Biradicals from Benzoenyne−Allenes. Application in the Synthesis of 11*H*-Benzo[*b*]fluoren-11-ols, 1*H*-Cyclobut[*a*]indenes, and Related Compounds

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Received May 4, 2001

New synthetic pathways to 11*H*-benzo[*b*]fluoren-11-ols, 1*H*-cyclobut[*a*]indenes, and related compounds via biradicals generated from benzoenyne−allenes were developed. Treatment of the diacetylenic propargylic alcohols **13**, derived from condensation between benzophenones and the lithium acetylide of 1-(2-ethynylphenyl)-2-phenylethyne, with thionyl chloride produced the 11-chloro-11*H*-benzo[*b*]fluorene **14** and, after hydrolysis, the corresponding 11*H*-benzo[*b*]fluoren-11-ols **15**. The transformation involved a sequence of reactions, including a biradical-forming C2−C6 cyclization (Schmittel cyclization) reaction of the chlorinated benzoenyne−allene intermediates followed by an intramolecular radical−radical coupling to form the formal Diels−Alder adducts. Interestingly, in the case of the diacetylenic propargylic alcohol **26**, obtained from dibenzosuberenone (**25**), an intramolecular [2 + 2] cycloaddition reaction of the chlorinated benzoenyne−allene intermediate occurred, furnishing the 1*H*-cyclobut[*a*]indene **27** exclusively. The dramatic change of the reaction pathway could be attributed to the emergence of a steric strain due to the nonbonded interactions with the chloro substituent along the pathway toward the formal Diels−Alder adduct **31**. On the other hand, the non-chlorinated benzoenyne−allene, derived from prototropic isomerization of the diacetylenic hydrocarbon **60**, underwent a formal Diels−Alder reaction to furnish the 11*H*-benzo[*b*]fluorene-type hydrocarbon **61** exclusively.

Introduction

We recently reported an efficient transformation of the monoprotected acenaphthenequinone **1** to the chloride **8** via condensation with the lithium acetylide **2** to form **3** followed by treatment of **3** with thionyl chloride (Scheme 1).[1] Apparently, thionyl chloride promoted a sequence of reactions with an initial formation of the chlorosulfite **4** followed by an S_Ni' reaction to produce in situ the chlorinated benzoenyne−allene **5**.[2] A Schmittel cyclization reaction[3] then generated the biradical **6** which in turn underwent an intramolecular radical−radical coupling to furnish the formal Diels−Alder adduct **7** and, after tautomerization, the chloride **8**. The chloride **8** was prone to hydrolysis to form the corresponding alcohol. It was possible to reduce the crude chloride with sodium borohydride to produce **9**. Deprotection then afforded **10** having a carbonyl group to allow a repeat of the condensation and the Schmittel cyclization sequence to give **11** having a carbon framework represented on the surface of C_{60}. The thionyl chloride-promoted cascade sequence was very facile at ambient and/or subambient temperatures, providing an efficient pathway to the polycyclic aromatic compounds.

To probe the scope and limitations of the thionyl chloride-induced cascade transformation, several representative aryl ketones were selected for condensation with **2**. A new synthetic route to the benzoenyne−allenes without a chloro substituent was also developed to allow a direct transformation to the corresponding polycyclic aromatic hydrocarbons.

Results and Discussion

11*H*-Benzo[*b*]fluoren-11-ols and Related Compounds. The reaction sequence outlined in Scheme 2 depicted the use of benzophenone (**12a**) for condensation with the lithium acetylide **2** to furnish the propargylic alcohol **13a** in 93% yield. Upon treatment with thionyl chloride in the presence of pyridine, the alcohol **13a** was converted to the chloride **14a** via the cascade sequence

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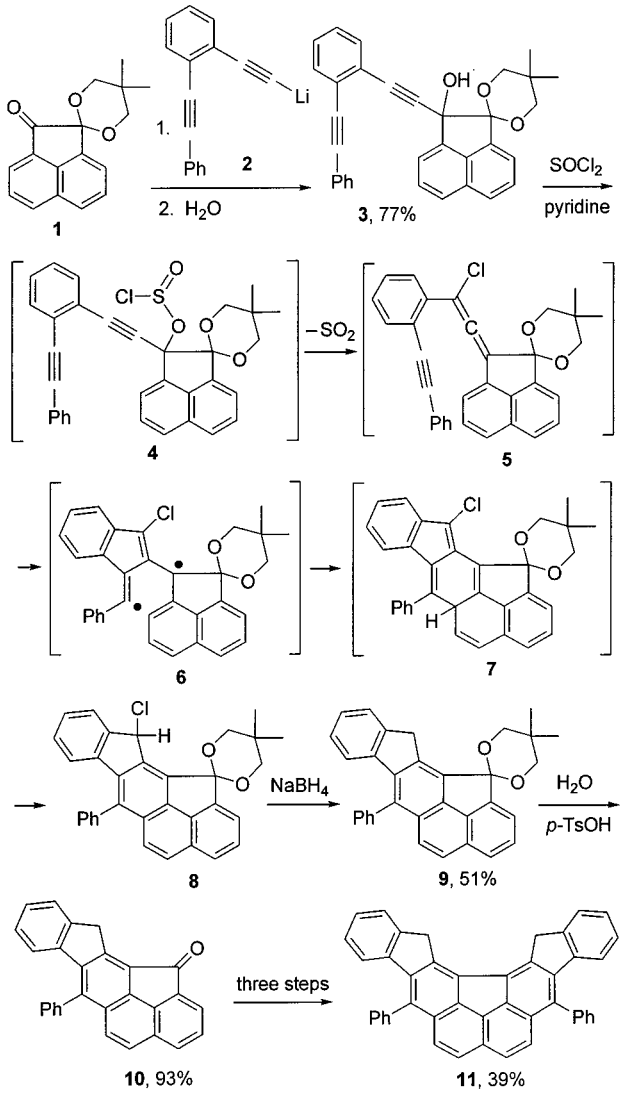
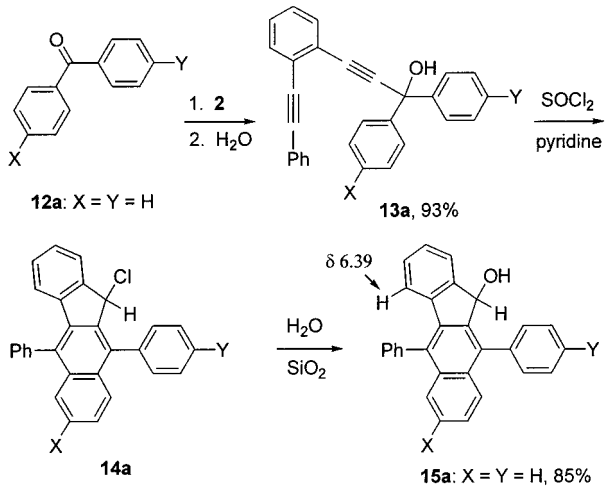
10.1021/jo0104577 CCC: $20.00
Published on Web 09/12/2001

Scheme 1



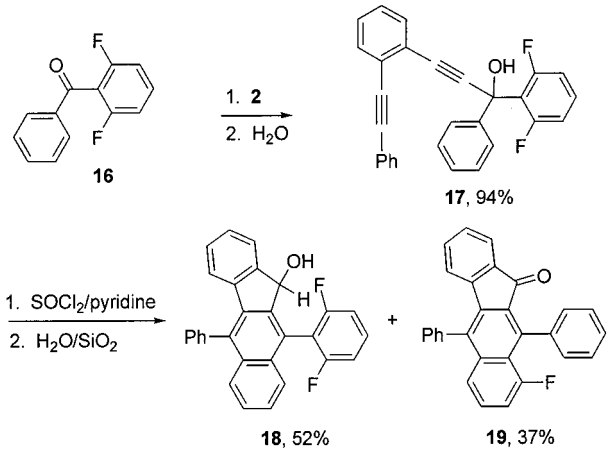
Scheme 2



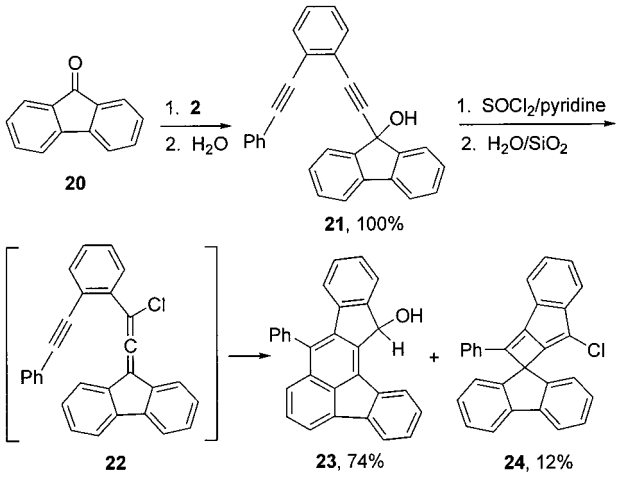
outlined in Scheme 1. The chloride **14a** was also prone to hydrolysis and, on exposure to water/silica gel, was converted to the corresponding 11*H*-benzo[*b*]fluoren-11-ol **15a** in 85% overall yield from **13a**.

The ^{13}C NMR spectrum of **15a** exhibited 27 signals for the aromatic carbons with the signal at δ 129.1 having twice the intensity of those from other aromatic methine

Scheme 3



Scheme 4



(CH) carbons. The observation of 27 aromatic signals, only one less than the number of 28 aromatic carbons, indicates that the two phenyl substituents are oriented perpendicular to the rest of the aromatic system, and the rates of their rotations are slower than the NMR time scale. In this conformation, all four *ortho* carbons of the two phenyl substituents are in different magnetic environments, as are the four *meta* carbons. They could thus exhibit the ^{13}C NMR signals with different chemical shifts. Furthermore, the aromatic hydrogen indicated with an arrow is shielded by the neighboring phenyl group, shifting its ^{1}H NMR signal upfield to δ 6.39 (doublet). In every case of this study, the adducts derived from the formal Diels−Alder reaction of benzoenyne−allenes exhibited an aromatic ^{1}H NMR signal with such an upfield shift.

Several other benzophenone derivatives were also used for the synthesis of 11*H*-benzo[*b*]fluoren-11-ols (Table 1). With **13c** and **13d**, the intramolecular radical−radical coupling slightly favored the attack of the benzene ring having a bromo or a methoxyl substituent. In the case of **17**, the attack of the benzene ring having the fluoro substituents resulted in the loss of one fluorine substituent, leading to the benzofluorenone **19** (Scheme 3).

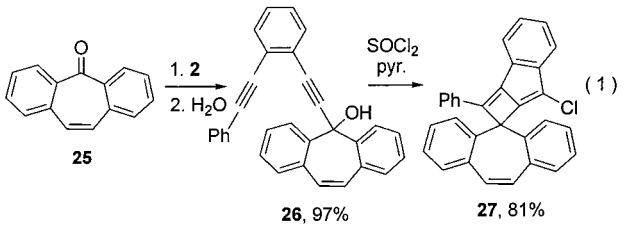
The use of 9-fluorenone (**20**) as a diaryl ketone produced **23** in 74% yield (Scheme 4). Interestingly, a small amount of the 1*H*-cyclobut[*a*]indene **24** (12%), produced from the intramolecular [2 + 2] cycloaddition reaction between the allenic and the acetylenic moieties in **22**, was

Table 1. Synthesis of 11*H*-Benzo[*b*]fluoren-11-ols

benzophenones	propargylic alcohols, isolated yield	11*H*-benzo[*b*]fluoren-11-ols, isolated yield
12b: X = Y = Br	**13b**, 88%	**15b**, 65%
12c: X = Br, Y = H	**13c**, 86%	**15c**: X = Br, Y = H, 37% **15c′**: X = H, Y = Br, 28%
12d: X = MeO, Y = H	**13d**, 74%	**15d**: X = MeO, Y = H, 45% **15d′**: X = H, Y = MeO, 25%

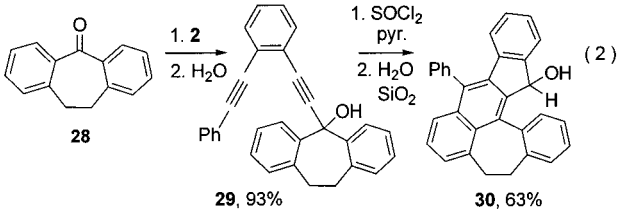
also isolated. The structure of **24** was unequivocally established by X-ray analysis. While an intramolecular [2 + 2] cycloaddition reaction of a benzoenyne−allene system was reported earlier,[4] no such precedent was observed for the benzoenyne−allenes having a phenyl substituent at the allenic terminus, which invariably resulted in the formation of the adducts derived only from the formal Diels−Alder reaction.

[4 + 2] Cycloaddition versus [2 + 2] Cycloaddition. We were surprised to observe that treatment of **26**, derived from dibenzosuberenone (**25**) and **2**, with thionyl chloride produced the [2 + 2] cycloaddition adduct **27** exclusively (eq 1). The structure of **27** was unequivocally



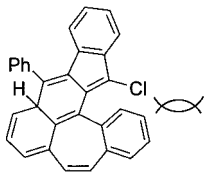
(1)

established by X-ray analysis. One the other hand, with **29**, derived from dibenzosuberone (**28**) and **2**, the formal [4 + 2] cycloaddition reaction of the chlorinated benzoenyne−allene was again the preferred pathway, leading to the formation of the alcohol **30** (eq 2). The reason for



(2)

such a dramatic change of the reaction pathway is not clear at this time. Molecular modeling suggests the emergence of a steric strain due to the nonbonded interactions between the chloro substituent and one of the neighboring benzene rings along the pathway toward the formal [4 + 2] cycloaddition reaction, leading to the Diels−Alder adduct **31**. Replacing the central carbon−carbon double bond in **26** with the dimethylene linkage in **29** appears to reduce the nonbonded interactions.



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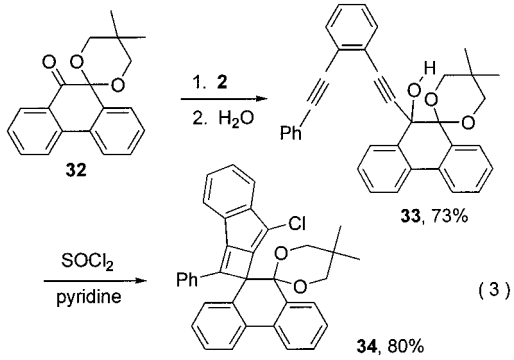
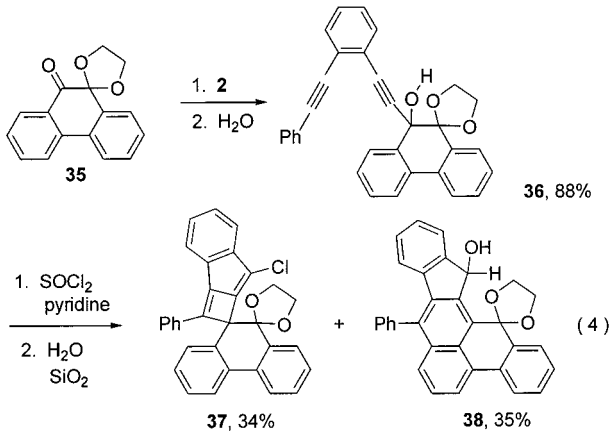
The importance of the steric interactions in determining the reaction pathway was supported by the following two cases of the monoprotected phenanthrenequinone. With a sterically more demanding 5,5-dimethyl-1,3-dioxane protective group in **33**, only the [2 + 2] cycloaddition adduct **34**[5] was obtained (eq 3). On the other hand,



(3)

with a sterically less demanding ethylene ketal protective group in **36**, an essentially 1:1 mixture of the [2 + 2] and the [4 + 2] cycloaddition adducts **37**[5] and **38** was produced (eq 4).

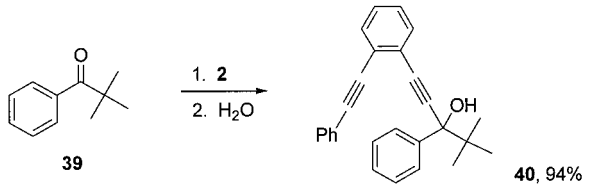


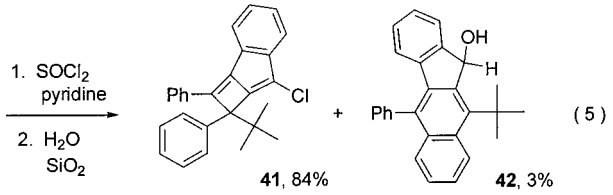
(4)

With **40**, derived from 2,2-dimethylpropiophenone (**39**), the [2 + 2] cycloaddition adduct **41**[5] was produced predominantly (eq 5). However, connecting one of the methyl groups in **40** to the benzene ring to form **45** and **46** appears to reduce the steric interactions between the *gem*-dimethyl group and the chloro substituent along the pathway of the [4 + 2] cycloaddition reactions. As a result, **49** and **50** were formed predominantly with the effect particularly dramatic in the case of **46** having a five-membered ring (eq 6).

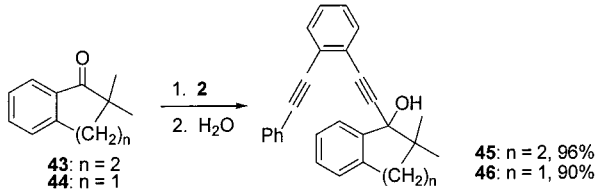
A New Pathway to Benzoenyne−Allenes. We have also developed a new synthetic pathway to benzoenyne−allenes without a chloro substituent. Treatment of **40** with triethylsilane followed by trifluoroacetic acid[6] pro-

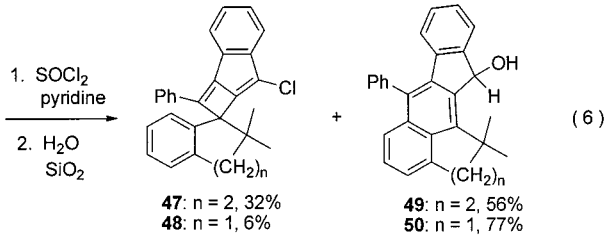
(5) The structure was unequivocally established by X-ray analysis.





(5)



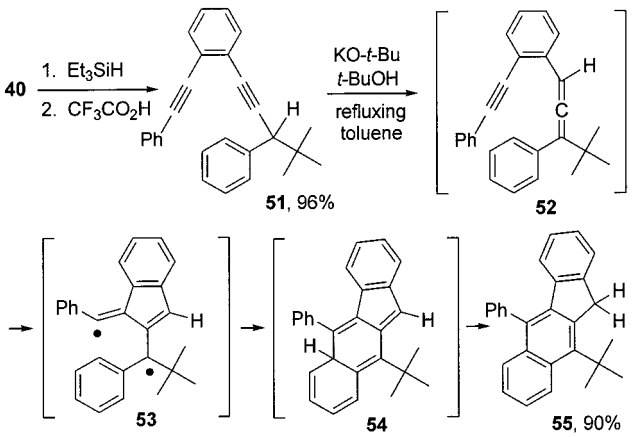


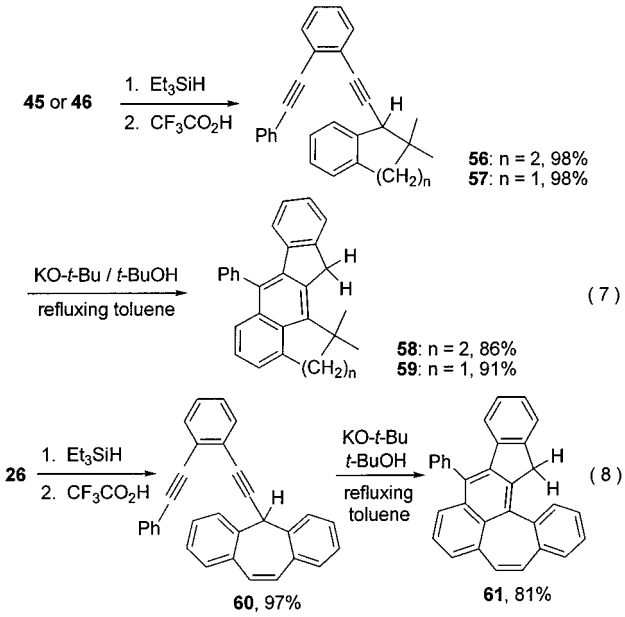
(6)

duced **51** in excellent yield (Scheme 5). Prototropic isomerization, promoted by potassium *tert*-butoxide in refluxing toluene,[7] produced the benzoenyne−allene **52** in situ, which in turn underwent a formal [4 + 2] cycloaddition reaction to furnish **54** and, after tautomerization, the hydrocarbon **55**. At room temperature, the formation of **52** as the major isomer in equilibrium with **51** (**52**:**51** = 6:1) was detected. The benzoenyne−allene **52** gave a ^{1}H NMR signal at δ 6.93 as a singlet for the allenic hydrogen and a ^{13}C NMR signal at δ 203.8 for the central allenic carbon. It is worth noting that only the [4 + 2] cycloaddition adduct **55** was produced from **52**, in sharp contrast with the formation of predominantly the [2 + 2] cycloaddition adduct **41** from the chlorinated system. The fact that replacing the chloro substituent with the sterically less demanding allenic hydrogen in **52** dramatically altered the course of the reaction is consistent with the proposition regarding the importance of the steric interactions in directing the reaction toward the [2 + 2] cycloaddition pathway. It is conceivable that removal of the chloro substituent could also alter the electronic nature of the system in favor of the formal Diels−Alder pathway.

Similarly, the exclusive formation of the [4 + 2] cycloaddition adducts **58**, **59**, and **61**[5] was also observed (eqs 7 and 8). It is worth noting that the X-ray structure of **61** clearly indicates that the phenyl substituent is essentially perpendicular to the central aromatic system as concluded for **15a**.

Scheme 5





(7)

(8)

Conclusions

The thionyl chloride-induced cascade cyclization of diacetylenic propargylic alcohols provides an efficient synthetic route to 11*H*-benzo[*b*]fluoren-11-ols and related compounds.[8] The simplicity of the synthetic sequence and the mildness of the reaction condition make this pathway especially attractive. Interestingly, in certain cases the intramolecular [2 + 2] cycloaddition reaction of the chlorinated benzoenyne−allene intermediates occurred preferentially to form 1*H*-cyclobut[*a*]indenes. Competition from the intramolecular [2 + 2] cycloaddition reaction could be avoided with the non-chlorinated benzoenyne−allenes, providing direct access to novel polycyclic aromatic hydrocarbons.[9]

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, thionyl chloride, pyridine (anhydrous), benzophenones, 9-fluorenone (**20**), diben-

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zosuberenone (**25**), dibenzosuberone (**28**), phenanthrenequinone, 2,2-dimethyl-1,3-propanediol, ethylene glycol, 2,2-dimethylpropiophenone (**39**), trifluoroacetic acid, triethylsilane, and potassium *tert*-butoxide (1.0 M) in THF were purchased from Aldrich and were used as received. The 2,2-dimethylpropylene monoketal **32** of phenanthrenequinone was prepared in 96% yield according to the reported procedure.[10] Similarly, **35** was prepared from phenanthrenequinone and ethylene glycol in 55% yield. 1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthylene (**43**)[11] and 2,2-dimethyl-1-indanone (**44**)[12] were prepared according to the reported procedures. Silica gel for flash column chromatography was purchased from ICN. Melting points were uncorrected. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) and $CDCl_3$ (^{13}C δ 77.00) as internal standards.

1,1-Diphenyl-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (13a). The following procedure is representative for the preparation of the diacetylenic propargylic alcohols. To 0.395 g (1.95 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne[1,3g,13] in 18 mL of THF under a nitrogen atmosphere at 0 °C was added 0.78 mL of a 2.5 M solution of *n*-butyllithium (1.95 mmol) in hexanes. After 30 min of stirring, 0.322 g (1.77 mmol) of benzophenone (**12a**) in 40 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/5% CH_2Cl_2 and 5% Et_2O in hexanes) to provide 0.633 g (1.65 mmol, 93% yield) of **13a** as a viscous liquid: R_f = 0.56 (hexanes:Et_2O = 2:1); IR 3545, 2217, 756, 692 cm^{-1}; ^{1}H NMR δ 7.79−7.75 (4 H, m), 7.60−7.53 (2 H, m), 7.43−7.23 (13 H, m), 3.00 (1 H, s); ^{13}C NMR δ 144.9, 132.2, 132.0, 131.8, 128.41, 128.36, 128.25, 127.9, 127.6, 126.1, 125.9, 124.8, 122.9, 95.6, 93.5, 88.1, 85.9, 75.0; MS *m*/*z* 384 (M$^+$), 367, 307, 279, 105; HRMS calcd for $C_{29}H_{20}O$ 384.1514, found 384.1520.

5,10-Diphenyl-11*H*-benzo[*b*]fluoren-11-ol (15a). The following procedure is representative for the synthesis of 11*H*-benzo[*b*]fluoren-11-ols. To 0.575 g (1.50 mmol) of **13a** in 50 mL of anhydrous diethyl ether under a nitrogen atmosphere at 0 °C was added a mixture of 0.12 mL of thionyl chloride (1.65 mmol) and 0.27 mL of pyridine (3.30 mmol) in 30 mL of anhydrous diethyl ether. The reaction mixture was then allowed to warm to room temperature. After 4 h, 50 mL of water was added, and the mixture was extracted with diethyl ether. The combined organic extracts were washed with a saturated sodium chloride solution (50 mL) and water (50 mL), dried over sodium sulfate, and concentrated to give the crude chloride **14a**. Purification by flash column chromatography (silica gel/5% CH_2Cl_2 and 5% Et_2O in hexanes) resulted in the conversion of the chloride to the alcohol **15a**, which was obtained (0.489 g, 1.27 mmol, 85% yield) as a light yellow solid: R_f = 0.30 (hexanes:Et_2O = 3:1); mp 142−144 °C; IR (KBr) 3448, 763, 701 cm^{-1}; ^{1}H δ 7.7−7.34 (15 H, m), 7.23 (1 H, t, *J* = 7.5 Hz), 7.06 (1 H, t, *J* = 7.5 Hz), 6.39 (1 H, d, *J* = 7.7 Hz), 5.83 (1 H, s), 1.84 (1 H, br s); ^{13}C δ 145.6, 141.0, 139.9, 138.6, 137.7, 136.6, 135.1, 134.1, 133.5, 132.3, 130.8, 130.1, 130.0, 129.3, 129.2, 129.1, 128.9, 128.6, 128.0, 127.96, 127.9, 126.6, 126.1, 126.06, 125.7, 125.2, 123.6, 73.5; MS *m*/*z* 384 (M$^+$), 367, 307; HRMS calcd for $C_{29}H_{20}O$ 384.1514, found 384.1500. Anal. Calcd for $C_{29}H_{20}O$: C, 90.60; H, 5.24. Found: C, 90.17; H, 5.34.

9-[[2-(Phenylethynyl)phenyl]ethynyl]-9*H*-fluoren-9-ol (21). The same procedure was repeated as described for **13a** except that 0.358 g of 1-(2-ethynylphenyl)-2-phenylethyne (1.77 mmol) and 0.360 g of 9-fluorenone (2.00 mmol) were used to afford **21** (0.676 g, 1.77 mmol, 100% yield) as a white solid: mp 126−127 °C; IR (KBr) 3406, 2217 cm^{-1}; ^{1}H δ 7.77 (2 H, d, *J* = 7.5 Hz), 7.63 (2 H, d, *J* = 7.5 Hz), 7.52−7.46 (2 H, m), 7.38 (2 H, td, *J* = 7.5 and 1.2 Hz), 7.31−7.21 (9 H, m), 2.72 (1 H, br OH); ^{13}C δ 147.0, 139.1, 132.3, 131.7, 129.6, 128.6, 128.3, 128.2, 127.8, 126.1, 124.8, 124.5, 123.0, 120.2, 93.4, 92.8, 87.8, 81.9, 75.2; MS *m*/*z* 382 (M$^+$), 365, 354; HRMS calcd for $C_{29}H_{18}O$ 382.1358, found 382.1350. Anal. Calcd for $C_{29}H_{18}O$: C, 91.07; H, 4.74. Found: C, 90.91; H, 4.87.

Alcohol 23 and 1*H*-Cyclobut[*a*]indene 24. The same procedure was repeated as described for **15a** except that 0.360 g of **21** (0.940 mmol) was used to afford **23** (0.265 g, 0.694 mmol, 74% yield) as a light yellow solid and **24**[5] (0.046 g, 0.115 mmol, 12% yield) as an orange solid. **23**: mp 222−223 °C; IR (KBr) 3322, 754, 702 cm^{-1}; ^{1}H δ 8.47−8.42 (1 H, m), 7.98−7.89 (2 H, m), 7.75 (1 H, d, *J* = 7.5 Hz), 7.63−7.55 (3 H, m), 7.55−7.41 (6 H, m), 7.31 (1 H, td, *J* = 7.5 and 1.0 Hz), 7.11 (1 H, t, *J* = 7.2 Hz), 6.57 (1 H, d, *J* = 7.9 Hz), 6.20 (1 H, s), 2.09 (1 H, br OH); ^{13}C δ 146.0, 140.2, 140.1, 139.5, 137.9, 137.6, 137.3, 137.1, 134.0, 133.2, 132.3, 130.9, 130.2, 129.9, 129.0, 128.8, 128.2, 128.1, 128.0, 127.8, 125.6, 125.3, 123.6, 121.4, 119.8, 73.6; MS *m*/*z* 382 (M$^+$), 366, 350, 305; HRMS calcd for $C_{29}H_{18}O$ 382.1358, found 382.1345. **24:** mp 183−184 °C; IR (KBr) 1195, 746, 682 cm^{-1}; ^{1}H δ 7.91−7.84 (3 H, m), 7.50−7.41 (6 H, m), 7.40−7.30 (1 H, m), 7.30−7.18 (5 H, m), 7.13−7.07 (2 H, m); ^{13}C δ 150.2, 149.2, 146.38, 146.35, 140.2, 140.1, 131.5, 130.0, 129.3, 128.9, 128.6, 127.83, 127.75, 124.89, 124.85, 123.9, 120.2, 120.1, 110.1, 64.6; MS *m*/*z* 400 (M$^+$), 365; HRMS calcd for $C_{29}H_{17}Cl$ 400.1019, found 400.1021.

1*H*-Cyclobut[*a*]indene 27. The same procedure was repeated as described for **15a** except that 0.313 g of **26** (0.767 mmol) was used to afford **27**[5] (0.266 g, 0.624 mmol, 81% yield) as an orange solid: compound turns dark at 205 °C and becomes black without melting at 217 °C; IR 1489, 1437, 731, 688 cm^{-1}; ^{1}H δ 8.12 (2 H, d, *J* = 7.1 Hz), 7.75 (3 H, d, *J* = 7.5 Hz), 7.61 (2 H, t, *J* = 7.4 Hz), 7.52 (1 H, t, *J* = 7.3 Hz), 7.41 (2 H, dd, *J* = 7.4 and 1.4 Hz), 7.34−7.15 (9 H, m); ^{13}C δ 148.8, 147.5, 144.0, 143.9, 140.1, 135.0, 134.3, 132.3, 130.2, 129.7, 129.6, 128.9, 128.4, 128.0, 127.3, 126.8, 125.0, 124.0, 120.5, 111.4, 67.6; MS *m*/*z* 426 (M$^+$), 391, 349, 313; HRMS calcd for $C_{31}H_{19}Cl$ 426.1175, found 426.1175. Anal. Calcd for $C_{31}H_{19}Cl$: C, 87.21; H, 4.49; Cl, 8.30. Found: C, 87.24; H, 4.41; Cl, 8.41.

1*H*-Cyclobut[*a*]indene 34. The same procedure was repeated as described for **15a** except that 0.159 g of the alcohol **33** (0.320 mmol) was used to afford **34**[5] (0.131 g, 0.255 mmol, 80% yield) as an orange solid: mp 185−187 °C; IR 1206, 758, 689 cm^{-1}; ^{1}H δ 8.1−7.9 (5 H, m), 7.80 (1 H, d, *J* = 7.3 Hz), 7.57 (1 H, td, *J* = 7.6 and 1.4 Hz), 7.5−7.13 (10 H, m), 3.60 (1 H, d, *J* = 11.3 Hz), 3.46 (1 H, d, *J* = 11.3 Hz), 3.37 (2 H, s), 0.99 (3 H, s). 0.70 (3 H, s); ^{13}C δ 148.9, 145.7, 139.6, 136.4, 134.9, 134.8, 133.3, 133.0, 129.82, 129.76, 129.4, 129.3, 128.8, 128.6, 128.0, 127.9, 127.7, 127.2, 126.8, 125.1, 124.7, 123.9, 123.6, 120.0, 111.3, 99.6, 71.7, 70.9, 68.1, 33.3, 24.9, 24.8; MS *m*/*z* 514 (M$^+$), 479, 428, 393, 365; HRMS calcd for $C_{35}H_{27}ClO_2$ 514.1700, found 514.1695. Anal. Calcd for $C_{35}H_{27}ClO_2$: C, 81.62; H, 5.28; Cl, 6.88. Found: C, 81.83; H, 5.53; Cl, 6.71. The broad ^{1}H NMR signal at δ 8.0 suggests a somewhat restricted rotation of the phenyl substituent and/or a relatively slow interconversion of the conformational isomers.

1*H*-Cyclobut[*a*]indene 37 and Alcohol 38. The same procedure was repeated as described for **15a** except that 0.123 g (0.27 mmol) of **36** was used to afford **37**[5] (0.044 g, 0.093 mmol, 34% yield) as an orange solid and **38** (0.043 g, 0.095 mmol, 35% yield) as a yellow solid. **37**: mp 246−247 °C; IR 1201, 734, 689 cm^{-1}; ^{1}H δ 7.94 (2 H, d, *J* = 7.7 Hz), 7.81−7.73 (3 H, m), 7.62 (1 H, dd, *J* = 7.7 and 1.3 Hz), 7.55 (1 H, td, *J* = 7.7 and 1.4 Hz), 7.43−7.17 (10 H, m), 4.14 (1 H, dt, *J* = 7.3 and 4.8 Hz), 3.95−3.88 (2 H, m), 3.83−3.75 (1 H, m); ^{13}C δ 148.9, 147.4, 146.0, 139.4, 136.2, 134.3, 132.9, 132.7, 129.71, 129.66, 129.3, 128.8, 128.7, 128.24, 128.19, 128.0, 124.8, 124.63, 124.55, 124.0, 123.9, 120.1, 111.4, 108.0, 67.4, 66.7, 65.2; MS *m*/*z* 472 (M$^+$), 437, 427, 393, 365; HRMS calcd for $C_{32}H_{21}ClO_2$ 472.1230, found 472.1235. **38:** IR 3492, 760 cm^{-1}; ^{1}H δ 8.22 (1 H, dd, *J* = 6.0 and 2.2 Hz), 8.13 (1 H, d, *J* = 7.7 Hz), 7.77 (1 H, dd, *J* = 7.6 and 1.5 Hz), 7.70 (1 H, d, *J* = 7.1 Hz), 7.63−7.38 (9 H, m), 7.28 (1 H, t, *J* = 7.3 Hz), 7.05 (1 H, t, *J* = 7.3

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Hz), 6.30 (1 H, d, J = 7.7 Hz), 6.06 (1 H, d, J = 1.6 Hz), 4.97 (1 H, d, J = 2.0 Hz), 4.76−4.69 (2 H, m), 4.21−4.05 (2 H, m); ^{13}C δ 145.1, 142.9, 139.3, 138.4, 137.3, 135.3, 134.8, 134.0, 133.1, 130.1, 129.7, 129.2, 129.15, 129.10, 128.7, 128.2, 128.0, 127.5, 127.3, 126.8, 126.4, 125.2, 124.7, 124.4, 123.6, 121.2, 107.1, 73.2, 67.3, 62.8.

4,4-Dimethyl-3-phenyl-1-[2-(2-phenylethynyl)phenyl]-1-pentyn-3-ol (40). The same procedure was repeated as described for **13a** except that **2** derived from 0.468 g of 1-(2-ethynylphenyl)-2-phenylethyne (2.31 mmol) and 0.341 g of 2,2-dimethylpropiophenone (**39**, 2.10 mmol) were used to afford **40** (0.722 g, 1.98 mmol, 94% yield) as a viscous liquid: IR (neat) 3562, 2215 cm^{-1}; ^{1}H δ 7.77−7.72 (2 H, m), 7.58−7.43 (4 H, m), 7.35−7.22 (8 H, m), 2.38 (1 H, s), 1.09 (9 H, s); ^{13}C δ 142.0, 132.2, 132.1, 131.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.3, 127.0, 125.8, 125.1, 123.0, 96.3, 93.2, 88.3, 84.5, 79.5, 39.7, 25.6; MS m/z 364 (M$^+$), 349, 307.

7-Chloro-1-(1,1-dimethylethyl)-1,2-diphenyl-1*H*-cyclobut[*a*]indene (41) and 10-(1,1-Dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluoren-11-ol (42). The same procedure was repeated as described for **15a** except that 0.431 g (1.18 mmol) of **40** was used to afford **41**[5] (0.379 g, 0.99 mmol, 84% yield) as an orange solid and **42** (0.013 g, 0.036 mmol, 3% yield) as a yellow solid. **41**: mp 156−157 °C; IR 1203, 753, 691 cm^{-1}; ^{1}H δ 8.01 (2 H, dd, J = 8.1 and 1.3 Hz), 7.66 (1 H, d, J = 7.5 Hz), 7.61−7.52 (4 H, m), 7.45 (2 H, t, J = 7.2 Hz), 7.37 (1 H, td, J = 7.5 and 1.1 Hz), 7.27 (2 H, t, J = 7.1 Hz), 7.20 (2 H, t, J = 7.3 Hz), 1.26 (9 H, s); ^{13}C δ 154.0, 148.5, 145.8, 143.2, 142.5, 135.0, 129.5, 129.2, 129.1, 128.9, 128.5, 128.4, 127.6, 126.4, 124.9, 123.4, 119.7, 112.5, 77.2, 37.1, 28.7; MS m/z 382 (M$^+$), 367, 347, 325, 289; HRMS calcd for $C_{27}H_{23}Cl$ 382.1488, found 382.1472. Anal. Calcd for $C_{27}H_{23}Cl$: C, 84.69; H, 6.05; Cl, 9.26. Found: C, 84.65; H, 6.20; Cl, 9.18. **42:** IR 3372, 768, 702 cm^{-1}; ^{1}H δ 8.59 (1 H, d, J = 8.9 Hz), 7.63−7.56 (4 H, m), 7.51 (1 H, dd, J = 8.3 and 1.6 Hz), 7.43 (1 H, td, J = 7.7 and 1.6 Hz), 7.39−7.29 (3 H, m), 7.22 (1 H, td, J = 7.5 and 1 Hz), 7.00 (1 H, td, J = 7.7 and 1 Hz), 6.33 (1 H, d, J = 10.1 Hz), 6.16 (1 H, d, J = 7.9 Hz), 1.95 (9 H, s), 1.83 (1 H, d, J = 10.1 Hz); ^{13}C δ 146.3, 144.7, 140.1, 139.2, 139.1, 135.9, 135.4, 133.2, 132.4, 130.2, 129.9, 129.3, 129.1, 128.7, 128.3, 127.83, 127.76, 127.3, 125.0, 124.5, 123.7, 74.2, 38.6, 33.4; MS m/z 364 (M$^+$), 331, 307; HRMS calcd for $C_{27}H_{24}O$ 364.1827, found 364.1816.

1*H*-Cyclobut[*a*]indene 48 and 2,11-Dihydro-1,1-dimethyl-6-phenyl-1*H*-indeno[1,7-*ab*]fluoren-11-ol (50). The same procedure was repeated as described for **15a** except that 0.276 g of **46** (0.760 mmol) was used to afford **48** (0.017 g, 0.045 mmol, 6% yield) as an orange solid and **50** (0.213 g, 0.588 mmol, 77% yield) as a yellow solid. **48:** IR 1200, 752, 738, 688 cm^{-1}; ^{1}H δ 7.76 (1 H, d, J = 7.5 Hz), 7.48 (1 H, dm, J = 7.5 and 1 Hz), 7.43 (1 H, td, J = 7.7 and 1 Hz), 7.36−7.24 (8 H, m), 7.20−7.10 (2 H, m), 3.23 (1 H, d, J = 15.8 Hz), 3.02 (1 H, d, J = 16.0 Hz), 1.32 (3 H, s), 1.17 (3 H, s); ^{13}C δ 153.0, 149.3, 145.8, 144.9, 141.4, 140.7, 133.9, 129.6, 129.0, 128.9, 128.1, 127.9, 127.1, 125.4, 125.1, 124.6, 123.5, 119.9, 111.1, 75.5, 47.3, 45.6, 28.7, 24.5; MS m/z 380 (M$^+$), 365, 345, 330; HRMS calcd for $C_{27}H_{21}Cl$ 380.1332, found 380.1344. **50:** mp 140−142 °C; IR 3389, 780, 763, 741, 703 cm^{-1}; ^{1}H δ 7.63 (1 H, d, J = 7.5 Hz), 7.6−7.53 (3 H, m), 7.47−7.35 (3 H, m), 7.29−7.19 (3 H, m), 7.04 (1 H, t, J = 7.6 Hz), 6.46 (1 H, d, J = 7.9 Hz), 5.96 (1 H, d, J = 10.3 Hz), 3.35 (2 H, s), 1.88 (1 H, d, J = 10.3 Hz), 1.77 (3 H, s), 1.74 (3 H, s); ^{13}C δ 150.5, 146.5, 143.6, 140.1, 138.3, 137.3, 135.5, 132.3, 131.0, 130.1, 129.9, 129.0, 128.8, 128.2, 127.8, 127.7, 125.0, 123.6, 121.6, 119.7, 73.0, 48.9, 45.0, 31.6, 26.5; MS m/z 362 (M$^+$), 347, 345, 329; HRMS calcd for $C_{27}H_{22}O$ 362.1671, found 362.1657. Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.32; H, 6.12.

4,4-Dimethyl-3-phenyl-1-[2-(2-phenylethynyl)phenyl]-1-pentyne (51). The following procedure is representative for the preparation of the diacetylenic hydrocarbons from the diacetylenic propargylic alcohols. To a mixture of the alcohol **40** (0.250 g, 0.686 mmol) and triethylsilane (0.120 g, 1.03 mmol) in 6 mL of methylene chloride was added 0.21 mL of trifluoroacetic acid (0.313 g, 2.74 mmol). After 5 min of stirring at room temperature, 0.290 g of sodium carbonate (2.74 mmol) was added followed by 10 mL of water and 40 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.64) provided 0.230 g (0.660 mmol, 96% yield) of **51** as a yellow liquid: IR 2215, 755, 701, 690 cm^{-1}; ^{1}H δ 7.56−7.51 (1 H, m), 7.49−7.40 (5 H, m), 7.34−7.18 (8 H, m), 3.70 (1 H, s), 1.05 (9 H, s); ^{13}C δ 139.2, 132.13, 132.07, 131.7, 129.8, 128.2, 127.9, 127.6, 127.3, 126.6, 126.3, 125.6, 123.3, 95.7, 92.8, 88.6, 82.4, 50.6, 35.5, 27.8; MS m/z 348 (M$^+$), 333, 318, 291; HRMS calcd for $C_{27}H_{24}$ 348.1878, found 348.1870.

10-(1,1-Dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluorene (55). The following procedure is representative for the preparation of the polycyclic aromatic hydrocarbons from the diacetylenic hydrocarbons. To 0.224 g of **51** (0.643 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere were added 0.70 mL of a 1.0 M solution of potassium *tert*-butoxide in THF (0.70 mmol) and 0.5 mL of *tert*-butyl alcohol. The reaction mixture was heated under reflux for 6 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 40 mL of diethyl ether were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.73) provided 0.202 g (0.580 mmol, 90% yield) of **55** as a yellow solid: mp 144−145 °C; IR 907, 764, 730, 702 cm^{-1}; ^{1}H δ 8.62 (1 H, d, J = 8.7 Hz), 7.65−7.27 (9 H, m), 7.20 (1 H, td, J = 7.3 and 0.8 Hz), 6.96 (1 H, t, J = 7.4 Hz), 6.26 (1 H, d, J = 7.9 Hz), 4.51 (2 H, s), 1.92 (6 H, s); ^{13}C δ 144.2, 141.0, 140.3, 139.8, 138.1, 137.5, 134.5, 133.1, 131.3, 130.2, 129.2, 127.9, 127.6, 127.5, 126.8, 126.2, 124.1, 123.9, 123.6, 123.3, 40.2, 38.9, 34.3; MS m/z 348 (M$^+$), 333, 291; HRMS calcd for $C_{27}H_{24}$ 348.1878, found 348.1866. Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 92.78; H, 6.93.

Diacetylene 60. The same procedure was repeated as described for **51** except that 0.409 g (1.00 mmol) of **26** was used to afford **60** (0.382 g, 0.973 mmol, 97% yield) as a light yellow solid: mp 45−47 °C; IR 2215, 796, 757, 690 cm^{-1}; ^{1}H δ 8.12 (2 H, br), 7.63 (2 H, br m), 7.49 (2 H, d, J = 7.3 Hz), 7.40−7.18 (11 H, m), 7.16 (2 H, s), 4.81 (1 H, s); ^{13}C δ 137.5, 134.0, 132.2, 132.1, 131.9, 131.3, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 126.2, 125.9, 125.8, 125.6, 123.0, 93.3, 92.1, 88.5, 86.0 (br), 40.8 (br); MS m/z 392 (M$^+$), 391, 315. The broad ^{1}H NMR signals at δ 8.12 and 7.63 and the ^{13}C NMR signals at δ 86.0 and 40.8 suggest a relatively slow conformational inversion of the central seven-membered ring.

Hydrocarbon 61. The same procedure was repeated as described for **55** except that 0.099 g (0.25 mmol) of **60** was used to afford **61**[5] (0.080 g, 0.20 mmol, 81% yield) as a light yellow solid: mp 197−198 °C; IR 727, 703 cm^{-1}; ^{1}H δ 7.67−7.55 (3 H, m), 7.50−7.27 (8 H, m), 7.25−7.17 (3 H, m), 7.00 (1 H, t, J = 7.7 Hz), 6.69 (1 H, d, J = 12.1 Hz), 6.62 (1 H, d, J = 11.9 Hz), 6.38 (1 H, d, J = 7.7 Hz), 4.63 (1 H, d, J = 22.6 Hz), 3.88 (1 H, d, J = 22.4 Hz); ^{13}C δ 144.0, 142.2, 140.8, 139.1, 139.0, 138.7, 137.9, 137.7, 136.0, 134.4, 134.1, 133.8, 133.6, 132.6, 130.5, 130.4, 129.9, 129.4, 129.3, 129.1, 128.7, 128.6, 127.9, 127.8, 127.1, 126.4, 125.1, 124.7, 124.3, 123.5, 38.4; MS m/z 392 (M$^+$), 315; HRMS calcd for $C_{31}H_{20}$ 392.1565, found 392.1571. Anal. Calcd for $C_{31}H_{20}$: C, 94.86; H, 5.14. Found: C, 94.56; H, 5.39. The observation of the two ^{1}H NMR signals at δ 4.63 and 3.88 attributable to the two hydrogens on the sp^3 carbon suggests a relatively slow interconversion of the two helical conformers of **61**. The relatively large geminal coupling constant of 22.5 Hz is consistent with the earlier report of J = −22.3 Hz for fluorene.[14]

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

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Supporting Information Available: Experimental procedures and spectroscopic data for **13b**−**d**, **15b**−**d**, **17**−**19**, **26**, **29**, **30**, **33**, **36**, **45**−**47**, **49**, and **56**−**59**, ^{1}H and ^{13}C NMR spectra for compounds **13a**−**13d**, **15a**−**d**, **17**−**19**, **21**, **23**, **24**, **26**, **27**, **29**, **30**, **33**, **34**, **36**−**38**, **40**−**42**, **45**−**51**, and **55**−**61**, and the ORTEP drawings and tables of crystallographic data for the X-ray diffraction analyses of **24**, **27**, **34**, **37**, **41**, and **61**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0104577