Thermolysis of Benzoenyne−Allenes To Form Biradicals and Subsequent Intramolecular Trapping with a Tetraarylallene To Generate Two Triarylmethyl Radical Centers

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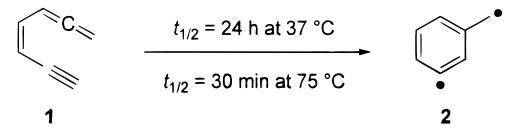
Received November 24, 1998

Thermolysis of the benzoenyne−allene **20** in 1,4-cyclohexadiene (1,4-CHD) at 75 °C produced the cycloaromatized adduct **23** in 22% yield. The reaction presumably proceeds through a cascade sequence involving an initial Myers cyclization reaction to form the biradical **21**. The subsequent trapping of the aryl radical center in **21** with the tetraarylallenic moiety intramolecularly affords **22**, having two stabilized triarylmethyl radical centers. Hydrogen-atom abstraction from 1,4-CHD by **22**, manifesting its radical character, then produces **23**. Similarly, thermolysis of benzoenyne−allenes **25** in 1,4-CHD furnished fluoranthenes **27** in essentially quantitative yields. The presence of the fused five-membered ring in **20** and **25** is necessary to direct the initial biradical-forming step toward the Myers cyclization reaction. Without the five-membered ring as in the cases of **31**, the C2−C6 cyclization reaction became the preferred pathway, leading to benzofluorenes **34**.

Introduction

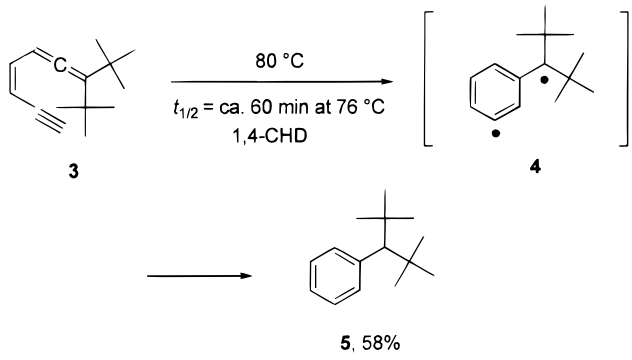
The use of the thermally-induced isomerization reactions of organic molecules to generate the carbon-centered biradicals has several potential advantages over the conventional chemical or photochemical methods.[1] Unlike the chemical methods where overoxidation or overreduction of an organic compound could occur,[2] such undesirable side reactions will not be a major concern in the thermal process because the two radical centers are generated simultaneously. In addition, the chemical reagent needed to promote the formation of radicals and the reaction byproducts of the chemical process have to be removed at the end. Moreover, since heat can easily permeate through material, a precursor could be incorporated inside an inert matrix and then be converted to a biradical by simple heat treatment. On the other hand, chemicals or light may not be able to penetrate through the matrix barrier to induce the formation of radicals.

Of the few reported methods for generating biradicals under thermal conditions, the Myers cyclization reaction of (*Z*)-1,2,4-heptatrien-6-ynes (enyne−allenes) to α,3-didehydrotoluene biradicals (eq 1) provides a particularly attractive pathway to carbon biradicals because the reaction occurs under mild thermal conditions and various synthetic routes to enyne−allenes with diverse chemical structures are becoming available.[3] While the aryl radical center in **2** is too reactive to be persistent because H-atom abstraction generates a strong aryl C−H bond, the benzylic radical center could become persistent or even stable[4] if proper substituents are placed at the terminus of the allenic end of **1**.



(1)

Scheme 1



We recently reported that the enyne−allene **3** undergoes a facile Myers cyclization reaction under refluxing benzene (80 °C) in the presence of an excess of 1,4-CHD to furnish **5** in 58% yield (Scheme 1).[5] The reaction presumably proceeds through the biradical **4** having an α,α-di-*tert*-butylbenzylic radical center, which was re-

† To whom correspondence concerning the X-ray structures should be addressed.

(1) (a) Borden, W. T. *Diradicals*; Wiley-Interscience: New York, 1982. (b) Platz, M. S. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum Press: New York, 1990.

(2) (a) Rajca, A.; Rajca, S. *J. Am. Chem. Soc.* **1996**, *118*, 8121−8126. (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893. (c) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235−9241. (d) Tukada, H.; Mutai, K. *Tetrahedron Lett.* **1992**, *33*, 6665−6668. (e) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552−2561.

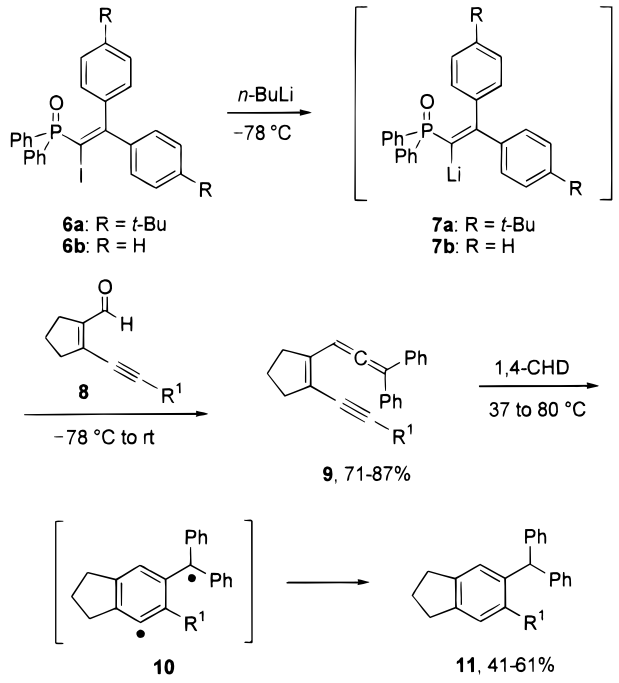
(3) (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (b) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 9130−9132. (c) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995−4998. (d) Nagata, R.; Yamanaka, H.; Murahashi, E.; Saito, I. *Tetrahedron Lett.* **1990**, *31*, 2907−2910. (e) Nicolaou, K. C.; Maligres, P.; Shin, J.; de Leon, E.; Rideout, D. *J. Am. Chem. Soc.* **1990**, *112*, 7825−7926. For recent reviews, see: (f) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222. (g) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−6518.

(4) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13−19.

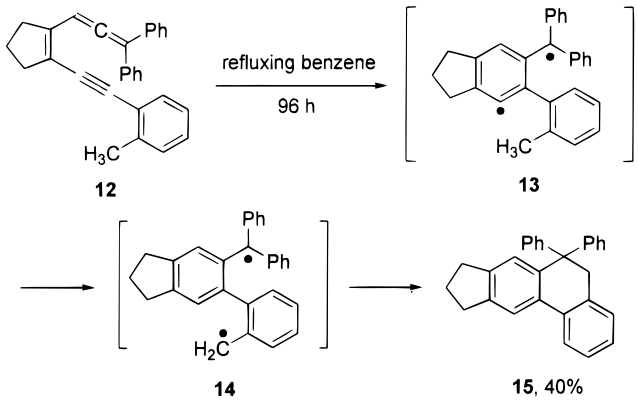
(5) Wang, K. K.; Wang, Z.; Sattsangi, P. D. *J. Org. Chem.* **1996**, *61*, 1516−1518.

10.1021/jo982326k CCC: $18.00
Published on Web 02/06/1999

Scheme 2



Scheme 3

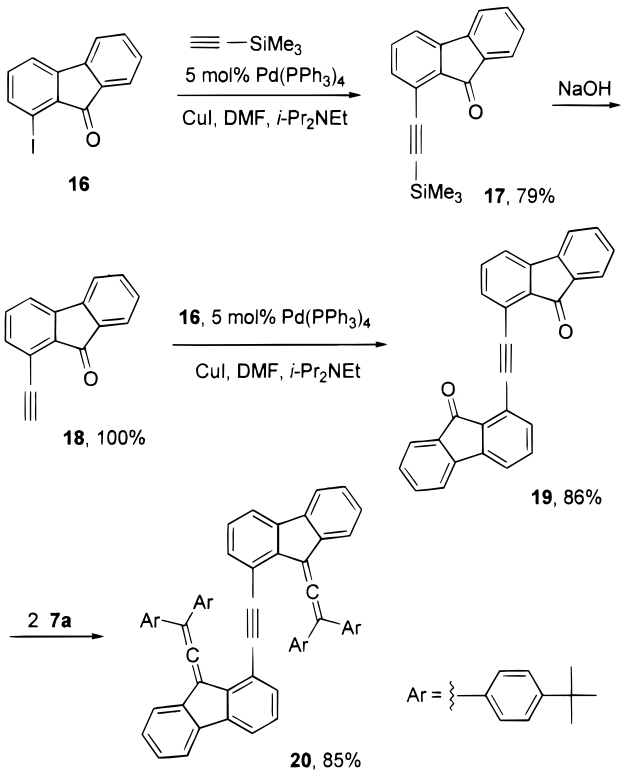


ported to be persistent in dilute solution at room temperature for several days.[6] The EPR spectrum of the α,α-di-*tert*-butylbenzylic radical indicates that it prefers a conformation in which the p orbital of the radical center is perpendicular to the π bonds of the benzene ring in order to minimize steric interactions.

Enyne−allenes **9** having two phenyl substituents at the allenic terminus were synthesized by using readily available enynyl aldehydes **8** for the Horner reaction with phosphinoxy carbanion **7b**.[7] Thermolysis of these enyne−allenes under mild thermal conditions produced the cycloaromatized adducts **11** via biradicals **10** having a stabilized triarylmethyl radical center (Scheme 2).

In the absence of 1,4-CHD, thermolysis of **12** under refluxing benzene for 96 h afforded the cycloaromatized adduct **15** in 40% yield (Scheme 3). Apparently, a 1,5-hydrogen shift of the initially formed α,3-didehydrotoluene biradical **13** to form **14** followed by an intramolecular radical−radical combination led to **15**. This example demonstrates the feasibility of converting the reactive

Scheme 4



aryl radical to the more stable benzylic radical via a 1,5-hydrogen shift.

Results and Discussion

The success in producing a stabilized triarylmethyl radical and in transforming the aryl radical to the benzylic radical shown in Scheme 3 prompted us to design new ways to capture the aryl radical intramolecularly. Examples of trapping the aryl radical center with an intramolecular double or triple bond have been reported.[8] We envisioned that if the aryl radical could be captured by a tetraarylallenic moiety intramolecularly, then the initially formed biradical could be transformed to a new biradical having two triarylmethyl radical centers. To test the feasibility of this strategy, the benzoenyne−allene **20** was synthesized from 1-iodo-9-fluorenone **16**[9] (Scheme 4). The $Pd(PPh_3)_4$-catalyzed cross-coupling reaction between **16** and (trimethylsilyl)-acetylene furnished **17**, which was desilylated to form **18**. Cross-coupling between **18** and **16** was also promoted by $Pd(PPh_3)_4$ to afford **19**, which was readily converted to **20** by treatment with phosphinoxy carbanion **7a** for the Horner reaction.

Thermolysis of **20** in 1,4-CHD at 75 °C produced the cycloaromatized adduct **23** in 22% yield (Scheme 5). The structure assignment of **23** is based on the high-resolution mass spectrum and the ^1H and ^{13}C NMR spectra.

(6) Schreiner, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 144−145.

(7) Liu, B.; Wang, K. K.; Petersen, J. L. *J. Org. Chem.* **1996**, *61*, 8503−8507.

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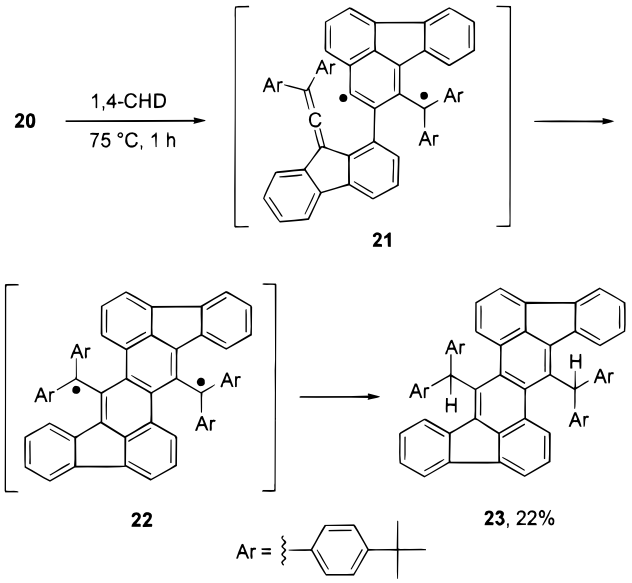
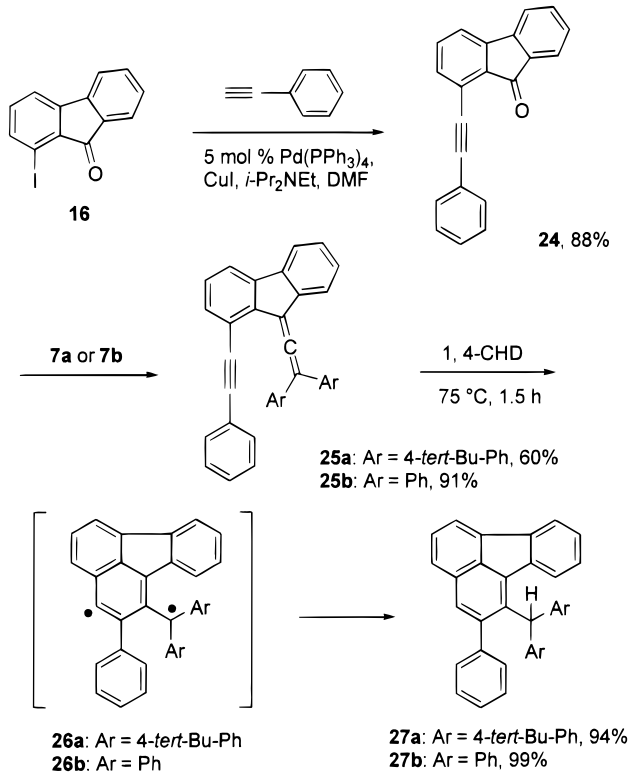
(9) (a) Huntress, E. H.; Pfister, K., III.; Pfister, K. H. T. *J. Am. Chem. Soc.* **1942**, *64*, 2845−2849. (b) Kharasch, N.; Bruice, T. C. *J. Am. Chem. Soc.* **1951**, *73*, 3240−3244.

Scheme 5



Scheme 6



The molecular ion was detected by a high-resolution mass spectrometer (m/z = 932.5297). The presence of only one *tert*-butyl signal in the ^{1}H NMR spectrum suggests that **23** is a symmetrical molecule. The appearance of a set of AB doublets in the aromatic region is also consistent with the presence of the *para*-disubstituted benzene rings in **23**. While the ^{1}H NMR signal for the two tertiary hydrogens on the sp^3 carbons is buried in the aromatic region, their presence can be clearly discerned in the ^{13}C NMR spectrum. The ^{13}C NMR signal at δ 54.77 was found to arise from the methine carbon attached with one hydrogen by using the DEPT technique and can be attributed to the two sp^3 C−H carbons in **23**. The ^{13}C NMR signals for one type of *tert*-butyl group were also observed. In the aromatic region, nine signals are from the C−H carbons and the remaining 10 signals are from carbons without hydrogen attached to them, consistent with what can be expected from the structure of **23**. The four signals with higher intensities at δ 148.97, 138.22, 129.36, and 125.01 can be attributed to the carbons on the *para*-disubstituted benzene rings.

Apparently, the transformation from **20** to **23** proceeded through an initial Myers cyclization reaction to produce the biradical **21**. The aryl radical center in **21** was then captured by the allenic moiety to form **22** having two stabilized triarylmethyl radical centers. Because of nonbonded steric interactions, the molecular model of **22** indicates that it cannot achieve the planar quinonoid form and can be best regarded as a biradical with the p orbital of the radical centers perpendicular to the π bonds of the central chrysene ring. In addition, the quinonoid form of **22** would cause a complete disruption of aromaticity of the central chrysene system. This is reminiscent of a sterically hindered Chichibabin hydrocarbon, which also cannot achieve coplanarity and consequently exhibits paramagnetic properties.[10] The subsequent hydrogen-atom abstraction from 1,4-CHD by **22**, manifesting its radical behavior, then furnished **23**.

To probe more closely the Myers cyclization reaction from **20** to the biradical **21**, the benzoenyne−allenes **25** were synthesized from **16** by using a similar reaction sequence outlined in Scheme 6. Thermolysis of **25** in 1,4-CHD at 75 °C for 1.5 h produced the cycloaromatized adducts **27** in essentially quantitative yields.

The structure of **27a** was unequivocally established by an X-ray structural analysis.[11] It is interesting to note that the benzylic C−H bond lies essentially on the plane of the fluoranthene ring with only a 17° twist angle and is pointed toward the phenyl substituent in the crystal lattice. The two 4-*tert*-butylphenyl groups are situated above and below the plane of the fluoranthene ring.

Compared to **9**, the fixed *s-cis* benzoenyne−allene system in **25** presumably is an important factor in promoting cycloaromatization efficiently.[12] This result also suggests that the initial Myers cyclization reaction from **20** to **21** probably is not responsible for relatively low yield in producing **23**.

The presence of the fused five-membered ring in **20** and **25** is crucial in directing the initial biradical-forming step toward the Myers cyclization reaction. By using the benzophenones **30**, readily prepared from **28**[13] (Scheme 7), for condensation with phosphinoxy carbanion **7a** or **7b**, the 11*H*-benzo[*b*]fluorenes **34** were produced (Scheme 8). The structures of **34a** and **34b** were established by X-ray structural analyses.[11] Presumably, the initial Horner reactions produced the benzoenyne−allenes **31**, which then underwent a facile C2−C6 cyclization at room temperature to form the biradicals **32**. The subsequent intramolecular radical−radical coupling produced **33**, leading to the 11*H*-benzo[*b*]fluorenes **34** through tau-

(10) Müller, E.; Rieker, A.; Scheffler, K.; Moosmayer, A. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 6−15.

(11) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(12) Naoe, Y.; Kikuishi, J.; Ishigaki, K.; Iitsuka, H.; Nemoto, H.; Shibuya, M. *Tetrahedron Lett.* **1995**, *36*, 9165−9168.

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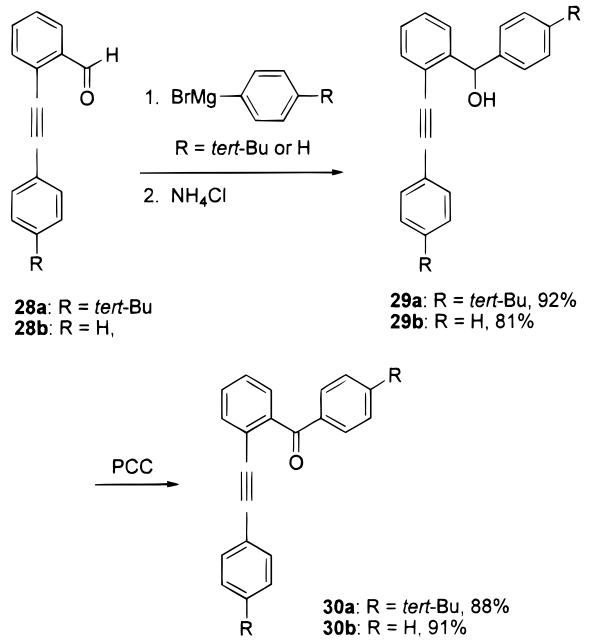
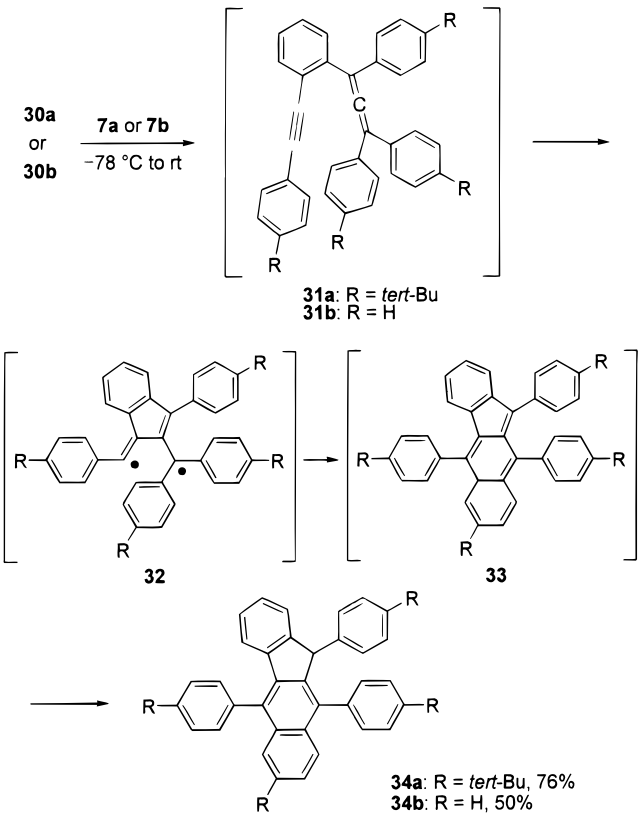
Scheme 7



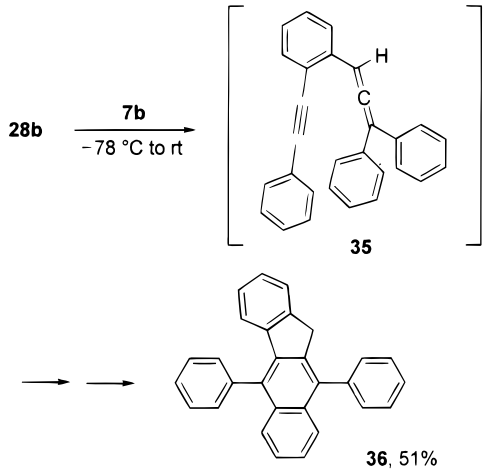
Scheme 8



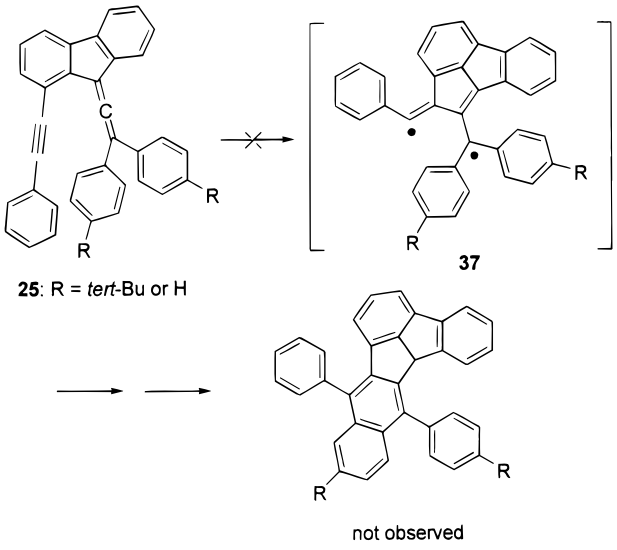
tomerization. There are ample precedents in the literature to support the formation of the formal Diels−Alder adducts **33** through a two-step C2−C6 cyclization involving a biradical intermediate.[14] Similarly, the 11*H*-benzo[*b*]fluorene **36** was obtained from condensation between **28b** and **7b** (Scheme 9).

The preference for **20** and **25** to undergo the Myers cyclization reaction can be attributed to the emergence of substantial ring strains in the resulting biradicals had the reaction proceeded through the C2−C6 cyclization. For example, the C2−C6 cyclization of **25** would produce

Scheme 9



Scheme 10



37 having a strained bicyclo[3.3.0]octatrienyl system (Scheme 10). Apparently, the emergence of a similar ring strain also prevented **9** from undergoing the C2−C6 cyclization. The effect of ring strain in deciding the biradical-forming pathway from thermolysis of enyne−allenes was clearly delineated by Schmittel and coworkers previously.[14a]

Conclusions

The success in capturing the aryl radical center in **21**, derived from thermolysis of the benzoenyne−allene **20**, with the tetraarylallenic moiety intramolecularly demonstrates the feasibility of generating **22** having two triarylmethyl radical centers under mild thermal conditions. Because of steric interactions, **22** cannot exist in the planar quinonoid form and behaves like a biradical.

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The central five-membered ring of the fluorene system in **20** and **25** is crucial in directing the reaction toward the Myers cycloaromatization pathway.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from benzophenone ketyl prior to use. Pyridinium chlorochromate, diisopropylethylamine, 1,4-cyclohexadiene, 2-bromobenzaldehyde, fluoranthene, $Pd(PPh_3)_4$, CuI, 2.5 M solution of *n*-butyllithium in hexanes, 1.7 M solution of *tert*-butyllithium in pentane, 1.0 M solution of phenylmagnesium bromide in THF, and 2.0 M solution of 4-*tert*-butylphenylmagnesium bromide in diethyl ether were purchased from Aldrich Chemical Co. and were used as received. Phenylacetylene, (4-*tert*-butylphenyl)acetylene, and (trimethylsilyl)acetylene were purchased from Farchan Laboratories Inc. and were used without further purification. 1-Iodo-9-fluorenone was prepared from fluoranthene according to the reported procedure.[9] Diphenyl(2,2-diphenyl-1-iodoethenyl)phosphine oxide (**6b**) was prepared by treatment of diphenyl(phenylethynyl)phosphine oxide with phenylmagnesium chloride in the presence of CuBr followed by iodine as reported previously.[7] Similarly, diphenyl[2,2-di(4-*tert*-butylphenyl)-1-iodoethenyl]phosphine oxide (**6a**) was synthesized from diphenyl[(4-*tert*-butylphenyl)ethynyl]phosphine oxide and 4-*tert*-butylphenylmagnesium bromide in 83% yield as a pale yellow solid. 2-(Phenylethynyl)benzaldehyde (**28b**) was prepared according to the reported procedure.[13] Melting points are uncorrected. Silica gel (230−400 mesh) was purchased from Baker. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) or $CDCl_3$ (^{13}C δ 77.00) as internal standard unless otherwise indicated.

1-[2-(Trimethylsilyl)ethynyl]-9-fluorenone (17). The procedure for the preparation of **28b** was adopted.[13] To a degassed solution containing 0.116 g of $Pd(PPh_3)_4$ (0.100 mmol), 0.061 g of CuI (0.32 mmol), 0.60 g of 1-iodo-9-fluorenone[9] (1.96 mmol), and 0.78 g of diisopropylethylamine (6.0 mmol) in 3 mL of *N*,*N*-dimethylformamide (DMF) was added via cannula a degassed solution of 0.79 g of (trimethylsilyl)acetylene (8.1 mmol) in 1.8 mL of DMF. After 12 h at room temperature, the reaction mixture was poured into a beaker containing 30 mL of a saturated NH_4Cl solution and 100 mL of pentane. After filtration, the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel/2% diethyl ether in hexanes) to afford 0.427 g of **17** (1.55 mmol, 79%) as a viscous yellow liquid: IR (neat) 2155, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.67 (1 H, dt, J = 7.3 and 1 Hz), 7.5 (2 H, m), 7.48−7.45 (1 H, m), 7.41 (1 H, t, J = 7.5 Hz), 7.35−7.27 (2 H, m), 0.33 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 191.77, 144.70, 142.92, 134.48, 134.03, 133.72, 133.65, 129.39, 124.21, 120.62, 120.18, 120.04, 101.87, 101.05, −0.18; MS *m*/*z* 276 (M^+), 261, 202; HRMS calcd $C_{18}H_{16}OSi$ 276.0970, found 276.0961.

1-Ethynyl-9-fluorenone (18). To 0.356 g of **17** (1.29 mmol) in 50 mL of diethyl ether was added a mixture of 20 mL of 10% NaOH and 50 mL of methanol. After 30 min at room temperature, 50 mL of diethyl ether and 50 mL of water were added, and the organic layer was separated, washed with 2 N HCl and water, and dried over $MgSO_4$. Evaporation of solvent furnished 0.263 g of **18** (1.29 mmol, 100%) as a yellow solid: mp 129−131 °C; IR (KBr) 3244, 2109, 1708, 750, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.68 (1 H, dt, J = 7.5 and 1 Hz), 7.54−7.49 (3 H, m), 7.44 (1 H, t, J = 7.5 Hz), 7.37 (1 H, dd, J = 7.6 and 1.3 Hz), 7.32 (1 H, ddd, J = 7.3, 6.3, and 2.2 Hz), 3.50 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 191.73, 144.84, 142.90, 134.66, 133.97, 133.90, 129.47, 124.41, 120.46, 120.24, 119.57, 83.40, 79.90; MS *m*/*z* 204 (M^+), 176; HRMS calcd $C_{15}H_8O$ 204.0575, found 204.0573. Anal. Calcd for $C_{15}H_8O$: C, 88.22; H, 3.95. Found: C, 88.24; H, 3.94.

Diketone 19. The same procedure was repeated as described for **17** except that 0.403 g of 1-iodo-9-fluorenone (**16**, 1.31 mmol) and 0.263 g of 1-ethynyl-9-fluorenone (**18**, 1.29 mmol) were used to afford 0.425 g of **19** (1.11 mmol, 86%) as orange crystalline needles: mp 281−283 °C; IR (KBr) 3057, 1714, 753, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.72−7.67 (4 H, m), 7.58−7.48 (8 H, m), 7.33 (2 H, td, J = 7.2 and 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 191.92, 144.80, 143.17, 134.55, 134.15, 134.05, 133.98, 133.66, 129.40, 124.28, 120.59, 120.36, 120.29, 92.21; MS *m*/*z* 382 (M^+), 354, 353, 324, 191; HRMS calcd for $C_{28}H_{14}O_2$ 382.0994, found 382.0982. Anal. Calcd for $C_{28}H_{14}O_2$: C, 87.94; H, 3.69. Found: C, 87.70; H, 3.61.

Diallene 20. To a solution of diphenyl[2,2-di(4-*tert*-butylphenyl)-1-iodoethenyl]phosphine oxide (**6a**, 2.41 g, 3.90 mmol) in 120 mL of THF was added 4.6 mL (7.8 mmol) of a 1.7 M solution of *tert*-butyllithium in pentane at −78 °C. After 30 min at −78 °C, the resulting mixture was added via cannula to a solution of diketone **19** (0.573 g, 1.50 mmol) in 280 mL of THF at 0 °C. The reaction mixture was stirred at room temperature for 5 h before 50 mL of water was added. The solution was concentrated in vacuo to about 150 mL, and then 100 mL of water and 200 mL of methylene chloride were introduced. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel/2% diethyl ether in pentane) to furnish 1.186 g of **20** (1.28 mmol, 85%) as a yellow solid: IR 3052, 1916, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75 (2 H, d, J = 7.3 Hz), 7.65 (2 H, dd, J = 7.4 and 1.0 Hz), 7.60 (2 H, d, J = 7.1 Hz), 7.36 (2 H, td, J = 7.4 and 1.0 Hz), 7.28 (2 H, td, J = 7.4 and 1.0 Hz), 7.07 (16 H, s), 6.98 (2 H, t, J = 7.5 Hz), 6.90 (2 H, dd, J = 7.7 and 1.0 Hz), 1.15 (36 H, s); ^{13}C NMR ($CDCl_3$) δ 207.41, 150.17, 138.81, 138.24, 138.04, 137.66, 132.59, 131.15, 128.52, 127.55, 127.16, 126.68, 124.82, 122.48, 119.91, 119.54, 119.14, 116.36, 107.30, 92.59, 34.26, 31.05; MS *m*/*z* 930 (M^+), 929, 915, 914, 913, 905, 889, 873, 812, 797; HRMS calcd for $C_{72}H_{65}$ ($M^+ - 1$) 929.5086, found 929.5115.

Chrysene 23. A degassed solution of diallene **20** (0.368 g, 0.396 mmol) in 10 mL of 1,4-CHD was heated at 75 °C, and the progress of the reaction was monitored by TLC. The color of the solution became dark green gradually. After 1 h at 75 °C, the starting diallene **20** disappeared completely. The reaction mixture was concentrated, and the residue was purified by flash chromatography (silica gel/2% CH_2Cl_2 in hexanes) to afford 0.080 g of **23** (0.086 mmol, 22%) as a yellow solid that gradually turns to brown color beginning at 180 °C in a sealed capillary tube. At 220 °C, it starts to soften and eventually melts and decomposes at 332 °C to produce a brown liquid. **23**: IR 3057, 1510 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.16 (2 H, d, J = 8.5 Hz), 7.85 (2 H, d, J = 6.9 Hz), 7.80 (2 H, d, J = 7.3 Hz), 7.4−7.2 (24 H, m), 6.93 (2 H, td, J = 7.6 and 0.8 Hz), 1.27 (36 H, s); ^{1}H NMR (CD_2Cl_2) δ 8.16 (2 H, d, J = 8.3 Hz), 7.89 (2 H, d, J = 6.9 Hz), 7.84 (2 H, d, J = 7.5 Hz), 7.38 (8 H, d, J = 8.7 Hz), 7.4−7.3 (6 H, m), 7.30 (8 H, d, J = 8.5 Hz), 7.23 (2 H, t, J = 7.3 Hz), 6.96 (2 H, td, J = 7.6 and 1.0 Hz), 1.28 (36 H, s); ^{13}C NMR ($CDCl_3$) δ 148.97, 140.90, 139.35, 138.22, 137.69, 137.62, 136.39, 135.93, 132.58, 129.36, 128.62, 127.70, 127.02, 126.67, 126.40, 126.18, 125.01, 120.07, 118.49, 54.77, 34.35, 31.32; MS *m*/*z* 932 (M^+), 875, 797, 279; HRMS calcd for $C_{72}H_{68}$ 932.5321, found 932.5297.

1-(Phenylethynyl)-9-fluorenone (24). The same procedure was repeated as described for **17** except that 1.013 g of 1-iodo-9-fluorenone (3.308 mmol) in 5 mL of DMF and 0.505 g of phenylacetylene (4.95 mmol) in 4 mL of DMF were used to afford 0.818 g of **24** (2.92 mmol, 88%) as a yellow solid: mp 98−99 °C; IR (KBr) 2213, 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74−7.66 (3 H, m), 7.5−7.27 (9 H, m); ^{13}C NMR ($CDCl_3$) δ 191.91, 144.78, 142.95, 134.44, 134.06, 133.81, 133.28, 132.88, 132.14, 129.32, 128.80, 128.32, 124.08, 122.92, 120.91, 120.20, 119.76, 95.77, 86.28; MS *m*/*z* 280 (M^+), 252, 250; HRMS calcd for $C_{21}H_{12}O$ 280.0888, found 280.0889. Anal. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.31. Found: C, 89.96; H, 4.40.

9-[Di(4-*tert*-butylphenyl)vinylidene]-1-(phenylethynyl)-9*H*-fluorene (25a). To a solution of 0.587 g of diphenyl[2,2-di(4-*tert*-butylphenyl)-1-iodoethenyl]phosphine oxide (**6a**, 0.950 mmol) in 35 mL of THF was added 1.1 mL (1.9 mmol) of a 1.7 M solution of *tert*-butyllithium in pentane at −78 °C, and the color of the solution changed to dark red immediately. After 30 min at −78 °C, the reaction mixture was introduced via

cannula to a flask containing 0.206 g of **24** (0.736 mmol) in 50 mL of THF at 0 °C. After 5 h at room temperature, 40 mL of diethyl ether and 60 mL of water were added. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.246 g of **25a** (0.44 mmol, 60%) as a pale yellow solid: IR 1918, 1599, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83−7.78 (2 H, m), 7.73 (1 H, dd, J = 6.4 and 1.2 Hz), 7.53 (1 H, dd, J = 7.7 and 1.0 Hz), 7.5−7.3 (11 H, m), 7.25−7.1 (5 H, m), 1.33 (18 H, s); ^{13}C NMR ($CDCl_3$) δ 207.51, 150.75, 139.42, 138.22, 137.76, 137.55, 132.80, 131.81, 131.56, 128.71, 127.95, 127.84, 127.79, 127.52, 127.36, 125.37, 123.15, 122.53, 120.18, 119.98, 119.31, 116.48, 107.65, 95.30, 87.38, 34.57, 31.31.

9-(Diphenylvinylidene)-1-(phenylethynyl)-9*H*-fluorene (25b). The same procedure was repeated as described for **25a** except that 0.83 g of diphenyl(2,2-diphenyl-1-iodoethenyl)phosphine oxide (**6b**, 1.6 mmol), 1.9 mL of a 1.7 M solution of *tert*-butyllithium (3.2 mmol) in pentane, and 0.352 g of **24** (1.26 mmol) were used to afford 0.508 g of **25b** (1.15 mmol, 91%) as an orange solid: IR 1924, 1597, 1493, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82−7.78 (2 H, m), 7.72 (1 H, dd, J = 7.3 and 1.2 Hz), 7.54−7.28 (14 H, m), 7.2−7.1 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 207.51, 139.49, 138.03, 137.82, 137.35, 135.73, 131.74, 131.53, 129.01, 128.48, 128.07, 127.99, 127.93, 127.78, 127.72, 127.44, 123.02, 122.53, 120.27, 120.06, 119.42, 116.87, 107.84, 95.47, 87.15; MS m/z 442 (M^+), 365, 289; HRMS calcd for $C_{35}H_{22}$ 442.1722, found 442.1713.

1-[Di(4-*tert*-butylphenyl)methyl]-2-phenylfluoranthene (27a). A solution of 0.231 g of **25a** (0.417 mmol) in 5 mL of 1,4-CHD was heated at 75 °C, and the progress of the reaction was monitored by TLC. After 1.5 h at 75 °C, the benzoenyne−allene **25a** disappeared completely. The reaction mixture was concentrated, and the residue was purified by flash chromatography (silica gel/hexanes) to afford 0.218 g of **27a** (0.392 mmol, 94%) as a pale yellow solid: mp 227−229 °C; IR (KBr) 3059, 752, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.99 (1 H, d, J = 6.7 Hz), 7.91 (1 H, d, J = 7.5 Hz), 7.85 (1 H, d, J = 8.3 Hz), 7.81 (1 H, s), 7.67 (1 H, dd, J = 8.2 and 7.0 Hz), 7.4−7.3 (3 H, m), 7.28−7.2 (7 H, m), 7.12 (4 H, d, J = 8.3 Hz), 7.01 (1 H, d, J = 7.9 Hz), 6.91 (1 H, td, J = 7.5 and 1 Hz), 6.17 (1 H, s), 1.31 (18 H, s); ^{13}C NMR ($CDCl_3$) δ 148.79, 145.88, 142.69, 139.81, 139.56, 139.39, 139.27, 136.69, 136.38, 132.97, 129.63, 128.88, 128.40, 127.75, 127.63, 127.17, 126.90, 126.81, 126.56, 126.28, 125.04, 120.44, 119.15, 52.07, 34.30, 31.34; MS m/z 556 (M^+), 555, 541, 499, 423, 421, 365, 289, 279; HRMS calcd for $C_{43}H_{40}$ 556.3130, found 556.3155. Anal. Calcd for $C_{43}H_{40}$: C, 92.76; H, 7.24. Found: C, 92.59; H, 7.27. The fluoranthene **27a** was recrystallized from a mixture of 5:3 ethanol and pentane for the X-ray structure determination.[11]

1-(Diphenylmethyl)-2-phenylfluoranthene (27b). The same procedure was repeated as described for **27a** except that 0.156 g of **25b** (0.353 mmol) in 4.8 mL of 1,4-CHD was heated at 75 °C for 1.5 h to afford 0.155 g of **27b** (0.349 mmol, 99%) as a yellow solid: mp 230−232 °C; IR (KBr) 3057, 1598, 740, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (1 H, dd, J = 6.9 and 0.6 Hz), 7.85 (2 H, t, J = 7.9 Hz), 7.80 (1 H, s), 7.66 (1 H, dd, J = 8.1 and 6.9 Hz), 7.35−7.1 (16 H, m), 7.04 (1 H, d, J = 7.9 Hz), 6.88 (1 H, td, J = 7.6 and 1.0 Hz), 6.15 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 145.87, 142.47, 141.84, 139.83, 139.07, 138.92, 136.74, 136.65, 132.96, 129.55, 129.34, 128.88, 128.49, 128.20, 127.84 (two overlapping signals), 127.07, 126.96, 126.83, 126.74, 126.33, 126.12, 120.58, 119.30, 52.84; MS m/z 444 (M^+), 367, 289, 165; HRMS calcd for $C_{35}H_{24}$ 444.1878, found 444.1862. Anal. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.27; H, 5.51.

2-[(4-*tert*-Butylphenyl)ethynyl]benzaldehyde (28a). The same procedure was repeated as described for **28b**[13] except that 2.22 g of (4-*tert*-butylphenyl)acetylene (14.1 mmol) and 1.85 g of 2-bromobenzaldehyde (10.0 mmol) were used to afford 2.025 g of **28a** (7.73 mmol, 77%) as a yellow solid: mp 62.5−64.5 °C; IR (KBr) 2214, 1698, 835, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.64 (1 H, s), 7.93 (1 H, d, J = 7.7 Hz), 7.62 (1 H, d, J = 7.7 Hz), 7.56 (1 H, t, J = 7.4 Hz), 7.5−7.36 (5 H, m), 1.32 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 191.82, 152.49, 135.75, 133.74, 133.15, 131.41, 128.39, 127.19, 127.13, 125.52, 119.25, 96.60, 84.26, 34.88, 31.12; MS m/z 262 (M^+), 247, 229, 219, 202; HRMS calcd for $C_{19}H_{18}O$ 262.1358, found 262.1348. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.15; H, 6.77.

4-*tert*-Butyl-2′-[(4-*tert*-butylphenyl)ethynyl]benzhydrol (29a). To a solution of 0.715 g of **28a** (2.73 mmol) in 10 mL of THF was added 1.7 mL of a 2.0 M solution of 4-*tert*-butylphenylmagnesium bromide (3.4 mmol) in diethyl ether at −30 °C under a nitrogen atmosphere. The reaction mixture then was allowed to warm to room temperature. After 1.5 h, 18 mL of a dilute NH_4Cl solution and 100 mL of diethyl ether were introduced. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (silica gel/6% diethyl ether in hexanes) to furnish 0.995 g of **29a** (2.51 mmol, 92%) as a white solid: mp 103−104 °C; IR (KBr) 3359, 2216, 834, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60 (1 H, d, J = 7.4 Hz), 7.50 (1 H, dd, J = 7.7 and 1.2 Hz), 7.4−7.2 (10 H, m), 6.34 (1 H, d, J = 3.7 Hz), 2.45, (1 H, d, J = 3.7 Hz), 1.31 (9 H, s), 1.28 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 151.76, 150.31, 145.58, 140.23, 132.33, 131.21, 128.61, 127.24, 126.32, 126.23, 125.37, 125.30, 121.36, 120.00, 94.76, 86.90, 73.89, 34.81, 34.48, 31.33, 31.16; MS m/z 396 (M^+), 381, 247; HRMS calcd for $C_{29}H_{32}O$ 396.2453, found 396.2452. Anal. Calcd for $C_{29}H_{32}O$: C, 87.83; H, 8.13. Found: C, 87.54; H, 8.18.

2-(Phenylethynyl)benzhydrol (29b). To a solution of 1.59 g of 2-(phenylethynyl)benzaldehyde[13] (**28b**, 7.72 mmol) in 18 mL of THF was added 9.3 mL of a 1.0 M solution of phenylmagnesium bromide (9.3 mmol) in THF at −30 °C under a nitrogen atmosphere. The reaction mixture then was allowed to warm to room temperature. After 1.5 h, 18 mL of a dilute NH_4Cl solution and 100 mL of diethyl ether were introduced. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was recrystallized from hexanes to furnish 1.77 g of **29b** (6.23 mmol, 81%) as a white solid: mp 99−101 °C; IR (KBr) 3333, 755, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (1 H, dm, J = 7.9 and 0.6 Hz), 7.54 (1 H, dm, J = 7.6 and 1 Hz), 7.5−7.43 (4 H, m), 7.41−7.22 (8 H, m), 6.39 (1 H, s), 2.55 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 145.45, 143.05, 132.40, 131.46, 128.83, 128.48, 128.38, 127.51, 127.39, 126.65, 126.34, 122.94, 121.21, 94.58, 87.40, 74.03; MS m/z 284 (M^+), 206, 178; HRMS calcd for $C_{21}H_{16}O$ 284.1201, found 284.1198.

4-*tert*-Butyl-2′-[(4-*tert*-butylphenyl)ethynyl]benzophenone (30a). To 0.646 g of pyridinium chlorochromate (3.00 mmol), suspended in 4 mL of anhydrous methylene chloride, was added 0.719 g of **29a** (1.82 mmol) in 4 mL of methylene chloride at room temperature. After 2 h, the black reaction mixture was diluted with 40 mL of diethyl ether, and the solvent was decanted. The remaining black residue was washed with diethyl ether. The combined organic layers were passed through a short Florisil column. Solvent was then evaporated, and the black residue was purified by flash chromatography (silica gel/2% diethyl ether in hexanes) to furnish 0.632 g of **30a** (1.60 mmol, 88%) as a white solid: mp 110-111 °C; IR (KBr) 2217, 1663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (2 H, d, J = 8.4 Hz), 7.56 (1 H, td, J = 7.7 and 1.9 Hz), 7.5−7.38 (5 H, m), 7.17 (2 H, d, J = 8.4 Hz), 6.90 (2 H, d, J = 8.4 Hz), 1.31 (9 H, s), 1.24 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 196.82, 156.81, 151.62, 141.80, 134.75, 132.29, 131.12, 130.26, 130.13, 128.63, 128.01, 125.29, 124.96, 122.00, 119.61, 95.36, 87.06, 35.14, 34.70, 31.08; MS m/z 394 (M^+), 379; HRMS calcd for $C_{29}H_{30}O$ 394.2297, found 394.2299. Anal. Calcd for $C_{29}H_{30}O$: C, 88.28; H, 7.66. Found: C, 88.36; H, 7.64.

(2-Phenylethynyl)benzophenone (30b). The same procedure was repeated as described for **30a** except that 0.345 g of pyridinium chlorochromate (1.60 mmol) and 0.284 g of **29b** (1.00 mmol) were used to afford 0.256 g of **30b** (0.91 mmol, 91%) as a yellow liquid: IR (neat) 2216, 1665, 755, 704, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93−7.90 (1 H, m), 7.90−7.87 (1 H, m), 7.66−7.41 (7 H, m), 7.28−7.16 (3 H, m), 7.09−7.03 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 197.04, 141.53, 137.34, 133.12, 132.53, 131.39, 130.29, 130.22, 128.66, 128.37, 128.16, 128.05, 122.57, 121.82, 95.12, 87.42; MS m/z 282 (M^+), 281, 265, 253, 252, 176;

HRMS calcd for $C_{21}H_{13}O$ ($M^+ - 1$) 281.0966, found 281.0959. Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.31; H, 5.00.

7-*tert*-Butyl-5,10,11-tri(4-*tert*-butylphenyl)-11*H*-benzo[*b*]fluorene (34a). To a solution of 1.446 g of diphenyl[2,2-di(4-*tert*-butylphenyl)-1-iodoethenyl]phosphine oxide (**6a**, 2.340 mmol) in 95 mL of dry THF at −78 °C was added 2.8 mL (4.76 mmol) of a 1.7 M solution of *tert*-butyllithium in pentane under a nitrogen atmosphere. After 30 min at −78 °C, 0.839 g of **30a** (2.13 mmol) in 15 mL of THF was introduced. After 5 h, the reaction mixture was gradually warmed to room temperature. After an additional 12 h at room temperature, 200 mL of diethyl ether and 100 mL of water were added. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel/hexanes) to afford 1.077 g of **34a** (1.61 mmol, 76%) as a white solid: mp 288−290 °C; IR (KBr) 3059, 833, 765, 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68−7.61 (2 H, m), 7.56 (1 H, d, J = 2.2 Hz), 7.53 (1 H, d, J = 9 Hz), 7.46 (2 H, dt, J = 8.2 and 2 Hz), 7.42−7.35 (2 H, m), 7.30 (1 H, dd, J = 7.9 and 2.0 Hz), 7.14−7.03 (2 H, m), 7.0−6.89 (2 H, m), 6.84 (2 H, d, J = 8.2 Hz), 6.48 (1 H, d, J = 7.7 Hz), 6.4−6.33 (3 H, m), 5.08 (1 H, s), 1.49 (9 H, s), 1.38 (9 H, s), 1.23 (9 H, s), 1.19 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 150.59, 149.76, 149.27, 148.07, 147.66, 144.33, 140.87, 139.12, 136.82, 136.09, 135.89, 135.60, 133.17, 133.07, 130.49, 129.93, 129.78, 128.91, 127.74, 127.29, 126.68, 125.83, 125.77, 125.60, 125.24, 124.90, 124.43, 123.85, 123.53, 121.60, 53.21, 34.80, 34.77, 34.47, 34.15, 31.58, 31.55, 31.36, 31.07; MS m/z 668 (M^+), 653, 611, 535; HRMS calcd for $C_{51}H_{56}$ 668.4382, found 668.4385. Anal. Calcd for $C_{51}H_{56}$: C, 91.56; H, 8.44. Found: C, 91.49; H, 8.54. Benzofluorene **34a** was recrystallized from a 2:1 mixture of methanol and methylene chloride for the X-ray structure determination.[11]

5,10,11-Triphenyl-11*H*-benzo[*b*]fluorene (34b). The same procedure was repeated as described for **34a** except that 0.141 g of **30b** (0.500 mmol) and 0.253 g of **6b** (0.500 mmol) were used to afford 0.11 g of **34b** (0.25 mmol, 50%) as a white solid: mp 197−199 °C; IR 1595, 1493, 762, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7−7.3 (14 H, m), 7.13−6.9 (6 H, m), 6.57−6.48 (3 H, m), 5.15 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 149.67, 144.20, 142.19, 140.32, 139.05, 138.36, 136.76, 136.42, 133.21, 133.05, 132.25, 130.46, 130.25, 130.21, 129.42, 129.17, 129.13, 128.29, 128.16, 127.82, 127.68, 126.91, 126.80, 126.38, 125.88, 125.70, 125.40, 125.27, 123.57, 53.69; MS m/z 444 (M^+), 367; HRMS calcd for $C_{35}H_{24}$ 444.1878, found 444.1904. Anal. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.51; H, 5.49. Benzofluorene **34b** was recrystallized from a 2:1 mixture of methanol and methylene chloride for the X-ray structure determination.[11]

5,10-Diphenyl-11*H*-benzo[*b*]fluorene (36). The same procedure was repeated as described for **34b** except that 0.206 g of **28b** (1.00 mmol) was used to afford 0.189 g of **36** (0.51 mmol, 51%) as a white solid: mp 194−196 °C; IR 3060, 762, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7−7.35 (15 H, m), 7.21 (1 H, td, J = 7.4 and 1.2 Hz), 7.04 (1 H, t, J = 7.7 Hz), 6.51 (1 H, d, J = 7.9 Hz), 3.89 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 144.28, 141.40, 139.47, 139.25, 139.13, 136.91, 135.23, 133.15, 132.96, 131.50, 130.16, 129.95, 129.10, 128.65, 127.75, 127.39, 127.05, 126.49, 126.46, 125.75, 125.23, 125.07, 124.79, 123.71, 36.57; MS m/z 368 (M^+), 291; HRMS calcd for $C_{29}H_{20}$ 368.1565, found 368.1561. Anal. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.63; H, 5.56.

Acknowledgment. The financial support of the National Science Foundation (CHE-9618676) to K.K.W. is gratefully acknowledged. J.L.P. acknowledges the support (CHE-9120098) provided by the Chemical Instrumentation Program of the National Science Foundation for the acquisition of a Siemens P4 X-ray diffractometer in the Department of Chemistry at West Virginia University.

Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **6a**, **17**−**20**, **23**, **24**, **25a**,**b**, **27a**,**b**, **28a**, **29a**,**b**, **30a**,**b**, **34a**,**b**, and **36** and the ORTEP drawings of the crystal structures of **27a**, **34a**, and **34b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO982326K