JOC Article
pubs.acs.org/joc

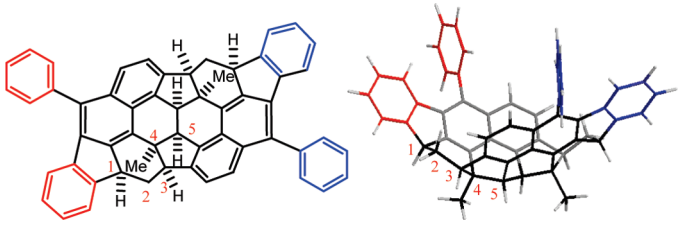
Synthesis of a Basket-Shaped $C_{56}H_{38}$ Hydrocarbon as a Precursor toward an End-Cap Template for Carbon [6,6]Nanotubes

Hu Cui, Novruz G. Akhmedov, Jeffrey L. Petersen, and Kung K. Wang*

C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

kung.wang@mail.wvu.edu

Received January 25, 2010



A basket-shaped $C_{56}H_{38}$ hydrocarbon (**3**) possessing a 30-carbon difluorenonaphthacenyl core that can be mapped onto the surface of C_{78} was synthesized from 4-bromo-1-indanone. The first stage of the synthesis involved the preparation of tetraketone **10** as a key intermediate. The use of cascade cyclization reactions of benzannulated enyne−allenes as key features in the next stage of the synthetic sequence provides an efficient route to **3** from 4-bromo-1-indanone in 12 steps. The all-*cis* relationship among the methyl groups and the methine hydrogens causes the two benzofluorenyl units in **3** to be in an essentially perpendicular orientation to each other. Hydrocarbon **3** and its derivatives could serve as attractive precursors leading to a geodesic $C_{68}H_{26}$ end-cap template for carbon [6,6]-nanotubes.

Introduction

The use of open geodesic polyarenes as end-cap seeds for growing single-walled carbon nanotubes (SWNTs) is an attractive strategy for the construction of SWNTs with a uniform diameter.[1] The advantages of such a rational synthetic approach over empirical methods, such as arc-discharge, laser ablation, and chemical vapor deposition,[2] were eloquently stated in the proposition for the synthesis of a geodesic $C_{60}H_{12}$ end-cap template for growing an armchair C_{3v} carbon [6,6]nanotube.[1a] Our continuing interest in the synthesis of bowl-shaped and basket-shaped polycyclic aromatic compounds[3] led us to select **1**, a $C_{66}H_{12}$ polycyclic aromatic hydrocarbon, and its partially hydrogenated and methylated derivative **2** ($C_{68}H_{26}$) as alternative end-cap templates for carbon [6,6]nanotubes (Figure 1). The structure of **1** can be regarded as having an interior 30-carbon framework of difluoreno[2,1,9,8,7-*defghi*:2′,1′,9′,8′,7′-*mnopqr*]-naphthacene[4] fused at the rim with a [6]cycloparaphenylene, which represents a nanohoop segment[5] of carbon [6,6]-nanotubes. Compared to **1**, the presence of 10 sp^3-hybridized carbons in the interior 30-carbon core of **2** appears to alleviate the molecular strain significantly. We have made progress toward the construction of **2** by successfully synthesizing **3**, a $C_{56}H_{38}$ hydrocarbon, as its potential precursor (Figure 2). The structure of **3** retains the 30-carbon interior core of **2**. However, two phenyl groups of the [6]cycloparaphenylene rim are removed along with the cleavage of four

*To whom correspondence should be addressed. Tel: (304) 293-3068, ext 6441. Fax: (304) 293-4904.

(1) (a) Hill, T. J.; Hughes, R. K.; Scott, L. T. *Tetrahedron* **2008**, *64*, 11360–11369. (b) Fort, E. H.; Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 16006–16007. (c) Steinberg, B. D.; Jackson, E. A.; Filatov, A. S.; Wakamiya, A.; Petrukhina, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 10537–10545. (d) Jackson, E. A.; Steinberg, B. D.; Bancu, M.; Wakamiya, A.; Scott, L. T. *J. Am. Chem. Soc.* **2007**, *129*, 484–485.

(2) Dai, H. *Acc. Chem. Res.* **2002**, *35*, 1035–1044.

(3) (a) Wang, K. K.; Wang, Y.-H.; Yang, H.; Akhmedov, N. G.; Petersen, J. L. *Org. Lett.* **2009**, *11*, 2527–2530. (b) Kim, D.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2006**, *8*, 2313–2316. (c) Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 7996–7999.

(4) (a) Hagen, S; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed.* **1997**, *36*, 406–408. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.

(5) (a) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647. (b) Steinberg, B. D.; Scott, L. T. *Angew. Chem., Int. Ed.* **2009**, *48*, 5400–5402. (c) Merner, B. L.; Dawe, L. N.; Bodwell, G. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5487–5491.

Published on Web 02/24/2010 DOI: 10.1021/jo100132v

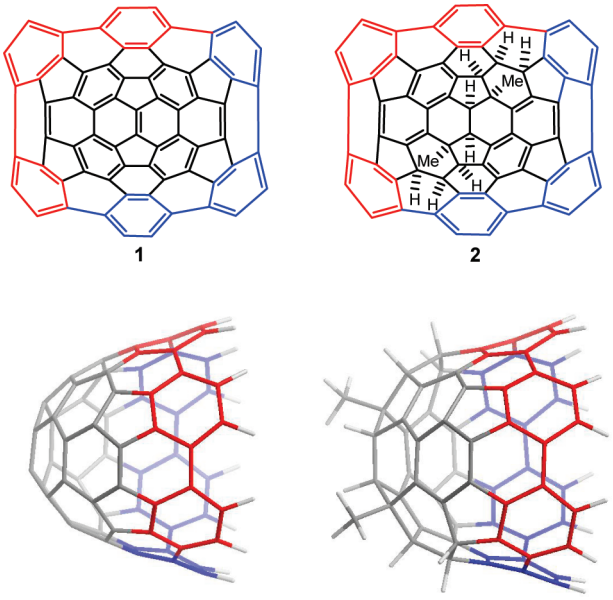


FIGURE 1. MM2-optimized structures of **1** and **2**.

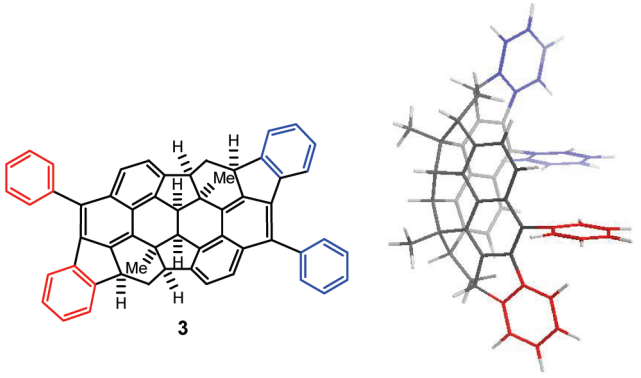


FIGURE 2. MM2-optimized structure of **3**.

additional carbon−carbon bonds connecting two of the four remaining phenyl groups on the rim to the rest of the molecule.

Results and Discussion

The synthetic sequence outlined in Scheme 1 illustrates the preparation of tetraketone **10** as a key intermediate leading toward **3**. Treatment of the commercially available 4-bromo-1-indanone[6] with triisopropylsilyl trifluoromethanesulfonate produced the corresponding silyl enol ether **4** in quantitative yield.[7] As an indene derivative, the methylene hydrogens in **4** are relatively acidic,[8] allowing lithiation with lithium diisopropylamide (LDA) to form the corresponding carbanion. Treatment of the resulting carbanion with Cu(II) chloride for the coupling reaction[9] followed by desilylation with tetrabutylammonium fluoride (TBAF) then produced

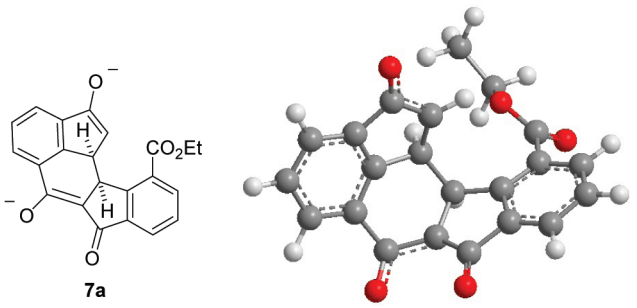


FIGURE 3. MM2-optimized structure of dienolate **7a**.

an essentially 1:1 mixture of the *rac*-**5** and *meso*-**5** isomers in 82% combined yield. The use of the corresponding trimethylsilyl enol ether for coupling gave only ca. 50% yield of a 1:1 mixture. While it was possible to separate small fractions of pure *rac*-**5** and *meso*-**5** by silica gel column chromatography for structure elucidation, the majority of the fractions are still mixtures of the *rac* and *meso* isomers. It was later discovered that the *rac* and *meso* isomers could be more readily separated after the subsequent carboethoxylation step. The structures of *rac*-**5** and *meso*-**5** were established by X-ray structure analyses.

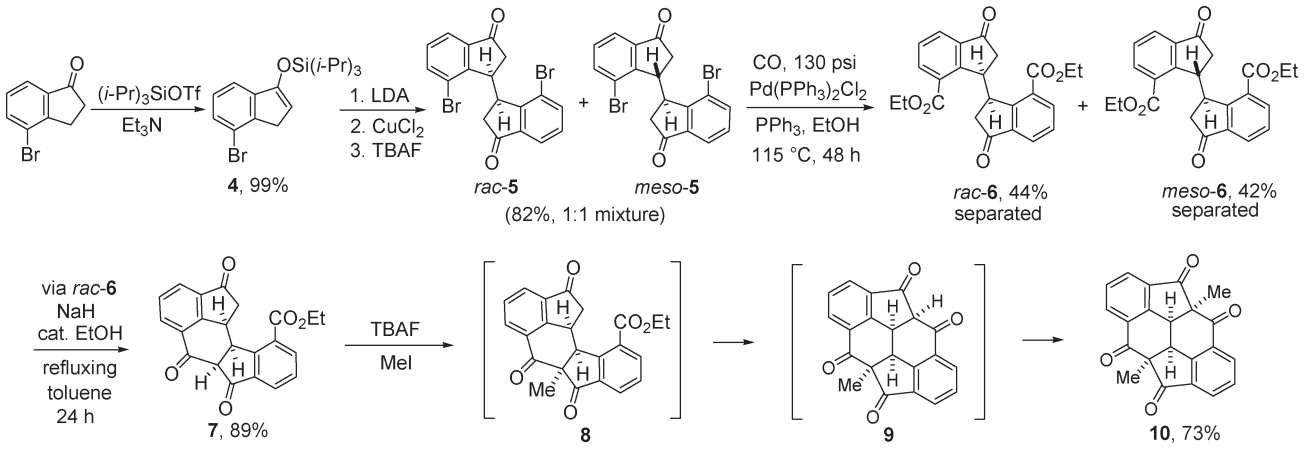
The palladium-catalyzed carboethoxylation reactions[10] of a 1:1 mixture of *rac*-**5** and *meso*-**5** produced a 1:1 mixture of the corresponding diketodiesters *rac*-**6** and *meso*-**6**. It was possible to separate the resulting two isomers by silica gel column chromatography to give *rac*-**6** in 44% isolated yield and *meso*-**6** in 42% isolated yield with a combined yield of 86%. A sample of pure *rac*-**5** was also subjected to the same reaction condition for carboethoxylation to form *rac*-**6** in 90% yield for structure identification.

Treatment of *rac*-**6** with sodium hydride in the presence of ethanol promoted an intramolecular Claisen-type condensation to form triketone **7**. The hydrogen between the two keto carbonyls is *cis* to the two central methine hydrogens as indicated by NOE measurements. However, the second intramolecular Claisen-type condensation did not occur to form the corresponding tetraketone. The lack of a second intramolecular Claisen-type condensation to form the corresponding tetraketone may be attributed to the difficulty of producing dienolate **7a** depicted in Figure 3 after an enolate is formed from deprotonation of the more acidic α hydrogen between the two keto carbonyls. Perhaps more importantly, the formation of the enolate between the two keto carbonyls causes dienolate **7a** to adopt a more planar geometry as shown in Figure 3, preventing the positioning of the ester carbonyl in a parallel orientation on top of the π electrons of the second enolate for condensation.

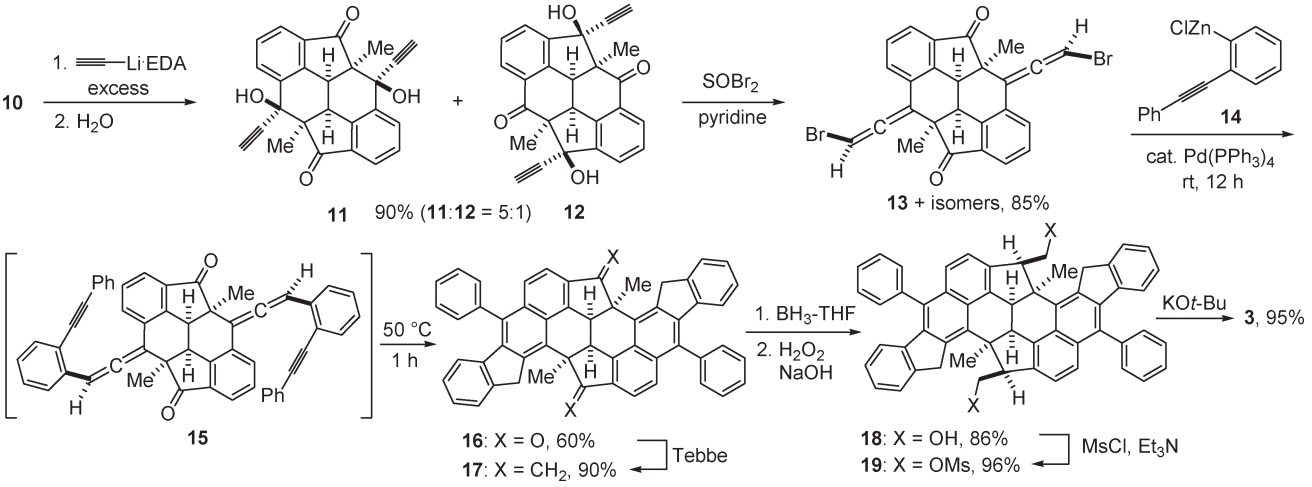
In an attempt to replace the acidic hydrogen between the two keto carbonyls with a methyl group by methylation with methyl iodide in the presence of tetrabutylamonium fluoride at room temperature,[11] it was gratifying to observe that the second Claisen-type condensation also occurred along with a subsequent methylation to give tetraketone **10** directly. Presumably after an initial methylation to form **8**, the second condensation occurred readily even under such a

(6) Adamczyk, M.; Watt, D. S.; Netzel, D. A. *J. Org. Chem.* **1984**, *49*, 4226–4237.
(7) Yu, J.-Q.; Wu, H.-C.; Corey, E. J. *Org. Lett.* **2005**, *7*, 1415–1417.
(8) Streitwieser, A., Jr.; Ciuffarin, E.; Hammons, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 63–67.
(9) (a) Heimer, N. E.; Hojjatie, M.; Panetta, C. A. *J. Org. Chem.* **1982**, *47*, 2593–2598. (b) Nicolet, P.; Sanchez, J.-Y.; Benaboura, A.; Abadie, M. J. M. *Synthesis* **1987**, 202–203.
(10) (a) El-ghayoury, A.; Ziessel, R. *J. Org. Chem.* **2000**, *65*, 7757–7763. (b) Charbonnière, L. J.; Weibel, N.; Ziessel, R. F. *Synthesis* **2002**, 1101–1109.
(11) Page, P. C. B.; Hamzah, A. S.; Leach, D. C.; Allin, S. M.; Andrews, D. M.; Rassias, G. A. *Org. Lett.* **2003**, *5*, 353–355.

SCHEME 1



SCHEME 2



mild reaction condition because the ester carbonyl could now be placed in a parallel orientation on top of the π electrons of the enolate or the corresponding enol for condensation to form **9**. A subsequent methylation then produced **10**.

The ^{1}H NMR spectrum gave the first indication that a symmetrical molecule was produced from **7** because only three signals in the aromatic region along with one methine signal and one methyl signal in the aliphatic region were observed. The presence of a C_2 symmetry in tetraketone **10** was confirmed by X-ray structure analysis. The methyl groups and the methine hydrogens in **10** are all *cis* to one another, indicating that the two methylation reactions occurred from the less hindered convex side. The all-*cis* relationship causes **10** to have a bent structure with the two benzene rings in essentially perpendicular orientation.

The next stage of the synthetic pathway outlined in Scheme 2 involved condensation between **10** and lithium acetylide−ethylenediamine complex to produce propargylic diol **11** as the major product (**11**:**12** = 5:1). The structure of **11** was established by X-ray structure analysis. The lithium acetylide attacked preferentially the keto carbonyls on the six-membered rings of **10** from the convex side. It is also interesting to note that even in the presence of large excess of lithium acetylide-ethylenediamine complex, only symmetrical diols **11** and **12** were produced. The unsymmetrical diols, triols, and tetraols were not detected. Similarly, with large excess of lithium (trimethylsilyl)acetylide, which formed a homogeneous solution with **10** in THF, only symmetrical diols **11** and **12** were obtained after desilylation.

Treatment of the mixture of **11** and **12** (5:1) with thionyl bromide[12] then produced allenic dibromide **13** and its isomers. The NMR spectrum indicated that the symmetrical allenic dibromide **13** was produced as the major product (71%), most likely via an S_Ni' pathway[13] with both of the two bromo substituents pointing toward the concave side. The structure of **13** was established by X-ray structure analysis. Minor amounts of an unsymmetrical dibromide (13%), presumably with one of the two bromo substituents pointing toward the convex side and a symmetrical dibromide (16%), presumably derived from **12**, were also observed. The palladium-catalyzed coupling reactions[14] between **13** and arylzinc chloride **14** produced, in situ, the benzannulated enyne−allene **15**. After 12 h at room temperature, the ^{1}H NMR spectrum indicated that a mixture of **15**, the corresponding monocyclized adduct, and the dicyclized benzofluorenyl dione **16** was formed in ratios of 1.0:1.6:1.1. When the

(12) Conde, J. J.; Mendelson, W. *Tetrahedron Lett*. **2000**, *41*, 811–814.
(13) Jacobs, T. L.; Fenton, D. M. *J. Org. Chem*. **1965**, *30*, 1808–1812.
(14) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett*. **1981**, *22*, 1451–1452.

reaction mixture was heated at 50 °C for 1 h, the mixture was transformed to **16** completely. The first indication of the successful formation of **16** came from the appearance of the characteristic AB splitting pattern in the ^{1}H NMR spectrum with a large coupling constant of 23.0 Hz that can be attributed to the two groups of methylene hydrogens on the five-membered rings of the benzofluorenyl structures.[15] Presumably, the transformation proceeded through Schmittel cyclization reactions of **15** to produce the corresponding biradicals followed by intramolecular radical−radical couplings and prototropic rearrangements to regain aromaticity as reported previously.[16]

Methylenation of **16** with the Tebbe reagent[17] produced diene **17**, which on treatment with BH_3−THF followed by oxidation provided diol **18**. The hydroboration reactions also occurred from the convex side. As a result, the two hydroxymethyl groups were forced to point inward toward the endohedral (concave) side of **18**. The orientation of the two hydroxymethyl groups toward the endohedral side of **18** was of crucial importance to the success of the subsequent intramolecular carbon−carbon bond-forming reactions. Diol **18** was then transformed to the corresponding methanesulfonate **19** with methanesulfonyl chloride in the presence of triethylamine. The methylene hydrogens on the five-membered rings of the benzofluorenyl structures are relatively acidic, making the corresponding carbanions readily accessible as observed previously.[3a] Treatment of **19** with potassium *tert*-butoxide for the intramolecular alkylation reactions then produced **3** in excellent yield. The close proximities between the carbons bearing the mesylate groups and the respective neighboring methylene carbons on the benzofluorenyl structures also contribute to the high efficiencies of the intramolecular alkylation reactions.

The structure of **3** was elucidated by ^{1}H and ^{13}C NMR spectroscopy and high-resolution MS. The presence of symmetry was apparent on the ^{1}H NMR spectrum with the appearance of only a singlet signal for the two methyl groups and five additional signals for the remaining 10 hydrogens on the sp^3-hybridzed carbons. The assignments and connectivity of these aliphatic hydrogens were established on the basis of their coupling patterns and NOE measurements (Figure 4). The all-*cis* relationship among the methine hydrogens (H1, H3, and H5) and the methyl groups was confirmed by irradiating the methyl signal at δ 2.12 and observing significant NOE enhancements for the signals of the methine hydrogens at δ 4.33 (H1), 4.28 (H3), and 4.14 (H5). Additional NOE experiments by irradiating H1, H3, H5, and H2$_{exo}$ signals further confirmed the structure assignment. In addition, irradiations of the H1 and H3 signals also resulted in significant NOE enhancements for the aromatic signals at δ 7.54 and 6.83, respectively. Furthermore, irradiation of the H2$_{exo}$ signal also caused significant NOE enhancements for

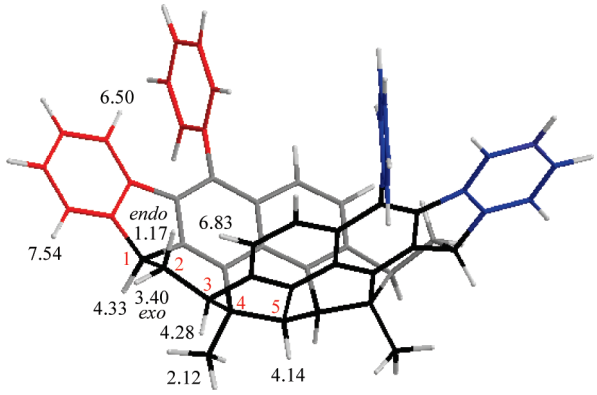


FIGURE 4. Assignments of ^{1}H NMR signals in δ values to the MM-2-optimized structure of **3**.

both of these two aromatic signals. The MM2-optimized structure of **3** indicates that the six-membered ring containing C1 to C4 carbons would adopt a boat conformation with H1 and the methyl group on C4 assuming the flagpole positions. Such a conformation is supported by the observation of a large coupling constant of 12.4 Hz between H1 and H2$_{endo}$ indicating an *anti* relationship and a coupling constant of 9.7 Hz between H2$_{exo}$ and H3 indicating a near eclipsed relationship. The upfield shift of an aromatic hydrogen at δ 6.50 is typical of a 5-phenylbenzofluorenyl structure with the phenyl substituent in essentially perpendicular orientation with respect to the benzofluorenyl group, placing one of the neighboring aromatic hydrogens in a shielding region of the induced magnetic field as observed previously.[3c]

Conclusions

A 12-step synthetic pathway from 4-bromo-1-indanone to the basket-shaped $C_{56}H_{38}$ hydrocarbon **3** is established. The ability to employ the same type of reaction twice for most of the synthetic steps greatly enhances the overall efficiency of the process. The molecule is chiral, possessing only a C_2 symmetry. The structure of **3** contains a 30-carbon difluorenonaphthacenyl core that can be mapped onto the surface of C_{78}. Compared to an earlier synthesis of a basket-shaped $C_{56}H_{40}$ hydrocarbon,[3a] the 30-carbon core in **3** is fully connected. The presence of 10 sp^3-hybridized carbons in the 30-carbon core appears to relieve substantial molecular strain associated with the corresponding fully aromatized system. The synthetic sequence could be adopted to allow the introduction of two additional phenyl groups at the periphery for further construction of a rim containing a unit of [6]cycloparaphenylene, which represents a nanohoop segment of carbon [6,6]nanotubes. Such a rim construction process could be initiated by condensation of **16** with 2 equiv of 2,6-dichlorobenzylmagnesium bromide followed by dehydration, attaching two more functionalized phenyl groups to the 30-carbon core for subsequent intramolecular arylation reactions.[1c,d,3b] The presence of 10 sp^3-hybridized carbons in the interior core places the phenyl groups at the periphery in close proximity to one another, making it feasible to connect them to form a paraphenylene rim.

Experimental Section

Triisopropylsilyl Enol Ether 4. To a mixture of 0.330 g (1.56 mmol) of 4-bromo-1-indanone[6] and 0.30 mL (2.2 mmol)

(15) Li, H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804–7810.

(16) (a) Li, H.; Zhang, H.-R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662–6668. (b) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999–1002. (c) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843–1845. (d) Wang, K. K. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 1091−1126.

(17) (a) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165–167. (b) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

of triethylamine in 20 mL of chloroform was added 0.46 mL (1.72 mmol) of triisopropylsilyl trifluoromethanesulfonate under argon. After 30 min of stirring at room temperature, 10 mL of a saturated sodium bicarbonate solution was introduced. The organic layer was separated, and the aqueous layer was extracted with methylene chloride (3 × 10 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (basic aluminum oxide/hexanes) to provide 0.570 g (1.55 mmol, 99%) of **4** as a colorless oil: IR (neat) 1596, 1563, 1355, 866 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.39 (1 H, d, J = 7.5 Hz), 7.36 (1 H, d, J = 7.9 Hz), 7.21 (1 H, t, J = 7.6 Hz), 5.49 (1 H, t, J = 2.3 Hz), 3.25 (2 H, d, J = 2.4 Hz), 1.34 (3 H, septet, J = 7.5 Hz), 1.16 (18 H, d, J = 7.6 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 153.5, 143.8, 142.5, 128.2, 128.0, 118.9, 117.4, 106.0, 35.2, 17.9, 12.5; MS m/z 369, 367 (MH^+); HRMS calcd for $C_{18}H_{28}BrOSi$ (MH^+) 367.1087, found 367.1090.

Dibromides *rac*-5 and *meso*-5. To a mixture of 0.330 g (1.55 mmol) of **4** in 20 mL of THF at −78 °C was added 1.0 mL of a 1.8 M solution (1.8 mmol) of lithium diisopropylamide under argon. The reaction mixture was stirred at −78 °C for 10 min before it was transferred via cannula to a flask containing 0.240 g (1.80 mmol) of copper(II) chloride and 10 mL of THF at −78 °C. The color of the solution turned black immediately. The solution was allowed to warm to −30 °C and stirred for 30 min before it was quenched with 10 mL of a saturated sodium dihydrogen phosphate solution. Water (50 mL) was introduced, and the organic layer was separated. The aqueous layer was back-extracted with methylene chloride (3 × 15 mL). The combined organic layers were treated with 5 mL of a 1.0 M solution of TBAF in THF under argon. After 1 h of stirring, the solution was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel/10% ethyl acetate in methylene chloride) to provide 0.270 g (0.64 mmol, 82%) of an essentially 1:1 mixture of *rac*-**5** and *meso*-**5** as a light yellow solid. *rac*-**5**: mp 242−244 °C; IR 1711, 1590, 1260, 793 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.84 (2 H, d, J = 7.8 Hz), 7.73 (2 H, d, J = 7.5 Hz), 7.35 (2 H, t, J = 7.7 Hz), 4.80 (2 H, d, J = 7.6 Hz), 2.42 (2 H, dd, J = 19.6, 8.2 Hz), 1.79 (2 H, dd, J = 19.7, 1.5 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 203.3, 154.4, 140.1, 138.9, 130.2, 123.0, 121.3, 38.9, 37.3; MS m/z 423, 421, 419 (MH^+); HRMS calcd for $C_{18}H_{13}Br_2O_2$ (MH^+) 418.9277, found 418.9280. *meso*-**5**: mp 258−259 °C; IR 1717, 1588, 1261, 793 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.65 (2 H, d, J = 7.6 Hz), 7.64 (2 H, d, J = 7.8 Hz), 7.29 (2 H, t, J = 7.6 Hz), 4.33 (2 H, d, J = 7.8 Hz), 2.86 (2 H, dd, J = 18.6, 7.9 Hz), 2.30 (2 H, d, J = 18.6 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 203.1, 152.9, 140.3, 138.3, 130.4, 123.2, 122.8, 42.5, 42.2; MS m/z 423, 421, 419 (MH^+); HRMS calcd for $C_{18}H_{13}Br_2O_2$ (MH^+) 418.9277, found 418.9281. In a separate run, additional silica gel column chromatography allowed the separation of a fraction of pure *rac*-**5** and a fraction of pure *meso*-**5** for structure elucidation. Recrystallization of the separated *rac*-**5** and *meso*-**5** from methylene chloride/hexanes produced crystals suitable for X-ray structure analyses.

Diketodiesters *rac*-6 and *meso*-6. To a solution of 0.270 g (0.64 mmol) of a 1:1 mixture of *rac*-**5** and *meso*-**5** in 6.0 mL of ethanol and 1.0 mL (7.19 mmol) of triethylamine in a 15-mL heavy wall cylindrical glass vessel were added 0.050 g (7.1×10^{-5} mmol) of bis(triphenylphosphine)palladium(II) dichloride and 0.100 g (0.38 mmol) of triphenylphosphine. The vessel was pressurized to 130 psi with carbon monoxide and heated to 115 °C for 48 h before it was allowed to cool to room temperature. The extra carbon monoxide was then released in a well ventilated hood, and the solution was concentrated in vacuo. The residue was dissolved in methylene chloride and purified by column chromatography (silica gel/15% ethyl acetate in hexanes) to afford 0.113 g (0.28 mmol, 44%) of *rac*-**6** as a light yellow solid and 0.110 g (0.27 mmol, 42%) of *meso*-**6** as a light yellow solid. *rac*-**6**: mp 145−146 °C; IR 1717, 1259, 1134, 754 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 8.21 (2 H, dd, J = 7.6, 1.2 Hz), 7.92 (2 H, dd, J = 7.6, 1.2 Hz), 7.52 (2 H, t, J = 7.6 Hz), 4.93 (2 H, dd, J = 4.5, 2.4 Hz), 4.45 (2 H, dq, J = 10.8, 7.2 Hz), 4.38 (2 H, dq, J = 10.8, 7.1 Hz), 2.46 (2 H, dd, J = 19.4, 8.2 Hz), 1.82 (2 H, dd, J = 19.4, 2.1 Hz), 1.41 (6 H, t, J = 7.1 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 204.2, 165.8, 156.6, 138.8, 136.7, 129.6, 128.4, 127.7, 61.5, 40.5, 39.6, 14.3; MS m/z 407 (MH^+), 379, 361; HRMS calcd for $C_{24}H_{23}O_6$ (MH^+) 407.1489, found 407.1492. *meso*-**6**: mp 183−184 °C; IR 1716, 1259, 1133, 754 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 8.04 (2 H, dd, J = 7.6, 1.2 Hz), 7.79 (2 H, dd, J = 7.6, 1.1 Hz), 7.45 (2 H, t, J = 7.5 Hz), 4.94 (2 H, d, J = 7.8 Hz), 4.17 (2 H, dq, J = 10.8, 7.1 Hz), 4.10 (2 H, dq, J = 10.8, 7.2 Hz), 2.79 (2 H, dd, J = 18.4, 7.8 Hz), 2.24 (2 H, dd, J = 18.5 Hz), 1.32 (6 H, t, J = 7.1 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 203.6, 165.2, 154.5, 139.0, 135.8, 130.2 128.4, 127.2, 60.9, 42.5, 42.1, 14.0; MS m/z 407 (MH^+), 379, 361; HRMS calcd for $C_{24}H_{23}O_6$ (MH^+) 407.1489, found 407.1492.

By using the same experimental procedure, pure *rac*-**5** was converted to *rac*-**6** in 90% isolated yield.

Triketone 7. To 0.359 g (0.884 mmol) of *rac*-**6** in 10 mL of anhydrous toluene under an argon atmosphere was added 0.20 g (5.0 mmol) of a 60% sodium hydride by weight in mineral oil followed by 0.05 mL (0.85 mmol) of absolute ethanol. The color of the solution immediately turned green. The reaction mixture was heated to reflux for 24 h before it was allowed to cool to room temperature. A saturated sodium dihydrogen phosphate solution (30 mL) was introduced followed by 30 mL of methylene chloride. After 30 min of stirring, the organic layer was separated, and the aqueous layer was extracted with methylene chloride (3 × 30 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was washed with a solution of 50% diethyl ether in hexanes (3 × 15 mL) to remove dark color materials and mineral oil from sodium hydride. The resulting gray residue was dissolved in methylene chloride and purified by column chromatography (silica gel/50% ethyl acetate in hexanes) to afford 0.284 g (0.789 mmol, 89%) of **7** as a white solid: mp 244−245 °C; IR 1718, 1693, 1290, 1261 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 8.40 (1 H, dd, J = 7.6, 0.6 Hz), 8.04 (1 H, d, J = 7.5 Hz), 7.92 (1 H, d, J = 7.5 Hz), 7.82 (1 H, d, J = 7.6 Hz), 7.55 (1 H, t, J = 7.6 Hz), 7.51 (1 H, t, J = 7.5 Hz), 5.40 (1 H, dd, J = 11.1, 7.5 Hz), 4.50 (1 H, qd, J = 7.0, 3.2 Hz), 4.48 (1 H, qd, J = 7.0, 3.2 Hz), 4.17 (1 H, dt, J = 11.1, 7.0 Hz), 4.07 (1 H, d, J = 7.5 Hz), 2.99 (2 H, dd, J = 17.9, 7.0 Hz), 2.08 (2 H, dd, J = 17.9, 7.0 Hz), 1.49 (3 H, t, J = 7.1 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 202.8, 197.4, 191.2, 165.1, 156.7, 154.4, 137.4, 137.2, 136.1, 132.6, 130.7, 129.7, 129.5, 129.3, 129.1, 128.7, 63.6, 61.8, 43.4, 39.5, 35.4, 14.3; MS m/z 361 (MH^+); HRMS calcd for $C_{22}H_{17}O_5$ (MH^+) 361.1071, found 361.1073. Triketone **7** is not very stable and needs to be used immediately for the preparation of tetraketone **10**.

Tetraketone 10. To a 50-mL flask containing 0.120 g (0.333 mmol) of **7** and 0.073 g (1.74 mmol) of sodium fluoride in 35 mL of anhydrous acetonitrile under an argon atmosphere at room temperature was added 0.40 mL (6.4 mmol) of methyl iodide followed by dropwise addition of 1.4 mL of a 1.0 M solution (1.4 mmol) of TBAF in THF. After 2 h of stirring at room temperature, the solution was concentrated in vacuo. The residue was purified by column chromatography (silica gel/10% ethyl acetate in hexanes) to provide 0.083 g (0.243 mmol, 73%) of **10** as a white solid: mp 311 °C dec; IR 1727, 1257, 962 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.93 (2 H, dd, J = 7.6, 0.9 Hz), 7.87 (2 H, dd, J = 7.5, 0.8 Hz), 7.47 (2 H, t, J = 7.6 Hz), 4.05 (2 H, s), 1.91 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 196.9, 189.6, 155.0, 136.1, 132.8, 130.1, 130.0, 128.9, 67.0, 40.8, 19.9; MS m/z 343 (MH^+); HRMS calcd for $C_{22}H_{15}O_4$ (MH^+) 343.0965, found 343.0967. Recrystallization of tetraketone **10** from methylene chloride/diethyl ether produced a crystal suitable for X-ray structure analysis.

Propargylic Diols 11 and 12. To a flask containing 0.325 g (3.51 mmol) of lithium acetylide−ethylenediamine complex in 100 mL of THF at −78 °C was added via cannula 0.150 g (0.439 mmol) of tetraketone **10** in 90 mL of THF. The solution was then allowed to warm to 0 °C in 2 h before it was quenched with 0.5 mL of a 2.0 M solution of hydrochloric acid. The solution was then allowed to warm to room temperature and stirred for 10 min. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography (basic aluminum oxide/30% ethyl acetate in methylene chloride) to provide 0.156 g (0.396 mmol, 90%) of a mixture of **11** and **12** (5:1) as a white solid. **11**: IR 3400, 3305, 1690 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.73 (2 H, dd, J = 7.3, 1.2 Hz), 7.31 (2 H, d, J = 7.8 Hz), 7.26 (2 H, t, J = 7.6 Hz), 5.55 (2 H, s), 4.03 (2 H, s), 2.75 (2 H, s), 1.90 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 210.3, 151.6, 138.9, 134.1, 129.45, 129.36, 123.2, 81.0, 74.9, 72.8, 57.5, 44.5, 19.9; MS m/z 395 (MH^+), 381 376, 359; HRMS calcd for $C_{26}H_{19}O_4$ (MH^+) 395.1278, found 395.1280. Recrystallization of **11** from ethyl acetate/hexanes produced a crystal suitable for X-ray structure analysis.

A minor set of ^1H NMR signals (partial) attributable to **12** were observed at δ 7.67 (2 H, dd, J = 7.5, 1.0 Hz), 7.57 (2 H, dd, J = 7.9, 0.9 Hz), 6.10 (2 H, s), 3.94 (2 H, s), 2.76 (2 H, s), 1.86 (6 H, s).

Allenic Dibromide 13. To a mixture of 0.156 g (0.396 mmol) of **11** and **12** (5:1) in 20 mL of methylene chloride at −78 °C was added 0.3 mL (3.72 mmol) of pyridine followed by 0.08 mL (1.03 mmol) of thionyl bromide. The solution was allowed to warm to 0 °C in 1 h before it was quenched with 20 mL of a 2.0 M solution of hydrochloric acid. Water (10 mL) was introduced, and the organic layer was separated. The aqueous layer was back-extracted with methylene chloride (2 × 10 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/30% ethyl acetate in methylene chloride) to provide 0.176 g (0.338 mmol, 85%) of a mixture of the symmetrical allenic dibromide **13** (71%), the corresponding unsymmetrical allenic dibromide (13%), and a symmetrical allenic dibromide (16%) derived from **12** as a yellow solid. In a separated run, additional silica gel column chromatography allowed the separation of a fraction containing essentially only the symmetrical allenic dibromide **13** for structure elucidation. **13**: mp 198 °C dec; IR 1941, 1717 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.57 (2 H, d, J = 7.5 Hz), 7.39 (2 H, d, J = 7.5 Hz), 7.29 (2 H, t, J = 7.5 Hz), 6.71 (2 H, s), 3.63 (2 H, s), 1.77 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 203.4, 203.0, 149.0, 135.4, 132.7, 129.3, 128.1, 124.6, 110.8, 78.7, 54.1, 42.3, 22.7; MS m/z 523, 521, 519 (MH^+), 441, 439; HRMS calcd for $C_{26}H_{17}Br_2O_2$ (MH^+) 518.9590, found 518.9592. Recrystallization of **13** from methylene chloride produced a crystal suitable for X-ray structure analysis.

Benzofluorenyl Dione 16. To a mixture of 0.700 g (2.72 mmol) of 1-bromo-2-(phenylethynyl)benzene in 10 mL of THF at −78 °C was added dropwise 1.70 mL of a 1.6 M solution (2.72 mmol) of butyllithium in hexanes. The solution was stirred at −78 °C for 10 min before 2.74 mL of a 1.0 M solution (2.74 mmol) of zinc chloride in diethyl ether was introduced to form **14**. The solution was allowed to warm to −30 °C and stirred for 1 h. In a separate flask, 0.176 g (0.338 mmol) of a mixture of **13** and its isomers and 0.078 g (0.068 mmol) of tetrakis(triphenylphosphine)palladium were dissolved in 10 mL of THF. The mixture was stirred at room temperature for 15 min before it was transferred via cannula into the flask containing the zinc reagent **14**. The mixture was stirred at room temperature for 12 h and then heated at 50 °C for 1 h before it was allowed to cool to room temperature. The reaction mixture was quenched with 1.0 mL of a 2.0 M solution of hydrochloric acid. The solution was then filtered through a short aluminum oxide column and concentrated in vacuo. The residue was purified by column chromatography (silica gel/5% ethyl acetate in hexanes) to afford 0.145 g (0.203 mmol, 60%) of **16** as a light yellow solid: mp 355 °C dec; IR 1709, 1616, 778 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.62 (2 H, d, J = 7.6 Hz), 7.58 (2 H, dt, J = 7.4, 1.2 Hz), 7.53 (2 H, tt, J = 7.4, 1.4 Hz), 7.50 (2 H, td, J = 7.5, 1.2 Hz), 7.37 (2 H, d, J = 8.6 Hz), 7.34−7.31 (4 H, m), 7.27 (2 H, t, J = 7.5 Hz), 7.20 (2 H, d, J = 7.3 Hz), 6.98 (2 H, t, J = 7.6 Hz), 6.34 (2 H, d, J = 7.9 Hz), 4.95 (2 H, d, J = 23.0 Hz), 4.47 (2 H, t, J = 23.0 Hz), 4.16 (2 H, s), 2.33 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 202.9, 150.1, 145.1, 143.2, 142.7, 139.8, 138.2, 136.0, 133.9, 129.9, 129.8, 129.6, 129.3, 129.2, 128.8, 128.1, 128.0, 127.1, 126.3, 124.64, 124.61, 124.1, 119.1, 58.8, 44.5, 36.8, 19.8; MS m/z 715 (MH^+); HRMS calcd for $C_{54}H_{35}O_2$ (MH^+) 715.2632, found 715.2639.

A minor set of ^1H NMR signals (partial) presumably arising from the presence of an isomeric benzofluorenyl dione (8%) derived from the allenic dibromide from **12** were observed at δ 7.13 (2 H, d, J = 9.0 Hz), 7.01 (2 H, t, J = 7.8 Hz), 6.59 (2 H, d, J = 7.8 Hz), 4.71 (2 H, d, J = 23.0 Hz), 4.55 (2 H, s), 4.42 (2 H, d, J = 23.0 Hz), 2.38 (6 H, s).

Benzofluorenyl Diene 17. To 0.050 g (0.070 mmol) of **16** in 10 mL of THF at 0 °C was added 0.8 mL of a 0.5 M solution (0.4 mmol) of the Tebbe reagent ($Cp_2TiCl(CH_2)Al(CH_3)_2$) in toluene. The solution was then allowed to warm to room temperature. After 1 h, it was quenched with 1 mL of a 2.0 M solution of hydrochloric acid at 0 °C. The solution was filtered through a short aluminum oxide column and then concentrated in vacuo. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.045 g (0.063 mmol, 90%) of **17** as a yellow solid: IR 1463, 1264, 739 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.54 (2 H, td, J = 7.3, 1.6 Hz), 7.53 (2 H, d, J = 7.5 Hz), 7.50 (2 H, tt, J = 7.5, 1.4 Hz), 7.47 (2 H, td, J = 7.5, 1.8 Hz), 7.33 (2 H, d, J = 7.5 Hz), 7.24 (2 H, d, J = 8.5 Hz), 7.22 (2 H, dt, J = 7.0, 1.8 Hz), 7.185 (2 H, td, J = 7.5, 1.0 Hz), 7.179 (2 H, d, J = 8.8 Hz), 6.94 (2 H, t, J = 7.4 Hz), 6.30 (2 H, d, J = 7.9 Hz), 5.90 (2 H, s), 5.74 (2 H, s), 4.73 (2 H, d, J = 22.0 Hz), 4.21 (2 H, d, J = 22.0 Hz), 3.88 (2 H, s), 2.17 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 154.9, 144.1, 140.7, 140.3, 139.1, 138.9, 138.3, 137.0, 133.1, 132.6, 131.8, 130.0, 129.9, 129.0, 128.9, 127.6, 126.9, 126.2, 125.5, 124.3, 123.6, 118.4, 107.8, 57.7, 47.4, 36.6, 21.6; MS m/z 711 (MH^+), 710, 709; HRMS calcd for $C_{56}H_{39}$ (MH^+) 711.3046, found 711.3046.

The ^1H NMR spectrum indicates the presence of a small amount of an isomer presumably arising from the presence of the minor isomer in the sample of **16**.

Benzofluorenyl Diol 18. To a solution of 0.078 g (0.11 mmol) of **17** in 5 mL of THF at 0 °C was added 0.6 mL of a 1.0 M borane−THF solution (0.6 mmol) in THF. The solution was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was then cooled to 0 °C before 3 mL of 95% ethanol, 1.0 mL of a 1.0 M solution (1.0 mmol) of sodium hydroxide, and 0.09 mL of a 30% hydrogen peroxide solution (0.88 mmol, 9.8 M) were introduced sequentially. The solution was stirred at 40 °C for 1 h and then cooled to 0 °C before 15 mL of water and 10 mL of methylene chloride were introduced. The organic layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 10 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography (silica gel/20% ethyl acetate in hexanes) to provide 0.070 g (0.094 mmol, 86%) of **18** as a light yellow solid: IR 3576, 1463, 728 cm^{-1}; ^1H ($CDCl_3$, 600 MHz) δ 7.58−7.55 (4 H, m), 7.52 (2 H, tt, J = 7.3, 1.4 Hz), 7.50 (2 H, td, J = 7.3, 1.5 Hz), 7.38 (2 H, d, J = 7.5 Hz), 7.25−7.22 (4 H, m), 7.17 (2 H, d, J = 8.6 Hz), 7.07 (2 H, d, J = 8.6 Hz), 7.01 (2 H, t, J = 7.6 Hz), 6.40 (2 H, d, J = 7.9 Hz), 5.00 (2 H, d, J = 22.1 Hz), 4.38 (2 H, d, J = 22.0 Hz), 3.90 (2 H, s), 3.87 (6 H, s), 2.45 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 143.5, 140.8, 139.7, 138.9, 137.9, 137.5, 137.0, 133.2,

132.0, 131.5, 130.1, 129.8, 129.1, 128.9, 127.7, 127.6, 126.9, 126.4, 124.8, 124.3, 123.6, 121.5, 62.7, 62.5, 56.0, 52.6, 39.7, 28.8; MS *m*/*z* 747 (MH^+), 746, 710, 709; HRMS calcd for $C_{56}H_{43}O_2$ (MH^+) 747.3258, found 747.3222.

The ^{1}NMR spectrum indicates that the product derived from the minor isomer in the sample of **17** was removed by silica gel column chromatography.

Benzofluorenyl Dimethanesulfonate 19. To a mixture of 0.070 g (0.094 mmol) of **18** in 7 mL of methylene chloride at 0 °C was added 0.13 mL (0.94 mmol) of triethylamine followed by 0.06 mL (0.75 mmol) of methanesulfonyl chloride. The solution was stirred for 30 min before 10 mL of a 1.0 M solution of hydrochloric acid was added. The organic layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 5 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography (silica gel/20% ethyl acetate in hexanes) to provide 0.081 g (0.090 mmol, 96%) of **19** as a yellow solid: IR 1463, 1358, 1175, 944, 732 cm^{-1}; ^{1}H ($CDCl_3$, 600 MHz) δ 7.59−7.56 (4 H, m), 7.55−7.53 (4 H, m), 7.37 (2 H, dm, J = 7.5, 0.9 Hz), 7.31 (2 H, m), 7.26 (2 H, d, J = 4.0 Hz), 7.24 (2 H, td, J = 3.7, 1.0 Hz), 7.15 (2 H, d, J = 8.6 Hz), 7.02 (2 H, t, J = 7.4 Hz), 6.42 (2 H, d, J = 7.9 Hz), 4.65 (2 H, d, J = 21.8 Hz), 4.44 (2 H, d, J = 21.8 Hz), 4.34 (2 H, dd, J = 10.8, 5.2 Hz), 4.13 (2 H, t, J = 5.1 Hz), 4.03 (2 H, dd, J = 10.8, 4.9 Hz), 3.96 (2 H, s), 2.46 (6 H, s), 2.37 (6 H, s); ^{13}C ($CDCl_3$, 150 MHz) δ 143.0, 140.7, 139.5, 138.7, 138.4, 137.3, 135.2, 133.5, 132.3, 131.1, 130.1, 129.7, 129.3, 129.0, 127.8, 127.5, 127.2, 126.7, 125.3, 124.4, 123.7, 121.5, 70.1, 59.8, 55.0, 53.4, 40.0, 37.0, 29.7; MS *m*/*z* 903 (MH^+), 902, 808, 807; HRMS calcd for $C_{58}H_{47}O_6S_2$ (MH^+) 903.2809, found 903.2776.

$C_{56}H_{38}$ Hydrocarbon 3. To a solution of 0.055 g (0.061 mmol) of **19** in 10 mL of THF at 40 °C was added dropwise 2.0 mL of a 0.1 M solution of potassium *tert*-butoxide in THF. The solution was stirred for 30 min before 20 mL of a saturated ammonium chloride solution and 10 mL of methylene chloride were added sequentially. The organic layer was separated, and the aqueous layer was back-extracted with methylene chloride (2 × 10 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo to provide 0.041 g (0.058 mmol, 95%) of **3** as a gray solid: IR 1467, 737, 700 cm^{-1}; ^{1}H ($CDCl_3$, 600 MHz) δ 7.53 (4 H, m), 7.47 (2 H, d, J = 7.6 Hz), 7.45 (2 H, tt, J = 7.3, 1.4 Hz), 7.40 (2 H, td, J = 7.5, 0.8 Hz), 7.19 (2 H, td, J = 7.4, 0.9 Hz), 7.14 (2 H, d, J = 8.6 Hz), 7.09 (2 H, d, J = 7.6 Hz), 6.97 (2 H, t, J = 7.6 Hz), 6.83 (2 H, d, J = 8.6 Hz), 6.50 (2 H, d, J = 7.8 Hz), 4.33 (2 H, dd, J = 12.4, 6.9 Hz), 4.28 (2 H, dd, J = 9.7, 6.2 Hz), 4.13 (2 H, s), 3.41 (2 H, ddd, J = 12.9, 9.7, 6.9 Hz), 2.12 (6 H, s), 1.17 (2 H, td, J = 12.6, 6.2 Hz); ^{13}C ($CDCl_3$, 150 MHz) δ 149.0, 143.3, 142.5, 142.2, 138.7, 136.1, 135.1, 131.9, 131.7, 130.9, 130.4, 129.8, 128.7, 128.6, 127.4, 126.81, 126.76, 125.1, 125.0, 124.5, 123.3, 121.8, 53.13, 53.09, 45.2, 40.3, 33.2, 26.3; MS *m*/*z* 711 (MH^+), 710, 709; HRMS calcd for $C_{56}H_{39}$ (MH^+) 711.3046, found 711.3005.

Acknowledgment. K.K.W. thanks the National Science Foundation (Grant No. CHE-0909613) for financial support. J.L.P. acknowledges the support (Grant No. CHE-9120098) provided by the National Science Foundation for the acquisition of a Siemens P4 X-ray diffractometer. The financial support of the NSF-EPSCoR (Grant No. 1002165R) for the purchase of a 600 MHz NMR spectrometer is also gratefully acknowledged.

Supporting Information Available: General experimental methods, ^{1}H and ^{13}C NMR spectra of compounds **3**−**7**, **10**, **11**, **13**, and **16**−**19**, ORTEP drawings of the crystal structures of *rac*-**5**, *meso*-**5**, **10**, **11**, and **13**, and X-ray crystallographic data of *rac*-**5**, *meso*-**5**, **10**, **11**, and **13** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.