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Novel Synthesis of 4,5-Diarylphenanthrenes via C^2−C^6 Cyclization of Benzannulated Enyne−Allenes

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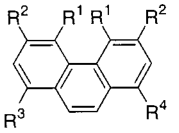
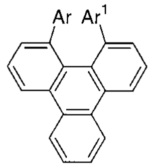
A new synthetic pathway to the 4,5-diarylphenanthrenes **8** having a helical twist in their structures was developed. The synthetic sequence involves condensation of the diketone **5** with 2 equiv of the lithium acetylides derived from the diacetylenes **4** followed by protonation to produce the propargylic alcohols **6**. Reduction of **6** with triethylsilane in the presence of trifluoroacetic acid furnished the tetraacetylenic hydrocarbons **7** in nearly quantitative yields. Treatment of **7** with potassium *tert*-butoxide under refluxing toluene at 110 °C for up to 10 h then furnished the 4,5-diarylphenanthrenes **8**. Apparently, the transformation from **7** to **8** involves initial prototropic isomerizations to form the benzannulated enyne−allenes **9**. Two subsequent formal intramolecular Diels−Alder reactions via the biradicals **10** and **12** derived from the C^2−C^6 cyclizations then led to **13**, which in turn underwent tautomerizations to give **8**. The structure of **8a** was established by the X-ray structure analysis, showing that the two phenyl substituents are bent away from each other and the central aromatic system is severely distorted with a helical twist. The existence of a helical twist in **8** imposed by the aryl groups at the 4- and 5-positions was also revealed with a set of AB ^{1}H NMR signals for the diastereotopic methylene hydrogens on the five-membered rings.

Introduction

Because of steric hindrance, the aromatic system of the 4,5-disubstituted phenanthrenes is twisted and the two substituents are bent out of the plane of the aromatic rings. Such structural distortion was first demonstrated with the partial resolution of the enantiomers of 4,5,8-trimethyl-1-phenanthrylacetic acid (**1a**) in 1947.[1] More recently, the activation barrier for racemization ($\Delta G^{\ddagger}_{\mathrm{rac}}$) of **1a** was determined to be 18.7 kcal/mol at −11 °C.[2] The X-ray structure of 4,5-dimethylphenanthrene (**1b**) was also reported, allowing direct measurement of a pronounced 27.9° twist between the mean planes of the outer rings and providing information regarding the distortion of the molecular geometry.[3] The enantiomers of **1b** were separated by chromatography on chiral stationary phases, and the $\Delta G^{\ddagger}_{\mathrm{rac}}$ was determined to be 16.1 kcal/mol at 25 °C.[3a] Other 4,5-disubstituted phenanthrene derivatives, including 4,5-diphenylphenanthrene (**1c**)[4] and closely related 4,5-diaryltriphenylenes (**2**)[4,5] and 13,14-bis(2-pyridyl)pentaphenes,[6] have also been reported. The presence of the diastereotopic hydrogens in the methylene group of **2a** and **2b** allowed the determination of $\Delta G^{\ddagger}_{\mathrm{rac}}$ through the analysis of the temperature-dependent NMR spectra. A $\Delta G^{\ddagger}_{\mathrm{rac}}$ of ca. 15.3 kcal/mol was determined for **2a**, whereas a significantly higher barrier of at least 21 kcal/mol was estimated for **2b**.[5] The steric hindrance also restricts the rotation of the aryl substituents in **2**. Analysis of the temperature-dependent NMR spectra gave the rotational barriers ($\Delta G^{\ddagger}_{\mathrm{rot}}$) of ca. 14.3, 15, and 15 kcal/mol for **2a**, **2b**, and **2c**, respectively.[5]



1a: $R^1 = R^3 = Me$, $R^2 = H$, $R^4 = CH_2CO_2H$
1b: $R^1 = Me$, $R^2 = R^3 = R^4 = H$
1c: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$
1d: $R^1 = R^2 = Me$, $R^3 = R^4 = H$
1e: $R^1 = R^2 = R^3 = R^4 = Me$



2a: Ar = Ph,
Ar^1 = 3-(bromomethyl)-5-methylphenyl
2b: Ar = 3,5-dimethylphenyl,
Ar^1 = 3-(bromomethyl)-5-methylphenyl
2c: Ar = Ar^1 = 3,5-dimethylphenyl

Several synthetic methods for 4,5-dimethylphenanthrenes and related compounds have been reported, including ozonolysis of pyrene,[7] intramolecular cyclization of 2,2′-bis(halomethyl)-6,6′-dimethylbiphenyls,[8] photochemically induced dehydrocyclization of stilbenes,[2,9] and desulfurization of a phenanthrene derivative containing two fused thiophene rings.[10] Photocyclization of 1-(8-phenyl-2-naphthyl)-4-phenyl-1-buten-3-yne (**3**) was reported to produce 4,5-diphenylphenanthrene (**1c**) in 65%

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(1) Newman, M. S.; Hussey, A. S. *J. Am. Chem. Soc.* **1947**, *69*, 3023−3027.

(2) Mannschreck, A.; Gmahl, E.; Burgemeister, T.; Kastner, F.; Sinnwell, V. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 270−271.

(3) (a) Armstrong, R. N.; Ammon, H. L.; Darnow, J. N. *J. Am. Chem. Soc.* **1987**, *109*, 2077−2082. (b) Cosmo, R.; Hambley, T. W.; Sternhell, S. *J. Org. Chem.* **1987**, *52*, 3119−3123. (c) Imashiro, F.; Saika, A.; Taira, Z. *J. Org. Chem.* **1987**, *52*, 5727−5729.

(4) (a) Tinnemans, A. H. A.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1115−1120. (b) Tinnemans, A. H. A.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 4617−4622.

(5) Tinnemans, A. H. A.; Laarhoven, W. H. *Tetrahedron* **1979**, *35*, 1537−1541.

(6) Fields, D. L.; Regan, T. H.; Graves, R. E. *J. Org. Chem.* **1971**, *36*, 2995−3001.

(7) (a) Newman, M. S.; Whitehouse, H. S. *J. Am. Chem. Soc.* **1949**, *71*, 3664−3667. (b) Munday, R.; Sutherland, I. O. *J. Chem. Soc. B* **1968**, 80−84.

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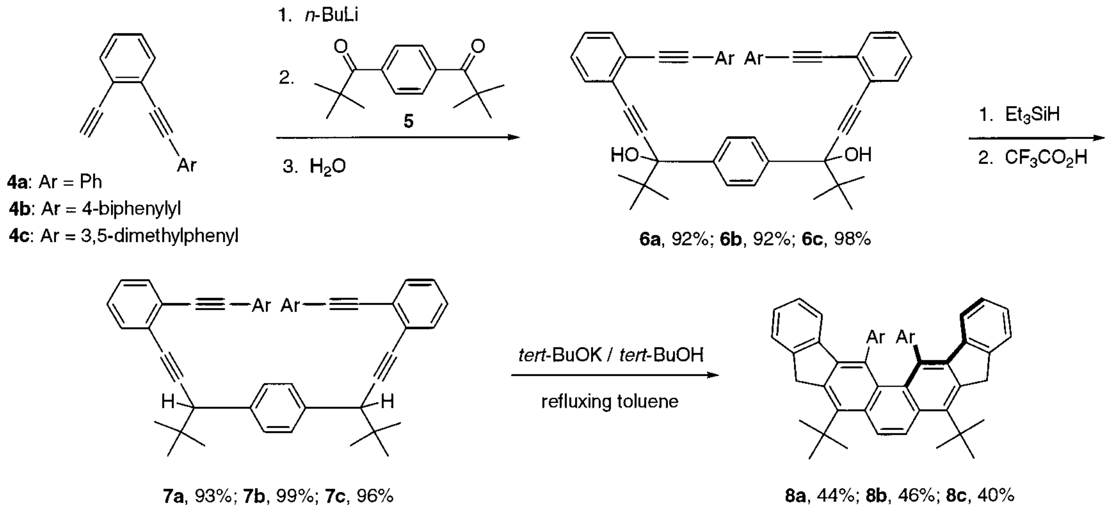
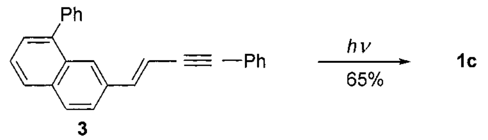
Scheme 1



yield (eq 1).[4] Similarly, 4,5-diaryltriphenylenes (**2**) were obtained by photocyclization of suitably substituted 1,4-diaryl-1-buten-3-ynes.[4,5]



(1)

We recently reported the use of the C^2–C^6 cyclization reaction of the benzannulated enyne–allenes for the synthesis of polycyclic aromatic hydrocarbons.[11] A similar reaction involving a benzannulated enyne–carbodiimide system led to the formation of an indolo-fused 4,7-phenanthroline derivative having a helical twist due to steric interactions as observed in **1b**.[12] We now report a successful extension of this strategy to the synthesis of 4,5-diarylphenanthrenes derived from benzannulated enyne–allenes.

Results and Discussion

Synthesis of 4,5-Diarylphenanthrenes. The synthetic sequence outlined in Scheme 1 involves lithiation of the diacetylenes **4** with 2 equiv of *n*-butyllithium followed by condensation with the diketone **5**[13] to afford the propargylic alcohols **6** as an essentially 1:1 mixture of diastereomers in excellent yields. Treatment of **6** with triethylsilane in the presence of trifluoroacetic acid[14] allowed an efficient conversion to the tetraacetylenic hydrocarbons **7** also as an essentially 1:1 mixture of diastereomers. On exposure to potassium *tert*-butoxide under refluxing toluene at 110 °C for up to 10 h, the hydrocarbons **7** were transformed to the 4,5-diarylphenanthrenes **8**.

Apparently, the transformation from **7** to **8** involved initial prototropic isomerizations[15] to form the benzannulated enyne–allenes **9** (Scheme 2). The formation of **9a** (Ar = Ph) was detected under milder reaction conditions. After 3 h of heating under refluxing THF at 65 °C, a major portion (ca. 80%) of the ^{1}H NMR signals belonging to the propargylic hydrogens in **7a** was converted to a singlet at δ 6.91, attributable to the allenic hydrogens in **9a**. A subsequent C^2–C^6 cyclization reaction generated the biradicals **10**, which in turn underwent an intramolecular radical–radical coupling to give **11**. Although the transformation from **9** to **11** could also be regarded as a Diels–Alder reaction, mechanistic and DNA-cleaving studies of analogous systems suggest a two-step biradical pathway.[16] A second formal Diels–Alder reaction of **11** then produced **13** and, after two subsequent tautomerizations, the 4,5-diarylphenanthrenes **8**.

The structure of **8a** was unequivocally established by the X-ray structure analysis. The ORTEP drawings of **8a** from three different perspectives are given in Figure 1 to illustrate the severity of the structural distortion. As expected, the two phenyl substituents are bent away from each other with overlaps of the carbon–carbon bonds occurring only at the C33–C34 edge and the C39–C44 edge. In addition, the two phenyl groups are oriented essentially parallel to each other (within 1.3°), but are at a 53.1° angle from the central aromatic system. The perpendicular distance between the planes of the two nearly parallel phenyl groups is ca. 2.9 Å much shorter than the usual π-system van der Waals contact distance of ca. 3.4 Å between parallel aromatic hydrocarbons in crystals[17] or even the graphite layer distance of 3.35 Å. A pronounced 46.1° twist between the mean planes of the outer rings (planes 1–2–3–4–4a–10a and 4b–5–

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(8) (a) Newman, M. S.; Lilje, K. C. *J. Org. Chem.* **1979**, *44*, 4944–4946. (b) Bestmann, H. J.; Häberlein, H.; Eisele, W. *Chem. Ber.* **1966**, *99*, 28–34. (c) Karnes, H. A.; Kybett, B. D.; Wilson, M. H.; Margrave, J. L.; Newman, M. S. *J. Am. Chem. Soc.* **1965**, *87*, 5554–5558. (d) Wittig, G.; Zimmermann, H. *Chem. Ber.* **1953**, *86*, 629–640.

(9) (a) Grimme, S.; Pischel, I.; Nieger, M.; Vögtle, F. *J. Chem Soc., Perkin Trans. 2* **1996**, 2771–2774. (b) Fritsch, R.; Hartmann, E.; Andert, D.; Mannschreck, A. *Chem. Ber.* **1992**, *125*, 849–855. (c) Scherübl, H.; Fritzsche, U.; Mannschreck, A. *Chem. Ber.* **1984**, *117*, 336–343.

(10) MacDowell, D. W. H.; Childers, R. L. *J. Org. Chem.* **1962**, *27*, 2630–2631.

(11) Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 7996–7999.

(12) Shi, C.; Zhang, Q.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 925–932.

(13) Bennett, G. B.; Nadelson, J.; Alden, L.; Jani, A. *Org. Prep. Proced. Int.* **1976**, *8*, 13–18.

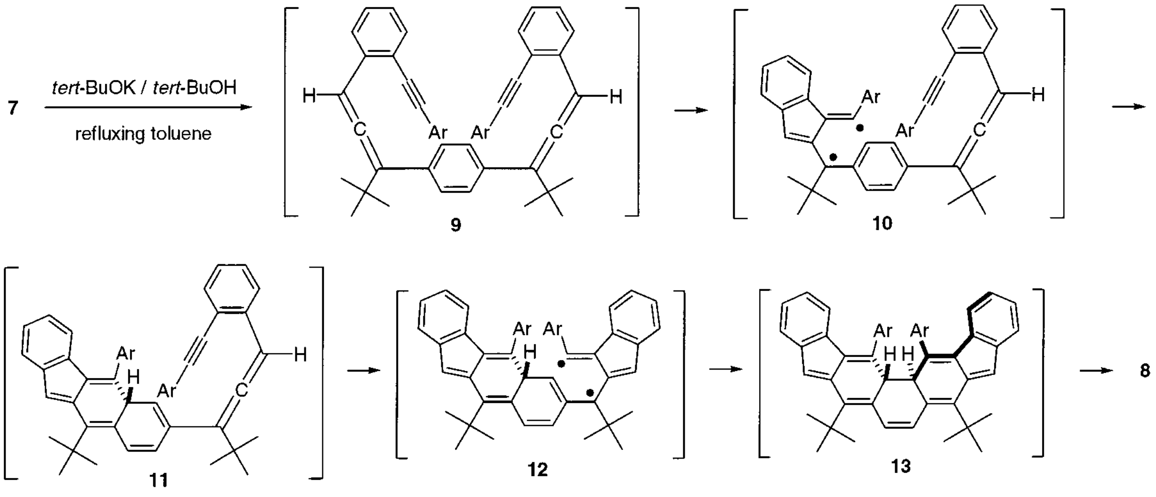
(14) Carey, F. A.; Hsu, C.-L. W. *J. Organomet. Chem.* **1969**, *19*, 29–41.

(15) Landor, P. D. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London 1982; Vol. 1, pp 44–47.

(16) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843–1845. (b) Schmittel, M.; Maywald, M.; Strittmatter, M. *Synlett* **1997**, 165–166. (c) Musch, P. W.; Engels, B. *J. Am. Chem. Soc.* **2001**, *123*, 5557–5562.

(17) Robertson, J. M. *Organic Crystals and Molecules*; Cornell University Press: Ithaca, New York, 1953; pp 206–214.

Scheme 2

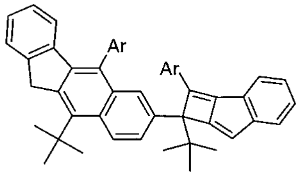


6−7−8−8a) of the phenanthrene system of **8a** is much larger than that of **1b** at 27.9°, further indicating a profound structural distortion due to nonbonded steric interactions.

The structures of **8** were also elucidated with high-resolution mass spectroscopy and ^{1}H and ^{13}C NMR spectroscopy. The molecular ions with the correct exact mass were detected. The ^{1}H NMR spectra showed the right numbers of signals and patterns of multiplicity consistent with the structures of **8**. The chemical shift assignments for **8a** are shown in Figure 2. It is interesting to note that the helical twist in **8a** was manifested with a set of signals from the diastereotopic methylene hydrogens on the five-membered rings. An AB pattern at δ 4.39 and 4.15 with a large geminal coupling constant of 21.0 Hz was observed. Such an AB pattern was also observed for **8b** and **8c**. The upfield shift aromatic signal at δ 6.20, attributable to the two aromatic hydrogens closest to the phenyl substituents, indicates that the phenyl substituents are oriented, to a large degree, perpendicular to the central aromatic system as observed in the X-ray structure. Such an orientation will place the neighboring aromatic hydrogens in the shielding region of the induced aromatic ring current as in other similar structures.[11] The signal for the ortho hydrogens of the phenyl substituents was shifted upfield to δ 6.52, consistent with the reported chemical shift of δ 6.43 for those of 4,5-diphenylphenanthrene (**1c**).[4a] In the ^{13}C NMR spectrum of **8a**, three signals in the aliphatic region for the *tert*-butyl groups and the methylene carbons were observed. In addition, 16 signals in the aromatic region were clearly discernible along with a broad hump at around δ 132.5. The presence of such a hump was also observed in the cases of **8b** and **8c**, indicating that the coalescence temperatures for some of the ^{13}C signals are at or around the ambient temperature, presumably due to somewhat restricted rotation of the aryl substituents.

The formation of **8** in nearly 50% yields may indicate that the rate of transformation from **11** to **13** is at least competitive with that of the tautomerization of **11** to **14** (Scheme 3). A rapid initial tautomerization could lead to the formation of the linearly fused hydrocarbons **16** as the major products from **15** because of reduced nonbonded steric interactions in the step for the intramolecular radical−radical coupling. Without tautomerization, the biradicals **12** would not be able to cyclize to form **16**. It is also interesting to note that photocyclization of **3** produced 4,5-diphenylphenanthrene (**1c**) instead of the sterically less congested 1,5-diphenylanthracene (eq 1).[4] The higher reactivity of the α- than the β-position of naphthalene in homolytic addition may be responsible for the high regioselectivity in producing **1c**. A similar preference could also account for the formation of **8** from **15** in the event of a rapid tautomerization from **11** to **14**. The ^{1}H NMR spectra of the crude reaction mixtures before separation and purification by column chromatography indicated that the hydrocarbons **16** were either not formed or were produced only in minute quantities. The four methylene hydrogens in **16** are magnetically equivalent and could be expected to exhibit a singlet ^{1}H NMR signal at around δ 4.5.

It is worth noting that in the cases of **8b** and **8c**, minor amounts of **17b** (9%) and **17c** (12%) were also isolated.



17a: Ar = Ph
17b: Ar = 4-biphenylyl, 9%
17c: Ar = 3,5-dimethylphenyl, 12%

Although **17a** was not isolated, the ^{1}H NMR spectrum of the crude reaction mixture before column chromatography indicated the presence of a substantial amount of **17a** (**8a**/**17a** = 1.8:1). The amount of **17a** diminished after prolonged heating of the reaction mixture. Apparently, direct coupling of the radical centers depicted in **12** led to the formation of the [2 + 2] cycloaddition adducts having the 1*H*-cyclobut[*a*]indene moiety. Similar examples of the intramolecular [2 + 2] cycloaddition reaction of the benzannulated enyne−allene systems leading to 1*H*-cyclobut[*a*]indenes were reported previously.[18] Unlike **8**, the ^{1}H and ^{13}C NMR spectra of **17** clearly showed a lack of symmetry in their structures. For example, in the case of **17b**, the ^{1}H NMR signals for

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[18] (a) Gillmann, T.; Hulsen, T.; Massa, W.; Wocadlo, S. *Synlett* **1995**, 1257−1259. (b) Li, H.; Zhang, H.-R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662−6668.

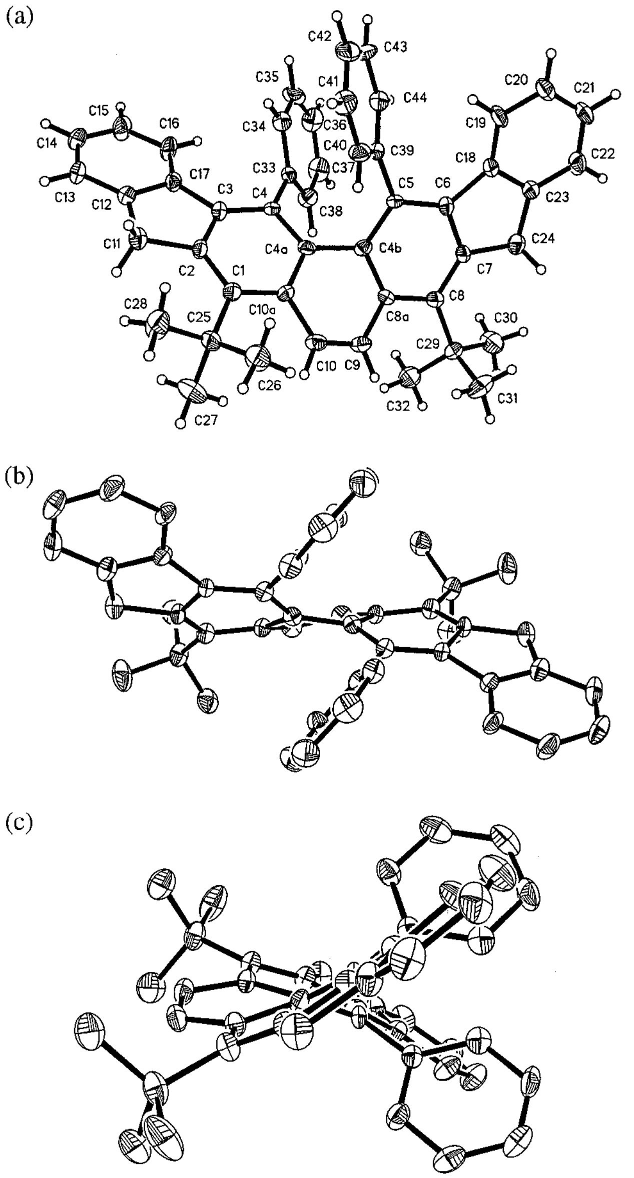


Figure 1. ORTEP drawings of the crystal structure of **8a** from three different perspectives: (a) viewing along the axis perpendicular to the phenanthrene ring, (b) viewing along the crystallographic C_2 axis with hydrogen atoms omitted for clarity, and (c) viewing along the C4a−C4b axis with hydrogen atoms omitted for clarity.

the two *tert*-butyl groups were observed at δ 1.87 and 1.12. The methylene hydrogens became essentially a singlet at δ 4.47. A new signal as a singlet at δ 6.19 attributable to the alkenyl hydrogen on the five-membered ring also appeared. The isolated aromatic hydrogen on the naphthalene ring gave a signal at δ 7.91 as a doublet due to a long-range coupling (J = 2.2 Hz). The signals for the other two aromatic hydrogens meta or para to the isolated aromatic hydrogen on the naphthalene ring occurred at δ 7.67 (dd, J = 9.3, 2.2 Hz) and δ 8.51 (d, J = 9.3 Hz), respectively. A ^{13}C NMR signal at δ 75.7 for the sp^3 carbon in the four-membered ring was also observed.

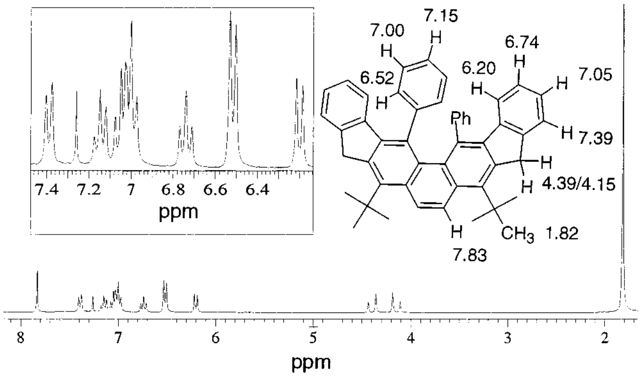
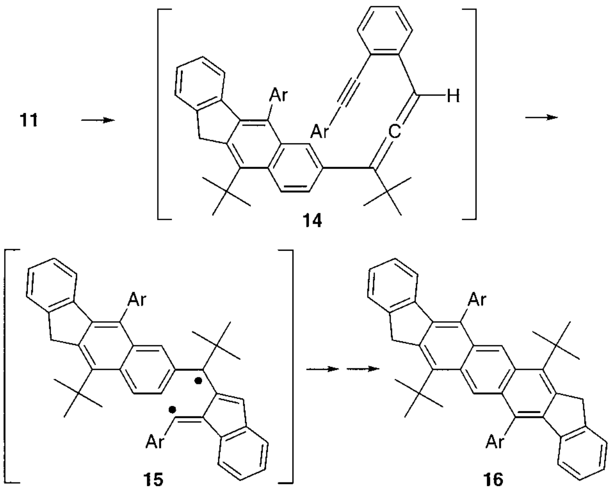


Figure 2. ^{1}H NMR spectrum of the 4,5-diarylphenanthrene **8a** in $CDCl_3$.

Scheme 3



The well resolved AB pattern of the ^{1}H NMR signals for the methylene hydrogens in **8** provided an opportunity to determine the activation barriers for racemization by dynamic NMR studies. However, the AB signals of **8a** in 1,1,2,2-tetrachloroethane-d_2 remained well separated and exhibited no line broadening even at 125 °C, indicating that the rate of the helix inversion is relatively slow on the NMR time scale. The $\Delta G^{\ddagger}_{\mathrm{rac}}$ of **8a** is estimated to be at least 19.4 kcal/mol on the basis of the AB signals at δ 4.42 and 4.19 ($\delta_A - \delta_B = 60.7$ Hz) with a coupling constant of 20.8 Hz at 125 °C.

It was reported that due to buttressing effect of the two methyl groups at the 3- and 6-positions, the $\Delta G^{\ddagger}_{\mathrm{rac}}$ of **1d** at 25 °C is 23.1 kcal/mol, which is 7 kcal/mol higher than that of **1b**.[3a] Introducing two more methyl groups at the 1- and 8-positions further increases the $\Delta G^{\ddagger}_{\mathrm{rac}}$ of **1e** at 49 °C to 25.1 kcal/mol.[2,19] Therefore, it could be expected that **8a** having two fused indeno rings at the 2,3- and 6,7-positions and two sterically demanding *tert*-butyl groups at the 1- and 8-positions would have a relatively high value for $\Delta G^{\ddagger}_{\mathrm{rac}}$.

Synthesis of the Diacetylenes 4. The diacetylene **4a** was prepared from 1-bromo-2-iodobenzene (**18**) via two consecutive palladium-catalyzed cross-coupling reactions with phenylacetylene and (trimethylsilyl)acetylene followed by desilylation as described previously (Scheme 4).[11] The diacetylenes **4b** and **4c** were likewise synthesized. However, direct coupling of the bromide **20a** or **20b** with (trimethylsilyl)acetylene was sluggish, requiring 3 days of heating at 60 °C and giving a low yield in the case of **23b**. This problem was circumvented by treatment of the bromides **20** with n-butyllithium at −78 °C

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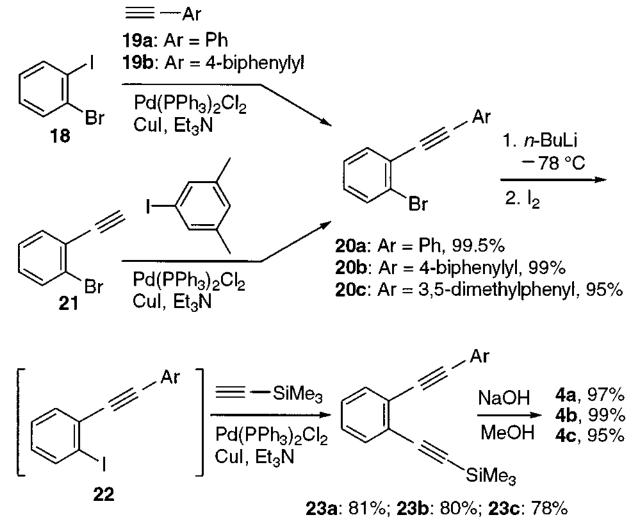
(19) Mannschreck, A.; Hartmann, E.; Buchner, H.; Andert, D. *Tetrahedron Lett.* **1987**, *28*, 3479−3482.

Scheme 4



followed by iodine to convert them to the iodides **22**. The subsequent coupling reaction went to completion within 1 h at room temperature and gave good overall yields for the two-step procedure.

Conclusions

The reaction sequence outlined in Scheme 1 represents a new synthetic route to the indeno-fused 4,5-diarylphenanthrenes. The formal Diels–Alder reaction involving a C^2–C^6 cyclization reaction followed by a radical–radical coupling reaction of the benzannulated enyne–allenes is key to the efficient assembly of the phenanthrene system. The buttressing effects due to the indeno-fused rings and the two *tert*-butyl groups at the 1- and 8-positions are responsible for increasing the activation barrier for the helix inversion of the resulting 4,5-diarylphenanthrenes.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, *tert*-butyllithium (1.7 M) in pentane, CuBr·SMe$_2$, terephthaloyl chloride, trifluoroacetic acid, triethylsilane, potassium *tert*-butoxide (1.0 M) in THF, 4-bromobiphenyl, 5-iodo-*m*-xylene (1-iodo-3,5-dimethylbenzene), Pd(PPh$_3$)$_2$Cl$_2$, copper(I) iodide, and triethylamine were purchased from Aldrich and were used as received. (Trimethylsilyl)acetylene and 1-bromo-2-iodobenzene were purchased from GFS Chemicals, Inc., and Alfa, respectively. 4-Iodobiphenyl was prepared from 4-bromobiphenyl using the procedure described for **22**. 1-Bromo-2-ethynylbenzene (**21**)[20] was obtained by desilylation of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene[21] with sodium hydroxide as described for **4**. Silica gel for flash column chromatography was purchased from ICN. Melting points were uncorrected. ^{1}H (270 MHZ) and ^{13}C (67.9 MHZ) NMR spectra were recorded in CDCl$_3$ using CHCl$_3$ (^{1}H δ 7.26) and CDCl$_3$ (^{13}C δ 77.00) as internal standards.

Diketone 5.[13] To a suspension of 4.52 g of CuBr·SMe$_2$ (22.0 mmol) in 100 mL of THF was added 12.9 mL of a 1.7 M solution of *tert*-butyllithium (22.0 mmol) in pentane at −50 °C. After 30 min of stirring, a solution of 2.03 g of terephthaloyl chloride (10.0 mmol) in 40 mL of THF was introduced dropwise via cannula. After an additional 4 h, the reaction mixture was allowed to warm to room temperature and then quenched with 50 mL of a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was back-extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 2.36 g of **5** (9.58 mmol, 96% yield) as a white solid: mp 83–84 °C (lit.[13] mp 80.5–82 °C); IR 1672, 962 cm^{-1}; ^{1}H δ 7.67 (4 H, s), 1.34 (18 H, s); ^{13}C δ 208.4, 140.2, 127.1, 44.0, 27.5; MS *m/z* 246 (M$^+$), 190, 189, 161.

Propargylic Alcohol 6a. The following procedure is representative for the preparation of the propargylic alcohols **6**. To 0.404 g (2.00 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne (**4a**) in 20 mL of THF under a nitrogen atmosphere at 0 °C was added 0.80 mL of a 2.5 M solution of *n*-butyllithium (2.00 mmol) in hexanes. After 30 min of stirring, a solution of 0.223 g of **5** (0.90 mmol) in 40 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) provided 0.540 g of **6a** (0.830 mmol, 92% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. Diastereomer **1**: mp 177–178 °C; IR 3568, 3459, 2215 cm^{-1}; ^{1}H δ 7.60 (4 H, s), 7.59–7.55 (2 H, m), 7.74–7.49 (2 H, m), 7.47–7.41 (4 H, m), 7.36–7.20 (10 H, m), 2.27 (2 H, s), 1.05 (18 H, s); ^{13}C δ 141.1, 132.2, 131.7, 128.4, 128.3, 128.1, 127.9, 126.5, 125.9, 125.2, 123.0, 96.3, 93.2, 88.3, 84.6, 79.4, 39.7, 25.6; MS *m/z* 673 (MNa$^+$), 633, 593, 576; HRMS calcd for $C_{48}H_{42}O_2Na$ (MNa$^+$) 673.3083, found 673.3114. Diastereomer **2**: mp 189–190 °C; IR 3562, 3455, 2216 cm^{-1}; ^{1}H δ 7.60 (4 H, s), 7.58–7.54 (2 H, m), 7.52–7.45 (6 H, m), 7.35–7.25 (10 H, m), 2.40 (2 H, s), 1.06 (18 H, s); ^{13}C δ 141.0, 132.2, 131.7, 128.4, 128.3, 128.0, 127.9, 126.5, 125.7, 125.1, 123.0, 96.2, 93.2, 88.3, 84.6, 79.4, 39.8, 25.6.

Propargylic Alcohol 6b. The same procedure was repeated as described for **6a** except that 0.123 g (0.50 mmol) of **5** was treated with the lithium acetylide derived from 0.343 g of **4b** (1.23 mmol) and 0.49 mL of a 2.5 M solution of *n*-butyllithium (1.23 mmol) in hexanes to afford 0.370 g of **6b** (0.461 mmol, 92% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. Diastereomer **1**: mp 213–215 °C; IR 3568, 3456, 2215 cm^{-1}; ^{1}H δ 7.73 (4 H, s), 7.58–7.48 (16 H, m), 7.42–7.32 (6 H, m), 7.31–7.22 (4 H, m), 2.37 (2 H, s), 1.08 (18 H, s); ^{13}C δ 141.1, 141.0, 140.1, 132.2, 132.1, 128.7, 128.1, 127.9, 127.5, 127.0, 126.9, 126.6, 125.8, 125.1, 121.8, 96.3, 93.2, 89.0, 84.7, 79.4, 39.7, 25.6; MS *m/z* 825 (MNa$^+$), 785, 745, 728; HRMS calcd for $C_{60}H_{50}O_2Na$ (MNa$^+$) 825.3709, found 825.3729. Diastereomer **2**: mp 258–259 °C; IR 3376, 2215 cm^{-1}; ^{1}H δ 7.62 (4 H, s), 7.58–7.50 (14 H, m), 7.49–7.38 (6 H, m), 7.36–7.23 (6 H, m), 2.37 (2 H, s), 1.04 (18 H, s); ^{13}C δ 141.0, 140.2, 132.25, 132.17, 132.11, 128.8, 128.1, 127.9, 127.6, 126.97, 126.94, 126.5, 125.8, 125.1, 121.9, 96.2, 93.2, 88.9, 84.6, 79.4, 39.8, 25.6.

Propargylic Alcohol 6c. The same procedure was repeated as described for **6a** except that 0.443 g of **5** (1.80 mmol) was treated with the lithium acetylide derived from 0.984 g of **4c** (4.27 mmol) and 1.71 mL of a 2.5 M solution of *n*-butyllithium (4.27 mmol) in hexanes to afford 1.243 g of **6c** (1.76 mmol, 98% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. Diastereomer **1**: IR 3549, 3464, 2209 cm^{-1}; ^{1}H δ 7.59 (4 H, s), 7.56–7.52 (2 H, m), 7.50–7.46 (2 H, m), 7.34–7.23 (4 H, m), 7.14 (4 H, s), 6.89 (2 H, s), 2.31 (2 H, s), 2.24 (12 H, s), 1.06 (18 H, s); ^{13}C δ 141.0, 137.8, 132.1, 130.3, 129.4, 128.0, 127.7, 126.4, 126.0, 125.1, 122.6, 96.2, 93.7, 87.6, 84.6, 79.4, 39.7, 25.6, 21.1; MS *m/z* 729 (MNa$^+$), 689, 649, 632; HRMS calcd for $C_{52}H_{50}O_2Na$ (MNa$^+$) 729.3709, found 729.3692. Diastereomer **2**: mp 194–195 °C; IR 3567, 3469, 2209 cm^{-1}; ^{1}H

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[20] Guo, L.; Bradshaw, J. D.; McConville, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, *16*, 1685–1692.

[21] Schmittel, M.; Strittmatter, M. *Tetrahedron* **1998**, *54*, 13751–13760.

δ 7.61 (4 H, s), 7.56−7.52 (2 H, m), 7.49−7.45 (2 H, m), 7.33−7.22 (4 H, m), 7.18 (4 H, s), 6.95 (2 H, s), 2.38 (2 H, s), 2.28 (12 H, s), 1.06 (18 H, s); ^{13}C δ 141.0, 137.8, 132.17, 132.12, 130.4, 129.4, 128.0, 127.8, 126.5, 125.9, 125.1, 122.6, 96.1, 93.6, 87.6, 84.6, 79.4, 39.7, 25.6, 21.1.

Tetraacetylenic Hydrocarbon 7a. The following procedure is representative for the preparation of the tetraacetylenic hydrocarbons **7**. To a mixture of 0.310 g of **6a** (0.476 mmol) and 0.168 g of triethylsilane (1.42 mmol) in 10 mL of methylene chloride was added 0.29 mL of trifluoroacetic acid (0.433 g, 3.80 mmol). After 5 min of stirring at room temperature, 0.202 g of sodium carbonate (1.90 mmol) was added followed by 10 mL of water and 50 mL of diethyl ether. The organic layer was separated, washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/5% diethyl ether in hexanes, $R_f = 0.49$) provided 0.274 g of **7a** (0.443 mmol, 93% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2216, 755 cm^{-1}; ^{1}H (1:1 mixture) δ 7.57−7.40 (8 H, m), 7.32−7.22 (14 H, m), 3.64 and 3.62 (2 H, two singlets, 1:1 ratio), 1.00 (18 H, s); ^{13}C (1:1 mixture) δ 137.4, 137.3, 132.12, 132.05, 131.6, 128.9, 128.2, 127.8, 127.3, 126.33, 126.30, 125.58, 125.51, 123.25, 123.18, 95.76, 95.70, 92.82, 92.76, 88.66, 88.60, 82.44, 82.41, 50.2, 35.45, 35.41, 27.8; MS *m/z* 618 (M^+), 561, 505.

Tetraacetylenic Hydrocarbon 7b. The same procedure was repeated as described for **7a** except that 0.160 g of **6b** (0.20 mmol) was treated with 0.070 g of triethylsilane (0.60 mmol) and 0.12 mL of trifluoroacetic acid (1.6 mmol) in 40 mL of methylene chloride to afford 0.153 g of **7b** (0.198 mmol, 99% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2217, 761 cm^{-1}; ^{1}H (1:1 mixture) δ 7.59−7.52 (12 H, m), 7.48−7.40 (6 H, m), 7.38−7.31 (8 H, m), 7.29−7.22 (4 H, m), 3.67 and 3.63 (2 H, two singlets, 1:1 ratio), 1.03 and 1.02 (18 H, two singlets, 1:1 ratio); ^{13}C (1:1 mixture) δ 140.8, 140.3, 140.2, 137.5, 137.4, 132.2, 132.13, 132.10, 129.0, 128.8, 128.7, 127.8, 127.53, 127.48, 127.3, 127.0, 126.9, 126.8, 126.3, 125.65, 125.59, 122.2, 122.1, 95.8, 92.7, 89.3, 82.6, 82.4, 50.3, 35.5, 27.8; MS *m/z* 770 (M^+), 713, 657; HRMS calcd for $C_{60}H_{50}$ (M^+) 770.3913, found 770.3899.

Tetraacetylenic Hydrocarbon 7c. The same procedure was repeated as described for **7a** except that 0.442 g of **6c** (0.626 mmol) was treated with 0.160 g of triethylsilane (1.38 mmol) and 0.39 mL of trifluoroacetic acid (5.0 mmol) in 10 mL of methylene chloride to afford 0.404 g of **7c** (0.599 mmol, 96% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2214, 848 cm^{-1}; ^{1}H (1:1 mixture) δ 7.56−7.49 (2 H, m), 7.47−7.39 (2 H, m), 7.30−7.21 (8 H, m), 7.18−7.14 (4 H, m), 6.94 and 6.90 (2 H, two singlets, 1:1 ratio), 3.65 and 3.63 (2 H, two singlets, 1:1 ratio), 2.28 and 2.25 (12 H, two singlets, 1:1 ratio), 1.02 (18 H, s); ^{13}C (1:1 mixture) δ 137.7, 137.4, 137.3, 132.2, 132.1, 130.2, 129.4, 128.9, 127.7, 127.3, 126.31, 126.24, 125.75, 125.71, 122.9, 95.6, 93.2, 88.0, 82.5, 50.3, 35.5, 29.2, 27.8, 21.1; MS *m/z* 674 (M^+), 617, 561.

4,5-Diarylphenanthrene 8a. The following procedure is representative for the synthesis of the 4,5-diarylphenanthrenes **8**. To 0.191 g of **7a** (0.309 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere were added 0.65 mL of a 1.0 M solution of potassium *tert*-butoxide (0.65 mmol) in THF and 0.5 mL of 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 3 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 50 mL of methylene chloride were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/10% methylene chloride in hexanes, $R_f = 0.73$) provided 0.084 g of **8a** (0.136 mmol, 44% yield) as a yellow solid: mp >340 °C; IR 1464, 705 cm^{-1}; ^{1}H δ 7.83 (2 H, s), 7.39 (2 H, d, $J = 7.3$ Hz), 7.15 (2 H, t, $J = 7.4$ Hz), 7.05 (2 H, t, $J = 7.3$ Hz), 7.00 (4 H, t, $J = 7.3$ Hz), 6.74 (2 H, t, $J = 7.5$ Hz), 6.52 (4 H, d, $J = 7.1$ Hz), 6.20 (2 H, d, $J = 8.1$ Hz), 4.39 (2 H, d, $J = 21.0$ Hz), 4.15 (2 H, d, $J = 21.0$ Hz), 1.82 (18 H, s); ^{13}C δ 144.2, 141.2, 139.43, 139.36, 139.0, 137.1, 135.3, 132.5 (br), 131.9, 131.7, 128.1, 126.5, 126.0, 125.3, 123.6, 123.0, 122.0, 39.8, 37.8, 33.4; MS *m/z* 618 (M^+), 561; HRMS calcd for $C_{48}H_{42}$ (M^+) 618.3287, found 618.3296. Recrystallization of **8a** from CH_2Cl_2/hexanes produced a crystal suitable for the X-ray structure analysis.

4,5-Diarylphenanthrene 8b and 1*H*-Cyclobut[*a*]indene 17b. The same procedure was repeated as described for **8a** except that 0.153 g of **7b** (0.198 mmol) was treated with a mixture of 0.48 mL of a 1.0 M solution of potassium *tert*-butoxide (0.48 mmol) in THF and 0.5 mL of 2-methyl-2-propanol in 10 mL of anhydrous toluene under reflux for 10 h to afford 0.070 g of **8b** (0.091 mmol, 46% yield) as a yellow solid and 0.014 g of **17b** (0.018 mmol, 9% yield) as an orange solid. **8b**: mp 249−251 °C; IR 1486, 696 cm^{-1}; ^{1}H δ 7.92 (2 H, s), 7.70 (4 H, d, $J = 7.3$ Hz), 7.51−7.35 (12 H, m), 7.09 (2 H, t, $J = 7.0$ Hz), 6.78 (2 H, t, $J = 7.8$ Hz), 6.72 (4 H, d, $J = 8.5$ Hz), 6.42 (2 H, t, $J = 7.9$ Hz), 4.44 (2 H, d, $J = 21.0$ Hz), 4.20 (2 H, d, $J = 21.0$ Hz), 1.87 (18 H, s); ^{13}C δ 144.2, 141.1, 140.9, 139.7, 139.5, 139.0, 138.2, 137.2, 134.7, 132.2 (br), 131.9, 131.5, 128.7, 127.1, 126.9, 126.8, 126.1, 125.3, 123.7, 123.1, 122.0, 39.9, 37.8, 33.4; MS *m/z* 770 (M^+), 714, 659; HRMS calcd for $C_{60}H_{50}$ (M^+) 770.3913, found 770.3925. **17b**: mp 269−272 °C; IR 1487, 696 cm^{-1}; ^{1}H δ 8.51 (1 H, d, $J = 9.3$ Hz), 7.97 (1 H, dd, $J = 7.9, 2.0$ Hz), 7.91 (1 H, d, $J = 2.2$ Hz), 7.83−7.76 (4 H, m), 7.72 (1 H, dd, $J = 7.9, 1.8$ Hz), 7.67 (1 H, dd, $J = 9.3, 2.2$ Hz), 7.66 (1 H, d, $J = 7.1$ Hz), 7.53−7.44 (7 H, m), 7.41−7.22 (8 H, m), 7.17 (1 H, td, $J = 7.5, 1$ Hz), 7.07 (1 H, td, $J = 7.3, 1.4$ Hz), 6.94 (1 H, t, $J = 7.3$ Hz), 6.19 (1 H, s), 4.47 (2 H, s), 1.87 (9 H, s), 1.12 (9 H, s); spin decoupling indicates that the signal at δ 8.51 is coupled to the signal at δ 7.67, which is also coupled to the signal at δ 7.91; ^{13}C δ 154.0, 152.3, 150.7, 148.0, 144.2, 141.2, 140.7, 140.5, 140.3, 139.9, 139.8, 139.1, 138.3, 138.2, 137.2, 134.0, 133.7, 132.7, 130.8, 130.6, 129.8, 129.6, 129.1, 128.9, 128.8, 127.8, 127.5, 127.4, 127.2, 127.0, 126.9, 126.8, 126.2, 125.8, 123.9, 123.6, 123.5, 121.5, 111.4, 75.7, 40.1, 38.8, 37.2, 34.3, 28.5; MS *m/z* 771 (MH^+), 770, 713; HRMS calcd for $C_{60}H_{51}$ (MH^+) 771.3991, found 771.3987.

4,5-Diarylphenanthrene 8c and 1*H*-Cyclobut[*a*]indene 17c. The same procedure was repeated as described for **8a** except that 0.270 g of **7c** (0.40 mmol) was treated with a mixture of 0.96 mL of a 1.0 M solution of potassium *tert*-butoxide (0.96 mmol) in THF and 0.5 mL of 2-methyl-2-propanol in 15 mL of anhydrous toluene under reflux for 10 h to afford 0.108 g of **8c** (0.16 mmol, 40% yield) as a yellow solid and 0.033 g of **17c** (0.049 mmol, 12% yield) as an orange solid. **8c**: mp 265−270 °C; IR 1462, 707 cm^{-1}; ^{1}H δ 7.81 (2 H, s), 7.44 (2 H, d, $J = 7.3$ Hz), 7.10 (2 H, t, $J = 7.2$ Hz), 6.84 (2 H, d, $J = 7.9$ Hz), 6.81 (2 H, s), 6.49 (2 H, d, $J = 7.9$ Hz), 6.27 (4 H, s), 4.41 (2 H, d, $J = 21.0$ Hz), 4.20 (2 H, d, $J = 21.0$ Hz), 2.10 (12 H, s), 1.84 (18 H, s); ^{13}C δ 144.2, 141.4, 139.1, 139.0, 138.2, 136.6, 136.2, 135.5, 132.4, 131.7, 130.2 (br), 128.0, 125.9, 125.4, 123.6, 122.9, 121.8, 39.7, 37.7, 33.3, 21.3; MS *m/z* 674 (M^+), 617, 561; HRMS calcd for $C_{52}H_{50}$ (M^+) 674.3913, found 674.3935. **17c**: mp 212−215 °C; IR 1595, 1435 cm^{-1}; ^{1}H δ 8.40 (1 H, d, $J = 9.3$ Hz), 7.67 (1 H, d, $J = 2.2$ Hz), 7.64−7.57 (2 H, m), 7.54 (2 H, s), 7.46 (1 H, d, $J = 7.5$ Hz), 7.36−7.15 (4 H, m), 7.10−7.03 (2 H, m), 6.99 (1 H, t, $J = 7.5$ Hz), 6.92 (2 H, d, $J = 6.5$ Hz), 6.48 (1 H, d, $J = 7.7$ Hz), 5.88 (1 H, s), 4.46 (2 H, s), 2.43 (3 H, s), 2.41 (6 H, s), 2.31 (3 H, s), 1.85 (9 H, s), 1.14 (9 H, s); ^{13}C δ 154.8, 152.4, 151.3, 147.7, 144.1, 140.5, 140.2, 139.5, 138.6, 138.3, 138.1, 137.6, 137.0, 135.3, 134.1, 133.5, 131.0, 129.7, 129.2, 128.8, 128.6, 127.8, 127.7, 127.1, 126.7, 126.6, 126.1, 124.7, 123.8, 123.3, 121.4, 111.0, 75.3, 40.1, 38.7, 36.9, 34.3, 28.6, 21.6, 21.44, 21.36; MS *m/z* 675 (MH^+), 674, 617, 560; HRMS calcd for $C_{52}H_{50}$ (M^+) 674.3913, found 674.3922.

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Supporting Information Available: Experimental procedures and spectroscopic data for **4b**,**c**, 4-[(trimethylsilyl)ethynyl]-1,1′-biphenyl, **19b**, **20b**,**c**, and **23a**–**c**, and ^{1}H and ^{13}C NMR spectra for compounds **4b**,**c**, **5**, **6a**–**c**, **7a**–**c**, **8a**–**c**, **17b**,**c**, 4-[(trimethylsilyl)ethynyl]-1,1′-biphenyl, **19b**, **20b**,**c**, and **23b**,**c**, and tables of crystallographic data for the X-ray diffraction analysis of **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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