm; EI-MS: m/z: 938 ([M^+], 100), 859 (60), 769 (100).

8,16,24-Trimethoxybenzo[*e*]diacephenanthrylene[4,5-*j*;4′,5′-*l*]fluoranthene (11): A mixture of **10** (500 mg, 0.53 mmol), $Pd(OAc)_2$ (357 mg, 0.53 mmol), $BnMe_3NBr$ (244 mg, 1.06 mmol), and Cs_2CO_3 (1.69 g, 5.3 mmol) in DMA (25 mL) was heated at 140 °C for 36 h. After being cooled to room temperature, the mixture was filtered and the insoluble solid was washed with CH_2Cl_2 and acetone. The filtrate was diluted with CH_2Cl_2, then washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (hexane/Et_2O, 10:3) to give **11** as a yellow solid (146 mg, 40%); m.p. 200–202 °C; R_f = 0.15 (hexane/Et_2O, 10:3); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80 (d, J = 10.1 Hz, 3H), 7.64 (dd, J = 8.1, 1.2 Hz, 3H), 7.34 (td, J = 7.7, 1.2 Hz, 3H), 7.20 (dd, J = 7.3, 1.6 Hz, 3H), 7.09 (d, J = 4.1 Hz, 3H), 7.08 (s, 3H), 6.88 (dd, J = 5.3, 4.5 Hz, 3H), 3.90 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 154.52 (C), 140.85 (C), 139.29 (C), 138.67 (C), 138.66 (C), 132.93 (CH), 132.32 (CH), 131.27 (C), 129.98 (C), 129.50 (C), 129.07 (CH), 127.97 (CH), 126.85 (CH), 124.13 (C), 116.81 (CH), 111.21 (CH), 56.11 ppm (CH_3); MALDI-MS (dithranol): m/z: 691.9 ([M^++1]).

***syn*-5,10,15-Tris(1-bromo-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (12a) and *anti*-5,10,15-tris(1-bromo-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (12b)**: *n*BuLi (1.3 mL, 2.5 M solution in hexanes, 3.25 mmol) was added to **1** (342 mg, 1 mmol) in THF (25 mL) at −78 °C. The resulting mixture was then slowly allowed to warm to −10 °C over 4 h to give a red solution, to which a solution of 1-bromo-2-(bromomethyl)naphthalene (975 mg, 3.25 mmol) in THF (10 mL) was added. After 30 min, the mixture was diluted with EtOAc, washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. The residue was triturated with hexanes to give *anti*-trialkylated truxene **12b** as a white solid. **12b**: m.p. 181 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48–8.25 (m, 5H), 7.85–7.31 (m, 17H), 7.22 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 7.07–6.95 (m, 3H), 6.67 (d, J = 6.9 Hz, 1H), 6.53 (d, J = 7.7 Hz, 1H), 5.26 (dd, J = 10.5, 4.8 Hz, 1H), 5.19–5.14 (m, 2H), 4.35–4.24 (m, 2H), 4.13 (dd, J = 13.7, 4.8 Hz, 1H), 3.13 (dd, J = 13.7, 9.7 Hz, 1H), 2.99 (dd, J = 13.7, 10.1 Hz, 1H), 3.13 ppm (dd, J = 14.1, 10.9 Hz, 1H); ^{13}C NMR (360 MHz, $CDCl_3$): δ = 146.77, 146.61, 146.52, 141.59, 140.58, 140.47, 140.14, 139.83, 139.66, 137.32, 136.96, 136.87, 136.76, 133.39, 132.47, 132.41, 129.18, 129.04, 128.87, 128.03, 127.67, 127.34, 127.20, 127.11, 126.89, 126.11, 125.97, 125.86, 125.64, 125.55, 125.13, 125.08, 124.99, 122.93, 122.87, 122.54, 46.80, 46.52, 46.41, 40.32, 40.16 ppm (the rest of the signals are not observed); EI-MS: m/z (%): 1000 ([M^+], 1), 779 (56), 699 (10), 559 (63), 479 (19), 340 (100). The solid was suspended in *t*BuOH (25 mL) and KO*t*Bu (112 mg, 1 mmol) was added. The mixture was heated under reflux conditions for 12 h. After being cooled to room temperature, it was diluted with water and the solid was filtered off and washed with water and acetone to give **12a** as a white solid (622 mg, 62%). **12a**: m.p. >300 °C; ^{1}H NMR (300 MHz, [D]$_2$-1,1,2,2-tetrachloroethane, 130 °C): δ = 8.30 (brs, 6H), 8.06 (brs, 3H), 7.65–7.44 (brm, 9H), 7.22 (brs, 3H), 6.97 (brs, 9H), 4.99 (brs, 3H), 3.96 (brs, 3H), 3.41 ppm (brs, 3H); EI-MS: m/z (%): 1000 ([M^+], 2), 779 (54), 698 (13), 560 (19), 480 (14), 339 (100); elemental analysis calcd (%) for $C_{60}H_{39}Br_3\cdot 0.75\,H_2O$: C 70.19, H 4.12; found: C 70.16, H 4.44.

***syn*-5,10,15-Tris(1-hydroxy-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[3,2-*a*;3′,2′-*c*]fluorene (14)**: BBr_3 (6 mL, 1 M solution in CH_2Cl_2, 6 mmol) was added to **13** (853 mg, 1 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The mixture was stirred for 1 h at −78 °C and then for 12 h at room temperature. It was then treated with water and extracted with CH_2Cl_2. The organic layer was separated and concentrated. The residue was triturated with EtOAc to give **14** as a beige powder (670 mg, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.1 Hz, 6H), 7.72–7.68 (m, 3H), 7.50–7.37 (m, 9H), 7.25–7.17 (m, 6H), 6.85–6.76 (m, 6H), 4.80 (s, 3H), 4.50 (dd, J = 9.4, 4.1 Hz, 3H), 3.49 (dd, J = 15.6, 4.3 Hz, 3H), 2.43 ppm (dd, J = 14.5, 11.8 Hz, 3H); ^{13}C NMR (360 MHz, $CDCl_3$): δ = 148.87, 147.31, 140.78, 140.08, 135.48, 133.36, 128.65, 127.51, 126.31, 125.58, 125.28, 125.19, 122.60, 120.98, 119.78, 118.36, 118.25, 46.60, 33.07 ppm (one carbon signal was not observed); EI-MS: m/z (%): 811 ([M^+], 6), 653 (41), 496 (20), 339 (67), 154 (100); elemental analysis calcd (%) for $C_{60}H_{42}O_3\cdot 0.75\,CH_2Cl_2$: C 78.72, H 4.83; found: C 78.82, H 4.83.

***syn*-5,10,15-Tris(1-trifluoromethanesulfonyloxy-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[3,2-*a*;3′,2′-*c*]fluorene (15)**: Tf_2O (500 μL, 3 mmol) was added to a mixture of **14** (420 mg, 0.5 mmol), 4-dimethylaminopyridine (4 mg, 0.03 mmol), and 2,6-lutidine (350 μL, 3 mmol) in CH_2Cl_2 (20 mL) at −30 °C. The resulting mixture was allowed to warm to 0 °C over 1 h. It was then treated with water and extracted with CH_2Cl_2. The organic layer was separated and concentrated. The residue was triturated with EtOAc to give **15** as a white powder (312 mg, 52%). **15**: m.p. 249 °C (decomp); ^{1}H NMR (300 MHz, [D]$_2$-1,1,2,2-tetrachloroethane, 100 °C): δ = 7.91 (d, J = 8.4 Hz, 3H), 7.83 (d, J = 8.6 Hz, 3H), 7.72 (d, J = 7.9 Hz, 3H), 7.58 (d, J = 8.5 Hz, 3H), 7.54–7.40 (m, 6H), 7.35–7.31 (m, 3H), 7.13–7.06 (m, 6H), 6.88 (d, J = 7.9 Hz, 3H), 4.62 (dd, J = 8.2, 4.7 Hz, 3H), 3.81 (dd, J = 14.5, 4.7 Hz, 3H), 3.25 ppm (dd, J = 14.6, 8.5 Hz, 3H); EI-MS: m/z (%): 1207 ([M^+], 1), 917 (16), 628 (15), 494 (16), 339 (100); elemental analysis calcd (%) for $C_{63}H_{39}S_3O_9F_9\cdot 0.5\,CH_2Cl_2$: C 61.22, H 3.21; found: C 61.57, H 3.25.

Benzo[1,2-*e*:3,4-*e*′:5,6-*e*″]tribenzo[*l*]acephenanthrylene (2): **Method 1a**: A mixture of **12a** (150 mg, 0.15 mmol), $Pd(OAc)_2$ (34 mg, 0.15 mmol), $BnMe_3NBr$ (69 mg, 0.3 mmol), and K_2CO_3 (207 mg, 1.5 mmol) in DMA (8 mL) was stirred at 140 °C for 36 h. It was then cooled to 23 °C and the precipitated solid was filtered off and washed with CH_2Cl_2 and acetone. This solid was suspended in saturated aqueous NaCN solution and stirred for 1 h. It was then filtered off and washed sequentially with water and acetone to give **2** as a clear brown powder (47 mg, 42%).

Method 1b: As Method 1a but with Cs_2CO_3 (488 mg, 1.5 mmol) instead of K_2CO_3. Yield: 60 mg, 53%.

Method 2: A mixture of **15** (120 mg, 0.1 mmol), [$Pd(PPh_3)_2Cl_2$] (70 mg, 0.15 mmol), and NaOPiv (74 mg, 0.6 mmol) in DMA (5 mL) was stirred at 120 °C for 36 h. It was then cooled to 23 °C and the precipitated solid was separated by centrifugation and washed with CH_2Cl_2 and acetone. This solid was suspended in saturated aqueous NaCN solution and stirred for 1 h. It was then separated by centrifugation and washed sequentially with water and acetone to give **2** as a clear brown powder (8 mg, 11%). ^{1}H NMR (300 MHz, [D]$_2$-1,1,2,2-tetrachloroethane, 130 °C): δ = 9.26–9.01 (m, 12H), 8.13–8.02 (m, 12H), 7.80–7.69 ppm (m, 6H); ^{13}C NMR (solid state, 100.6 MHz): δ = 134.99, 131.48, 128.32, 124.56, 121.16 ppm; EI-MS (probe temperature: 600 °C, ion source: 300 °C, 90 eV): m/z (%): 750 ([M^+], 100), 375 ([M^{2+}], 30), 248 ([M^{3+}], 2).

***syn*-2,7,13-Tributyl-5,10,15-tris(1-bromo-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (17a)**: *n*BuLi (0.31 mL, 0.784 mmol, 2.5 M in hexane) was added to a suspension of **16a** (100 mg, 0.196 mmol) in THF (10 mL) at −78 °C. The red solution was allowed to warm to 0 °C, whereupon a solution of 1-bromo-2-(bromomethyl)naphthalene (235 mg, 0.784 mmol) in THF (3 mL) was added. The resulting mixture was warmed to 23 °C and the yellow solution obtained was stirred at this temperature for 17 h. After extractive workup (EtOAc), the solvent was evaporated to give crude **17a** and its *anti* isomer (137 mg, 62%). Recrystallization from EtOAc afforded pure **17a:** m.p. 125–127 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.32 (d, J = 8.5 Hz, 3H), 8.02 (d, J = 8.1 Hz, 3H), 7.77 (d, J = 7.3 Hz, 3H), 7.60–7.56 (m, 6H), 7.51–7.46 (m, 3H), 7.14 (dd, J = 7.7 Hz, 1.6 Hz, 3H), 7.05 (d, J = 6.9 Hz, 3H), 6.28 (s, 3H), 4.60–4.55 (m, 3H), 4.05 (dd, J = 13.3, 5.3 Hz, 3H), 3.06 (dd, J = 13.7, 9.7 Hz, 3H), 2.43–2.29 (m, 6H), 1.33–1.11 (m, 12H), 0.79 ppm (t, J = 9.3 Hz, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.92, 140.28, 140.00, 137.74, 137.66, 135.87, 133.25, 132.39, 129.07, 127.90, 127.65, 127.17, 127.09, 126.89, 125.95, 125.61, 125.08, 122.24, 46.10, 40.38, 35.69, 33.41, 22.34, 13.94 ppm; FAB-MS: m/z (%): 1167 ([M^+], 15), 947 (85), 727 (38), 507 (100).

2,7,13-Triphenyl-5,10,15-tris(1-bromo-2-naphthylmethyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (17b): *n*BuLi (0.84 mL, 2.10 mmol, 2.5 M in hexane) was added to a suspension of **16b** (300 mg, 0.52 mmol) in THF (15 mL) at −78 °C. The red solution was allowed to warm to 10 °C, whereupon a solution of 1-bromo-2-(bromomethyl)naphthalene (1300 mg, 4.20 mmol) in THF (4 mL) was added. The resulting mixture was warmed to 23 °C and the yellow solution obtained was stirred at this temperature for 3 h. After extractive work-up (EtOAc), the solvent was evaporated to give crude **17b** as an *anti*/*syn* mixture (ca. 5.5:1) (450 mg, 71%). The mixture could be separated by column chromatography. ***anti***-

17b: Yellow solid; m.p. 226–228 °C; R_f = 0.53 (hexane/CH_2Cl_2, 2:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.54–8.33 (m, 9H), 7.91–6.94 (m, 30H), 6.75 (s, 1H), 6.63 (s, 1H), 6.59 (s, 1H), 5.33–5.20 (m, 3H), 4.51–4.42 (m, 3H), 3.23–3.15 (m, 1H), 3.07–2.94 (m, 1H), 2.87–2.79 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 147.03, 146.95, 141.81, 140.84, 140.67, 139.17, 138.91, 138.72, 138.61, 138.55, 137.62, 137.60, 137.27, 136.60, 136.49, 133.50, 132.55, 129.40, 129.20, 129.07, 128.48, 128.07, 128.02, 127.76, 127.56, 126.95, 126.25, 125.81, 125.39, 124.52, 124.33, 123.10, 122.68, 46.93, 46.79, 46.70, 40.41, 40.32, 40.16 ppm (several carbon signals were not observed); FAB-MS: *m*/*z* (%): 1227.5 ([M^+], 2), 1147.4 ([M^+ −Br], 1), 1023.2 ([M^+−$C_{10}H_6Br$], 1), 1007.2 ([M^+−$C_{11}H_8Br$], 9), 927.3 ([M^+−$C_{11}H_8Br$−Br], 3), 787.3 ([M^+−2$C_{11}H_8Br$], 5), 707.3 ([M^+ −2$C_{11}H_8Br$−Br], 4), 567.3 ([M^+−3$C_{11}H_8Br$], 21).

***syn*-17b**: Yellow solid; m.p. 144–146 °C; R_f = 0.40 (hexane/CH_2Cl_2, 2:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.37 (d, J = 8.1 Hz, 3H), 8.17 (d, J = 8.1 Hz, 3H), 7.7–7.6 (m, 12H), 7.53 (td, J = 7.9, J = 1.2 Hz, 6H), 7.39 (d, J = 8.5 Hz, 3H), 7.05 (t, J = 7.1 Hz, 6H), 6.89 (t, J = 8.7 Hz, 9H), 6.79 (d, J = 7.7 Hz, 6H), 5.88 (s, 3H), 4.06 (dd, J = 10.7, J = 6.1 Hz, 3H), 3.96 (dd, J = 13.3, J = 5.5 Hz, 3H), 2.68 ppm (dd, J = 13.5, J = 10.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.72, 140.75, 140.22, 138.86, 137.57, 137.43, 135.03, 133.22, 132.25, 129.18, 128.09, 127.84, 127.48, 127.20, 126.94, 126.22, 125.86, 125.27, 124.73, 124.41, 122.43, 45.96, 40.08 ppm (one carbon signal was not observed); FAB-MS: *m*/*z* (%): 2453 ([2M^+], 1), 1227 ([M^+], 4), 1147 ([M^+−Br], 3), 1007 ([M^+ −$C_{11}H_8Br$], 20), 927 ([M^+−$C_{11}H_8Br$−Br], 4), 787 ([M^+−2$C_{11}H_8Br$], 9), 707 ([M^+−2$C_{11}H_8Br$−1Br], 8), 567 ([M^+−3$C_{11}H_8Br$], 40); HR-FAB-MS: *m*/*z* calcd for $C_{78}H_{50}Br_3$ ([M^+−H]): 1227.1422; found 1227.1450.

1,11,21-Tributyl-benzo[1,2-*e*:3,4-*e*′:5,6-*e*″]tribenzo[*l*]acephenanthrylene (18a): A mixture of **17a** and its *anti* isomer (100 mg, 0.085 mmol), $Pd(OAc)_2$ (39 mg, 0.17 mmol), $BnMe_3NBr$ (39.1 mg, 0.17 mmol), and Cs_2CO_3 (277 mg, 0.85 mmol) was heated in DMA (6 mL) at 130 °C for 24 h. After being cooled, the mixture was partitioned between CH_2Cl_2 and 10% aqueous HCl. The organic extract was washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. The residue was chromatographed (hexane/CH_2Cl_2, 3:1) to give **18a** as an orange solid (20 mg, 26%): R_f = 0.30 (hexane/CH_2Cl_2, 3:1); m.p. 131–132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.52–8.39 (m, 9H), 8.09–8.05 (m, 3H), 7.93–7.87 (m, 3H), 7.76–7.66 (m, 9H), 7.53–7.48 (m, 3H), 3.82–3.17 (m, 6H), 1.37–1.22 (m, 2H), 1.15–0.83 (m, 2H), 0.69–0.61 ppm (m, 3H); ^{1}H NMR ([D_2]-1,1,2,2-tetrachloroethane, 300 MHz, 120 °C): δ = 9.10 (s, 3H), 8.98 (d, J = 7.3 Hz, 3H), 8.42 (d, J = 7.3 Hz, 3H), 8.14 (d, J = 8.8 Hz, 3H), 8.03 (d, J = 8.9 Hz, 6H), 7.87 (d, J = 8.2 Hz, 3H), 7.63–7.59 (m, 6H), 3.25 (t, J = 7.6 Hz, 6H), 0.96–0.87 (m, 12H), 0.57 ppm (t, J = 7.3 Hz, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.99, 140.71, 140.35, 136.37, 133.81, 133.58, 132.97, 132.89, 131.55, 131.82, 130.44, 130.34, 129.07, 127.51, 127.34, 126.67, 125.56, 124.69, 123.21, 122.99, 35.61, 35.57, 35.39, 34.08, 33.97, 33.77, 22.84, 22.61, 14.11, 13.77 ppm; MALDI-MS (dithranol or without a matrix): *m*/*z*: 918 ([M^+]); HR-FAB-MS: *m*/*z* calcd. for $C_{72}H_{54}$: 918.4225; found: 918.4083.

1,11,21-Triphenyl-benzo[1,2-*e*:3,4-*e*′:5,6-*e*″]tribenzo[*l*]acephenanthrylene (18b): A mixture of **17b** (*syn*/*anti* mixture; 84 mg, 0.069 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol), $BnMe_3NBr$ (16 mg, 0.07 mmol), and K_2CO_3 (99 mg, 0.70 mmol) was heated in DMA (5 mL) at 160 °C for 24 h. After being cooled, the mixture was partitioned between CH_2Cl_2 and 10% aqueous HCl. The organic extract was washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. The residue was chromatographed (hexane/CH_2Cl_2, 3:1) to give **18b** as a yellow solid (50 mg, 38%), m.p. 196–198 °C; R_f = 0.30 (hexane/CH_2Cl_2, 3:1); MALDI-MS (dithranol): *m*/*z*: 979.0 ([M^+]), 903 ([M^+−C_6H_5+H^+]).

***syn*-5,10,15-Tris(1-bromo-2-naphthylmethyl)-4,9,13-trimethoxy-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4a) and *anti*-5,10,15-tris(1-bromo-2-naphthylmethyl)-4,9,13-trimethoxy-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4b)**: *n*BuLi (1.94 mL, 2.5 M solution in hexanes, 4.86 mmol) was added to **3** (600 mg, 1.39 mmol) in THF (55 mL) at −78 °C, and the mixture was slowly allowed to warm to −10 °C over a period of 4 h. Thereafter, a solution of 1-bromo-2-(bromomethyl)naphthalene (1.67 g, 5.56 mmol) in THF (20 mL) was added to the red solution. After 30 min, the mixture was diluted with EtOAc and washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. The residue was chromatographed (hexane/CH_2Cl_2, 2:1) to give a 3:1 mixture of *anti*- and *syn*-trialkylated derivatives (1.36 g, 90%).

***syn*-4a**: Yellow solid; m.p. 180–182 °C; R_f = 1.10 (hexane/CH_2Cl_2, 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.5 Hz, 3H), 7.66 (d, J = 7.9 Hz, 3H), 7.50–7.46 (m, 6H), 7.37 (td, J = 6.9, 1.0 Hz, 3H), 7.05 (dd, J = 8.5, 6.9 Hz, 6H), 6.77 (dd, J = 9.7, 7.9 Hz, 6H), 5.46 (t, J = 6.1 Hz, 3H), 3.66 (dd, J = 13.8, 6.0 Hz, 3H), 3.37 ppm (dd, J = 13.8, 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.23, 149.50, 142.29, 137.63, 135.57, 133.18, 132.29, 129.52, 128.19, 127.96, 127.68, 127.54, 126.88, 126.62, 125.60, 125.38, 117.90, 109.65, 55.64, 50.57, 41.20 ppm; MALDI-MS (dithranol): *m*/*z*: 1089 ([M^+]).

***anti*-4b:** Yellow solid; m.p. 252–254 °C; R_f = 1.20 (hexane/CH_2Cl_2, 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28–8.17 (m, 2H), 7.78–7.24 (m, 16H), 7.14–6.91 (m, 4H), 6.85–6.63 (m, 4H), 6.40 (d, J = 7.3 Hz, 1H), 5.76 (dd, J = 8.1, 5.7 Hz, 1H), 5.66 (t, J = 6.1 Hz, 1H), 5.49 (t, J = 5.7 Hz, 1H), 4.10 (s, 3H), 4.05 (s, 3H), 4.02 (s, 3H), 3.82 (dd, J = 14.2, 6.1 Hz, 1H), 3.70 (dd, J = 14.2, 5.7 Hz, 1H), 3.51 (dd, J = 14.2, 5.3 Hz, 1H), 3.41 (dd, J = 13.8, 7.7 Hz, 1H), 3.23 (dd, J = 14.2, 8.5 Hz, 1H), 2.86 ppm (dd, J = 14.2, 9.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.38, 154.32, 154.27, 150.07, 150.04, 150.00, 149.97, 148.90, 148.87, 142.83, 142.21, 141.17, 141.02, 138.13, 138.09, 137.73, 137.70, 137.59, 136.20, 136.11, 135.85, 135.61, 133.14, 133.10, 132.22, 132.18, 129.63, 129.59, 129.45, 129.40, 128.46, 128.43, 128.37, 128.34, 128.04, 127.82, 127.70, 127.63, 127.42, 126.84, 126.73, 126.49, 126.45, 125.75, 125.65, 125.46, 125.22, 118.15, 117.66, 117.59, 110.01, 109.95, 109.83, 109.74, 55.94, 55.83, 55.48, 50.89, 49.96, 49.47, 42.69, 41.58, 41.48 ppm; FAB-MS: *m*/*z* (%): 1089 ([M^+], 16), 1009 ([M^+−Br], 3), 869 ([M^+−$C_{11}H_8Br$], 100), 789 ([M^+−$C_{11}H_8Br$−Br], 10), 649 ([M^+−2$C_{11}H_8Br$], 47), 568 ([M^+ −2$C_{11}H_8Br$−Br], 7), 430 ([M^+−3$C_{11}H_8Br$], 56).

1,11,21-Trimethoxy-benzo[1,2-*e*:3,4-*e*′:5,6-*e*″]tribenzo[*l*]acephenanthrylene (5): A mixture of **4a,b** (586 mg, 0.54 mmol), $Pd(OAc)_2$ (362 mg, 0.54 mmol), $BnMe_3NBr$ (248 mg, 1.08 mmol), and Cs_2CO_3 (1.75 g, 5.38 mmol) in DMA (35 mL) was heated at 140 °C for 36 h. After being cooled to room temperature, the mixture was diluted with CH_2Cl_2 and washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. The residue was chromatographed (hexane/CH_2Cl_2, 1:1) to give **5** as a yellow solid (300 mg, 66%); m.p. >300 °C; R_f = 1.12 (hexane/CH_2Cl_2, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.25 (d, J = 8.7 Hz, 3H), 9.13 (d, J = 9.1 Hz, 3H), 8.53 (s, 3H), 8.09 (d, J = 8.7 Hz, 3H), 8.07 (d, J = 8.7 Hz, 3H), 7.94 (d, J = 8.7 Hz, 3H), 7.81 (dd, J = 7.2, 7.1 Hz, 3H), 7.70 (dd, J = 7.9, 6.9 Hz, 3H), 7.62 (d, J = 9.1 Hz, 3H), 4.10 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 130.13, 129.09, 128.71, 125.87, 114.48, 55.51 ppm (other signals were not observed); FAB-MS: *m*/*z* (%): 841 ([M^+], 10).

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