New Molecular Devices: In Search of a Molecular Ratchet

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The triptycene-substituted [3]- and [4]helicenes **1** and **2** were examined as possible molecular versions of mechanical ratchets, where the triptycene serves as the ratchet wheel and the helicenes as pawl and spring. The syntheses of **1** and **2b** are described. ^{1}H NMR was employed to examine rotation around the triptycene/helicene single bond; at 20 °C rotation is frozen for both **1** and **2b**, but the NMR of **1** revealed a plane of symmetry, indicating that **1** cannot function as a unidirectional ratchet. In contrast, NMR revealed that, like a ratchet, triptycyl[4]helicene **2b** lacks the symmetry of **1** and has a barrier to rotation of 24.5 kcal/mol, but spin polarization transfer NMR experiments indicated the triptycene in **2b** nonetheless rotates equally in both directions. That outcome is rationalized from the standpoint of thermodynamics.

Introduction

The dynamics and control of rotational motion about single bonds has engaged the attention of chemists for decades. Once-forefront issues such as rotation around the carbon−carbon bond in ethane have been superseded over time by more subtle aspects of conformational isomerism.[1] Interest in recent years has been further fueled by conceptual linkages between macromechanical issues of rotation and molecular variations on the same themes, as illustrated by reports of molecular gears,[2] brakes,[3] and turnstiles.[4] A key issue is identifying which everyday mechanical concepts can be extrapolated to the molecular scale.

In conjunction with a longer-term goal of devising a molecule that functions as a motor, this laboratory has been exploring various aspects of rotary motion at the molecular level. To that end, we reported in 1994 work culminating in the development of a molecular brake.[3a] More recently, we described in a brief communication[5] our examination of molecules that might function as molecular ratchets. We now present in greater detail our efforts to construct molecular ratchets and address some of the conceptual issues that pertain.

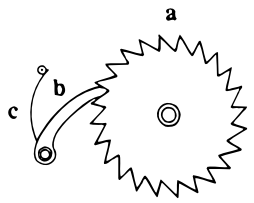
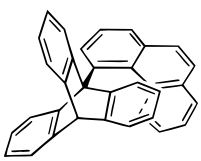


Figure 1. Simple mechanical ratchet: (a) a ratchet wheel; (b) a pawl; (c) a spring that holds the pawl against the wheel.

Commonly, ratchets are devices that allow rotary motion in only one direction; in their simplest form they consist of three components (Figure 1): (a) a toothed ratchet wheel; (b) a pawl that prevents unintended rotation of the ratchet wheel; and (c) a spring that holds the pawl in place. In seeking to translate the macroscopic concept of the ratchet to the molecular scale, we chose compounds **1** and **2** as possible candidates, where the



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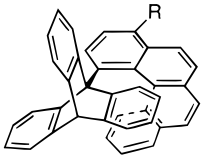

2 **a**, R= H
b, R= Me

triptycene[6] acts as the wheel and the helicenes[7] function as the pawl and spring. Examination of models, particularly of **2**, indicates a distinctly helical conformation of the [4]helicene unit; that asymmetry is evident in Figure 2, which is a stereoview of an electron density

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(1) (a) For a leading reference see: Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994. (b) See also: Oki, M. *Top. Stereochem.* **1983**, *14*, 1−81 (note especially Section III).

(2) (a) Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175−182. (b) Mislow, K. *Chemtracts: Org. Chem.* **1989**, *2*, 151−174. (c) Nakamura, M.; Oki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2106−2111. (d) Oki, M.; Fukuda, T.; Asakura, M.; Toyota, S. *Ibid.* **1996**, *69*, 3267−3272. (e) Yamamoto, G. *Tetrahedron* **1990**, *46*, 2761−2772. (f) Kawada, Y.; Sakai, H.; Oguri, M.; Koga, G. *Tetrahedron Lett.* **1994**, *35*, 139−143. (g) Stevens, A. M.; Richards, C. J. *Ibid.* **1997**, *38*, 7805−7808. (h) Gakh, A. A.; Sachleben, R. A.; Bryan, J. C. *Chem Tech* **1997**, *27*, 26−33.

(3) (a) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; García, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657−3658. See the supplementary material appended thereto for detailed synthetic procedures. See also: (b) Casares, J. A.; Coco, S.; Espinet, P.; Lin, Y.-S. *Organometallics* **1995**, *14*, 3058−3067. (c) Fanizzi, F. P.; Lanfranchi, M.; Natile, G.; Tiripicchio, A. *Inorg. Chem.* **1994**, *33*, 3331−3339.

(4) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662−10671.

(5) Kelly, T. R.; Tellitu, I.; Sestelo, J. P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1866−1868. For a "Highlight" featuring this paper see: Davis, A. P. *Ibid.* **1998**, *37*, 909−910.

(6) For a review of triptycenes see: Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev.* **1974**, *43*, 951−966.

(7) For reviews of helicene chemistry, see: (a) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649−660. (b) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63−130. (c) Meurer, K. P.; Vögtle, F. *Ibid.* **1985**, *127*, 1−76. Some more recent papers: (d) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983−3986. (e) Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093−1094. (f) Janke, R. H.; Haufe, G.; Würthwein, E.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031−6035.

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Figure 2. Stereoview of an electron-density surface map of the lowest energy conformation of **2a**.

surface map of the lowest energy conformation of **2a**. Manual rotation of the triptycene in models of **2** forces the helicene further and further out of planarity until the energy maximum is reached. That rotation is accomplished much more easily with a clockwise instead of a counterclockwise turning of the triptycene (as viewed from the left, for the enantiomer of **2** that is shown in Figure 2), as would be expected of a ratchet.

The conformation and chirality of helicenes have attracted the attention of many researchers over the years.[7] We chose to enlist helicenes as springs because they have an inherent helicity and because they resist deformation. Their resistance to being further twisted is not insurmountable because they can be caused to racemize, but their tendency to oppose deformation, and to return to their original geometry, reflects the characteristics of a spring. Several studies[8] have shown that the energy of activation for racemization of helicenes depends on the size and substituents in the helicene.

Preliminary Studies

A key parameter leading to the decision to investigate triptycylhelicene systems as possible ratchets was the barrier to rotation around the triptycene/helicene bond. We sought molecules with a barrier on the order of 18−27 kcal/mol in order to facilitate measurement by NMR. Molecules possessing a barrier to rotation in that range do not rotate on the NMR time scale at room temperature but will at temperatures accessible with a variable-temperature NMR probe. Guided by computer modeling of barriers to rotation, we chose **1** and **2** as possible candidates. Calculations[9] indicated that the barriers (in terms of $\Delta H^{\ddagger}$) to rotation in **1** and **2** were 27 and 22 kcal/mol, respectively. To our minds, those calculated barriers to rotation were invested with some credibility when the same calculations were applied to rotation around the

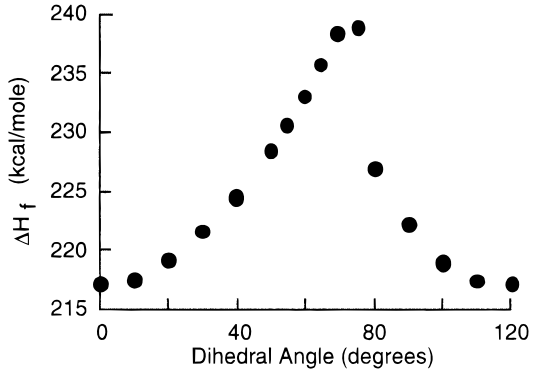
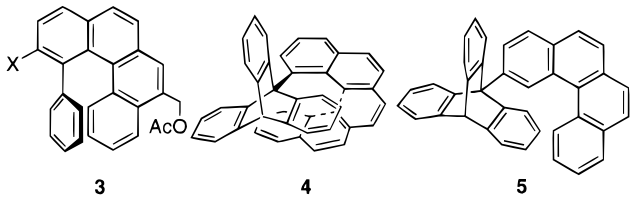


Figure 3. Calculated[9a] (AM1) energetics for clockwise[9b] rotation around the triptycene/[4]helicene bond in **2a**. Clockwise rotation of the triptycene in **2a** corresponds to a left-to-right progression on the *x* axis.

phenyl/[4]helicene bond in **3** (X = H). Laarhoven[10] has previously determined the barrier ($\Delta G^{\ddagger}$) experimentally to be 12.8 ± 0.3 kcal/mol. Our calculated barrier ($\Delta H^{\ddagger}$, not $\Delta G^{\ddagger}$) is 9.6 kcal/mol. Using $\Delta H^{\ddagger}$ values to predict $\Delta G^{\ddagger}$ values is not rigorous, but we hoped it would serve as a useful guide. If it developed that the calculated $\Delta H^{\ddagger}$ barriers for **1** and **2** also underestimated the actual barriers ($\Delta G^{\ddagger}$), then the barriers might be too high to quantitate using NMR. In that event, we could use a pentahelicene pawl as in **4**, since the calculated barrier to rotation is only 16 kcal/mol. On the other hand, if the actual barriers in **1** and **2** proved substantially lower than the calculated barriers, then they could be increased by introduction of substituents on the helicene ortho to the triptycene, as substituents ortho to the phenyl ring (i.e., X ≠ H) in analogues of **3** can increase the barrier to rotation by several kcal/mol.[10]



3 **4** **5**

Since the calculated barriers proved, in retrospect, to be remarkably (to us) accurate in predicting the experimentally observed barriers to rotation in **1**−**3**, mention of two additional points seems warranted. First, and not surprisingly, the site of attachment of the triptycene to the helicene has a major impact on the barrier to rotation, as would be expected if the helicene is functioning as a spring and pawl in **2**. Thus, in contrast to **2**, where the calculated barrier ($\Delta H^{\ddagger}$) to rotation is 22 kcal/mol, the calculated barrier for the rotation of the helicene in **5** is only 4 kcal/mol.

Second, the barrier to rotation is calculated to be higher in **1** than in **2**. It was counterintuitive to us that a bigger pawl (as in **2**) would lead to a smaller barrier. But since experiments bear out the calculations, an explanation is required. We suggest that the barrier to rotation in **2** is less than in **1** because in **2** the interaction between the one-ring-longer helicene and the blade of the triptycene prevents the molecule from relaxing to as stable a

(8) (a) Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* **1972**, 3707−3708. (b) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 347−349. (c) Scherübl, H.; Fritzsche, U.; Mannschreck, A. *Chem. Ber.* **1984**, *117*, 336−343.

(9) (a) Calculations (AM1) were carried out using the coordinate drive feature of the Spartan molecular modeling program (Wavefunction, Inc., Irvine, CA), Version 4.0, on a Silicon Graphics workstation. (b) The same calculations (Spartan AM1 coordinate drive) give a significantly different potential energy curve for counterclockwise (120° → 0° dihedral angle) rotation. The calculations for counterclockwise rotation give an energy maximum ca. 5 kcal/mol higher than for clockwise rotation and, in contrast to clockwise rotation, are accompanied by inversion of the helicity of the helicene. In contrast, experimental determinations (vide infra) indicate that helicene inversion is an appreciably higher energy process[7] than triptycene rotation. Given the principle of microscopic reversibility, we attribute the clockwise/counterclockwise difference to a limitation of the calculational program, at least as employed by us.

(10) Laarhoven, W. H.; Peters, W. H. M.; Tinnemans, A. H. A. *Tetrahedron* **1978**, *34*, 769−777.

Figure 4. Space-filling models of calculated minimum (left) and maximum energy conformations of **2a**.

ground-state conformation (relative to the energy maximum) as is accessible to **1**. The even lower calculated barrier for rotation in **4** can be accounted for analogously.

Figure 3 presents a plot of the calculated energy of **2a** as a function of rotation around the triptycene/helicene bond. The asymmetry of the peak is consistent with what might be expected if **2a** rotated unidirectionally. Figure 4 depicts space-filling models corresponding to the minimum and maximum energy conformations of **2a**. Note the difference in the position of the helicene.

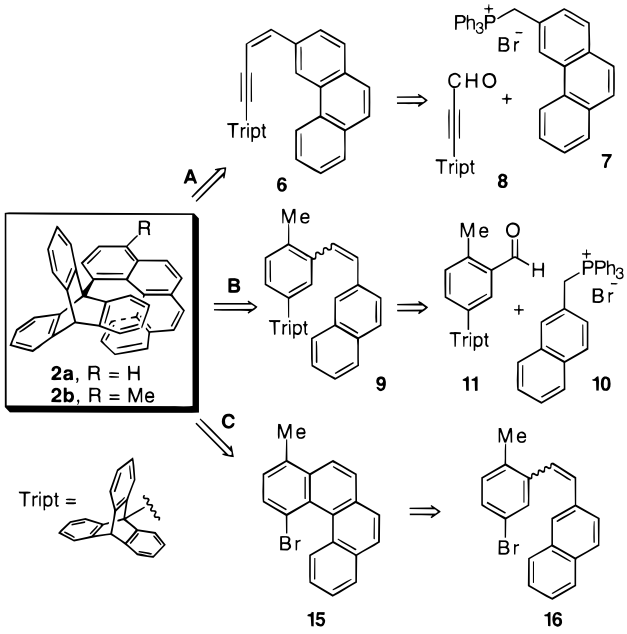
On the basis of the foregoing considerations, we decided to first undertake the synthesis of the 1-triptycyl[4]-helicenes **2**, whose anticipated barrier to rotation seemed most amenable to assessment by NMR. To study and compare the theoretical calculations, the synthesis of the 4-triptycylphenanthrene **1** was also carried out.

Results and Discussion

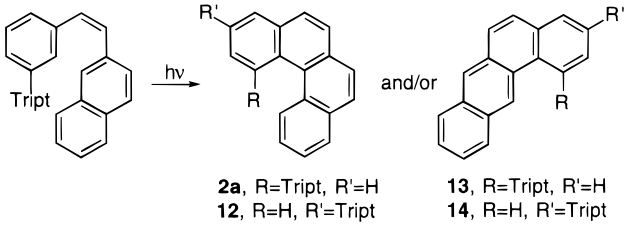
Synthetic Considerations. From retrosynthetic analysis, we envisioned the synthesis of the triptycene-helicene systems being based on photocyclization approaches. To date, carbohelicenes have been mainly synthesized by using stilbene photocyclizations,[11] although lately, alternative synthetic strategies have been reported.[7d−f] Relatively few examples of the synthesis of 1-substituted helicenes have been reported, and yields are generally low.[7,10] Nevertheless, Tinnemans and Laarhoven[12] have reported the synthesis of 4-phenylphenanthrene and 1-phenylbenzo[*c*]phenanthrene (**3**)-from 1,4-diarylenynes using an enyne photocyclization. On the basis of these stilbene and enyne photocyclization precedents, we considered three different approaches to the 1-triptycyl[4]helicene system (Scheme 1).

Approach **A** is based on the photocyclization of the enyne **6** obtained from Wittig reaction between the ylide of the phosphonium salt **7** and the propargylic aldehyde **8**. The regioselectivity of the photocyclization should be controlled by electronic effects.[12] Approach **B** entails the photocyclization of a stilbene (**9**) where the triptycene unit has already been installed. Although electronic effects should favor[11] the formation of the benzo[*c*]-phenanthrene over the benzo[*c*]anthracene isomers (**13** and **14**, Scheme 2), it was nonetheless likely that predominant—if not exclusive—formation of the undesired 3-substituted benzo[*c*]phenanthrene regiosomer (**12**) instead of the desired (**2a**) would occur because of the steric bulk of the triptycene. It should[11] be possible, however, to suppress cyclization at the undesired site by

Scheme 1



Scheme 2



blocking it with, e.g., a methyl group as in **9** (Scheme 1), thereby obtaining **2b**, the methylated analogue of **2a**. The stilbene **9** would be formed by Wittig reaction between the ylide derived from **10** and the triptycene−aldehyde unit **11**, available from the known[13] 5-bromo-*o*-tolualdehyde via Stille coupling with a 9-stannylanthracene and subsequent benzyne addition.

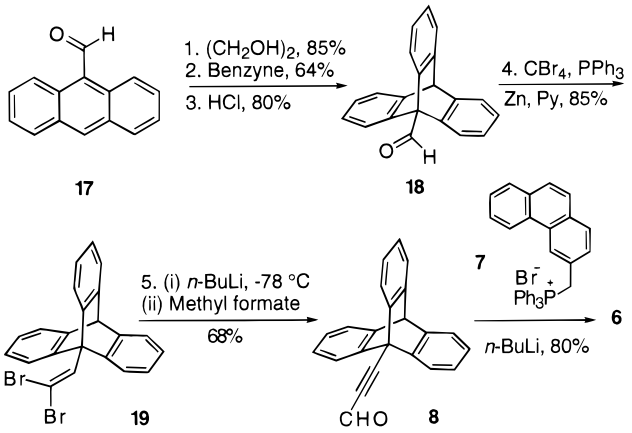
Alternatively, approach **C** was considered in the case of a stilbene photocyclization failure due to the steric bulk of the triptycene. In approach **C**, incorporation of the triptycene (or a precursor to it) would be achieved at the end of the synthesis through the 1-bromobenzo[*c*]phenanthrene **15**. Analogous synthetic strategies were planned for constructing 4-triptycylphenanthrene **1**, although for this compound nonphotochemical routes were also envisaged.

Enynic Route. The synthesis began with a known[3a] preparation of triptycene aldehyde **18** starting from the commercially available anthracene-9-carboxaldehyde **17** (Scheme 3). Carbonyl protection with ethylene glycol, triptycene generation via benzyne addition, and subsequent deprotection afforded the aldehyde **18** in moderate yield. A Corey−Fuchs reaction[14] gave the vinyl dibromide **19**, which was transformed through treatment with *n*-BuLi at −78 °C and trapping of the resulting alkynyllithium with methyl formate to give the desired propargylic aldehyde **8** in good yield. Treatment of [(3-

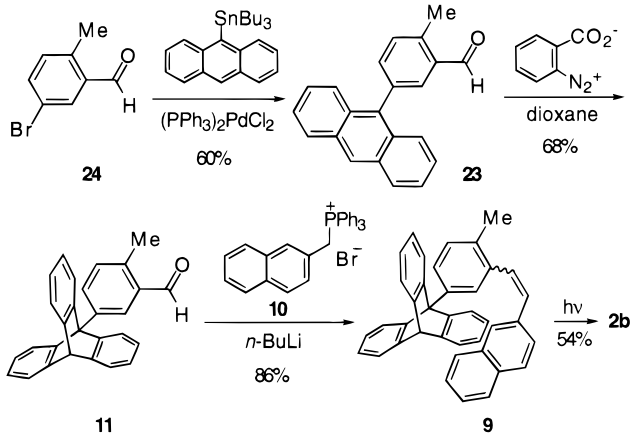
(11) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1−456.
(12) (a) Tinnemans, A. H. A.; Laarhoven, W. H. *Tetrahedron Lett.* **1973**, 817−820. (b) Tinnemans, A. H. A.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1111−1115. (c) Tinnemans, A. H. A.; Laarhoven, W. H. *Ibid.* **1976**, 1115−1121.

(13) Stoilov, I.; Watt, D. S.; Goodman, J. P.; Pyrek, J. St. *J. Heterocycl. Chem.* **1993**, *30*, 1645−1651.
(14) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769−3772.

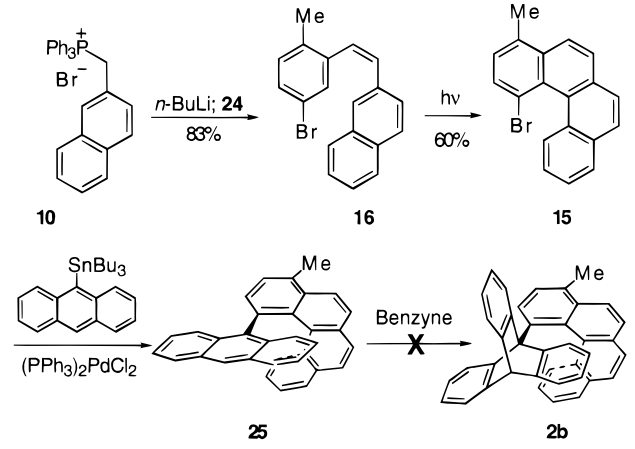
Scheme 3



Scheme 4



Scheme 5



phenanthryl)methyl]triphenylphosphonium bromide[15] (**7**) with *n*-BuLi and Wittig reaction of the resulting ylide with the aldehyde **8** led in 80% yield to the formation of the enyne **6** in the form of a 2:3 mixture of *cis:trans* isomers as established by ^{1}H NMR.

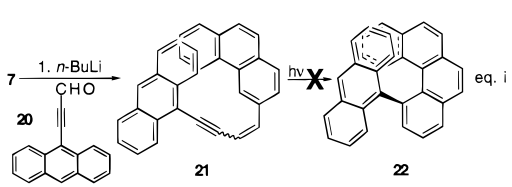
Irradiation[12] of the enyne **6** in several solvents (benzene, cyclohexane, methanol), under oxidative [I_2 (5 to 100 mol %), O_2 atmosphere] or nonoxidative (argon, deoxygenation of the system) conditions, with a mercury lamp (100 or 450 W) in a quartz apparatus with or without various filters (Pyrex, Vycor) did not afford, in any case, the desired photocyclized product. Only reduced (alkyne reduction mainly) or oxidized products were isolated. Since all the enynic photocyclizations reported[10,12] use 1,4-diarylenynes, we are inclined to attribute the failure of our reactions to the nonaromatic triptycene unit.[16]

Stilbenic Route. After the foregoing disappointing results, we abandoned approach **A** and moved to the stilbenic route (approach **B**, Scheme 1). Key steps in this route are the preparation of the aldehyde **11** and the stilbene photocyclization (Scheme 4). Starting with 5-bromo-*o*-tolualdehyde (**24**, obtained from *o*-tolualdehyde by treatment with Br_2 and $AlCl_3$),[13] we incorporated the anthracene unit using a Stille[17] coupling reaction with 9-(tributylstannyl)anthracene,[18] obtaining the aldehyde **23** in moderate yield. Regioselective addition of benzyne, generated from benzenediazonium 2-carboxylate,[19] afforded the desired triptycene aldehyde **11** in good yield. A Wittig reaction between the ylide generated from the naphthyl phosphonium salt **10**,[20] and the aldehyde **11** gave a cis/trans mixture (1:1) of stilbenes **9** in excellent yield. Irradiation[21] of the stilbene mixture with a medium-pressure mercury lamp (100 W) through a Pyrex filter in dry benzene using I_2 (1 equiv) and propylene oxide (100 equiv) over 40 h afforded the desired 1-triptycyl[4]-helicene **2b** in 54% yield. As mentioned previously, the methyl group in **9** was included for the purpose of blocking photocyclization at the undesired but otherwise less hindered position para to the triptycene. Notwithstanding that precaution, a side product was formed and identified (by ^{1}H NMR and MS) as compound **12** resulting from cyclization onto the methyl-bearing carbon of **9** with loss of the methyl group. This product (**12**) is generated in a 1:4 ratio with respect to the desired helicene **2b**.

Parallel to the development of the successful route described above, we also examined (Scheme 5) the approach **C** where key steps are the synthesis of the 1-bromobenzo[*c*]phenanthrene **15** and the attachment of the triptycene unit to it. A Wittig reaction between the ylide derived from **10**[20] and the aldehyde **24**[13] led to the formation of stilbene **16** as a 1:2.3 mixture of cis/trans isomers in excellent yield. Irradiation of the mixture with a medium-pressure mercury lamp (100 W) through a Pyrex filter for 20 h produced the desired 1-bromo[4]-

(15) (a) Akiyama, S.; Nakasuji, N.; Nakagama, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2231−2236. (b) Mallory, F. B.; Mallory, C. W. *J. Org. Chem.* **1983**, *48*, 526−532.

(16) We note, however, that when we replaced the 9-triptycyl unit in **6** by an anthracene (**21**) the results of the attempted photocyclization were equivalent (eq i). Propargylic aldehyde **20** was prepared from the corresponding dibromide (**38**): see the Experimental Section.



(17) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524.

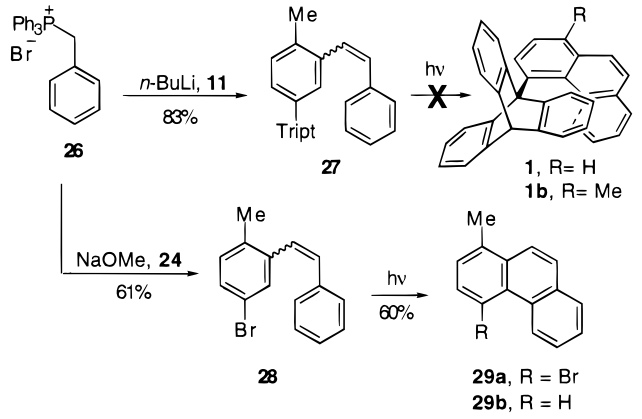
(18) Prepared[3a] from 9-bromoanthracene by metalation with *n*-BuLi and reaction of the resulting aryllithium with tributyltin chloride (98% yield).

(19) Logullo, F. M.; Seitz, A. H.; Friedman, L. *Organic Syntheses*; 1973; Collect. Vol. 5, pp 54−59.

(20) Geerts, J. P.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1960**, *60*, 563−569.

(21) See the Experimental Section for general conditions of irradiation. See also: Lui, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769−3775.

Scheme 6



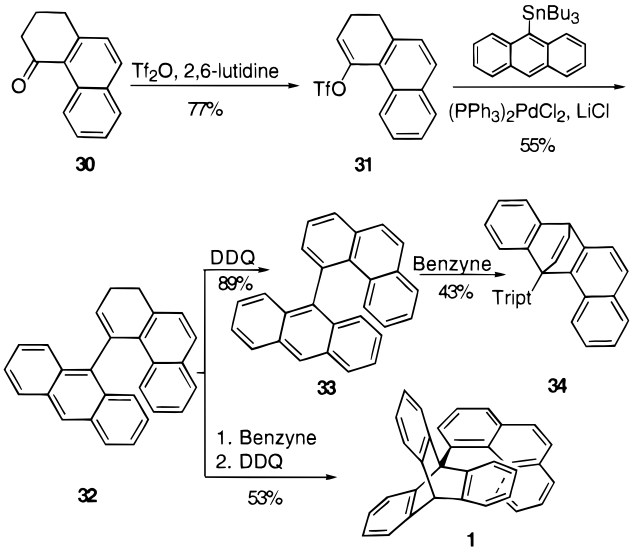
helicene **15** in good yield. Literature precedents[22] indicate that bromine substituents on benzene rings normally direct photocyclizations away from their ortho positions. In our case, however, the methyl group functions as a blocking agent and directs the reaction ortho to the bromine. Palladium-catalyzed coupling of **15** with 9-(tributylstannyl)anthracene[18] gave the desired coupled product **25** as part of a complex mixture of products.[23] Unfortunately, benzyne addition to that **25**-containing mixture, under the same experimental conditions used for the synthesis of **11**, never afforded any of the desired 1-triptycyl[4]helicene **2b**, even though by then we had an authentic sample of **2b** (from approach B) to use as an aid in assaying the outcome of the reaction.

In summary, using the convergent (four steps, 20% overall yield) stilbene photocyclization route summarized in Scheme 4, the 1-triptycyl[4]helicene **2b** was synthesized.

Synthesis of 4-(9-Triptycyl)phenanthrene (1). On the basis of the experience obtained from the synthesis of the [4]helicene **2b**, in undertaking the synthesis of 4-(9-triptycyl)phenanthrene (**1**), we initially used the stilbenic strategy (approach **B**) directly (Scheme 6). Following standard procedures we prepared the stilbene **27** as a 1:1 cis/trans mixture of isomers. Surprisingly, irradiation of the mixture under the same conditions effective for cyclizing **9** and **16** did not afford any of the desired cyclized product; instead, only cis/trans isomerization was observed. Further studies using different filters, oxidative conditions, lamps (100 or 450 W), and/or solvents failed to result in formation of any of the desired product.

These unexpected results led us to investigate alternative routes. One of them involved the introduction of the triptycene unit after construction of a 4-substituted phenanthrene (such as **29a**). The synthesis of **29a**, from **28**, was expected to be complicated by the above-noted[22] propensity of a bromo substituent to direct photocyclization away from the ortho position, but as before, an extra methyl group was expected to overcome that difficulty. A Wittig reaction between the phosphonium salt **26** and the aldehyde **24** delivered the stilbene **28** (cis/trans mixture) in good yield. Irradiation under standard

Scheme 7



conditions[15] led, unfortunately, to the photocyclization product with loss of the bromide (**29b**).[24]

Given the foregoing results, we undertook the preparation of the 4-substituted phenanthrene using a nonphotochemical route (Scheme 7). The known ketone **30**[25] was transformed into the enol triflate **31** in satisfactory yield. Palladium-catalyzed coupling of **31** with 9-(tributylstannyl)anthracene afforded **32**. Dehydrogenation[26] of **32** with DDQ afforded **33**, but reaction of the latter with benzyne failed to give any detectable amount of the desired **1**. The major isolated product, obtained in 43% yield, is tentatively assigned structure **34** and results from the addition of two molecules of benzyne to **33**. Apparently, **1** is so strained that it is more reactive than **33** toward benzyne. When the order of reaction of **32** with DDQ and benzyne was reversed, the problem was solved, the benzyne adding only across the 9,10 positions of the anthracene. The desired 4-triptycylphenanthrene (**1**) was thus obtained from **30** in a three-pot sequence in 23% overall yield.

NMR Data Analysis. The ^{1}H NMR spectra of **1** and **2b** indicate that at room temperature rotation around the triptycene/helicene bond is frozen in both compounds but that the topology of the two is distinctly different. In particular, the ^{1}H NMR spectrum of **1** reveals a plane of symmetry since two (but not all three) of the rings of the triptycene unit are equivalent. The phenanthrene component of **1** is therefore either planar or exists as a rapidly racemizing mixture of two helicene enantiomers. Even at 160 °C, the upper temperature limit of the NMR probe, ^{1}H NMR spin polarization transfer experiments (see below) reveal no detectable rotation within two seconds of polarization, which indicates a barrier ($\Delta G^{\ddagger}$) to rotation around the triptycene/phenanthrene bond in excess of 27 kcal/mol.

The ^{1}H NMR room-temperature spectrum of **2b** reflects an absence of symmetry, where all three rings of the triptycene are nonequivalent. At 160 °C, but not at lower temperatures, however, some peak-broadening of trip-

(22) (a) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231−2234. (b) Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790−2791. (c) Liu, T.; Katz, T. J. *Tetrahedron Lett.* **1991**, *32*, 6831−6834.

(23) Compound **25** was identified by MS; its ^{1}H NMR spectrum suggests a mixture of two compounds.

(24) Haworth, R. D. *J. Chem. Soc.* **1932**, 1125−1133.

(25) Huggenberg, S.; Hesse, M. *Helv. Chem. Acta* **1980**, *63*, 2295−2301.

(26) Tashiro, M.; Yamato, T.; Kobayashi, K.; Arimura,T. *J. Org. Chem.* **1987**, *52*, 3196−3199.

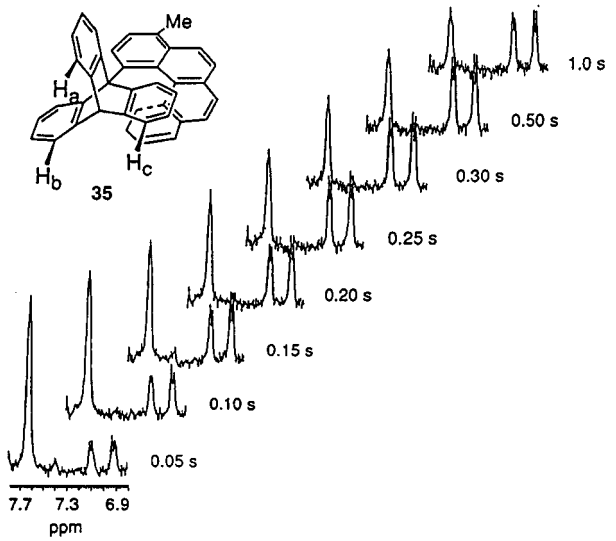


Figure 5. Results of spin polarization transfer experiment at 160 °C (calibrated temperature). The resonances for H_a, H_b, and H_c (see **35**) appear at δ 7.6, 7.1, and 6.9 ppm (not necessarily respectively). The spin of the proton resonating at δ 7.6 was polarized, and transfer of that polarization was monitored over time.

tycene (but not helicene) resonances is observed, indicating somewhat less retarded rotation. Extrapolation, based on analogy to our earlier work,[3a] suggested a coalescence temperature of about 220 °C, which corresponds to a $\Delta G^{\ddagger}$ of approximately 25 kcal/mol, a value that is corroborated by the studies described below and which is reassuringly close to the calculated barrier ($\Delta H^{\ddagger}$, not $\Delta G^{\ddagger}$) of 22 kcal/mol.

Given the above, it was of interest to establish the direction of rotation of the triptycene in **2b**. Preparation of isotopically labeled rotamers of **2b** should be possible but would require extensive synthetic, rotamer-separation, and structure-determination efforts. Fortunately, the spin polarization transfer NMR technique[27] affords the same information at a small fraction of the effort. In short, if one has a system that is conformationally mobile, but that mobility is slow on the NMR time scale, then one can polarize the spin of a slowly conformationally mobile atom, wait an appropriate time, and assay where (if anywhere) that polarization has moved to.

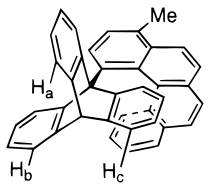
In the present case, where the experimentally determined barrier ($\Delta G^{\ddagger}$) to rotation is approximately 24.5 kcal/mol,[28] then at 160 °C a single rotamer has a half-life of about 0.17 s. Thus, if one selectively polarizes one of the three H_a, H_b, and H_c (see **35** in Figure 5) protons and—after appropriate time delays—assays for the location of that polarization, a clear-cut distinction between predominantly unidirectional rotation and bidirectional rotation is available. In the former case, a disproportionate share of the polarization that has moved should be transferred to a resonance for only one of the two other protons. In the latter case, the polarization that moves should be transferred equally to the remaining two resonances.

In the event, spin polarization of one (see **35**) of the three H_x protons in **2b** was achieved using a selective 180°-pulse-delay-observe sequence. As is evident from Figure 5, the triptycene rotates clockwise and counterclockwise to the same extent. Control experiments polarizing the spin of each of the other two H_x protons gave equivalent results.

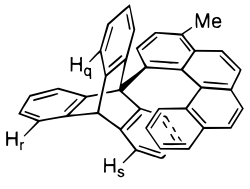
The spin polarization transfer results demonstrate unequivocally that rotation occurs equally in both directions. That is, **2b** (= **35**) does not behave as a ratchet.

Three points about the spin polarization transfer NMR experiment merit being addressed explicitly. First, although we discuss the interpretation of the results in terms of a single enantiomer of **2b**, the experiment was actually conducted on racemic material. Since enantiomers in an achiral environment give identical NMR spectra, carrying out the measurement on a single enantiomer would not have increased the information generated by the experiment and, therefore, would not have warranted the investment of effort required to develop a resolution of **2b**.

Second, since the spin polarization is transferred equally to both of the other two protons regardless of whether H_a, H_b, or H_c in **35** is polarized, it was not necessary to make specific assignments of the three relevant peaks at δ 7.6, 7.1, and 6.9. And even if polarization had transferred to only one peak, neither resolution of enantiomers nor specific peak assignments would have been necessary to distinguish between unidirectional rotation and racemization of the helicene. Consider, for example, **35** (= **2b**) and its enantiomer *ent*-**35** (= *ent*-**2b**). If unidirectional rotation of the helicene is occurring, then regardless of whether one polarizes (separately) H_a, H_b, or H_c, the spin will always transfer, and the transfer will not be degenerate; i.e., in no case will polarization transfer to two other peaks to a similar extent, and no peak will be the primary recipient of polarization transfer from more than one hydrogen. The possibility of unidirectional rotation is contradicted by the data in Figure 5.



35 (= **2b**)



ent-**35**

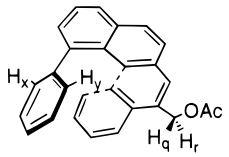
Third, since separate polarization of the resonances at 7.6, 7.1, and 6.9 is transferred equally, in each instance, to the other two resonances, one can also distinguish between uni/bidirectional rotation and helicene racemization. If the mechanism of polarization transfer were racemization of the helicene then, for example, polarization of the peak for H_b in **35** would transfer to the peak for H_s in *ent*-**35** (which is magnetically equivalent to H_c in **35**) and vice versa, but polarization would not transfer to or from H_a/H_r. The experimental results require that the rate of bidirectional rotation is, at minimum, substantially faster than that of helicene racemization. If the rate of helicene racemization were similar to or faster than the rate of bidirectional rotation, then the polariza-

(27) For leading references to the spin polarization transfer method, see: (a) Dahlquist, F. W.; Longmur, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406−410. (b) Frim, R.; Zilber, G.; Rabinovitz, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1202−1203. (c) Abdourazak, A. H.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3010−3011. For a more general review of the application of 2D NMR spectroscopy to the kinetics of exchange processes, see: Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

(28) The value of $\Delta G^{\ddagger}$ is calculated from the half−life obtained from the data in Figure 5. See, for example, Scudder, P. H. *Electron Flow in Organic Chemistry*; Wiley: New York, 1992; pp 38−40.

tion of, for instance, H_b would be transferred faster to H_s than it leaks out to H_a/H_r, which is not observed.

The present experiment avoids the complications Laarhoven faced[10] when seeking to determine the barrier to rotation around the phenyl/[4]helicene bond in **3** (X = H). NMR measurements of **3** (X = H) indicated that the resonances for H_x and H_y (see **36**) coalesce at −4 °C, but coalescence does not distinguish between equivalency arising from rotation around the phenyl/[4]helicene bond or racemization of the helicene. Laarhoven had to include a $-CH_2OAc$ unit in **3** to differentiate between the rotation and racemization mechanisms, where the persistence of an AB quartet for the methylene protons H_q and H_r in **36** under conditions where H_x and H_y become equivalent requires that rotation is occurring and excludes the helicene racemization mechanism.



36 (= **3**, X= H)

Thermodynamic Issues. For those who are fully aware of the more subtle consequences of the Second Law of Thermodynamics, the finding that the triptycene in **2b** rotates equally in both directions will come as no surprise. But for many, especially those who have manipulated models of **2**, the finding is counterintuitive. And for those who have been seduced by the models, the substantial asymmetry of the energy curve (Figure 3) for rotation around the triptycene/[4]helicene bond reinforces the expectation that rotation in one direction will be more facile than in the other. But Figure 3 contains a cautionary hint: the two energy minima flanking the energy maximum are equal in energy. More specifically, the expectation of a preferred direction of rotation overlooks an elementary consequence of energy diagrams, which requires that, unlike mountain climbing, it is only the height of the summit, not the steepness of the ascent, that matters. Put another way, the principle of microscopic reversibility rules.

The finding that **2b** does not function as a ratchet is reminiscent of the somewhat whimsical ratchet and pawl conundrum posed in 1962 by Nobel Laureate physicist Richard Feynman[29] and reiterated below.

> Let us try to invent a device that will violate the Second Law of Thermodynamics, that is, a gadget that will generate work from a heat reservoir with everything at the same temperature. Let us say we have a box of gas at a certain temperature, and inside there is an axle with vanes in it. (See Figure [6] but take $T_1 = T_2 = T$, say).

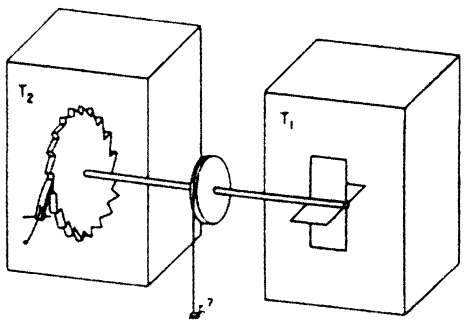


Figure 6. Ratchet and pawl machine (reproduced from ref 29).

> Because of the bombardments of gas molecules on the vane, the vane oscillates and jiggles. All we have to do is to hook onto the other end of the axle a wheel which can turn only one way—the ratchet and pawl. Then when the shaft tries to jiggle one way, it will not turn, and when it jiggles the other, it will turn. Then the wheel will slowly turn, and perhaps we might even tie a flea onto a string hanging from a drum on the shaft, and lift the flea! Now let us ask if this is possible. According to Carnot's hypothesis, it is impossible. But if we just look at it, we see, prima facie, that it seems quite possible.

If one imagines mentally taking Feynman's device (Figure 6), shrinking the axle length to zero and fusing the vanes to the ratchet wheel to give the assembly in Figure 7, then **2b** is the functional equivalent of that assembly, except that in **2b** the triptycene functions simultaneously as the wheel and the vanes, and the helicene serves double duty as the pawl and the spring. The finding that **2b** rotates equally in both directions is contrary to the Feynman scenario excerpted above. But as Feynman recognized, his argument, while tantalizing, is specious. For Feynman's device, or our **2b**, to rotate unidirectionally without an input of energy would require the violation of the Second Law of Thermodynamics.

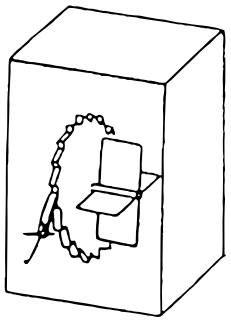


Figure 7. Machine of Figure 6 with axle length reduced to zero and vanes fused to wheel.

Conclusions. The synthesis of triptycyl[4]helicene **2b** successfully incorporates into a single molecule the essential components of a simple ratchet: the asymmetric combination of a ratchet wheel, a pawl, and a spring. Tantalizing as models of **2b** are, the experimental demonstration that **2b** rotates bidirectionally rather than unidirectionally illustrates the perils of extrapolating from macroscopic to molecular scales. It follows that molecular units such as **2** cannot be used to induce unidirectional rotation in an isothermal environment. Nonetheless, their ability to modulate the barrier to free rotation should make them useful components of more complex systems such as molecular motors and machines.

Experimental Section

General Materials and Methods. Unless otherwise stated, reactions were typically conducted under an argon atmosphere using dry, freshly distilled solvents under anhydrous conditions employing oven-dried glassware. Tetrahydrofuran (THF) and benzene were distilled from sodium/benzophenone; dichloromethane (CH_2Cl_2), triethylamine (NEt_3), and pyridine (Py) from calcium hydride (CaH_2). Anhydrous dioxane was purchased from Aldrich and used directly. Methyl formate was distilled from CaH_2 before use. All other reagents were purchased from Aldrich and used directly. For reactions

(29) Feynman, R. P.; Leighton, R. B.; Sands, M. *The Feynman Lectures on Physics*; Addison-Wesley: Reading, MA, 1963; Vol. 1, Chapter 46.

where a component was added by cannula, the total volume of solvent is given. Usually the compound was dissolved in 80% of that volume and the flask was then rinsed with the remaining 20% of fresh solvent.

Flash column chromatography was conducted according to the procedure of Still et al.[30] on silica gel purchased from Baxter Scientific Products (S/P brand silica gel 60 A, 230−400 mesh). ^{1}H NMR spectra were recorded on 300, 400, or 500 MHz spectrometers; chemical shifts are reported in ppm downfield from tetramethylsilane and are referenced to $CHCl_3$ as internal standard. ^{13}C NMR spectra were recorded at 100 MHz; chemical shifts are reported in ppm downfield from tetramethylsilane and are referenced to $CDCl_3$ as internal standard. Infrared spectra were recorded on an FT-IR spectrometer in CH_2Cl_2 solution. Silica gel GF plates were used for analytical TLC and visualized using short- and longwave UV lamps. Melting points are uncorrected. Elemental analyses were performed by Robertson Microlit Labs Inc., Madison, NJ. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were performed by the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, Urbana, IL.

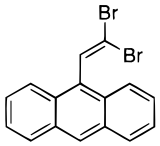
General Procedure for Photocyclizations.[21] The photoreactor, similar to Ace Glass catalog no. 7840, was a cylindrical glass vessel with an immersion well connected through a standard taper 60/40 ground glass joint. The vessel was flat-bottomed to allow a magnetic stirring bar to rotate. The immersion well was a double-walled quartz tube cooled by water containing a 100- or 450-W quartz Hg vapor lamp and, if necessary, a filter. The molarity of the solutions with respect to the starting stilbene or enyne was kept in the 10^{-3} M range. In stilbene photocyclizations, propylene oxide (PO) was used[21] to scavenge HI, and argon was bubbled through the stirred solution of stilbene and iodine for 20−30 min to deoxygenate the solution; the lamp was then turned on. The argon flow was maintained throughout the procedure, and the photoirradiation was monitored by ^{1}H NMR (aliquots taken via the angle joint, evaporating the solvent, and dissolving the residue in $CDCl_3$).

9-(2,2-Dibromoethenyl)triptycene (19). To a mixture of zinc dust (1.60 g, 24.7 mmol) and PPh_3 (6.47 g, 24.7 mmol) in CH_2Cl_2 (40 mL), cooled at 0 °C, was added CBr_4 (8.17 g, 24.7 mmol) in portions over 15 min. The mixture was allowed to reach rt and stirred for 20 min, and then dry pyridine (4 mL) was added. The brown reaction mixture was left stirring for an additional 1 h, and a solution of the aldehyde **18**[3a] (1.73 g, 6.17 mmol) in CH_2Cl_2 (6 mL) was added via cannula dropwise during 10 min. After 24 h, the reaction mixture was poured onto a silica gel (16 cm × 3 cm) chromatography column and the organic products were eluted with Et_2O (200 mL). The eluate was then evaporated under reduced pressure and the residue further purified by flash column chromatography (5% Et_2O/hexanes). The bromide **19** was obtained as a solid (1.48 g, 56%): mp 218−220 °C (crystallized from Et_2O/hexanes) and the starting aldehyde **18** was also recovered (0.80 g, 30%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (s, 1 H), 7.47 (m, 3 H), 7.41 (m, 3 H), 7.04 (m, 6 H), 5.40 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 142.4, 132.4, 125.7, 124.8, 124.2, 123.3, 96.6, 58.4, 54.4; IR (NaCl) 3062, 1608, 1464, 733 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* 437.9 (M^+, 45), 278.1 (100), 252 (15), 138 (30); HRMS (EI) calcd for $C_{22}H_{14}Br_2$ 435.9466, found 435.9462. Anal. Calcd for $C_{22}H_{14}Br_2$: C, 60.31; H, 3.22. Found: C, 60.47; H, 2.97.

3-(9-Triptycyl)propynal (8). To a solution of the vinyl dibromide **19** (515 mg, 1.17 mmol) in THF (10 mL) cooled at −78 °C was added a 2.3 M solution of *n*-BuLi in hexanes (1.22 mL, 2.8 mmol) dropwise via syringe over a 10 min period. The resulting light-yellow solution was stirred for 20 min at −78 °C and then transferred via cannula over a 10 min period to a cooled (−78 °C) solution of methyl formate (360 μL, 5.85 mmol) in THF (3 mL). The reaction mixture was slowly warmed to room temperature over 2 h, stirred at room temperature for an additional 4 h, and then quenched with saturated aqueous NH_4Cl (2 mL). The resulting solution was poured into a separatory funnel with Et_2O (50 mL) and washed with saturated aqueous NH_4Cl (30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated on a rotary evaporator. The crude residue was purified by flash column chromatography (5−15% Et_2O/hexanes), affording aldehyde **8** (270 mg, 68%) as a white solid: mp 263−265 °C (crystallized from Et_2O/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.73 (s, 1 H), 7.66 (m, 3 H), 7.42 (m, 3 H), 7.07 (m, 6 H), 5.45 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.6, 144.0, 142.6, 126.1, 125.3, 123.7, 122.0, 91.3, 90.9, 53.1, 53.0; IR (NaCl) 2219, 1671, 1451, 752 cm^{-1}; LRMS (EI) *m*/*z* 230 (100), 202 (65); HRMS (EI) calcd for $C_{23}H_{14}O$ $(M)^+$ 306.1045, found 306.1048. Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 89.89; H, 4.89.

1-(3-Phenanthryl)-4-(9-triptycyl)but-1-en-3-yne (6). To a cooled suspension of [(3-phenanthryl)methyl]triphenylphosphonium bromide (**7**)[15] (223 mg, 0.42 mmol) in THF at −78 °C was added dropwise a solution of 2.3 M *n*-BuLi in hexanes (182 μL, 0.42 mmol). The brown-red mixture was left warming to room temperature over a 1 h period, stirred for 30 min at room temperature, and cooled again to −78 °C. Then a solution of the aldehyde **8** (120 mg, 0.35 mmol) in THF (5 mL) was added over a 5 min period via cannula. The cooling bath was removed, and after 20 min the reaction mixture was quenched with saturated aqueous NH_4Cl (2 mL), poured into a separatory funnel with Et_2O (60 mL) and washed with saturated aqueous NH_4Cl (40 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography (3% Et_2O/hexanes), affording the enyne **6** (150 mg, 90%) as a mixture of cis/trans isomers (1:1.5). The mixture was dissolved in Et_2O (6 mL) and the trans isomer separated by precipitation. Trans isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (s, 1 H), 8.78 (d, J = 8.0 Hz, 1 H), 7.94 (d, J = 8.4 Hz, 2 H), 7.87 (m, 4 H), 7.79 (s, 1 H), 7.72 (m, 1 H), 7.65 (m, 2 H), 7.44 (d, J = 6.8 Hz, 4 H), 7.12 (m, 6 H), 6.87 (d, J = 16.4 Hz, 1 H), 5.48 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 144.5, 142.7, 134.4, 132.4, 132.4, 130.5, 130.3, 129.2, 128.8, 127.6, 126.9, 126.8, 126.6, 125.7, 125.3, 123.7, 123.5, 122.6, 122.0, 108.3, 92.0, 86.4, 53.4; LRMS (EI) *m*/*z* 480 (M^+, 100), 265 (40), 252 (35); HRMS (EI) calcd for $C_{38}H_{24}$ 480.1874, found 480.1874; UV (MeOH) λ_{max} 290, 310, 340 nm.

1-(9-Anthracenyl)-2,2-dibromoethene (38).



38

To a mixture of zinc dust (4.73 g, 72.8 mmol) and PPh_3 (19.0 g, 72.8 mmol) in CH_2Cl_2 (45 mL) at 0 °C was added CBr_4 (24.1 g, 72.8 mmol) in portions over a 20 min period (exothermic reaction). The mixture was stirred for 20 min at room temperature, and dry pyridine (4 mL) was added dropwise via syringe. The brown reaction mixture was left stirring for 1 h, and a solution of commercial 9-anthraldehyde (5.00 g, 6.17 mmol) in CH_2Cl_2 (12 mL) was added via cannula over a 10 min period. After 6 h of stirring, the reaction mixture was poured onto a chromatography column containing silica gel (10 cm × 5 cm), and the organic products were eluted with Et_2O (400 mL). The solvents were removed under reduced pressure, and the crude product was further purified by flash column chromatography (5% Et_2O/hexanes). Dibromide **38** (7.8 g, 86%) was obtained as a yellow solid: mp 116−117 °C (crystallized from Et_2O/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (s, 1 H), 8.12 (d, J = 8.4 Hz, 2 H), 8.10 (s, 1 H), 8.04 (d, J = 8.4 Hz, 2 H), 7.60 (dt, J = 8.2, 1.2 Hz, 2 H), 7.54 (dt, J = 8.2, 1.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.7, 131.4, 130.2, 129.0, 128.8, 128.1, 126.5, 125.6, 125.5, 95.5; IR (NaCl) 3044, 778 cm^{-1}. Anal. Calcd for $C_{16}H_{10}Br_2$: C, 53.08; H, 2.78; Br, 44.14. Found: C, 53.10; H, 2.67; Br, 44.04.

3-(9-Anthracenyl)propynal (20). To a solution of 1-(9-anthracenyl)-2,2-dibromoethene (**38**, 1.50 g, 4.0 mmol) in THF

(30) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923−2925.

(20 mL) cooled at −78 °C was added a 2.5 M solution of *n*-BuLi in hexanes (3.84 mL, 9.60 mmol) over a 10 min period via syringe. The resulting green mixture was stirred for 15 min at −78 °C and then transferred via cannula over a 5 min period to a solution of distilled methyl formate (495 μL, 8.0 mmol, 2.0 equiv) in THF (5 mL) cooled to −78 °C. The reaction mixture was slowly (1 h) warmed to room temperature, and stirred for an additional 1 h at room temperature, and then quenched with saturated aqueous NH_4Cl (2 mL), poured into a separatory funnel containing Et_2O (60 mL), and washed with saturated aqueous NH_4Cl (30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The crude residue was purified by flash column chromatography (5−15% Et_2O/hexanes), affording the aldehyde **20** (650 mg, 82%) as yellow, wooly needles: mp 147−149 °C (crystallized from AcOEt/hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.74 (s, 1 H), 8.62 (s, 1 H), 8.56 (d, J = 8.8 Hz, 2 H), 8.07 (d, J = 8.4 Hz, 2 H), 7.57 (dt, J = 6.8, 1.2 Hz, 2 H), 7.68 (dt, J = 6.8, 1.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 134.7, 132.3, 131.2, 129.3, 128.5, 126.4, 126.3, 112.8, 100.0, 92.8; IR (NaCl) 2168, 1653, 729 cm^{-1}; LRMS (EI) *m*/*z* 230 (M^+, 100), 202 (67); HRMS (EI) calcd for $C_{17}H_{10}O$ 230.0730, found 230.0731. Anal. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38. Found: C, 88.46; H, 4.33.

1-(9-Anthracenyl)-4-(3-phenanthryl)but-1-en-3-yne (21). To a cooled solution of [(3-phenanthryl)methyl]triphenylphosphonium bromide (**7**)[15] (239 mg, 0.45 mmol) in THF at −78 °C was added a 2.3 M solution of *n*-BuLi in hexanes (195 μL, 0.45 mmol). The cooling bath was removed, and the brown-red mixture was left stirring for 30 min at room temperature. The reaction mixture was cooled again to −78 °C, and a solution of the aldehyde **20** (100 mg, 0.431 mmol) in THF (9 mL) was added dropwise (5 min) via cannula. The reaction mixture was allowed to warm to room temperature and after 20 min quenched with saturated aqueous NH_4Cl (2 mL). The resulting solution was poured into a separatory funnel with Et_2O (60 mL) and washed with saturated aqueous NH_4Cl (50 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (3% Et_2O/hexanes), affording the enyne **21** (150 mg, 86%) as a mixture of cis/trans isomers (1.8:1): ^1H NMR of mixture ($CDCl_3$, 400 MHz) δ 9.45 (s), 8.75 (br s), 8.66 (d, J = 8.8 Hz), 8.50 (d, J = 8.4 Hz), 8.45 (d, J = 8.0 Hz), 8.30 (d, J = 8.4 Hz), 8.02 (m), 7.91 (m), 7.84 (d, J = 8.0 Hz), 7.70 (m), 7.76 (s), 7.65−7.37 (m), 7.16 (t, J = 8.1 Hz), 7.11 (d, J = 9.6 Hz), 6.93 (d, J = 16.0 Hz), 6.41 (d, J = 12.0 Hz); HRMS (EI) calcd for $C_{32}H_{20}$ 404.1562, found 404.1565; UV (hexanes) λ_{max} 285, 340, 425 nm.

5-(9-Anthracenyl)-2-methylbenzaldehyde (23). A solution of 5-bromo-2-methylbenzaldehyde[13] (1.0 g, 5 mmol) in dry dioxane (6 mL) was placed into a Schlenk tube under argon, and a solution of 9-(tributylstannyl)anthracene[18] (4.84 g, 10.4 mmol) in dioxane (4 mL) and $(PPh_3)_2PdCl_2$ (175 mg, 5%) were added. The tube was closed, and the mixture was heated at 130 °C for 60 h with magnetic stirring. Then the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel, washing the solids with Et_2O (100 mL). The combined filtrate and washes were evaporated, and the crude product was purified by flash column chromatography (3−10% AcOEt/hexanes). The coupling product **23** was obtained as a light yellow solid (930 mg, 62%): mp 147−148 °C (crystallized from CH_2Cl_2/hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 10.38 (s, 1 H), 8.58 (s, 1 H), 8.11 (d, J = 5.6 Hz, 2 H), 7.92 (d, J = 1.6 Hz, 1 H), 7.65 (d, J = 8.8 Hz, 2 H), 7.61 (dd, J = 8.8, 1.6 Hz, 1 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.51 (t, J = 6.0 Hz, 2 H), 7.41 (t, J = 8.0 Hz, 2 H), 2.90 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1, 140.0, 137.2, 136.6, 135.4, 135.3, 134.4, 132.3, 131.5, 130.3, 128.7, 127.3, 126.5, 125.9, 125.4, 19.9; IR (NaCl) 3049, 1696, 740 cm^{-1}; LRMS (EI) *m*/*z* 296.2 (M^+, 100), 252 (60); HRMS (EI) calcd for $C_{22}H_{16}O$ 296.1201, found 296.1201. Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 88.94; H, 5.34.

2-Methyl-5-(9-triptycyl)benzaldehyde (11). To a refluxing solution of 5-(9-anthracenyl)-2-methylbenzaldehyde (**23**) (600 mg, 2.03 mmol) in dioxane (20 mL) in a two-necked round-bottomed flask was added a previously prepared suspension of benzenediazonium-2-carboxylate[19] (16.2 mmol, 8.0 equiv) in dioxane (10 mL) portionwise over a 2 h period via Pasteur pipet (CAUTION: when dry, benzenediazonium-2-carboxylate detonates violently on being scraped or heated). The reaction was monitored by ^1H NMR by removing aliquots, evaporating the dioxane, and dissolving the residue in $CDCl_3$. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The black crude product was purified by flash column chromatography (5% Et_2O/hexanes), affording the triptycene **11** (460 mg, 62%) as a white crystalline solid: mp 236 °C (crystallized from Et_2O/hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 10.38 (s, 1 H), 8.61 (d, J = 2 Hz, 1 H), 8.22 (dd, J = 8.0, 2.0 Hz, 1 H), 7.57 (d, J = 8.0 Hz, 2 H), 7.45 (d, J = 7.2 Hz, 3 H), 7.20 (d, J = 7.2 Hz, 3 H), 7.02 (d, J = 7.6 Hz, 3 H), 6.96 (t, J = 7.6 Hz, 3 H), 2.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.3, 147.0, 146.6, 139.9, 137.1, 135.8, 135.2, 134.7, 132.4, 125.6, 125.0, 124.4, 124.1, 60.0, 55.4, 19.8; IR (NaCl) 3065, 1695, 1456, 749 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* 372 (M^+, 50), 252 (69), 117 (71), 116 (64), 115 (80); HRMS (EI) calcd for $C_{28}H_{20}O$ 372.1514, found 372.1514. Anal. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.06; H, 5.58.

1-[2-Methyl-5-(9-triptycyl)phenyl]-2-(2-naphthyl)ethene (9). To a solution of [(2-naphthyl)methyl]triphenylphosphonium bromide[20] (315 mg, 0.64 mmol) in THF (20 mL) cooled at −78 °C, was added via syringe a 2.3 M solution of *n*-BuLi in hexanes (280 μL, 0.64 mmol) dropwise over a 10 min period. The reaction mixture was allowed to warm to room temperature by removing the bath and stirred at room temperature for 30 min. The red ylide was then cooled to −78 °C, and a solution of the aldehyde **11** (203 mg, 0.54 mmol) in THF (5 mL) was added via cannula dropwise over a 5 min period. The cooling bath was removed, and the reaction mixture was left stirring for an additional 1 h at room temperature and then quenched with saturated aqueous NH_4Cl (2 mL). The reaction mixture was poured into a separatory funnel with Et_2O (60 mL) and washed with saturated aqueous NH_4Cl (40 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The resulting crude residue was purified by flash column chromatography (10% Et_2O/hexanes) to give stilbene **9** (230 mg, 85%) as a mixture of cis/trans isomers (1:1): ^1H NMR of mixture ($CDCl_3$, 400 MHz) δ 8.44 (s), 7.99 (d, J = 8.0 Hz), 7.92 (dd, J = 8.2 Hz), 7.86 (m), 7.84 (s), 7.78 (d, J = 1.6 Hz), 7.77 (m), 7.70 (d, J = 8.0 Hz), 7.55 (d, J = 8.0 Hz), 7.51 (d, J = 8.0 Hz), 7.45 (m), 7.47 (d, J = 7.6 Hz), 7.40 (dd, J = 8.4, 1.6 Hz), 7.39 (d, J = 7.2 Hz), 7.32 (d, J = 6.8 Hz), 7.19 (d, J = 16.4 Hz), 7.02 (dt, J = 8.4, 1.6 Hz), 6.94 (s), 6.43 (dt, J = 12.8, 8.0 Hz), 5.51 (s), 5.31 (s), 2.72 (s), 2.60 (s); IR (NaCl) 3053, 2944, 1456, 747 cm^{-1}; LRMS (EI) *m*/*z* 496 (M^+, 87), 252 (M − Tript, 100); HRMS (EI) calcd for $C_{39}H_{28}$ 496.2192, found 496.2191; UV (benzene) λ_{max} 283, 321 nm. Anal. Calcd for $C_{39}H_{28}$: C, 94.32; H, 5.68. Found: C, 93.95; H, 5.47.

4-Methyl-1-triptycylbenzo[*c*]phenanthrene (2b). To a solution of stilbene **9** (193 mg, 0.39 mmol) in benzene (250 mL) in the photoreactor under an argon atmosphere were added I_2 (99 mg, 0.39 mmol) and propylene oxide (1 mL). The mixture was irradiated (100 W mercury lamp) through a Pyrex filter over 40 h, progress of the reaction being monitored by ^1H NMR. The solvent was evaporated, and the crude residue was purified by flash column chromatography (2 to 5% Et_2O/hexanes). The benzo[*c*]phenanthrene **2b** was further purified by crystallization (Et_2O/hexanes), obtaining transparent crystals (104 mg, 54%): mp 308−310 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.43 (m, 1 H), 8.33 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 7.2 Hz, 1 H), 7.96 (d, J = 7.5 Hz, 1 H), 7.87 (t, J = 8.4 Hz, 2 H), 7.76 (d, J = 8.1 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.57 (m, 1 H), 7.35 (m, 3 H), 7.05 (dd, J = 7.2, 1.5 Hz, 1 H), 6.88 (dd, J = 7.6, 1.2 Hz, 1 H), 6.82 (t, J = 7.8 Hz, 1 H), 6.61 (dq, J = 7.5, 1.8 Hz, 2 H), 6.48 (d, J = 8 Hz, 1 H), 6.38 (dt, J = 7.2, 1.2 Hz, 1 H), 5.92 (dt, J = 7.8, 1.2 Hz, 1 H), 5.87 (d, J = 7.8 Hz, 1 H), 5.79 (dt, J = 7.8, 1.2 Hz, 1 H), 5.10 (s, 1 H), 3.00 (s,

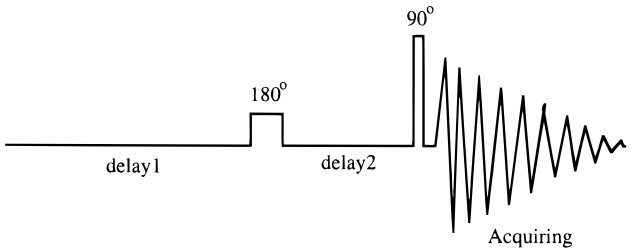


Figure 8. Pulse sequence for spin polarization transfer experiment.

3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 150.4, 147.0, 145.2, 143.8, 143.6, 137.3, 134.9, 134.4, 133.2, 131.5, 130.9, 130.8, 130.4, 129.9, 129.7, 127.9, 127.6, 126.4, 126.2, 126.1, 126.0, 125.9, 125.6, 125.5, 124.6, 124.2, 124.0, 124.0, 123.9, 123.9, 123.7, 123.5, 123.1, 122.7, 122.2, 65.8, 55.8, 20.6; LRMS (EI) 494 (M^+, 87), 252 (− Tript, 100); HRMS (EI) calcd for $C_{39}H_{26}$ 494.2030, found 494.2034. Anal. Calcd for $C_{39}H_{26}$: C, 94.70; H, 5.30. Found: C, 94.80; H, 5.13.

Spin Polarization Transfer Experiment on 2b. A Varian Unity 300 spectrometer was used with temperature control. The resonances for H_a, H_b, and H_c were identified by NOE's from the bridgehead proton, whose chemical shift (δ 5.10) is unique. ^{1}H T_1 values were measured using the inversion recovery method. T_1 values for the protons of interest (H_a, H_b, and H_c) are about 2 s. The exchange rate is faster than the relaxation rate but still slow enough to give resolved spectral lines. Therefore, a spin polarization transfer experiment can be used to measure the exchange rate. The pulse sequence is shown in Figure 8. A 10 s delay was used before the first pulse. The initial 180° pulse with a duration of 0.013 s is a selective pulse that inverts the H_a, H_b, or H_c resonance; it is followed by different delay times and then by a 90° detection pulse (17.5 μs). The data were acquired in DMSO at 160 °C. Each spectrum shown in Figure 5 represents the difference between the application of a 0.013 s, 180° selective pulse and a normal pulse sequence.

1-(2-Methyl-5-bromophenyl)-2-(2-naphthyl)ethene (16). To a solution of (2-naphthylmethyl)triphenylphosphonium bromide[20] (800 mg, 1.65 mmol) cooled at −78 °C was added a 2.30 M solution of *n*-BuLi in hexanes (1.65 mmol, 720 μL) over a 10 min period via syringe. The red solution was allowed to warm to room temperature by removing the cooling bath and stirred for an additional 30 min; then the resulting ylide was cooled again to −78 °C, and a solution of the aldehyde **24** (300 mg, 1.51 mmol) in THF (5 mL) was added via cannula over a 5 min period. The mixture was warmed to room temperature over 15 min and after an additional 1 h quenched with saturated aqueous NH_4Cl (1.5 mL). The reaction mixture was poured into a separatory funnel with Et_2O (80 mL) and washed with saturated aqueous NH_4Cl (30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (10% Et_2O/hexanes) to give the bromostilbene **16** (395 mg, 83%) as a mixture of cis/trans isomers (1:2.3): ^{1}H NMR of mixture ($CDCl_3$, 300 MHz) δ 7.88 (m), 7.84 (d, J = 2.0 Hz), 7.80−7.73 (m), 7.67 (s), 7.63 (d, J = 8.8 Hz), 7.56−7.50 (m), 7.49−7.44 (m), 7.40 (s), 7.38−7.33 (m), 7.22 (dd, J = 8.4, 1.2 Hz), 7.16 (s), 7.12 (d, J = 8.4 Hz), 6.85 (d, AB system, J = 12.0 Hz), 6.67 (d, AB system, J = 12.0 Hz), 2.43 (s), 2.21 (s); LRMS (EI) 324 (M^+, 100), 322 (95), 228 (45); HRMS (EI) calcd for $C_{19}H_{15}Br$ 322.0357, found 322.0357. Anal. Calcd for $C_{19}H_{15}Br$: C, 70.60; H, 4.68. Found: C, 70.55; H, 4.51.

1-Bromo-4-methylbenzo[*c*]phenanthrene (15). A solution of stilbene **16** (350 mg, 1.04 mmol) and I_2 (289 mg, 1.14 mmol) in benzene (700 mL) was prepared in the photoreactor under an argon atmosphere, and propylene oxide (2.5 mL) was added following standard procedures. The mixture was irradiated with a medium-pressure mercury lamp (100 W) through a Pyrex filter during 20 h (monitored by GC−MS). The solvent was evaporated in vacuo, and the crude product was purified by flash column chromatography (3% Et_2O/hexanes) to give the bromobenzo[*c*]phenanthrene **15** (150 mg, 50%) as a white solid: mp 163−165 °C (crystallized from Et_2O/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30 (m, 1 H), 7.99 (m, 3 H), 7.86 (d, J = 8 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 2 H), 7.60 (m, 2 H), 7.35 (d, J = 8.0 Hz, 1 H), 2.79 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.7, 134.0, 132.5, 132.3, 132.1, 131.9, 129.0, 128.9, 128.7, 128.0, 127.5, 127.4, 127.1, 126.1, 125.6, 124.8, 122.7, 119.5, 19.9; LRMS (EI) 322 (M^+, 65), 320 (65), 241 (100), 226 (90); HRMS (EI) calcd for $C_{19}H_{13}Br$ 320.0200, found 320.0200. Anal. Calcd for $C_{19}H_{13}Br$: C, 71.05; H, 4.08; Br, 24.88. Found: C, 70.93; H, 3.82; Br, 24.73.

1-Methyl-2-styryl-4-triptycylbenzene (27). To a solution of commercial benzyltriphenylphosphonium chloride (112 mg, 0.29 mmol) in THF (8 mL) at room temperature was added a 25 wt % solution of NaOMe (66 μL, 0.29 mmol) in MeOH dropwise over a 10 min period via syringe. The red solution was stirred for 1 h, and a solution of the aldehyde **11** (112 mg, 0.29 mmol) in THF (5 mL) was added via cannula over a 10 min period. The reaction mixture was stirred for 15 min, quenched with saturated aqueous NH_4Cl (2 mL), poured into a separatory funnel with Et_2O (60 mL), and washed with saturated aqueous NH_4Cl (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated under reduced pressure. Purification of the residue by flash column chromatography (10% AcOEt/hexanes) afforded stilbene **27** (95 mg, 76%) as a mixture of cis/trans isomers (1:1): ^{1}H NMR of the mixture ($CDCl_3$, 400 MHz) δ 8.35 and 7.81 (d, J = 2.4 Hz, 1 H), 7.88 and 7.85 (dd, J = 11, 2.4 Hz, 1 H), 7.54−7.43 (m, 4 H), 7.34 (d, J = 8.0 Hz, 3 H), 7.25 (d, J = 8.0 Hz, 3 H), 7.05−6.9 (m, 7 H), 6.85−6.70 (m, 3 H), 5.44 and 5.33 (s, 1 H), 2.62 and 2.52 (s, 3 H); HRMS (EI) calcd for $C_{35}H_{26}$ 446.2000, found 446.2001.

4-Bromo-1-methyl-2-styrylbenzene (28). To a solution of commercial benzyltriphenylphosphonium bromide (1.12 g, 2.59 mmol) in THF (25 mL) at room temperature was added a 25 wt % solution of NaOMe (0.69 mL, 3.0 mmol) in MeOH dropwise over a 10 min period via syringe. The orange solution was stirred for 45 min, and a solution of the aldehyde **24** (430 mg, 2.16 mmol) in THF (15 mL) was added via cannula over a 10 min period. The reaction mixture was stirred overnight, quenched with saturated aqueous NH_4Cl (2 mL), poured into a separatory funnel with Et_2O (60 mL), and washed with saturated aqueous NH_4Cl (40 mL). The organic layer was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure. Purification of the residue by flash column chromatography (hexanes) afforded stilbene **28** (356 mg, 61%) as a mixture of cis/trans isomers (1:1): ^{1}H NMR of the mixture ($CDCl_3$, 400 MHz) δ 7.72 (d, J = 2.8 Hz), 7.53 (d, J = 7.6 Hz), 7.39 (t, J = 7.3 Hz), 7.27 (m), 7.18 (m), 7.05 (m), 6.99 (d, J = 16 Hz), 6.65 (d, AB system, J = 12.0 Hz), 6.55 (d, AB system, J = 12 Hz), 2.37 (s), 2.11 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 138.4, 137.1, 136.4, 135.0, 134.6, 131.9, 131.7, 131.6, 131.4, 131.2, 130.2, 130.1, 128.8, 128.7, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.3, 127.1, 126.9, 126.8, 126.7, 125.1, 119.8, 119.1; HRMS (EI) calcd for $C_{15}H_{13}Br$ 272.0200, found 272.0163.

1-Methylphenanthrene (29b). A solution of stilbene **28** (120 mg, 0.44 mmol) and I_2 (11 mg, 0.04 mmol) in benzene (220 mL) was prepared in the photoreactor under an argon atmosphere, and propylene oxide (3 mL) was added following standard procedures. The mixture was irradiated with a medium-pressure mercury lamp (100 W) through a Pyrex filter during 12 h (monitored by GC−MS), and no reaction was observed. The filter was replaced with a Vycor filter, and the reaction mixture was irradiated for 7 h. The solvent was evaporated in vacuo and the crude product purified by flash column chromatography (hexanes) to give the phenanthrene **29b**[24] (25 mg, 21%), recovering part of the starting stilbene **28** (35 mg, 30%): ^{1}H NMR of **29b** ($CDCl_3$, 300 MHz) δ 8.70 (d, J = 10.8 Hz, 1 H), 8.58 (d, J = 10.8 Hz, 1 H), 7.95 (d, J = 12.0 Hz, 1 H), 7.89 (dd, J = 12.0, 2.0 Hz, 1 H), 7.78 (d, J = 12.0 Hz, 1 H), 7.60 (m, 3 H), 7.74 (d, J = 7.6 Hz, 1 H), 2.76 (s, 3 H); LRMS (EI) 192 (M^+, 100), 191 (58), 189 (36), 165 (43).

4-[(Trifluoromethanesulfonyl)oxy]-1,2-dihydrophenanthrene (31). To a solution of phenanthrone **30**[25] (750 mg, 3.82 mmol) and 2,6-lutidine (890 μL, 7.65 mmol) in CH_2Cl_2 (20 mL) was added at 0 °C trifluoromethanesulfonic anhydride (1.30 mL, 6.68 mmol) dropwise over a 5 min period via syringe. The reaction mixture was allowed to reach rt and stirred overnight. The solvent was evaporated under reduced pressure, and the resulting crude product was purified by flash column chromatography (hexanes) to give **31** (960 mg, 77%) as a white foam: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, J = 8.8 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.53−7.41 (m, 2 H), 7.27 (d, J = 8.0 Hz, 1 H), 6.23 (t, J = 5.2 Hz, 1 H), 2.90−2.84 (m, 2 H), 2.37−2.31 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.8, 137.6, 133.4, 129.9, 128.8, 128.1, 126.9, 125.8, 125.4, 125.0, 124.6, 123.3, 121.0, 120.1, 116.9, 113.8, 29.2, 22.1; LRMS (EI, 70 eV) *m/z* 329 ([M + H]$^+$, 10), 328 (M$^+$, 55), 167 (100), 165 (54); HRMS (EI) calcd for $C_{15}H_{11}O_3SF_3$ 328.0379, found 328.0379.

4-(9-Anthracenyl)-1,2-dihydrophenanthrene (32). A mixture of vinyl triflate **31** (1.33 g, 4.04 mmol), 9-(tributylstannyl)anthracene (2.83 g, 6.05 mmol), anhydrous LiCl (850 mg, 20.2 mmol), $Pd(PPh_3)_4$ (934 mg, 0.800 mmol), and dioxane (15 mL) was placed into a sealable tube. After several cycles of evacuation and addition of a N_2 atmosphere, the tube was sealed, and the solution was heated at 120 °C for 3 days. The solvent was removed under reduced pressure, and the corresponding crude reaction product was purified by flash column chromatography (hexanes), affording **32** (791 mg, 55%) as a yellow solid: mp 154−155 °C (needles crystallized from EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (s, 1H), 8.04−8.00 (m, 4H), 7.74 (d, J = 8.4 Hz, 1 H), 7.65 (d, J = 8.0 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H), 7.43−7.25 (m, 4 H), 7.10−7.00 (m, 1 H), 6.92 (d, J = 9.2 Hz, 1 H), 6.56−6.50 (m, 1 H), 6.41−6.37 (m, 1 H), 3.22−3.17 (m, 2 H), 2.62−2.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.0, 135.9, 135.7, 135.4, 133.5, 132.8, 131.7, 129.8, 129.7, 128.5, 128.4, 128.0, 126.8, 126.5, 126.3, 125.5, 125.4, 125.1, 124.6, 124.2, 30.5, 23.1; IR (neat) 3056, 2931−2829, 1437, 810, 737 cm^{-1}; LRMS (EI, 70 eV) *m/z* 357 ([M + H]$^+$, 29), 356 (M$^+$, 100); HRMS (EI) calcd for $C_{28}H_{20}$ 356.1565, found 356.1565. Anal. Calcd for $C_{28}H_{20}$: C, 94.35; H, 5.65. Found: C, 94.14; H, 5.61.

4-(9-Triptycyl)phenanthrene (1). To a refluxing solution of dihydrophenanthrene **32** (210 mg, 0.59 mmol) in dioxane (15 mL) in a two-neck round-bottomed flask was added a previously prepared[19] suspension of benzenediazonium-2-carboxylate (4.8 mmol, 8 equiv) in dioxane portionwise during 2 h via Pasteur pipet (CAUTION: when dry, benzenediazonium-2-carboxylate detonates violently on being scraped or heated). The reaction was monitored by ^{1}H NMR by removing aliquots, evaporating the dioxane, and dissolving the residue in $CDCl_3$. The reaction was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (10% EtOAc/hexanes), affording a pale yellow oil that was immediately dissolved in benzene (10 mL). Then, DDQ (163 mg, 0.72 mmol) was added, and the reaction mixture was heated at reflux for 10 h. The solvent was evaporated in a rotary evaporator and the crude residue was purified by flash column chromatography (20% CH_2Cl_2/hexanes) to give the desired triptycylphenanthrene **1** (127 mg, 51%) as a white solid: mp 316−317 °C (crystallized from CH_2Cl_2/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 7.87−7.80 (m, 2 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.56−7.54 (m, 1 H), 7.50 (d, J = 7.6 Hz, 2 H), 7.35−7.33 (m, 1 H), 7.21 (d, J = 8.8 Hz, 1 H), 7.17 (t, J = 7.3 Hz, 1 H), 7.00−6.96 (m, 2 H), 6.89−6.86 (m, 2 H), 6.79 (d, J = 7.6 Hz, 2 H), 6.59−6.55 (m, 2 H), 6.38−6.34 (m, 1 H), 5.46 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.2, 148.7, 145.3, 144.1, 134.6, 134.0, 132.2, 131.7, 131.6, 131.5, 130.6, 128.9, 127.5, 127.1, 126.9, 125.9, 125.3, 124.7, 124.5, 124.4, 123.5, 123.3, 122.0, 63.5, 55.2; IR (film) 3055, 2948, 1451, 746 cm^{-1}; LRMS (EI, 70 eV) *m/z* 431 ([M + H]$^+$, 45), 430 (M$^+$, 100), 253 (21), 252 (30); HRMS (EI) calcd for $C_{34}H_{22}$ 430.1721, found 430.1721.

4-(9-Anthracenyl)phenanthrene (33). A solution of dihydrophenanthrene **32** (160 mg, 0.45 mmol) and DDQ (153 mg, 0.67 mmol) in benzene (15 mL) was heated at reflux for 6 h. After cooling, the solvent was evaporated under vacuum, and the residue was purified by flash column chromatography (5% EtOAc/hexanes) to afford the phenanthrene **33** (142 mg, 89%) as an amorphous solid that was crystallized from hexanes: mp 139−140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (s, 1 H), 8.12−8.10 (m, 3 H), 7.94 (d, J = 9.0 Hz, 1 H), 7.81 (d, J = 9.0 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.74 (t, J = 7.6 Hz, 1 H), 7.48−7.42 (m, 5 H), 7.27−7.17 (m, 3 H), 7.09 (d, J = 8.8 Hz, 1 H), 6.66 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3, 136.2, 133.6, 133.1, 132.4, 131.7, 130.3, 129.9, 129.3, 128.4, 128.3, 127.9, 127.8, 126.7, 126.4, 126.0, 125.9, 125.8, 125.7, 125.4; IR (film) 3047, 1441, 1294, 907, 827, 753 cm^{-1}; HRMS (EI) calcd for $C_{28}H_{18}$ 354.1405, found 354.1408. Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.87; H, 4.99.

7,12-Etheno-12-(9-triptycyl)-3*H*-benz[*a*]anthracene (34). To a refluxing solution of phenanthrene **33** (105 mg, 0.30 mmol) in dioxane (25 mL), in a two-neck round-bottomed flask, was added a previously prepared[19] suspension of benzenediazonium-2-carboxylate (2.4 mmol, 8 equiv) in dioxane portionwise during 2 h via Pasteur pipet (CAUTION: when dry, benzenediazonium-2-carboxylate detonates violently on being scraped or heated). The reaction was monitored by ^{1}H NMR by removing aliquots, evaporating the dioxane, and dissolving the residue in $CDCl_3$. The mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The corresponding crude product was purified by flash column chromatography (5% EtOAc/hexanes) to give 65 mg (43%) of **34** (tentative structure assignment) as a pale yellow oil, which was crystallized from a mixture of Et_2O/hexanes as a yellowish solid: mp 328−329 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75−7.41 (m, 8 H), 7.28−7.24 (m, 1 H), 7.13−6.91 (m, 8 H), 6.69−6.48 (m, 6 H), 6.24−6.18 (m, 1 H), 5.60 (s, 1 H), 5.53 (dd, J = 8.2, 2.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.2, 148.1, 146.9, 145.7, 145.6, 145.5, 145.2, 145.1, 144.2, 143.5, 143.0, 136.3, 132.7, 132.0, 130.5, 130.2, 129.7, 129.1, 128.4, 127.7, 125.6, 125.3, 124.6, 124.4, 124.0, 123.5, 123.3, 123.2, 123.1, 123.0, 122.9, 122.8, 122.6, 122.3, 121.6, 60.9, 59.7, 55.3, 54.4; IR (film) 3050−3011, 2955−2854, 1457, 916, 740 cm^{-1}; LRMS (EI, 70 eV) *m/z* 507 ([M + H]$^+$, 3), 506 (M$^+$, 7), 86 (34), 85 (56), 84 (57), 83 (100); HRMS (EI) calcd for $C_{40}H_{26}$ 506.2034, found 506.2034.

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