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# Discovery of Deep-Seated Skeletal Rearrangements in the Photocyclizations of Some *tert*-Butyl-Substituted 1,2-Diarylethylenes

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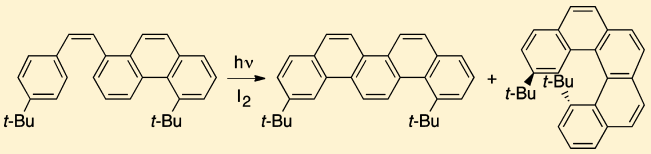
Supporting Information

**ABSTRACT:** The in-solution oxidative photocyclization of stilbenes to phenanthrenes is a well-known and synthetically valuable reaction. We report here our discovery that the oxidative photocyclization of several *tert*-butyl-substituted 1-styrylphenanthrenes resulted not only in the expected formation of *tert*-butyl-substituted picenes but also in the previously unknown rearrangement leading to the formation of *tert*-butyl-substituted pentahelicenes.




## INTRODUCTION

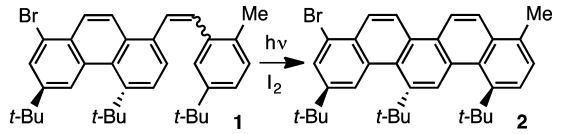
Stilbenes are widely known to undergo reversible *trans*-to-*cis* photoisomerizations in solution. The *cis* isomers can also undergo reversible photocyclization to produce 4a,4b-dihydrophenanthrene (DHP) intermediates. If the irradiated solution also contains iodine molecules, they are photochemically cleaved to give a pair of iodine atoms, each of which can abstract one of the 4a or 4b hydrogens on a DHP to give HI, followed by the abstraction of the second of these two bay hydrogens by an $I_2$ molecule to give a phenanthrene and another molecule of HI. The mechanism and synthetic value of this type of reaction have been well documented.[1]

This photocyclization reaction also extends to larger diarylethylenes in which one or both of the aryl groups are fused polycyclic aromatic systems. In recent years, we have used this reaction to develop multistep syntheses of a series of compounds having an extended zigzag pattern of *n* fused benzene rings. We proposed the name [*n*]phenacenes for these compounds because of their structural relationship to phenanthrene.[2] One of our goals has been to synthesize a series of [*n*]phenacenes with $n \geq 7$, which required us to overcome their prohibitively low solubility in organic solvents by attaching substituents such as *n*-alkyl, *tert*-alkyl, phenyl, or polyether groups. We previously published the photochemical syntheses of various solubilized [*n*]phenacenes with $n = 5$, 7, and 11.[2,3]

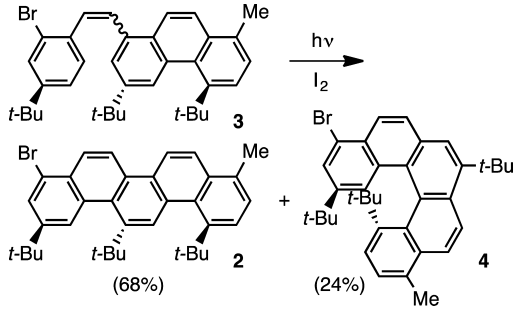
Our photocyclizations of the diarylethylenes described herein involve ultraviolet irradiation of purified *trans* isomers in a hydrocarbon solvent containing dissolved iodine. For space-saving reasons in the schemes that follow, the initial *trans*-to-*cis* step is not drawn, and also only one enantiomer is drawn for each of the reactants, intermediates, and final products.

Historically, in a earlier photocyclization of ours,[3b] compound **1** had given **2** in 67% yield.

We later needed to prepare additional **2**, but because we had only a very small remaining supply of **1** we chose instead to photocyclize the much larger sample we had on hand of the *trans* isomer of styrylphenanthrene **3**. To our great surprise and initial puzzlement, as shown in Scheme 1, the photocyclization of **3** gave a product mixture consisting of a 68% yield of the expected [5]phenacene **2** along with a 24% yield of the completely unexpected [5]helicene **4**! We established the structure of **4** by single-crystal X-ray analysis (see Figure 1) and proton NMR spectroscopy. In a subsequent reinvestigation of the photocyclization of **1** we confirmed that only compound **2** was formed with no detectable amount of any [5]helicene system.




**Scheme 1. Discovery of the Rearrangement**




## RESULTS AND DISCUSSION

To explore the scope and mechanism of this unprecedented photochemical rearrangement of **3** to **4** we undertook the

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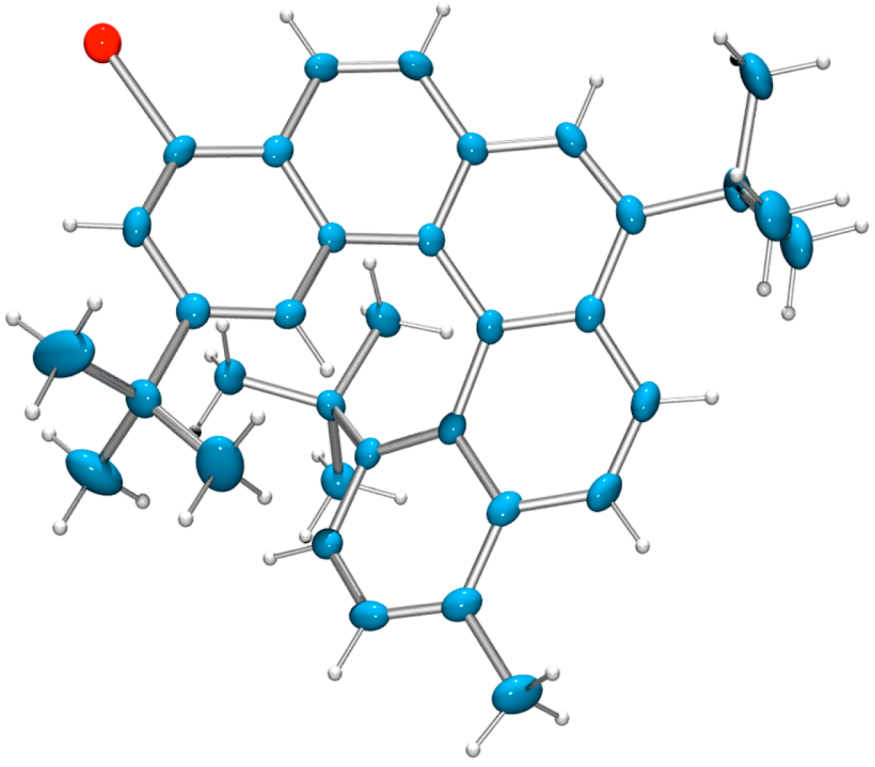
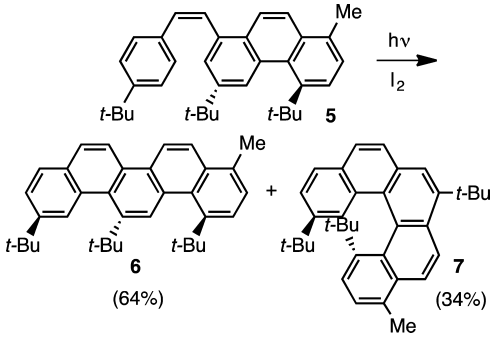


**Figure 1.** ORTEP representation of the X-ray crystallographic results for **4**.

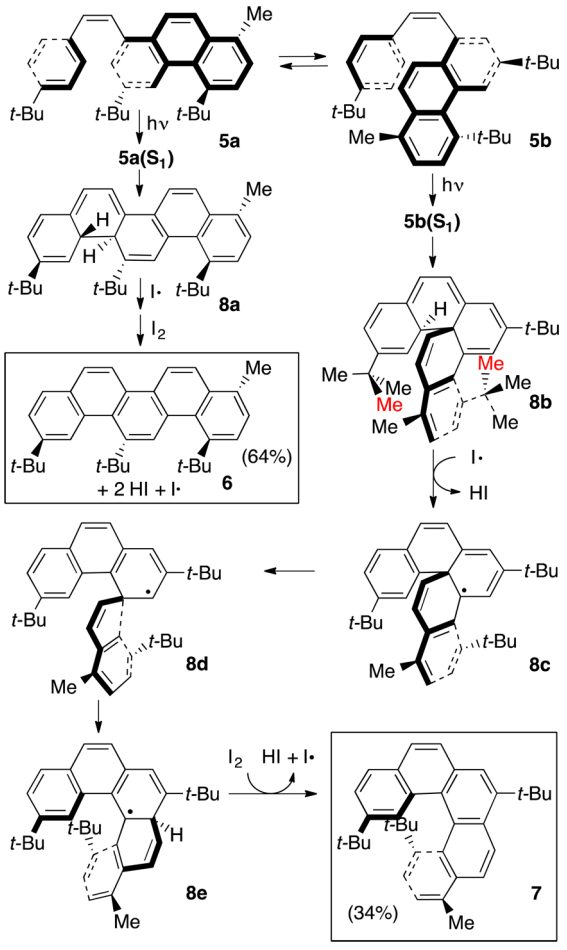
syntheses and photocyclizations of several previously unknown analogues of **3** lacking one or more of its five substituents. We began these experimental investigations by showing that the bromo substituent in **3** was not required for the rearrangement. Specifically, as shown in Scheme 2, we found that the photocyclization of **5** gave a 64% yield of the [5]phenacene **6** along with a 34% yield of the [5]helicene **7**.

**Scheme 2. Photocyclization of 5**




In Scheme 3, we present our mechanistic working hypotheses for the example of the photochemical formations of phenacene **6** and helicene **7** starting from the mixture of the two rapidly interconverting *cis* conformers **5a** and **5b**. We presume that the [5]phenacene **6** is formed from **5a** by the usual stilbene-like photocyclization to give a dihydroaromatic intermediate **8a** with two tertiary hydrogens, one of which is abstracted by an iodine atom (generated by the in situ photolysis of an $I_2$ molecule) to give HI and an intermediate radical from which the remaining tertiary hydrogen is subsequently abstracted by an $I_2$ molecule to give phenacene **6** along with another HI and an iodine atom. We propose that the first step in the formation of the [5]helicene **7**

**Scheme 3. Postulated Photocyclization Mechanisms**





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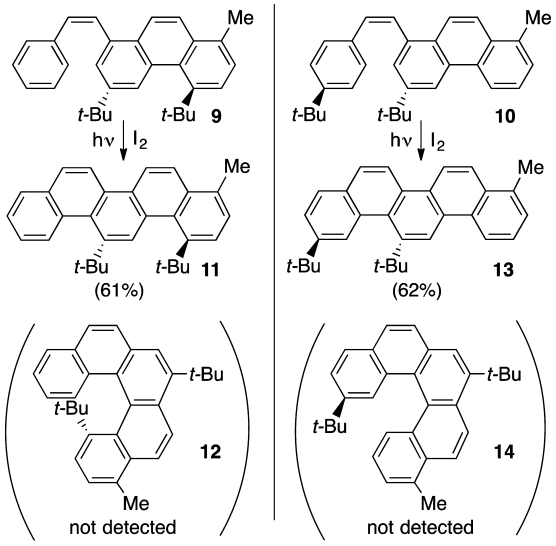
involves the photocyclization of **5b** (via its lowest energy excited singlet state $S_1$) to give intermediate **8b**. To our knowledge, this was the first example of a stilbene-like photocyclization that involves the formation of a new CC bond to an *angular* carbon of a polycyclic aromatic system. We postulate in Scheme 3 that the photochemical ring closure of **5b**($S_1$) to **8b** is assisted energetically by two separate intramolecular CH/$\pi$ stabilizations in which each of the two indicated red methyl groups on **8b** has one of its three hydrogens in close contact with the underneath face of the $\pi$-system of the preceding phenanthrene ring system. The lone tertiary hydrogen on **8b** subsequently undergoes an iodine-atom abstraction to produce an HI molecule along with the radical intermediate **8c**, which then undergoes two consecutive intramolecular rearrangements to give radical **8d** followed by radical **8e**. The subsequent abstraction by an $I_2$ molecule of the tertiary hydrogen from **8e** produces helicene **7** along with HI and a regenerated iodine atom.

As shown in Scheme 4, we began experimentally testing the scope of our proposed mechanism by photocyclizing compounds

**Scheme 4. Helicene Formation Requires Both "End" *tert*-Butyl Groups**

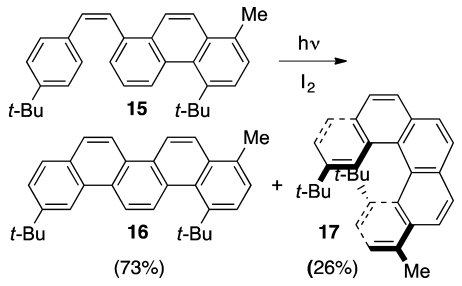



**9** and **10**, the two analogues of compound **5** that each lack one or the other of its two "end" *tert*-butyl groups. Compound **9** gave a 61% yield of the [5]phenacene **11** with no detectable amount of helicene **12**, and compound **10** gave a 62% yield of the [5]phenacene **13** with no detectable amount of helicene **14**. This supports our mechanistic hypothesis shown in Scheme 3 that intramolecular CH/$\pi$ interactions involving one hydrogen on each of the two red methyl groups shown on compound **8b** play a crucial role in the photochemical formation of [5]helicenes from styrylphenanthrenes.

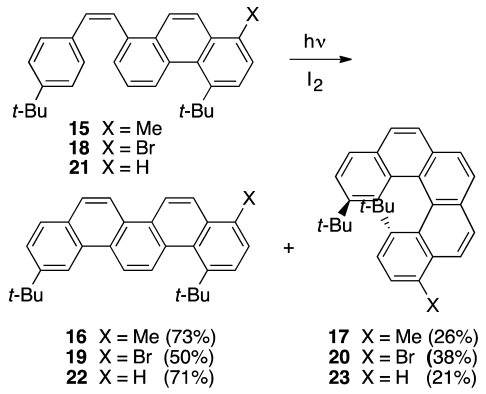
Scheme 5 shows that the photocyclization of **15** gives a **16**/**17** yield ratio of 73/26 = 2.8, which is somewhat larger than the **6**/**7** yield ratio of 64/34 = 1.9 shown in Scheme 2. We believe this is because the photocyclization to produce **16** does not create any intramolecular steric crowding between the two *tert*-butyl groups, whereas the photocyclization of stilbene **5** to **6** adds an additional steric crowding involving the "middle" *tert*-butyl group.

Scheme 6 illustrates that the photocyclization of compound **18** (X = Br) gave a 50% yield of phenacene **19** and a 38% yield of helicene **20** with a phenacene/helicene product ratio of 50/38 =

**Scheme 5. Photocyclization of 15**



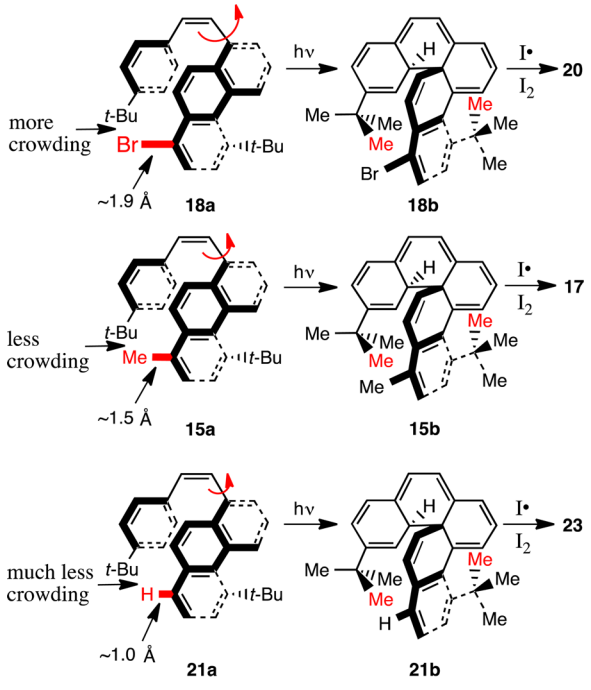

**Scheme 6. Product Yields in the Photocyclizations of 15, 18, and 21**




1.3, whereas the photocyclizations of compounds **15** (X = Me) and **21** (X = H) gave significantly larger phenacene/helicene product ratios of 73/26 = 2.8 for **15** and 71/21 = 3.4 for **21**.

To account mechanistically for the three different helicene/phenacene yield ratios indicated in Scheme 6 (26/73 = 0.4, 38/50 = 0.8, and 21/71 = 0.3) we illustrate in Scheme 7 the photocyclization steps of **15a**, **18a**, and **21a** to give the

**Scheme 7. Phenanthrene Ring Rotations of 15a, 18a, and 21a**





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corresponding three intermediates **15b**, **18b**, and **21b**, each of which subsequently undergo the usual multistep sequence of rearrangements to produce the corresponding helicenes **17**, **20**, and **23**. As indicated by the sizes of the three curved red arrows in Scheme 7, we expect that the amounts of twisting around the single bonds connecting the phenanthrene systems to the alkene double bonds in **15a**, **18a**, and **21a** depends on the intramolecular steric crowding between the red bromo, red methyl, and red hydrogen substituents on the corresponding phenanthrene rings and the *tert*-butyl substituents on the adjacent phenyl rings. This twisting is largest for **18a** because its red bromo substituent has a larger steric size and a longer covalent bond than either the red methyl group in **15a** or the red hydrogen in **21a**. As a consequence, we suggest this explains why the photocyclization of **18a** to **18b** would be expected to experience larger amounts of early CH/$\pi$ overlap interactions along the ring-closure path than the analogous photocyclizations of **15a** to **15b** or **21a** to **21b**. We believe this explains why the photocyclization of **18a** to **18b** is more efficient than the analogous photocyclizations of **15a** to **15b** and **21a** to **21b**.

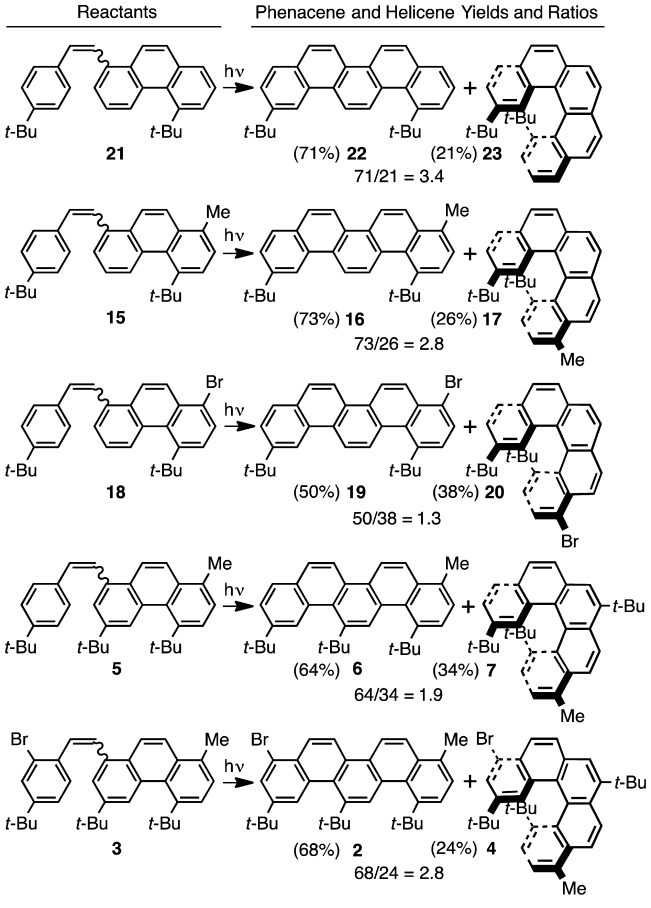
Scheme 8 presents a summary of the results of the five photocyclizations of compounds **3**, **5**, **15**, **18**, and **21** showing an average phenacene/helicene ratio of 2.4.

In contrast, as shown in Scheme 9, the photocyclization of the 1,2-diphenanthrylethylene **24**[4] produced a mixture of phenacene **25** and helicene **26** with a very high **25**/**26** ratio of 71/10 = 7.1.

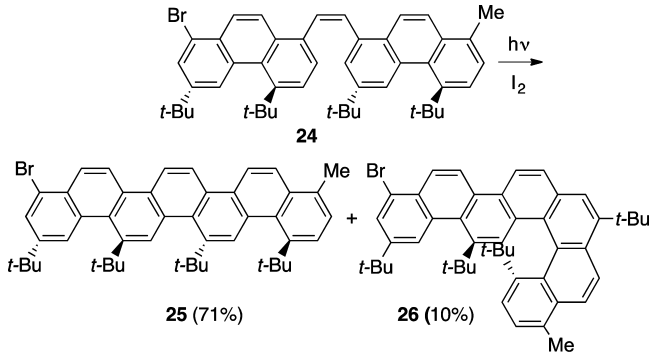
Our mechanistic explanation for this high ratio is illustrated in Scheme 10. Compound **24** presumably exists as a mixture of the four diastereomers **24a**, **24b**, **24c**, and **24d** of very similar energies. However, only **24a** has an excited singlet-state that readily undergoes photocyclization to **24a′** because it can benefit from the necessary two stabilizing CH/$\pi$ interactions. The photocyclization of the excited singlet-state of **24b** to **24b′** would not occur because there would be only one fully effective CH/$\pi$ stabilization interaction. Finally, we postulate that the photocyclizations of the excited singlet-states of both **24c** and **24d** would fail since these two ring-closures would each be sterically impeded because the pairs of *tert*-butyl groups indicated by the double-headed red arrows in **24c** and **24d** would not be able to squeeze past one another during the very short lifetimes of their photochemically excited singlet states.

Finally, as illustrated in Scheme 11, we recently carried out another test of our mechanistic reasoning that all of the various helicene side products summarized in Schemes 8 and 9 require *two* separate sets of CH/$\pi$ interactions. Specifically, the photocyclization of **27** in the presence of dissolved iodine gave a 92% yield of phenacene **28** but gave no detectable formation of

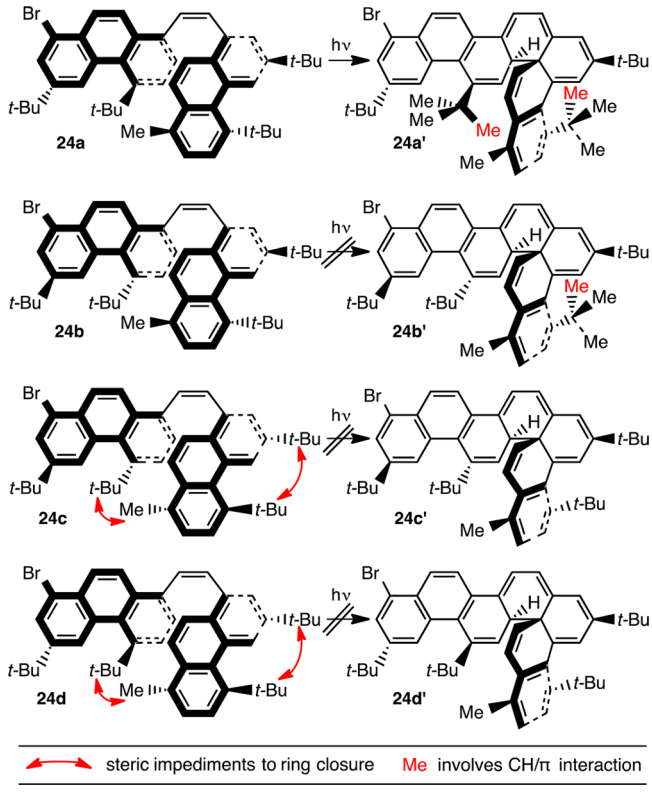
**Scheme 8. Summary of the Photocyclizations of 3, 5, 15, 18, and 21**




**Scheme 9. Product Yields from the Photocyclization of 24**




**Scheme 10. Steric Explanations for the Low Yield of 26**





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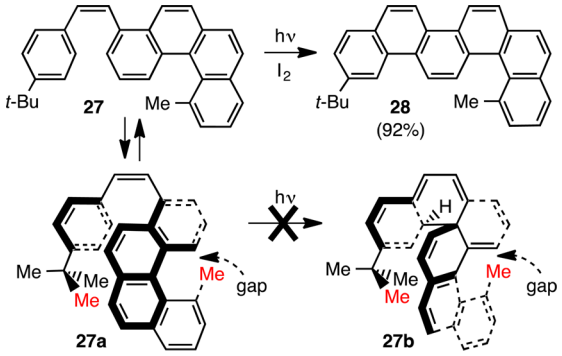
**Scheme 11. Compound 27 Fails To Yield 27b**

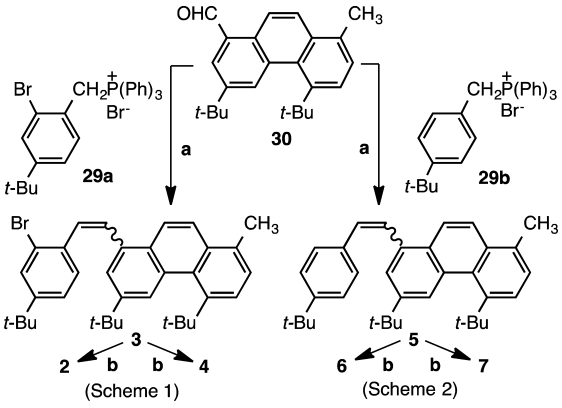



any helicene product! We believe this is because in **27a** there is only *one* effective CH/$\pi$ stabilization interaction that involves the red methyl group on the *tert*-butyl substituent. In contrast, the red methyl group attached directly to the benzo[*c*]phenanthrene ring in **27a** does not have a significant CH/$\pi$ overlap interaction with the back-side face of the ring at the other end of the benzo[*c*]phenanthrene system to produce **27b**.

## SYNTHESES

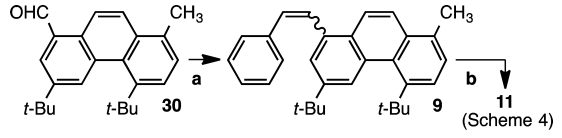
Our approach to the syntheses of the target molecules for this study was similar to that employed in previous work in which we reported on the syntheses of various [*n*]phenacenes.[3] The stilbene-to-phenanthrene type of photocyclization[1e] was key to the assembly of the polynuclear hydrocarbons reported here. The preparations of the 1,2-diarylethylene precursors were accomplished either by Wittig or Horner–Wadsworth–Emmons chemistry. Schemes 12–16 outline the individual syntheses of the diarylethylenes that led to our discovery and subsequent investigation of the scope of the special cases of photocyclizations that produce both helicenes and phenacenes.

**Scheme 12. Syntheses of Compounds 2–7**[a]



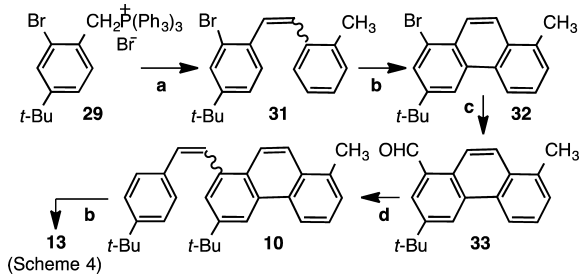

[a]Reagents and conditions: (a) *n*-BuLi, *i*-$Pr_2NH$; (b) *hν*, $I_2$, hexanes.

**Scheme 13. Syntheses of Compounds 9 and 11**[a]



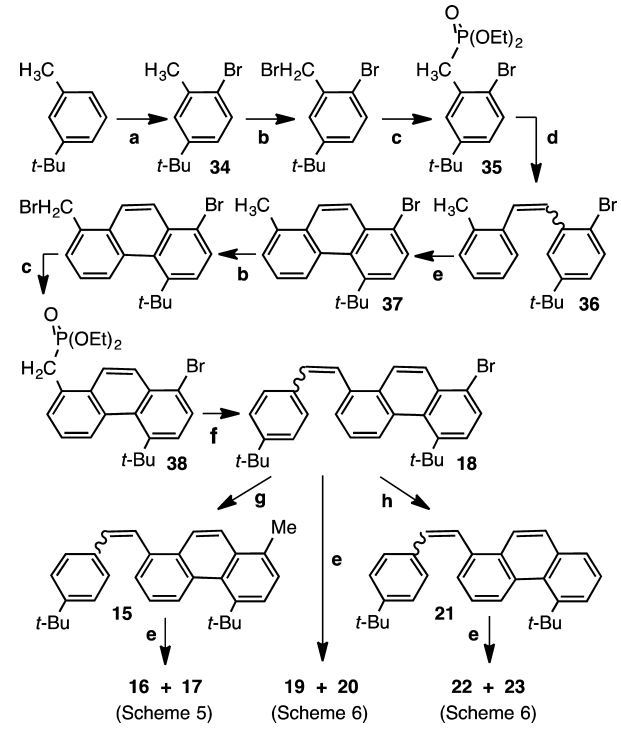

[a]Reagents and conditions: (a) *n*-BuLi, *i*-$Pr_2NH$, benzyltriphenylphosphonium bromide; (b) *hν*, $I_2$, hexanes.

**Scheme 14. Syntheses of Compounds 10 and 13**[a]




[a]Reagents and conditions: (a) 50% aq NaOH, $CH_2Cl_2$, *o*-tolualdehyde; (b) *hν*, $I_2$, hexanes; (c) (1) *n*-BuLi, (2) DMF; (d) *n*-BuLi, *i*-$Pr_2NH$, (4-*tert*-butylbenzyl)triphenylphosphonium bromide.

**Scheme 15. Syntheses of Compounds 15–23**[a]




[a]Reagents and conditions: (a) $Br_2$, Fe; (b) NBS, $CCl_4$; (c) $P(OEt)_3$ (d) NaH, 15-crown-5, *o*-tolualdehyde; (e) *hν*, $I_2$, hexanes; (f) NaH, 15-crown-5, 4-*tert*-butylbenzaldehyde; (g) (1) *n*-BuLi, (2) $Me_2SO_4$; (h) (1) *n*-BuLi, (2) $H_2O$.

## EXPERIMENTAL SECTION

**General Considerations.** Photocyclizations were carried out in stirred solutions in Pyrex vessels surrounded by 16 300 nm lamps. Dry-column chromatography utilizing silica gel wUV254 (Sorbent Technologies) and Nylon foil tubing as a support was employed to separate and purify compounds. After the column was developed, the appropriate bands were segmented and the silica gel was extracted in a Soxhlet. Silica G 2000 $\mu$m glass plates wUV254 (Sorbent Technologies) were used for all preparative thin-layer chromatography. $^1$H NMR and $^{13}C\{^1H\}$ NMR spectra were measured in $CDCl_3$ solution at ambient temperatures using TMS as an internal standard unless otherwise noted. Melting points were determined with an appropriate melting point apparatus and are uncorrected. Mass spectra were obtained using either GC–MS or HRMS instrumentation.

*(E)-1-(2-Bromo-4-tert-butylphenyl)-2-(3′,5′-di-tert-butyl-8′-methyl-1′-phenanthryl)ethene (3).* (2-Bromo-4-*tert*-butylbenzyl)-triphenylphosphonium bromide (**29a**)[3b] (4.38 g, 7.71 mmol) was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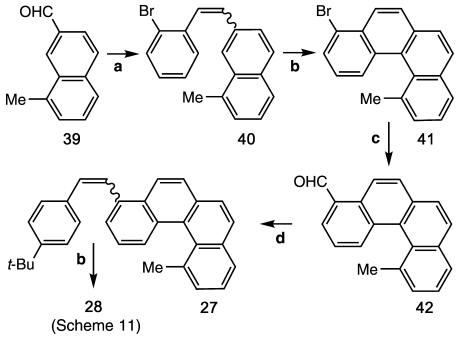
**Scheme 16. Syntheses of Compounds 27 and 28**[a]




[a]Reagents and conditions: (a) 50% aq NaOH, $CH_2CI_2$, *o*-tolualdehyde; (b) *hν*, $I_2$, hexanes; (c) (1) *n*-BuLi, (2) DMF; (d) *n*-BuLi, *i*-$Pr_2NH$, (4-*tert*-butylbenzyl)triphenylphosphonium bromide.

combined with 125 mL of THF under $N_2$. A solution of 5.47 mL (8.75 mmol) of 1.6 M *n*-BuLi in hexanes, 1.47 mL (10.5 mmol) of diisopropylamine, and 20 mL of THF was added slowly through an addition funnel. The reaction turned dark red indicating the formation of the ylide. A solution of 2.34 g (7.03 mmol) of 3,5-di-*tert*-butyl-8-methylphenanthrene-1-carboxaldehyde (**30**)[3b] dissolved in 5 mL of THF was added with a syringe to the reaction flask, turning the reaction mixture orange-yellow. The reaction mixture was heated slowly and allowed to stir at gentle reflux for 21 h. The clear dark yellow reaction was quenched by the addition of a saturated aq $NH_4Cl$ solution, and the aqueous layer was extracted 3 times with toluene. The combined organic layer was then washed with brine and dried over $Na_2SO_4$. The yellow solid that remained after rotary evaporation was dissolved in cyclohexane and stirred overnight with an equal volume of 70% EtOH to remove triphenylphosphine oxide. The layers were separated, and the organic layer was dried over $Na_2SO_4$ and filtered. Several crystals of iodine were added, and the purple solution was irradiated for 7 days with visible light from a 100-W tungsten bulb to achieve the *Z* to *E* isomerization. After the purple solution was washed with aq $NaHSO_3$ to remove the iodine it was dried over $Na_2SO_4$ and vacuum filtered through alumina and silica. The solvent was removed by rotary evaporation to give 3.29 g (86%) of a yellow solid that was recrystallized from a mixture of hexanes/toluene/95% EtOH to give **3** as a fluffy white solid: mp 151.5−152.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.25 (d, $J$ = 1.4 Hz, 1H), 7.98 (d, $J$ = 9.2 Hz, 1H), 7.82−7.73 (m, 5H), 7.63 (d, $J$ = 2.0 Hz, 1H), 7.46 (d, $J$ = 15.9 Hz, 1H), 7.40 (dd, $J$ = 8.1 Hz, 1.8 Hz, 1H), 7.32 (dd, $J$ = 7.8 Hz, 0.8 Hz, 1H), 2.66 (s, 3H), 1.56 (s, 9H), 1.48 (s, 9H), 1.35 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 152.5, 146.2, 144.4, 134.8, 133.0, 132.0, 131.93, 131.85, 131.4, 130.08, 130.06, 129.3, 129.1, 128.3, 128.2, 126.6, 126.5, 124.9, 124.1, 122.6, 122.5, 121.2, 38.0, 35.3, 34.7, 34.3, 31.6, 31.2, 19.3. Anal. Calcd for $C_{35}H_{41}Br$: C, 77.62; H, 7.63. Found: C, 77.83; H, 7.56.

*9-Bromo-1,11,13-tri-tert-butyl-4-methyl[5]phenacene (**2**)*[3b] *and 11-Bromo-1,7,13-tri-tert-butyl-4-methyl[5]helicene (**4**).* A solution of 0.250 g (0.46 mmol) of ethene **3** and 0.0291 g (0.12 mmol) of iodine in 2 L of silica-filtered hexanes was irradiated for 8 h. When the reaction was complete as judged by NMR analysis, the reaction solution was washed with aq $NaHSO_3$ to remove the iodine. The hexanes were removed by rotary evaporation, and the resulting crude solid was purified by dry column chromatography using 50% hexanes/50% $CH_2Cl_2$ as solvent. The solvent was removed by rotary evaporation and gave 0.228 g (92%) of a yellow powder, consisting of a mixture determined by NMR analysis to be 74% of the previously reported [5]phenacene **2**[3b] and 26% of the [5]helicene **4**. The crude solid was recrystallized from EtOH to separate the two products and gave as a first crop phenacene **2** with mp 246−248 °C (lit.[3b] mp 246.5−248.0 °C). Concentration of the filtrate gave on cooling helicene **4** as a pale yellow powder: mp 227−232 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.41 (d, $J$ = 9.1 Hz, 1H), 8.24 (d, $J$ = 8.8 Hz, 1H), 7.96 (d, $J$ = 9.1 Hz, 1H), 7.89 (s, 1H), 7.87 (d, $J$ = 8.8 Hz, 1H), 7.71 (d, $J$ = 1.8 Hz, 1H), 7.42 (d, $J$ = 7.9 Hz, 1H), 7.39 (d, $J$ = 7.7 Hz, 1H), 6.98 (d, $J$ = 1.8 Hz, 1H), 2.80 (s, 3H), 1.76 (s, 9H), 1.02 (s, 9H), 0.19 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 129.7, 129.0, 125.6, 112.9, 112.3, 112.0, 111.60, 111.55, 110.53, 110.51, 110.4, 110.0, 109.7, 109.13, 109.06, 108.7, 106.7, 105.7, 105.3, 104.8, 103.8, 103.2, 19.8, 17.6, 16.0, 14.2, 13.9, 12.4, 0.6. Anal. Calcd for $C_{35}H_{39}Br$: C, 77.91; H, 7.28. Found: C, 77.86; H, 7.28.

*(E)-1-(4-tert-Butylphenyl)-2-(3′,5′-di-tert-butyl-8′-methyl-1′-phenanthryl)ethane (**5**).* A procedure similar to that described for the preparation of ethene **3** was followed. From (4-*tert*-butylbenzyl)-triphenylphosphonium bromide (**29b**)[3a] (0.809 g, 1.65 mmol) and aldehyde **30**[3b] (0.500 g, 1.50 mmol) there was obtained a pale yellow oily solid that was mixed with a small amount of acetonitrile and sonicated for several hours to give 0.450 g (55%) of material that was recrystallized from hexanes/95% EtOH to give **5** as pale yellow crystals: mp 163.5−165 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.23 (d, $J$ = 1.6 Hz, 1H), 7.99 (d, $J$ = 9.2 Hz, 1H), 7.88 (d, $J$ = 16.0 Hz, 1H), 7.80−7.75 (m, 3H), 7.59−7.57 (m, 2H), 7.45−7.43 (m, 2H), 7.32 (dd, $J$ = 7.8 Hz, 0.6 Hz, 1H), 7.14 (d, $J$ = 16.0 Hz, 1H), 2.66 (s, 3H), 1.56 (s, 9H), 1.47 (s, 9H), 1.37 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 150.8, 146.2, 144.4, 135.1, 133.4, 132.1, 132.0, 131.8, 131.33, 131.30, 128.7, 128.3, 128.1, 126.44, 126.39, 126.36, 125.7, 122.4, 122.0, 121.3, 38.0, 35.2, 34.7, 34.3, 31.6, 31.3, 19.3. Anal. Calcd for $C_{35}H_{42}$: C, 90.85; H, 9.15. Found: C, 90.59; H, 9.11.

*1,11,13-Tri-tert-butyl-4-methyl[5]phenacene (**6**) and 1,7,13-Tri-tert-butyl-4-methyl[5]helicene (**7**).* A solution of 0.200 g (0.43 mmol) of the ethene **5** and 0.0274 g (0.11 mmol) of iodine in 150 mL of silica-filtered hexanes was irradiated for 2.5 h. The reaction was complete as judged by NMR analysis, and the reaction solution was washed with aq $NaHSO_3$ to remove the iodine. The solvent was removed by rotary evaporation, and the resulting 0.194 g (98%) of yellow powder was shown by NMR analysis to be a mixture of 65% [5]phenacene **6** and 35% [5]helicene **7**. The solid was recrystallized from EtOH to separate the two products. The phenacene **6** precipitated first as an ivory crystalline solid: mp 199.5−201.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.68 (s, 1H), 8.61 (d, $J$ = 9.1 Hz, 1H), 8.52−8.50 (m, 2H), 8.02 (d, $J$ = 9.2 Hz, 1H), 7.88−7.81 (m, 3H), 7.63 (dd, $J$ = 8.4 Hz, 1.9 Hz, 1H), 7.39 (dd, $J$ = 7.8 Hz, 0.8 Hz, 1H), 2.75 (s, 3H), 1.59 (s, 9H), 1.56 (s, 9H), 1.51 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 146.2, 145.6, 138.5, 133.2, 132.1, 132.0, 131.7, 131.1, 130.7, 130.4, 129.6, 128.8, 128.2, 127.9, 127.0, 126.8, 126.5, 125.7, 124.2, 123.2, 120.8, 119.8, 38.0, 37.9, 35.4, 34.6 (3C), 33.9 (3C), 31.7 (3C), 19.4. Anal. Calcd for $C_{35}H_{40}$: C, 91.25; H, 8.75. Found: C, 90.96; H, 8.71.

Concentration of the filtrate from the recrystallization gave helicene **7** as a yellow powder: mp 227−229.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.39 (d, $J$ = 9.1 Hz, 1H), 7.94 (d, $J$ = 9.1 Hz, 1H), 7.87 (s, 1H), 7.78−7.75 (m, 3H), 7.44−7.38 (m, 3H), 7.01 (d, $J$ = 1.9 Hz, 1H), 2.81 (s, 3H), 1.76 (s, 9H), 1.05 (s, 9H), 0.19 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 147.5, 147.4, 143.1, 130.7, 130.5, 130.2, 130.1, 129.9, 129.8, 129.1, 129.0, 127.9, 127.6, 127.4, 127.2, 126.6, 125.5, 124.2, 123.9, 123.8, 123.2, 121.2, 38.2, 36.0, 34.4, 32.6, 32.4, 31.0, 19.1. Anal. Calcd for $C_{35}H_{40}$: C, 91.25; H, 8.75. Found: C, 91.36; H, 8.82.

*(E)-1-Phenyl-2-(3′,5′-di-tert-butyl-8′-methyl-1′-phenanthryl)-ethene (**9**).* A procedure similar to that described for the preparation of ethene **3** was followed. From 0.643 g, (1.65 mmol) of benzyltriphenyl-phosphonium chloride and 0.50 g (1.5 mmol) aldehyde **30**[3b] there was obtained 0.409 g (67%) of material that was mixed with a small amount of acetonitrile and sonicated for several hours to give **9** as a pale yellow powder: mp 147.5−150 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.24 (d, $J$ = 1.6 Hz, 1H), 7.99 (d, $J$ = 9.2 Hz, 1H), 7.92 (d, $J$ = 16.0 Hz, 1H), 7.81 (d, $J$ = 1.7 Hz, 1H), 7.77 (d, $J$ = 9.2 Hz, 1H), 7.76 (d, $J$ = 7.8 Hz, 1H), 7.63 (m, 2H), 7.42 (m, 2H), 7.33−7.30 (m, 2H), 7.16 (d, $J$ = 16.0 Hz, 1H), 2.66 (s, 3H), 1.57 (s, 9H), 1.47 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 146.2, 144.4, 137.9, 133.2, 132.1, 131.9, 131.8, 131.5, 131.4, 128.83, 128.76, 128.3, 128.2, 127.6, 127.2, 126.6, 126.4, 122.5, 122.1, 121.3, 38.0, 35.2, 34.3, 31.6, 19.3. Anal. Calcd for $C_{31}H_{34}$: C, 91.57; H, 8.43. Found: C, 91.38; H, 8.25.

*1,13-Di-tert-butyl-4-methyl[5]phenacene (**11**).* A solution of 0.20 g (0.493 mmol) of alkene **9** and 0.08 g (0.315 mmol) of iodine in 100 mL of benzene was irradiated for 43 h, after which time the reaction was judged complete by NMR analysis. Most of the solvent was removed by rotary evaporation, and the remaining solution was washed with aq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$NaHSO_3$ and then vacuum filtered through alumina and silica to remove residual iodine. The solvent was removed by rotary evaporation, and the resulting 0.122 g (61%) orange powder was first sonicated with a small amount of acetonitrile to remove colored impurities and then recrystallized from hexanes to give **11** as a white crystalline solid: mp 239.5−241.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.68 (s, 1H), 8.66 (d, $J$ = 9.1 Hz, 1H), 8.60 (br d, $J$ = 8.0 Hz, 1H), 8.51 (d, $J$ = 9.2 Hz, 1H), 8.03 (d, $J$ = 9.2 Hz, 1H), 7.94−7.89 (m, 2H), 7.82 (d, $J$ = 7.7 Hz, 1H), 7.57−7.48 (m, 2H), 7.39 (dd, $J$ = 7.7 Hz, 0.7 Hz, 1H), 2.75 (s, 3H), 1.58 (s, 9H), 1.54 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 146.2, 138.6, 133.3, 132.3, 132.2, 131.9, 131.81, 131.76, 131.3, 130.5, 129.7, 128.6, 128.3, 127.0, 126.9, 126.6, 126.0, 125.8, 123.3, 123.2, 121.4, 119.7, 37.89, 37.86, 34.6, 34.1, 19.5. Anal. Calcd for $C_{31}H_{32}$: C, 92.03; H, 7.97. Found: C, 91.88; H, 7.87.

*(E)-2-Bromo-4-tert-butyl-2′-methylstilbene (**31**).* *o*-Tolualdehyde (7.73 mL, 66.9 mmol) and (2-bromo-4-*tert*-butylbenzyl)-triphenylphosphonium bromide (**29a**)[3b] (34.6 g, 60.8 mmol) were stirred vigorously in 100 mL of $CH_2Cl_2$ at 0 °C. A 30 mL portion of 50% aq NaOH was added over 30 min. The reaction mixture turned orange, indicating formation of the ylide. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched with $H_2O$, and the aqueous layer was extracted with three 50 mL portions of $CH_2Cl_2$. The solvent was removed by rotary evaporation, and the residue was stirred in hexanes and 70% EtOH to remove triphenylphosphine oxide. The hexanes were subsequently washed with additional 70% EtOH and then dried over $Na_2SO_4$. Several crystals of iodine were added, and the purple solution was irradiated for 30 h with visible light from a 100-W tungsten bulb to achieve the $Z$ to $E$ isomerization. After the purple solution was washed with aq $NaHSO_3$ to remove the iodine it was dried over $Na_2SO_4$ and then vacuum filtered through alumina and silica. The solvent was removed by rotary evaporation to give 18 g (90%) of a yellow oil that was purified by reduced pressure distillation to yield **31** as a colorless oil: bp 151 °C at 0.012 mmHg; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.64−7.58 (m, 3H), 7.34 (dd, $J$ = 8.0 Hz, 2.0 Hz, 1H), 7.31 (d, $J$ = 15.9 Hz, 1H), 7.24−7.18 (m, 4H), 2.43 (s, 3H), 1.32 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 152.5, 136.3, 135.9, 134.7, 130.4, 130.0, 128.7, 128.6, 127.8, 126.5, 126.3, 125.8, 124.8, 124.1, 34.7, 31.1, 19.9. Anal. Calcd for $C_{19}H_{21}Br$: C, 69.30; H, 6.43. Found: C, 69.12; H, 6.19.

*1-Bromo-3-tert-butyl-8-methylphenanthrene (**32**).* The procedure was similar to that described for the preparation of **11**. A solution of 6.0 g (18.2 mmol) of alkene **31** and 1.6 g (6.30 mmol) of iodine in 2 L of filtered hexanes was irradiated for 46 h. After the usual workup, 5.63 g (95%) of **32** was obtained and purified by addition of acetonitrile and subsequent sonication to give a pale yellow oil. A second sonication with acetonitrile gave **32** as a colorless crystalline solid: mp 85.5−87 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.67 (d, $J$ = 1.6 Hz, 1H), 8.59 (br d, $J$ = 8.4 Hz, 1H), 8.18 (d, $J$ = 9.5 Hz, 1H), 7.99 (dd, $J$ = 9.4 Hz, 0.6 Hz, 1H), 7.95 (d, $J$ = 1.7 Hz, 1H), 7.56 (dd, $J$ = 8.3 Hz, 7.2 Hz, 1H), 7.46 (br d, $J$ = 7.1 Hz, 1H), 2.76 (s, 3H), 1.48 (s, 9H); $^{13}$C{$^1$H} NMR (acetone-$d_6$, 100.6 MHz) $\delta$ 150.5, 135.1, 132.1, 130.8, 130.2, 129.0, 128.4, 128.0, 126.8, 124.2, 124.0, 123.0, 121.3, 118.9, 35.1, 30.7, 18.9. Anal. Calcd for $C_{19}H_{19}Br$: C, 69.73; H, 5.85. Found: C, 70.00; H, 5.67.

*3-tert-Butyl-8-methylphenanthrene-1-carboxaldehyde (**33**).* Phenanthrene **32** (1.63 g, 4.97 mmol) was stirred in 75 mL of diethyl ether under $N_2$ at 0 °C. A 1.6 M solution of *n*-BuLi in hexanes (4.66 mL, 7.46 mmol) was added dropwise over 1 h. The yellow reaction mixture was stirred at 0 °C for an additional 2 h, and then DMF (0.962 mL, 12.4 mmol) was added dropwise over 0.5 h. The reaction mixture was allowed to warm to room temperature and then was stirred for an additional 2 h. The reaction was quenched by pouring into 75 mL of 5% $H_3PO_4$ and the aqueous layer was extracted with three 50 mL portions of diethyl ether. The combined ether layers were washed with 75 mL of aq $NaHCO_3$ and then with brine before drying over $Na_2SO_4$. The diethyl ether was removed by rotary evaporation resulting in a yellow oil that was sonicated with acetonitrile to give 1.24 g (90%) of **33** as a yellow crystalline solid: mp 92−95 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 10.56 (s, 1H), 9.11 (d, $J$ = 9.5 Hz, 1H), 9.01 (d, $J$ = 1.9 Hz, 1H), 8.62 (d, $J$ = 8.4 Hz, 1H), 8.17 (d, $J$ = 2.0 Hz, 1H), 8.12 (dd, $J$ = 9.6 Hz, 0.5 Hz, 1H), 7.59 (dd, $J$ = 8.3 Hz, 7.3 Hz, 1H), 7.49 (d, $J$ = 7.1 Hz, 1H), 2.79 (s, 3H), 1.54 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 193.8, 148.5, 135.1, 133.3, 131.5, 131.2, 130.9, 130.0, 128.2, 128.1, 126.5, 125.4, 125.2, 121.7, 120.9, 35.3, 31.4, 19.9. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.12; H, 7.44.

*(E)-1-(4-tert-Butylphenyl)-2-(3′-tert-butyl-8′-methyl-1′-phenanthryl)ethene (**10**).* A procedure similar to that described for the preparation of ethene **3** was followed. From 0.538 g (1.1 mmol) of (4-*tert*-butylbenzyl)triphenylphosphonium bromide (**29b**)[3a] and 0.277 g (1.0 mmol) of aldehyde **33** there was obtained 0.339 g (83%) of a yellow oil which was purified by recrystallization from EtOH to give **10** as a white powder: mp 132.0−134.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.69 (br s, 1H), 8.63 (br d, $J$ = 8.3 Hz, 1H), 8.14 (d, $J$ = 9.3 Hz, 1H), 7.96−7.89 (m, 3H), 7.59−7.53 (m, 3H), 7.46−7.43 (m, 3H), 7.14 (d, $J$ = 16.0 Hz, 1H), 2.77 (s, 3H), 1.54 (s, 9H), 1.37 (s, 9H); $^{13}$C{$^1$H} NMR (acetone-$d_6$, 100.6 MHz) $\delta$ 150.7, 149.0, 135.4, 135.1, 134.7, 131.6, 130.8, 130.74, 130.65, 127.6, 127.5, 126.6, 126.2, 125.5, 125.4, 122.5, 122.2, 122.1, 121.2, 118.5, 35.1, 34.3, 30.9, 30.7, 19.0; HRMS (TOF MS CI+) calcd for $C_{31}H_{34}$ ($M^+$) 406.2675, found 406.2661.

*2,14-Di-tert-butyl-9-methyl[5]phenacene (**13**).* The procedure was as described for the preparation of **11**. A solution of 0.339 g (0.834 mmol) alkene **10** and 0.16 g (0.630 mmol) of iodine in 200 mL of hexanes was irradiated for 7 h. After the usual workup there was obtained 0.209 g (62%) of a pale yellow solid that was recrystallized from toluene/95% EtOH to give **13** as an off-white, shiny crystalline solid: mp 196.5−198 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 9.07 (s, 1H), 8.67 (d, $J$ = 8.3 Hz, 1H), 8.62 (d, $J$ = 8.7 Hz, 1H), 8.60 (d, $J$ = 8.7 Hz, 1H), 8.44 (d, $J$ = 1.8 Hz, 1H), 8.12 (d, $J$ = 9.4 Hz, 1H), 7.86 (d, $J$ = 8.6 Hz, 2H), 7.63−7.59 (m, 2H), 7.47 (br d, $J$ = 7.0 Hz, 1H), 2.81 (s, 3H), 1.69 (s, 9H), 1.47 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 145.8, 145.5, 134.9, 131.2, 130.9, 130.5, 130.4, 130.3, 129.9, 128.13, 128.07, 127.4, 126.5, 126.3, 126.2, 126.0, 124.2, 124.0, 122.8, 122.4, 121.0, 120.7, 38.6, 35.3, 34.6, 31.6, 19.8. HRMS (TOF MS CI+) calcd for $C_{31}H_{32}$ ($M^+$) 404.2504, found 404.2506.

*2-Bromo-5-tert-butyltoluene (**34**).*[5] Iron powder (0.1 g, 1.8 mmol) was added to 11.9 g (80 mmol) of 3-*tert*-butyltoluene and the reaction mixture heated to 95−100 °C in an oil bath. Bromine (12.7 g, 80 mmol) was added dropwise to the stirred reaction mixture over the course of 2.5 h. When the addition was complete, the reaction mixture was stirred for an additional 30 min at 95−100 °C. The mixture was cooled to room temperature and poured into 50 mL of water. Diethyl ether (100 mL) was added, and the layers were separated. The ether solution was extracted with three 100-mL portions of aq $NaHSO_3$ solution, followed by 100 mL of water and then dried over $Na_2SO_4$. The ether was evaporated and the resulting oil distilled under vacuum (bp 49 °C, 0.02 mmHg) to give 14.8 g (81%) of **34** as a colorless oil: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.42 (d, $J$ = 8.4 Hz, 1H), 7.23 (d, $J$ = 2.5 Hz, 1H), 7.06 (dd, $J$ = 8.4 Hz, 2.5 Hz, 1H), 2.38 (s, 3H), 1.28 (s, 9H); GC−MS $m/z$ 226/228 ($M^+$).

*Diethyl (2-Bromo-5-tert-butylbenzyl)phosphonate (**35**).* A solution of 9.1 g (40 mmol) of **34**, 7.8 g (44 mmol) of *N*-bromosuccinimide, and a small amount of benzoyl peroxide in 100 mL of $CCl_4$ was heated under reflux for 22.5 h. During the course of the reaction, the mixture was also irradiated with an incandescent light. The reaction mixture was allowed to cool, and the solution was filtered through a pad of Celite to remove the succinimide. The filtrate was concentrated by rotary evaporation to give 12.2 g of the benzyl bromide as an amber oil. Without purification this material was dissolved in 10.5 mL (10.0 g, 60 mmol) of triethyl phosphite, and the stirred reaction mixture was heated under reflux for 2 h. The reaction mixture was distilled under reduced pressure (35−60 °C, 0.02 mmHg) to remove the excess triethyl phosphite. The residue was dissolved in 75 mL of toluene and passed through a 125 g plug of silica gel. The silica gel was washed with an additional 250 mL of toluene and then extracted with ethyl acetate in a Soxhlet. The ethyl acetate was removed by rotary evaporation and the sample pumped under vacuum to give 10.9 g (75%) of **35** as an amber oil: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.48−7.45 (m, 2H), 7.12 (dt, $J$ = 8.5 Hz, 2.4 Hz, 1H), 4.05 (M, 4H), 3.38 (d, $J_P$ = 22.0 Hz, 2H), 1.30 (s, 9H), 1.26 (t, $J$ = 7.0 Hz, 6H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 150.6, 150.5, 132.4, 132.3, 131.2, 131.1, 129.0, 128.9, 125.7, 125.72, 125.68, 121.6, 62.2, 62.1, 34.5, 34.2, 32.8,


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31.1, 16.4, 16.3; HRMS (TOF MS ES+) calcd for $C_{15}H_{25}O_3PBr$ (M + 1) 363.0725, found 363.0721.

*(E)-2-Bromo-5-tert-butyl-2′-methylstilbene (**36**).* Sodium hydride (60% dispersion in mineral oil) was washed with hexanes, centrifuged, and decanted to remove the mineral oil. To a stirred suspension of the treated sodium hydride (7.2 g, 180 mmol) and a small amount of 15-crown-5 in 190 mL of THF at 0 °C was added a mixture of 16.3 g (45 mmol) of the phosphonate ester **35** and 5.4 g (45 mmol) of *o*-tolualdehyde dissolved in 110 mL of THF dropwise under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature where it was maintained for an additional 1 h before being quenched with 100 mL of $H_2O$. The layers were separated, and the aqueous phase was extracted three times with diethyl ether. The combined organic extracts were dried over $Na_2SO_4$, and the solvent was removed by rotary evaporation. The resulting solid was recrystallized from methanol to give 11.3 g (76%) of **36** as a white solid: mp 76−77 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.66 (d, $J$ = 2.4 Hz, 1H), 7.62 (br dd, $J$ = 6.6 Hz, 1.8 Hz, 1H), 7.51 (d, $J$ = 8.4 Hz, 1H), 7.33 (d, $J$ = 16.0 Hz, 1H), 7.24 (d, $J$ = 16.0 Hz, 1H), 7.25−7.20 (m, 2H), 7.18 (dd, $J$ = 8.4 Hz, 2.4 Hz, 1H), 2.46 (s, 3H), 1.36 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 150.7, 136.9, 136.3, 135.9, 132.6, 130.4, 129.5, 129.1, 127.9, 126.4, 126.3, 126.0, 123.9, 121.0, 34.7, 31.3, 12.0. HRMS (TOF MS FD+) calcd for $C_{19}H_{21}Br$ ($M^+$) 328.0827, found 328.0826.

*1-Bromo-4-tert-butyl-8-methylphenanthrene (**37**).* The general procedure was as described for the preparation of **11**. A solution of 1.15 g (3.5 mmol) of stilbene **36** and 0.25 g (1.0 mmol) of iodine in 1 L of hexanes was irradiated for 148 h after which time the reaction was judged to be ∼85% complete by GC−MS analysis. (Further irradiation resulted in an increase in byproducts.) After the usual workup the crude product was obtained as a dark-brown viscous oil that was chromatographed on a dry silica gel column (1.125 in. × 22 in.) using a mixture of 75% hexanes/25% $CH_2Cl_2$. The band corresponding to $R_f$ = 0.55 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was removed and the resulting solid recrystallized from methanol to give 0.63 g (55%) of **37** as a white solid: mp 79−80 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.22 (bd, $J$ = 8.1, 1H), 8.07 (d, $J$ = 9.2 Hz, 1H), 7.90 (d, $J$ = 9.2 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.39 (d, $J$ = 7.1 Hz, 1H), 7.31 (dd, $J$ = 8.1 Hz, 7.1 Hz, 1H), 2.76 (s, 3H), 1.52 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 148.2, 134.1, 133.1, 131.3, 131.2, 130.8, 130.3, 129.1, 128.8, 127.9, 125.3, 125.2, 122.7, 119.9, 38.2, 34.3, 19.9; HRMS (TOF MS CI+) calcd for $C_{19}H_{19}Br$ ($M^+$) 326.0670, found 326.0673.

*Diethyl (1-Bromo-4-tert-butyl-8-phenanthrylmethyl)-phosphonate (**38**).* A solution of 0.60 g (1.8 mmol) of phenanthrene **37**, 0.39 g (2.2 mmol) of *N*-bromosuccinimide, and a small amount of benzoyl peroxide in 20 mL of $CCl_4$ was heated under reflux for 4 h. During the course of the reaction, the mixture was also irradiated with an incandescent light. The reaction mixture was allowed to cool in the freezer overnight, and the solution was then filtered through a pad of Celite to remove the succinimide. The filtrate was concentrated on a rotary evaporator to give a dark viscous oil that was chromatographed on a dry silica gel column (1.125 in. × 20 in.) using a mixture of 50% hexanes/50% $CH_2Cl_2$. The band corresponding to $R_f$ = 0.55 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was removed to give 0.5 g of the bromomethyl compound as a light brown viscous liquid that was dissolved in 5.0 mL (4.8 g, 28.7 mmol) of triethyl phosphite. This mixture was stirred and heated under reflux for 6 h and then distilled at reduced pressure (35−60 °C, 0.02 mmHg) to remove the excess triethyl phosphite. The residue was dissolved in 25 mL of toluene and passed through a 20 g plug of silica gel. The silica gel was washed with an additional 50 mL of toluene and then extracted with ethyl acetate in a Soxhlet. The ethyl acetate was removed by rotary evaporation and the sample pumped under vacuum to give 0.44 g (52%) of the phosphonate ester **38** as a yellow oil: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.26 (dd, $J$ = 8.2 Hz, 2.2 Hz, 1H), 8.08 (d, $J$ = 9.3 Hz, 1H), 7.97 (d, $J$ = 9.3 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.67 (d, $J$ = 8.4 Hz, 1H), 7.55 (dd, $J$ = 7.0 Hz, 2.2 Hz, 1H), 7.31 (dd, $J$ = 8.2 Hz, 7.0 Hz, 1H), 3.94 (m, 4H), 3.68 (d, $J_P$ = 21.8 Hz, 2H), 1.49 (s, 9H), 1.15 (t, $J$ = 7.1 Hz, 6H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 148.2, 134.0, 131.5, 131.4, 131.28, 131.25, 131.13, 131.10, 131.05, 129.5, 129.5, 129.3, 129.1, 127.0, 126.9, 125.7, 123.26, 123.25, 122.71, 122.67, 119.8, 62.3, 62.2, 38.2, 34.3, 31.9, 30.5, 16.4, 16.3; HRMS (TOF MS ES+) calcd for $C_{23}H_{28}O_3NaPBr$ (M + Na) 485.0857, found 485.0858.

*(E)-1-(4-tert-Butylphenyl)-2-(8′-bromo-5′-tert-butyl-1′-phenanthryl)ethene (**18**).* A procedure similar to that employed for the preparation of **36** was used. From 0.40 g (0.86 mmol) of the phosphonate ester **38** and 0.14 g (0.86 mmol) of 4-*tert*-butylbenzaldehyde there was obtained after recrystallization from methanol 0.21 g (52%) of **18** as a yellow crystalline solid: mp 143−144 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.26 (bd, $J$ = 8.2 Hz, 1H), 8.08 (d, $J$ = 9.3 Hz, 1H), 8.04 (d, $J$ = 9.3 Hz, 1H), 7.85 (d, $J$ = 16.1 Hz, 1H), 7.78 (bd, $J$ = 7.4 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.57 (bd, $J$ = 8.2 Hz, 2H), 7.44 (bd, $J$ = 8.2 Hz, 2H), 7.40 (bdd, $J$ ∼ 8.2 Hz, ∼ 7.4 Hz, 1H), 7.15 (d, $J$ = 16.1 Hz, 1H), 1.52 (s, 9H), 1.37 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 151.1, 148.3, 134.8, 134.1, 134.0, 132.1, 131.7, 131.3, 131.2, 130.3, 129.3, 129.1, 126.4, 125.7, 125.6, 125.4, 124.6, 123.2, 122.9, 119.8, 38.2, 34.7, 34.4, 31.3; HRMS (TOF MS CI+) calcd for $C_{30}H_{31}Br$ ($M^+$) 470.1609, found 470.1630.

*4-Bromo-1,11-di-tert-butyl[5]phenacene (**19**) and 4-Bromo-1,13-di-tert-butyl[5]helicene (**20**).* A solution of 0.175 g (0.37 mmol) of ethene **18** and 0.10 g (0.40 mmol) of iodine in a mixture of 126 mL of hexane and 14 mL of 1-epoxybutane was irradiated for 5 h, after which time the reaction was judged to be ∼97% complete by GC−MS analysis. The reaction mixture was washed with four 75 mL portions of aq $NaHSO_3$ followed by 75 mL of water. The organic phase was dried over $Na_2SO_4$, and the hexanes were removed by rotary evaporation to give a viscous brown oil that was chromatographed on a dry silica gel column (0.625 in. × 21 in.) using a solvent mixture of 50% hexanes/50% $CH_2Cl_2$. The band corresponding to $R_f$ = 0.62 was isolated, and the silica gel extracted with diethyl ether in a Soxhlet. The ether was evaporated to give 0.151 g (88%) of a yellow solid which was shown by NMR to be a mixture of 57% **19** and 43% **20**. This mixture was then dissolved in hot EtOH and slowly allowed to cool to room temperature whereupon a pale yellow solid crystallized out. This solid was then recrystallized a second time from EtOH to give pure phenacene **19**: mp 193−194 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.80 (d, $J$ = 1.8 Hz, 1H), 8.71−8.67 (m, 3H), 8.60 (d, $J$ = 9.2 Hz, 1H), 8.30 (d, $J$ = 9.3 Hz, 1H), 8.00 (d, $J$ = 9.1 Hz, 1H), 7.95 (d, $J$ = 8.3 Hz, 1H), 7.79−7.77 (m, 2H), 7.75 (dd, $J$ = 8.3 Hz, 1.8 Hz, 1H) 1.59 (s, 9H), 1.54 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.4, 148.0, 133.6, 130.9, 130.3, 129.8, 129.5, 129.3, 129.0, 128.8, 128.6, 127.9, 127.3, 126.7, 125.8, 125.0, 122.3, 120.9, 119.8, 118.3, 117.3, 38.1, 35.1, 34.2, 31.3; HRMS (TOF MS CI+) calcd for $C_{30}H_{29}Br$ ($M^+$) 468.1453, found 468.1466.

The mixture of **19** and **20** obtained from the filtrate from the first crystallization described above was chromatographed on a silica gel preparative thin layer plate using a 30% $CH_2Cl_2$/70% hexane mixture. The band corresponding to $R_f$ = 0.48 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was removed to give helicene **20** as an amorphous yellow solid: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.22 (d, $J$ = 8.6 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.88−7.79 (m, 6H), 7.50 (dd, $J$ = 8.4 Hz, 1.9 Hz, 1H), 7.41 (d, $J$ = 8.2 Hz, 1H), 7.23 (d, $J$ = 1.9 Hz, 1H), 1.08 (s, 9H), 0.21 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.2, 147.7, 131.6, 131.4, 130.7, 130.5, 130.1, 129.8, 129.6, 129.0, 127.6, 127.4, 126.9, 126.5, 125.9, 125.3, 125.1, 125.02, 124.96, 123.8, 119.0, 39.0, 34.4, 32.4, 31.0; HRMS (TOF MS CI+) calcd for $C_{30}H_{29}Br$ ($M^+$) 468.1453, found 468.1458.

*(E)-1-(4-tert-Butylphenyl)-2-(5′-tert-butyl-8′-methyl-1′-phenanthryl)ethene (**15**).* A solution of 0.254 g (0.54 mmol) of **18** in 25 mL of dry diethyl ether was cooled to 0 °C under an argon atmosphere. *n*-BuLi (0.173 g, 2.7 mmol) as a 2.5 M solution in hexane was added dropwise to the reaction mixture over 10 min. The reaction mixture was stirred at 0 °C for 1 h during which time a dark red color developed. Dimethyl sulfate (0.68 g, 5.4 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature and was then heated under reflux for 1 h. The mixture was diluted with an additional 75 mL of diethyl ether and extracted with two 50 mL portions of 10% aq NaOH and then with 50 mL of $H_2O$ and 25 mL of brine. The organic layer was dried over $Na_2SO_4$ and the solvent removed by rotary evaporation. The resulting solid was recrystallized from EtOH to give 0.127 g (58%) of **15** as a pale yellow solid: mp 163−164 °C; $^1$H NMR


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($CDCl_3$, 400 MHz) $\delta$ 8.31 (d, $J$ = 8.2 Hz, 1H), 8.03 (d, $J$ = 9.2 Hz, 1H), 7.89 (d, $J$ = 16.0 Hz, 1H), 7.82 (d, $J$ = 9.2 Hz, 1H), 7.78−7.74 (m, 2H), 7.56 (d, $J$ = 8.3 Hz, 1H), 7.44 (d, $J$ = 8.3 Hz, 1H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.33 (dd, $J$ = 7.8 Hz, 0.7 Hz, 1H), 7.15 (d, $J$ = 16.0 Hz, 1H), 2.76 (s, 3H), 1.54 (s, 9H), 1.37 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 150.9, 146.3, 135.0, 133.8, 131.9, 131.8, 131.7, 131.5, 131.4, 130.1, 128.3, 126.6, 126.4, 125.8, 125.7, 123.8, 123.1, 122.3, 121.4, 37.9, 34.5, 31.3, 19.2; HRMS (TOF MS CI+) calcd for $C_{31}H_{34}$ ($M^+$) 406.2661, found 406.2654.

*1,11-Di-tert-butyl-4-methyl[5]phenacene (**16**) and 1,13-Di-tert-butyl-4-methyl[5]helicene (**17**).* A solution of 0.128 g (0.31 mmol) of ethene **15** and 0.096 g (0.37 mmol) of iodine in a mixture of 108 mL of hexanes and 12 mL of 1-epoxybutane was irradiated for 2 h after which time the reaction was judged complete by GC−MS analysis. The reaction mixture was washed with three 75 mL portions of aq $NaHSO_3$ followed by 75 mL of water. The organic phase was dried over $Na_2SO_4$, and the hexanes were removed by rotary evaporation to give a pale yellow solid that was chromatographed on a dry silica gel column (0.625 in. × 21 in.) using a mixture of 70% hexanes/30% $CH_2Cl_2$. The band corresponding to $R_f$ = 0.48 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was evaporated to give 0.126 g (99%) of a pale yellow solid that was shown by NMR analysis to be a mixture of 74% **16** and 26% **17**. The solid was dissolved in hot EtOH and allowed to cool slowly to room temperature whereupon a pale yellow solid crystallized out. A second recrystallization from EtOH gave pure phenacene **16**: mp 203−204 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.80 (d, $J$ = 1.7 Hz, 1H), 8.69 (d, $J$ = 9.2 Hz, 1H), 8.67 (s, 2H), 8.63 (d, $J$ = 9.3 Hz, 1H), 8.07 (d, $J$ = 9.2 Hz, 1H), 7.97 (d, $J$ = 9.2 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 7.84 (d, $J$ = 7.7 Hz, 1H), 7.73 (dd, $J$ = 8.4 Hz, 1.8 Hz, 1H), 7.39 (dd, $J$ = 7.7 Hz, 0.72 Hz, 1H), 2.74 (s, 3H), 1.61 (s, 9H), 1.54 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.5, 146.3, 131.9, 131.8, 131.6, 131.0, 130.0, 129.9, 129.8, 129.1, 128.5, 128.4, 128.2, 127.7, 126.60, 126.55, 125.0, 123.5, 121.3, 120.8, 118.6, 117.0, 38.0, 35.4, 34.6, 31.6, 19.3; HRMS (TOF MS CI+) calcd for $C_{31}H_{32}$ ($M^+$) 404.2504, found 404.2505.

The filtrate from the first crystallization was chromatographed on a silica gel preparative thin layer plate with a 30% $CH_2Cl_2$/70% hexane mixture. The band corresponding to $R_f$ = 0.54 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was evaporated and the resulting material recrystallized from EtOH to give helicene **17** as a pale yellow solid: mp 213.0−214.5 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.99 (d, $J$ = 8.5 Hz, 1H), 7.88−7.83 (m, 2H), 7.81−7.78 (m, 3H), 7.75 (d, $J$ = 8.5 Hz, 1H), 7.47 (dd, $J$ = 8.4 Hz, 1.9 Hz, 1H), 7.44−7.43 (m, 2H), 7.23 (d, $J$ =1.9 Hz, 1H), 2.81 (s, 3H), 1.06 (s, 9H), 0.22 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 147.4, 147.1, 132.0, 131.5, 131.1, 130.5, 130.4, 130.1, 129.8, 128.4, 128.1, 127.3, 127.2, 126.7, 126.4, 125.7, 125.3, 124.9, 124.70, 124.65, 123.9, 123.2, 38.5, 34.4, 32.6, 31.0, 19.3; HRMS (TOF MS CI+) calcd for $C_{31}H_{32}$ ($M^+$) 404.2504, found 404.2498.

*(E)-1-(4-tert-Butylphenyl)-2-(5′-tert-butyl-1′-phenanthryl)ethene (**21**).* A solution of 0.38 g (0.81 mmol) of **18** in 20 mL of dry diethyl ether was cooled to 0 °C under an argon atmosphere after which *n*-BuLi (0.103 g, 1.6 mmol) as a 2.5 M solution in hexane was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 1 h during which time it turned dark red. Water (8.0 mL) was then added dropwise over 20 min. The reaction mixture was allowed to warm to room temperature where it was maintained for 1 h. The mixture was diluted with an additional 50 mL of diethyl ether and washed successively with 50 mL of 5% $H_3PO_4$, 50 mL of aq $NaHCO_3$ and 50 mL of water. The organic layer was dried over $Na_2SO_4$ and the solvent removed by rotary evaporation. The resulting solid was recrystallized from a methanol/hexanes mixture to give 0.24 g (76%) of **21** as a white crystalline solid: mp 179−180 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.38 (bd, $J$ = 8.2 Hz, 1H), 7.99 (d, $J$ = 9.0 Hz, 1H), 7.88 (dd, $J$ = 7.7 Hz, 1.2 Hz, 1H), 7.86 (d, $J$ =16.0 Hz, 1H), 7.75 (d, $J$ = 7.2 Hz, 1H), 7.62−7.58 (m, 2H), 7.56−7.53 (m, 2H), 7.47 (t, $J$ = 7.6 Hz, 1H), 7.44−7.38 (m, 3H), 7.13 (d, $J$ = 16.0 Hz, 1H), 1.58 (s, 9H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 150.9, 135.0, 134.1, 133.3, 131.71, 131.69, 131.5, 128.7, 127.6, 126.4, 125.9, 125.7, 125.2, 123.9, 122.6, 121.8, 38.0, 34.7, 34.4, 31.3; HRMS (TOF MS CI+) calcd for $C_{30}H_{33}$ (M + 1) 393.2582, found 393.2574.

*1,11-Di-tert-butyl[5]phenacene (**22**) and 1,13-Di-tert-butyl[5]-helicene (**23**).* A solution of 0.177 g (0.45 mmol) of ethene **21** and 0.126 g (0.50 mmol) of iodine in a mixture of 162 mL of hexanes and 18 mL of 1-epoxybutane was irradiated for 3 h, after which time the reaction was judged complete by GC−MS analysis. The reaction mixture was extracted with four 75 mL portions of aq $NaHSO_3$ followed by 75 mL of water. The organic phase was then dried over $Na_2SO_4$ and, the hexanes were removed by rotary evaporation to give a pale yellow solid that was chromatographed on a dry silica gel column (0.625 in. × 21 in.) using a mixture of 50% hexanes/50% $CH_2Cl_2$. The band corresponding to $R_f$ = 0.57 was isolated, and the silica gel was extracted with diethyl ether in a Soxhlet. The ether was removed to give 0.162 g (92%) of a pale yellow solid shown by NMR analysis to be a mixture of 77% **16** and 23% **17**. This solid was dissolved in hot EtOH and allowed to cool slowly to room temperature whereupon a pale yellow solid crystallized out. A second recrystallization from EtOH gave pure phenacene **22**: mp 184−185 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.81 (d, $J$ = 1.3 Hz, 1H), 8.74−8.67 (m, 3H), 8.61 (d, $J$ = 9.0 Hz, 1H), 7.98−7.93 (m, 3H), 7.87 (d, $J$ = 9.0 Hz, 1H), 7.75−7.70 (m, 2H), 7.54 (t, $J$ = 7.6 Hz, 1H), 1.66 (s, 9H), 1.54 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.2, 148.2, 133.0, 131.3, 130.4, 129.7, 129.4, 129.3, 128.5, 128.2, 127.9, 127.7, 127.6, 126.4, 125.9, 125.0, 124.8, 121.1, 120.9, 118.4, 116.9, 37.9, 35.1, 34.3, 31.3; HRMS (TOF MS CI+) calcd for $C_{30}H_{30}$ ($M^+$) 390.2348, found 390.2338.

The filtrate from the first crystallization was chromatographed on a silica gel preparative thin layer plate with a 25% $CH_2Cl_2$/75% hexane mixture. The band corresponding to $R_f$ = 0.40 was isolated and the silica gel extracted with diethyl ether in a Soxhlet. The ether was evaporated and the resulting material recrystallized from methanol to give helicene **23** as a pale yellow solid: mp 163−164 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.88−7.74 (m, 7H), 7.71 (d, $J$ = 8.3 Hz, 1H), 7.57−7.56 (m, 2H), 7.48 (dd, $J$ = 8.4 Hz, 1.9 Hz, 1H), 7.30 (d, $J$ = 1.9 Hz, 1H), 1.05 (s, 9H), 0.26 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.2, 147.4, 133.1, 131.5, 131.4, 130.5, 130.0, 129.7, 128.5, 128.2, 127.4, 127.2, 126.7, 126.4, 125.9, 125.4, 125.3, 125.1, 125.0, 124.8, 124.7, 123.9, 38.8, 34.4, 32.5, 31.0; HRMS (TOF MS CI+) calcd for $C_{30}H_{30}$ ($M^+$) 390.2348, found 390.2332.

*1-Methyl-7-naphthaldehyde (**39**).* The aldehyde was prepared as described previously.[6,7] The crude product was recrystallized from hexanes to give **39** as a white crystalline solid (3.02 g, 80%): mp 54.5−55.5 °C (lit.[7] mp 55.5−56.5 °C).

*(E)-1-(2-Bromophenyl)-2-(8′-methyl-2′-naphthyl)ethene (**40**).* A procedure similar to that employed for the preparation of **36** was used. From 5.45 g (17.7 mmol) of diethyl 2-bromobenzylphosphonate[8] and 3.02 g (17.7 mmol) of aldehyde **39**[7] there was obtained, after recrystallization of the crude product from EtOH, 4.04 g (71%) of **40** as white needles: mp 115−116 °C; $^1H$ NMR ($C_6D_6$, 400 MHz) $\delta$ 7.90 (br s, 1H), 7.78 (d, $J$ = 16.1 Hz, 1H), 7.72 (dd, $J$ = 8.6 Hz, 1.7 Hz, 1H), 7.64 (d, $J$ = 8.6 Hz, 1H), 7.54 (d, $J$ = 8.2 Hz, 1H), 7.43 (dd, $J$ = 8.1 Hz, 1.1 Hz, 1H), 7.41 (dd, $J$ = 7.4 Hz, 1.6 Hz, 1H), 7.20 (t, $J$ = 7.0 Hz, 1H), 7.12 (d, $J$ = 6.9 Hz, 1H), 7.04 (d, $J$ = 16.2 Hz, 1H), 6.95 (td, $J$ = 7.5 Hz, 0.6 Hz, 1H), 6.70 (td, $J$ = 7.6 Hz, 1.6 Hz, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 137.2, 134.5, 134.4, 133.4, 133.1, 132.8, 132.0, 129.1, 128.8, 127.6, 127.2, 126.7, 126.2, 125.9, 124.2, 123.9, 123.0, 19.4; HRMS (TOF MS CI+) calcd for $C_{19}H_{15}Br$ ($M^+$) 322.0357, found 322.0364.

*9-Bromo-1-methylbenzo[c]phenanthrene (**41**).* The general procedure was similar to that described for the preparation of **11**. Ethene **40** (2.00 g, 6.2 mmol) and iodine (0.39 g, 1.5 mmol) were dissolved in a mixture of hexanes (800 mL) and toluene (200 mL) and irradiated for 18 h. After the usual workup there was obtained a tan material that was recrystallized from EtOH to give **41** (1.58 g, 79%) as an off-white solid: mp 97−98 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.40 (dd, $J$ = 8.8 Hz, 1.7 Hz, 1H), 7.99 (br d, $J$ = 8.4 Hz, 1H), 7.97 (d, $J$ = 8.8 Hz, 1H), 7.89−7.84 (m, 2H), 7.85 (dd, $J$ = 7.5 Hz, 1.1 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 1H), 7.62 (t, $J$ = 7.5 Hz, 1H), 7.54 (br d, $J$ = 7.0 Hz, 1H), 7.39 (dd, $J$ = 8.4 Hz, 7.6 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 135.8, 134.3, 131.81, 131.77, 130.5, 129.87, 129.85, 129.51, 129.45, 128.5,


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127.5, 126.9, 126.2, 126.0, 125.54, 125.49, 125.2, 122.4, 24.8; HRMS (TOF MS CI+) calcd for $C_{19}H_{13}Br$ ($M^+$) 320.0201, found 320.0212.

*1-Methylbenzo[c]phenanthrene-9-carboxaldehyde (**42**).* A procedure similar to that used for the preparation of **33** was followed. From 1.58 g (4.9 mmol) of **41** a crude product was obtained that was purified by dry column chromatography using 90% $CH_2Cl_2$/10% hexanes as solvent. The relevant fractions were extracted from the silica in a Soxhlet using ethyl acetate to give, after removal of the solvent by rotary evaporations, **42** (0.84 g, 63%) as a pale yellow solid: mp 101.5−103 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 10.55 (s, 1H); 9.35 (dd, $J$ = 8.9 Hz, 0.7 Hz, 1H), 8.29 (d, $J$ = 8.4 Hz, 1H), 8.08 (dd, $J$ = 7.12 Hz, 1.3 Hz, 1H), 8.07 (d, $J$ = 9.0 Hz, 1H), 7.90 (d, $J$ = 8.5 Hz, 1H), 7.88 (br d, $J$ = 9.4 Hz, 1H), 7.78 (d, $J$ = 8.4 Hz, 1H), 7.70 (dd, $J$ = 8.4 Hz, 7.1 Hz, 1H), 7.64 (t, $J$ = 7.5 Hz, 1H), 7.56 (dd, $J$ = 7.2 Hz, 0.6 Hz, 1H), 2.37 (s, 3H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 193.6, 136.8, 135.6, 134.9, 134.3, 131.7, 130.9, 130.7, 130.0, 129.8, 129.4, 129.3, 128.6, 126.9, 126.3, 125.7, 125.5, 123.9, 123.2, 24.7; HRMS (TOF MS CI+) calcd for $C_{20}H_{14}O$ ($M^+$) 270.1045, found 270.1049.

*(E)-1-(4-tert-Butylphenyl)-2-(1′-methyl-9′-benzo[c]phenanthryl)-ethene (**27**).* A procedure similar to that employed for the preparation of **36** was used. From diethyl 4-*tert*-butylbenzylphosphonate[9] (0.375 g, 1.3 mmol) and aldehyde **42** (0.356 g, 1.3 mmol) **27** (0.236 g, 44%) was obtained after recrystallization from EtOH as a white solid: mp 168−171 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 8.55 (d, $J$ = 8.6 Hz, 1H), 8.19 (d, $J$ = 16.1 Hz, 1H), 8.04 (d, $J$ = 8.9 Hz, 1H), 7.99−7.95 (m, 4H), 7.88 (d, $J$ = 8.4 Hz, 1H), 7.74−7.72 (m, 2H), 7.68 (d, $J$ = 7.4 Hz, 1H), 7.67 (d, $J$ = 7.5 Hz, 1H), 7.61 (br d, $J$ = 7.2 Hz, 1H), 7.52−7.50 (m, 2H), 7.34 (d, $J$ = 16.1 Hz, 1H), 2.41 (s, 3H), 1.38 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$) $\delta$ 151.0, 135.9, 135.0, 134.7, 134.2, 131.9, 131.4, 130.7, 130.0, 129.97, 129.7, 129.6, 127.9, 127.4, 126.5, 126.0, 125.9, 125.8, 125.7, 125.6, 125.4, 124.7, 123.3, 123.2, 34.7, 31.3, 24.9; HRMS (TOF MS CI+) calcd for $C_{31}H_{28}$ ($M^+$) 400.2191, found 400.2206.

*2-tert-Butyl-14-methylbenzo[c]picene (**28**).* The general procedure was as described previously for the preparation of **11**. Ethene **27** (0.0483 g, 0.12 mmol) and iodine (0.0077 g, 0.03 mmol) were dissolved in hexanes (50 mL), and the solution was irradiated for 2 h. After the usual workup there was obtained **28** (0.0442 g, 92%) as a tan solid: mp 229−230.5 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.93 (d, $J$ = 8.7 Hz, 1H), 8.83−8.79 (m, 3H), 8.24 (d, $J$ = 9.3 Hz, 1H), 8.10 (d, $J$ = 8.8 Hz, 1H), 8.03 (d, $J$ = 9.1 Hz, 1H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.89 (br d, $J$ = 8.0 Hz, 1H), 7.88 (d, $J$ = 8.5 Hz, 1H), 7.82 (d, $J$ = 8.5 Hz, 1H), 7.75 (dd, $J$ = 8.4 Hz, 1.8 Hz, 1H), 7.65 (t, $J$ = 7.8 Hz, 1H), 7.58 (br d, $J$ = 6.1 Hz, 1H), 2.48 (s, 3H), 1.55 (s, 9H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.6 MHz) $\delta$ 149.5, 136.2, 134.3, 131.5, 130.1, 130.0, 129.7, 129.5, 129.1, 129.0, 128.9, 128.2, 128.0, 127.9, 127.5, 126.8, 126.3, 126.1, 125.7, 125.4, 125.1, 122.5, 121.2, 119.7, 118.6, 35.4, 31.6, 24.9; HRMS (TOF MS CI+) calcd for $C_{31}H_{26}$ ($M^+$) 398.2035, found 398.2023.

*11-Bromo-4-methyl-1,13,15,17-tetra-tert-butyl[7]phenacene (**25**)[3b] and 9-Bromo-3,11,13,15-tetra-tert-butyl-18-methylnaphtho-[1,2-a]picene (**26**).* A solution of 0.058 g (0.083 mmol) of (*E*)-1-(8-bromo-4,6-di-*tert*-butyl-1-phenanthryl)-2-(8′-methyl-3′,5′-di-*tert*-butyl-1′-phenanthryl)ethene (**24**)[3b] and 0.08 g (0.32 mmol) of iodine in 100 mL of hexanes was irradiated for 6 h after which time the reaction was judged to be complete by NMR analysis. The reaction mixture was washed with aq $NaHSO_3$ and then with water. The organic phase was dried over $Na_2SO_4$, and the hexanes were removed by rotary evaporation. The resulting solid, 0.047 g (81%), was shown by NMR analysis to be a mixture of 88% phenacene **25**[3b] and 12% helicene **26**.[4] Recrystallization from a 95% ethanol/toluene mixture gave a sample of **25** that was fully characterized by NMR and by single-crystal X-ray analysis as reported previously.[3b] We were unable to isolate a pure sample of the helicene **26** from the mixture.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Copies of $^1$H and $^{13}$C{$^1$H} NMR spectra, high-resolution mass spectra, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(4) We reported previously[3b] that the photocyclization of **24** gave a 63% yield of **25**. Recent reinvestigation of the NMR analysis showed that a small amount (10%) of the helicene **26** was also formed. The structure of **26** was deduced from careful analysis of the NMR spectrum of the mixture and comparison of the characteristic signals from the *tert*-butyl groups with those present in all the other helicenes isolated and reported in this paper.

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