2005

Synthesis of novel polycyclic aromatic compounds via cascade cyclizations of benzannulated enyne-allenes

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**Synthesis of Novel Polycyclic Aromatic Compounds via Cascade
Cyclizations of Benzannulated Enyne–Allenenes**

Yanzhong Zhang

Dissertation

Submitted to the Eberly College of Arts and Sciences

at

West Virginia University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in Organic Chemistry

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2005

Keyword: Schmittel Cyclization, Enyne–Allenenes, Biradical, Helicene

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ABSTRACT

Synthesis of Novel Polycyclic Aromatic Compounds via Cascade Cyclizations of Benzannulated Enyne–Allenenes

Yanzhong Zhang

Under mild conditions, a diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene was successfully synthesized through the thionyl chloride-induced cascade cyclizations of the corresponding enediynyl propargylic alcohol with the formation of four new rings in one operation. The diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene has a 41-carbon framework represented on the surface of C₆₀.

A variety of helicenes with one or two phenyl substituents at the most sterically hindered position were also successfully synthesized through a cascade sequence of reactions involving a Schmitt cyclization reaction of the corresponding benzannulated enyne–allenenes followed by an intramolecular radical–radical coupling reaction to afford the formal Diels–Alder adducts. The helical structures were produced either by increasing the *ortho* annulation number of the central aromatic ring systems or by replacing the phenyl substituents with two longer 4-(*tert*-octyl)phenyl groups.

The structures of these helicenes were established by NMR studies and in some cases were confirmed by X-ray structure analyses. The existence of a helical twist is manifested with a set of AB ¹H NMR signals with a large geminal coupling constant of the diastereotopic methylene hydrogens on the five-membered rings. The racemization barriers of these helicenes were also studied by temperature dependent studies. Due to steric hindrance, the rotation of the phenyl substituent in the helical compounds is restricted. The rotational barriers of the phenyl substituent were also studied by temperature dependent studies.

Dedicated to
My wife and my parents

ACKNOWLEDGEMENT

I would like to express my sincere appreciation to my research advisor, Dr. Kung K. Wang, for his instructive guidance and continuous encouragement during the course of my dissertation research. His patience and calmness in solving problems and his willingness to share his knowledge have been an inspiration. I was quite fortunate to have been associated with such an outstanding chemist and a patient teacher. I am greatly benefited by his great interest and extensive knowledge of chemistry.

I would also like to express my gratitude to my research committee members, Dr. Peter M. Gannett, Dr. George A. O'Doherty, Dr. Jeffrey L. Petersen, and Dr. Björn C. Söderberg for their helpful suggestions and valuable discussions. My special thanks go to Dr. Jeffrey L. Petersen for his valuable help and excellent work in X-ray structure analysis.

My appreciation is also extended to my group members, Xiaoqing Han, Dr. Hongbin Li, Dr. Xiaoling Lu, Dr. Yonghong Yang, Hua Yang, Weixiang Dai, Daehwan Kim, Yu-Hsuan Wang and many other people for helping me get through my graduate school by making every day special.

My deepest gratitude goes to my wife and my parents for their love, support and encouragement that have made this dissertation possible.

Financial support from the C. Eugene Bennett Department of Chemistry of West Virginia University and the National Science Foundation is also gratefully acknowledged.

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Chapter I

Cyclization Reactions of Enyne–Allenenes

1. Introduction

Under thermal conditions, (*Z*)-1,2,4-heptatrien-6-yne (enyne–allene) **1** could undergo cyclization reaction regioselectively, the reaction could proceed through either the C²–C⁷ pathway (Myers–Saito cyclization) leading to the α ,3-didehydrotoluene/naphthalene biradical **2**¹ or the C²–C⁶ pathway (Schmittel cyclization) affording the fulvene/benzofulvene biradical **3** (Scheme 1).²

Scheme 1. Cyclization reactions of enyne–allenenes.

The regioselectivity of the cyclization reaction is controlled by the acetylenic terminal substituent R. With a hydrogen or a sterically non-demanding alkyl group at the acetylenic terminus, the Myers–Saito cyclization reaction is the preferred pathway. Otherwise, with an aryl substituent or a sterically demanding group, such as *tert*-butyl or trimethylsilyl group, the Schmittel cyclization reaction becomes the favored one.

2. Myers–Saito (C²–C⁷) Cyclization Reaction

Myers and Saito *et al.* independently demonstrated that enyne–allene **4** undergoes cyclization reaction to form the α ,3-didehydrotoluene biradical **5** and then leads to toluene (**6**) upon hydrogen atom abstraction (Scheme 2).¹

Scheme 2. Myers–Saito cyclization reaction.

Mechanistic studies of thermolysis of **4** in various solvents were performed (Figure 1)^{1c} and the biradical intermediate was successfully trapped by 1,4-cyclohexadiene. Heating a solution of **4** in deoxygenated solvents of benzene and 1,4-cyclohexadiene forms toluene (**6**)

and adducts **7** and **8** as the detectable products. Theoretically **7** and **8** could be formed by either a radical chain aromatization pathway (Scheme 3) or a radical recombination pathway (Scheme 4). But the invariance of the ratio (**7** + **8**)/toluene (**6**) with the concentration of **4** suggests that the former pathway is at best a minor competitor with the simple recombination mechanism. All the products formed by thermolysis of **4** in various solvents are consistent with the intermediacy of the α , 3-didehydrotoluene biradical **5**.

Figure 1. Thermolysis of enyne-allene **4** in various solvents.

Scheme 3. Mechanism of radical chain aromatization.

Scheme 4. Mechanism of trapping the $\alpha,3$ -didehydrotoluene biradical with 1,4-CHD.

Myers and coworkers also found out that the cyclization reaction is a first-order reaction with the following activation parameters: $\Delta H^\ddagger = 21.8 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = -11.6 \pm 1.5$ eu ($E_a = 22.5$ kcal/mol, $\log A = 10.7$).

Obviously the Myers–Saito cyclization reaction belongs to the family of biradical cyclization reactions such as Bergman cyclization reaction of enediyne **14** (Scheme 5)³ and Moore cyclization reaction of enyne–ketene **16** (Scheme 6).⁴

Scheme 5. Bergman cyclization of enediyne **14**.

Scheme 6. Moore cyclization of enyne–ketene **16**.

The Myers–Saito and the Bergman cyclization reactions were awarded with substantial interest, because they represent the basis of the antitumor antibiotic efficacy of enyne–allenes and enediynes. For example, the biological activity of NCS chromophore **20** is attributed to its ability to cleave DNA irreversibly. The DNA damage is initiated by a triggering reaction to form a labile intermediate **21**. Subsequently a rapid Myers–Saito–type cyclization reaction leads to biradical **22**, followed by abstraction of two hydrogen atoms from DNA to cause DNA cleavage (Scheme 7).⁵ Similarly, calicheamicin **24** shows its biological activity through the involvement of a Bergman cyclization reaction (Scheme 8).⁶

Scheme 7. Mechanism of DNA cleavage by neocarzinostatin.

Scheme 8. Mechanism of DNA cleavage by calicheamicin.

Although the similarity exists, the prototypical Myers–Saito cyclization reaction differs from the prototypical Bergman cyclization reaction at least in the following two aspects:⁷

1. Myers–Saito cyclization reaction gives rise to a σ – π biradical while Bergman cyclization reaction produces a σ – σ biradical.
2. Myers–Saito cyclization reaction is exothermic ($\Delta H \approx -15 \pm 3$ kcal/mol), whereas Bergman cyclization reaction is endothermic ($\Delta H \approx 14$ kcal/mol).

3. Schmittel (C²–C⁶) Cyclization Reaction

In 1995, Schmittel *et al.* discovered a switch from the well-known Myers–Saito cyclization reaction (C²–C⁷ cyclization) to C²–C⁶ cyclization reaction (Scheme 9).^{2a} As above mentioned, the kinetic competition between the C²–C⁶ and C²–C⁷ cyclization reactions can be most conveniently steered through the proper choice of the substituent at the alkyne terminus: with an aryl group or a bulky group (*t*-Bu or TMS group) at C⁷, the C²–C⁶ cyclization reaction is preferred, whereas with a hydrogen or a *n*-alkyl substituent, the C²–C⁷ cyclization reaction mode is observed. The effect of the aryl substituent is attributed to its ability to stabilize the alkenyl radical. The sterically demanding group raises the cyclization barrier of the C²–C⁷ cyclization reaction above that of the C²–C⁶ cyclization reaction due to

steric hindrance.

Scheme 9. Switch from $\text{C}^2\text{-C}^7$ cyclization to $\text{C}^2\text{-C}^6$ cyclization.

Later, our group found similar reaction switch for enyne-ketene imines and enyne-carbodiimides,^{8a,b} Schmittel, Engels and coworkers also reported the similar observation,^{8c,d} showing that the $\text{C}^2\text{-C}^6$ cyclization reaction constitutes a general reaction motif (Scheme 10).

Scheme 10. Switch from $\text{C}^2\text{-C}^7$ cyclization to $\text{C}^2\text{-C}^6$ cyclization of hetero enyne-allenes.

Although most examples in the literature could be reconciled with a concerted ene or a Diels–Alder reaction, mechanistic and theoretical studies are clearly in favor of the fulvene biradical in the course of the C²–C⁶ cyclization reaction based on the following evidence: 1) The C²–C⁶ cyclization reaction does not involve a polar transition state or a polar intermediate.^{9, 2c} 2) From kinetic studies, the reaction is different from Diels–Alder process.^{2b} For a concerted Diels–Alder reaction mechanism, the activation barrier of the formation **34** would be expected to be much higher than that of formation **35** because of the steric effect of the bulky mesityl group. Instead these two reactions were found to have very similar activation barriers. 3) Kinetic isotope effect study,¹⁰ as a powerful diagnostic tool for the distinction between stepwise and concerted mechanism, suggests that the thermal C²–C⁶ cyclization reaction of enyne–allenes proceeds through a stepwise biradical mechanism, not a concerted one. 4) The postulated formation of the biradical intermediate is supported by the observation that the enyne–allenes **28** could induce DNA cleavage as demonstrated by the formation of the open circular DNA.¹¹ 5) The convincing evidence for a stepwise biradical mechanism comes from the direct trapping of the fulvene biradical through 1,4-cyclohexadiene (Scheme 11).¹² When **42** was heated for 18 h in the neat solvent of 1,4-cyclohexadiene, the benzofulvene derivatives (*Z*)-**43** (7%) and (*E*)-**43** (4%) were formed along with the C²–C⁷ cyclization reaction product **44** (3%). Clearly (*Z*)-**43** and (*E*)-**43** are both derived from the fulvene biradical through hydrogen abstraction.

Scheme 11. Products from the thermolysis of **42** in 1,4-cyclohexadiene.

In conclusion, cyclization reaction of benzoenyne–allenes provides an easy access to the naphthalene biradical or the benzofulvene biradical, which is directed by the nature of the substituent at the acetylenic terminus. Myers–Saito cyclization reaction and Schmittel cyclization reaction could be induced either thermally or photochemically.¹³

4. Construction of Polycyclic Ring Systems via Schmittel Cyclization of Enyne–Allenes

4.1. Synthesis of Carbocyclic Ring Systems

Although the current research on the thermal cyclization reaction of enyne–allenes is focused on the theoretical and synthetic studies of model compounds in order to find good anticancer drug candidates, considerable effort has gone into employing the potential of the cycloaromatization reaction for the construction of polycyclic ring systems.

From a synthetic point of view, the Schmittel cyclization reaction has become a valuable synthetic tool for the construction of carbocyclic¹⁴ and heterocyclic^{8,15} ring systems, since the biradical intermediate could undergo a follow-up reaction to give formal Diels–Alder adducts that provides a convenient access to polycyclic aromatic systems.

Hai-Ren Zhang of Dr. Wang's group developed an approach to the chlorinated enyne–allene, which could proceed via a cascade reactions involving a Schmittel cyclization reaction and a subsequent formal Diels–Alder reaction to afford novel polycyclic ring systems.¹⁶ This pathway was successfully adopted for the synthesis of a C₄₄H₂₆ hydrocarbon having a carbon framework represented on the surface of C₆₀ (Scheme 12).^{16a}

Scheme 12. Synthesis of a C₄₄H₂₆ hydrocarbon via the Schmittel cyclization reaction.

A new synthetic pathway to twisted 4,5-diarylphenanthrenes **60** via Schmitt cyclization reaction of benzannulated enyne-allenes was developed by Dr. Hongbin Li of Dr. Wang's group (Scheme 13).¹⁷

Scheme 13. Synthesis of twisted 4,5-diarylphenanthrenes.

Moreover, the Schmitt cyclization reaction was employed as a key step in the construction of the benzo[*b*]fluorine core of several metabolites structurally related to the kinamycin family of antibiotics (Scheme 14).^{14a}

Scheme 14. Synthesis of the benzo[*b*]fluorine core of kinamycins.

4.2. Synthesis of Heterocyclic Ring Systems

The synthetic applications of the biradical intermediates could be further extended to the systems of enyne-ketenimines and enyne-carbodiimides as described in Scheme 10. Dr. Wang group successfully adopted this strategy to synthesize several novel heterocyclic ring systems structurally related to the naturally occurring ellipticine and its derivatives

(Scheme 15).¹⁸

Scheme 15. Synthesis of novel heteroaromatics structurally related to ellipticine via thermolysis of pyridannulated enyne-carbodiimides.

5. Literature Survey on the Synthetic Methodologies for the Preparation of Enyne-Allenes

Due to wide synthetic applications of the thermal cyclization reactions of enyne-allenes, a variety of synthetic methods have been developed for the preparation of enyne-allenes with diverse structural features.¹⁹

The enyne-allene **4** could be easily synthesized from the enediynyl propargylic diazene **67** through a spontaneous sigmatropic rearrangement (Scheme 16).^{1a,b,c,20}

Scheme 16. Synthesis of enyne-allene **4** via a sigmatropic rearrangement.

Transition-metal catalyzed coupling reactions have been employed for the synthesis of a variety of enyne-allenes. For example, thermolabile enyne-allene ester **72** could be prepared by a Pd-catalyzed cross-coupling reaction between arylzinc halide **69a** or arylboronic acid **69b** and 2-haloallene carboxylates **70** under mild conditions (Scheme 17).²¹

Scheme 17. Synthesis of benzannulated enyne-allene **72** via Pd-catalyzed coupling.

Enyne-allenes could also be synthesized through the Horner–Wittig and related reactions. An example was reported by Finn *et al.* by using the metallated phosphorus methylene reagent **74**, which could undergo double olefination with aldehydes **73** to give enyne-allenes **77** as outlined in Scheme 18.²²

Scheme 18. Synthesis of benzannulated enyne-allenes **77** via titanium-substituted ylides.

The prototropic rearrangement of enediynes affords a simple and direct synthetic pathway to enyne-allenes. For example, enyne-allene **79** could easily be obtained from **78** through a prototropic rearrangement under basic conditions (Scheme 19).²³

Scheme 19. Synthesis of enyne-allene via prototropic rearrangement of enediynyl sulfone.

The [2,3]-sigmatropic rearrangement of enediynyl propargylic alcohols is widely used for the preparation of enyne-allenes. This approach was first reported by Sevin *et al.* in 1967²⁴ and later was adopted by Saito,^{1d,e} Nicolaou,²⁵ Grissom²⁶ and Schmittle^{2b,d} for the synthesis of a variety of allenyl phosphonates or phosphine oxides. For instance, Nicolaou *et al.* reported that phosphine oxides **84** could be obtained from propargylic alcohols **82** via a [2,3]-sigmatropic rearrangement induced by chlorodiphenylphosphine (Scheme 20).

Scheme 20. Synthesis of enyne-allenes via a [2,3]-sigmatropic rearrangement.

The synthetic strategy involving the use of a [3,3]-sigmatropic rearrangement of propargylic vinyl ethers for the preparation of enyne–allenes has also been reported. Grissom *et al.* discovered that a [3,3]-sigmatropic rearrangement of **85** was promoted by either thermolysis (150 °C) or a Lewis-acid catalyst AgBF₄ at room temperature to afford enyne–allene **87** (Scheme 21).²⁶

Scheme 21. Synthesis of enyne–allene **87** via a [3,3]-sigmatropic rearrangement.

Rearrangement of propargylic derivatives could also afford corresponding enyne–allenes. Schmittel *et al.*^{11b} reported that benzannulated enyne–allenes **91** and **92** were prepared from the propargylic acetates **90** by cuprate addition or by Pd-catalyzed addition of arylzinc chloride, respectively (Scheme 22).

Scheme 22. Synthesis of enyne–allenes via rearrangement of propargylic acetates.

Cunico *et al.* developed a method for in situ formation of enyne-allene **95** based on a facile elimination and trimethylsilyl (TMS) group migration within the propargylic framework of **94** (Scheme 23).²⁷

Scheme 23. Synthesis of enyne-allene **95** with keto substituent.

The strategy of a nucleophilic attack on the acetylenic ketone functionality to form benzannulated enyne-allenes was adopted by Lipton *et al.* for the preparation of the oxygen-substituted enyne-allenes **97**.²⁸ Treatment of acetylenic ketones **96** with cuprate followed by trapping the resultant enolates with acetic anhydride afforded enyne-allenes **97** in good yield (Scheme 24).

Scheme 24. Synthesis of enyne-allenes **97** via conjugate addition of dialkylcuprates.

Dr. Wang group reported several convenient approaches for the synthesis of enyne-allenes. An example is outlined in Scheme 25.^{14b,29} Condensation between allenic aldehydes **99** and $[\gamma$ -(trialkylsilyl)allenyl]borane **98** furnished the corresponding β -silyl alcohols **100**, which on subsequent elimination of the hydroxyl and the silyl groups produced enyne-allenes **101a** (*Z:E* = 96:4) and **101b** (*Z:E* = 99:1).^{29e}

Scheme 25. Synthesis of enyne-allenes **101** from condensation between allenic aldehydes and $[\gamma$ -(trialkylsilyl)allenyl]borane.

Chapter II

Synthesis of Diindeno-Fused 4*H*-Cyclopenta[*def*]phenanthrene via Benzannulated Enediynyl Propargylic Alcohol

1. Introduction

Our research group reported an efficient approach to produce chlorinated benzoenyne–allene **105** through S_N1' reaction promoted by treatment of benzannulated enediynyl propargylic alcohol **103** with thionyl chloride.³⁰ A subsequent Schmittel C^2-C^6 cyclization generated the biradical **106**, which in turn underwent an intramolecular radical–radical coupling to give the formal Diels–Alder adduct **107**. Tautomerization followed by hydrolysis then afforded **109** and minor [2 + 2] adduct **110**. The efficiency of the reaction sequence provides many opportunities for the assembly of novel aromatic structures.

Scheme 26. Schmittel cyclization of chlorinated benzoenyne–allene.

2. Research Objective

Derivatives of 4*H*-cyclopenta[*def*]phenanthrene could be used as precursors for the synthesis of polycyclic aromatic hydrocarbons with carbon frameworks represented on the surface of C₆₀. For example, 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene was used in the first synthesis of corannulene, a bowl-shaped C₂₀H₁₀ aromatic hydrocarbon.³¹ Based on the simple and efficient route to polycyclic aromatic compounds via chlorinated benzoenyne–allene, we envisioned that by replacing 9-fluorenone with 2,2-dimethylindene-1,3-dione, the synthetic sequence outlined in Scheme 26 could lead to diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene.

3. Literature Survey for the Synthesis of 4*H*-Cyclopenta[*def*]phenanthrene

Several synthetic methods have been reported for the synthesis of 4*H*-cyclopenta[*def*]phenanthrenes.^{32,31} The Friedel–Crafts cyclization of derivatives of phenanthrenes or acenaphthylenes was a key step for most approaches. We have also synthesized several derivatives of 4*H*-cyclopenta[*def*]phenanthren-4-one via the Schmitt cyclization of chlorinated benzoenyne–allenes.³³ My contribution in this project is summarized in the following section.

4. Results and Discussion

The benzannulated enediynyl propargylic alcohols are useful precursors of the corresponding enyne–allenes, which have found applications in the synthesis of polycyclic aromatic compounds.^{2b,c,16,17} We have successfully employed this synthetic pathway for efficient transformation of 1,3-indandione **111**³⁴ to the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene **118** (Scheme27).

Scheme 27. Synthesis of 4H-cyclopenta[def]phenanthrene.

Condensation between **111** and 2 equiv of **46** led to propargylic diols **112** as a mixture of the *trans* and *cis* isomers. Treatment of *trans*-**112a** with thionyl chloride then promoted a cascade sequence of reactions involving initially two $\text{S}_{\text{N}}\text{i}'$ reactions to produce in situ the benzannulated chloroenyne–allene **113** as described previously.^{16a,17} Two subsequent formal Diels–Alder reactions, presumably with each involving a Schmitt cyclization reaction to form the corresponding biradical^{2b,c} followed by an intramolecular radical–radical coupling reaction, then gave **114**, which in turn underwent two prototropic rearrangements to furnish the diindeno-fused 4H-cyclopenta[def]phenanthrene derivative **115**. It was operationally convenient to reduce the crude product of **115** without further purification with tributyltin hydride to furnish **116** in 43 % overall yield from *trans*-**112a**.

It is worth noting that four new rings were formed in one step under mild conditions, which demonstrates the efficiency of the approach for the construction of polycyclic aromatic structures.

Because the relative reaction rates of the steps of the cascade sequence have not been determined, it is also possible that the first unit of the benzannulated enediynyl propargylic alcohol moiety could undergo a formal Diels–Alder reaction and a prototropic rearrangement before the second unit would begin its cyclization sequence.

5. Conclusions

The success in using diols **112** for two cascade reaction sequences in a single operation further demonstrates the versatility of this synthetic pathway for the construction of novel polycyclic aromatic structures. The diindeno-fused 4H-cyclopenta[def]phenanthrene **116** has a 41-carbon framework, 38 carbons on the aromatic rings and three carbons on the

three five-membered rings, that is represented on the surface of C_{60} .

Chapter III

Helicenes

1. Introduction

Helicenes are a well-known representative of polycyclic aromatic compounds with a structure characterized by a series of *ortho*-condensed aromatic rings (Figure 2).³⁵ When the number of annulated arenas increases, the system can not be planar and then adopts a helical structure to release the steric congestion. Due to the nonplanar structures, helicenes are inherently chiral.

Figure 2. Examples of helicenes.

2. Potential Applications of Helicenes

For many years, helicenes were studied just for an academic curiosity. More recently, with the further studies of this kind of compound, more and more potential applications have been found out. Due to their extraordinary optical and electronic properties, helicenes could be potentially used as optical materials,³⁶ asymmetric catalysts,³⁷ asymmetric molecular recognition³⁸ and molecular devices.³⁹

It is worth noting that enantiopure helical hydrocarbons, [6]helicene **118** and [5]helicene **123** without any heteroatoms, could act as a chiral inducer in highly enantioselective synthesis of pyrimidyl alkanol **124** by addition of diisopropylzinc to 2-(2-*tert*-butylethynyl)pyrimidine-5-carbaldehyde (**122**) (Scheme 28).^{37g} When aldehyde **122**

(0.05 mmol) was treated with *i*-Pr₂Zn (0.15 mmol) in the presence of (*P*)-(+)-[6]helicene **118a** (6 mol%, >99.5% *ee*) at 0 °C in toluene, (*S*)-5-pyrimidyl alkanol (*S*)-**124a** was obtained (95% *ee*, 95% yield). On the other hand, in the presence of (*M*)-**118b** (7 mol%), the enantiomer (*R*)-**124b** was formed (93% *ee*, 93% yield). The same observation of the asymmetric induction was also found for [5]helicene **123**. The mechanism of asymmetric induction by the helical hydrocarbons was postulated to involve coordination of the chiral helicenes with the carbonyl moiety and the pyrimidine ring of the aldehyde **122**, so that the *Re* and *Si* faces of the carbonyl group may be differentiated. When *i*-Pr₂Zn is added, a nonracemic zinc alkoxide of the corresponding alkanol is formed.

Scheme 28. Asymmetric induction by helical hydrocarbons.

Because helicenes have such wide potential applications, there is a need for efficient and enantioselective approaches to the synthesis of this kind of compounds.

3. Literature Survey for the Synthesis of Helicenes

3. 1. Approaches for Racemic Helicenes

[6]Helicene was synthesized by Newman through Friedel–Crafts acylations and resolved by formation of a charge–transfer complex in 1955.⁴⁰ His brilliant work in this field opened the door for the study of this fascinating class of helical molecules.

The classical method for the synthesis of helicenes is based on the photocyclization of stilbene–type precursors (Scheme 29).⁴¹ Although useful, due to poor

regioselectivity in the photocyclization step, this method produced a mixture of isomers in some cases. This traditional approach also suffered from other fundamental drawbacks, such as highly dilute solution and low functional group tolerance.

Scheme 29. Synthesis of helicenes via photocyclization of stilbene-type precursors.

The first efficient non-photochemical route for the synthesis of racemic helicenes **129** was developed by Katz and coworkers through double Diels–Alder cycloaddition reactions⁴² between divinylarene **127** and 1,4-benzoquinone **128** (Scheme 30).

Scheme 30. Katz’s simple non-photochemical route to helicene quinones.

An approach for the synthesis of [7]helicene was reported by Gingras *et al.* in 1998 by using carbenoid coupling of aromatic bis(bromomethyl) moieties (Scheme 31)⁴³ or McMurry coupling of a dialdehyde. The carbenoid coupling could provide [7]helicene in 75% yield on a gram-scale.

Scheme 31. Gingras’s approach to [7]helicene by “carbenoid coupling” strategy.

A new route to [5]helicenes was developed by Harrowven *et al.*, involving a tin-mediated, non-reducing tandem radical cyclization of (Z,Z)-1,4-bis(2-iodostyryl)benzene

derivatives as a key step.⁴⁴ This short protocol could provide different substituted [5]helicenes with yields ranging from 35 to 58%. An example is outlined in Scheme 32.

Scheme 32. Synthesis of [5]helicene by iterative radical cyclization.

Transition metal-catalyzed cycloisomerization reactions have been employed for the synthesis of a variety of helicenes. This novel strategy was adopted by Stará *et al.*⁴⁵ through nickel(0)-catalyzed [2 + 2 + 2] cycloisomerization of *cis,cis*-dienetriyne to afford [6]helicene in 61% yield in one operation with the formation of three new rings. The new paradigm provided an efficient non-photochemical method for the synthesis of different substituted [5], [6] and [7]helicenes with yields ranging from 60 to 83%.

Scheme 33. Synthesis of [6]helicene by nickel(0)-catalyzed [2 + 2 + 2] cycloisomerization.

Vollhardt and coworkers reported another transition metal-catalyzed approach to angular [*n*]phenylenes by cobalt-catalyzed [2 + 2 + 2] cycloisomerization (Scheme 34).⁴⁶ [7]Phenylene **135**, the first helical phenylene, could be obtained through cobalt-catalyzed double cycloisomerization of hexayne **134** in 8% yield in one step with the formation of six new rings. A more efficient approach to [7]phenylene **135** involved cobalt-catalyzed triple cycloisomerization of nonayne **136** in low yield (2%), but forming nine rings in one step.

Scheme 34. Vollhardt's approach to [7] phenylene by cobalt-catalyzed double and triple cycloisomerizations.

3.2. Asymmetric Approaches for Helicenes

Despite remarkable progress in the synthetic methodology development of helicenes, there is still a major challenge to develop efficient asymmetric approaches to the helical compounds. Most of the asymmetric approaches reported to date were based on chromatographic, chemical or enzymatic resolutions of the racemic derivatives. Although several enantio- or diastereoselective syntheses have been reported, moderate asymmetric inductions have been achieved except in a few cases.

Carreño and coworkers reported the first enantioselective synthesis of 7,8-dihydro[5]helicene quinones and bisquinones based on a one-pot domino process (Scheme 35).⁴⁷ Treatment of vinyl 3,4-dihydrophenanthrene **136** with 2 equivalents of enantiopure (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**137**) afforded 7,8-dihydro[5]helicene quinone **138** in optically pure form with the absolute configuration *P*. The reaction sequence involved spontaneous elimination of the sulfoxide in the initially formed Diels–Alder adduct and *in situ* partial aromatization of the corresponding tetrahydroaromatic derivative in the

presence of an excess of the chiral sulfinylquinone. Interestingly, the enantiodivergent synthesis of either *P* or *M* helimer from the same intermediate depends on the different aromatizing reagents. The helicene (*P*)-**138** would be formed in 67% yield with 96% *ee* via aromatization of the B ring of **139** (R = TBDMS) with DDQ, whereas helicene (*M*)-**138** was obtained in 88% yield with 90% *ee* when the aromatization of **139** (R = Me) was effected with CAN.

Scheme 35. Carreño's domino process for the enantiodivergent synthesis of 7,8-dihydro[5]helicene quinones.

Another asymmetric approach to [5]helicene was developed by Karikomi and coworkers through an aromatic oxy-Cope rearrangement strategy (Scheme 36).⁴⁸ Condensation of chiral bicycle[2,2,2]ketone **140** with Grignard reagent **141** afforded (1*R*, 2*S*, 4*S*)-**142**, followed by an asymmetric aromatic oxy-Cope rearrangement to give pentacyclic fused-ring derivative **143** in 47% yield. (*P*)-**144** was obtained from **143** in 24% yield with 98% *ee* in four subsequent steps involving reduction, hydrolysis and dehydration, enolacetylation, and aromatization. The enantiomer (*M*)-**144** was likewise synthesized from

(1*S*,4*R*)-**140**.

Scheme 36. Synthesis of [5]helicene (*P*)-**144** via an aromatic oxy-Cope rearrangement.

More recently, Stará and coworkers developed a highly stereoselective cobalt-mediated [2 + 2 + 2] cycloisomerization of aromatic triynes to afford [7]helicene-like compounds (Scheme 37).⁴⁹ A central-to-helical chirality transfer could be easily controlled by the absolute configuration at the asymmetric center or by the presence of substitutes of the aromatic triynes.

Scheme 37. Asymmetric synthesis of [7]helicene-like compounds via [2 + 2 + 2] cycloisomerization

Chapter IV

Studies of Helical Molecules: Synthesis of Indeno-Fused Benzo[*c*]phenanthrene and Dibenzo[*c,g*]phenanthrene ([5]Helicene) with a Phenyl Substituent at the Most Sterically Hindered Position

1. Introduction

We recently reported an efficient synthetic pathway outlined in Scheme 38 to produce **153** as an 11*H*-benzo[*b*]fluorene derivative.^{16b} Condensation between lithium acetylide **46** and 2,2-dimethylpropiophenone (**147**) furnished propargylic alcohol **148**, which was then reduced with triethylsilane in the presence of trifluoroacetic acid to give the benzannulated enediyne **149**. Treatment of **149** with potassium *t*-butoxide under refluxing toluene then produced **153** in a sequence of cascade reactions. Presumably, an initial 1,3-prototropic rearrangement of **149** furnished the benzannulated enyne–allene **150**, which then underwent a Schmitt cyclization reaction to generate benzofulvene biradical **151**.² A subsequent intramolecular radical–radical coupling then gave the formal Diels–Alder adduct **152** and, after a prototropic rearrangement, 11*H*-benzo[*b*]fluorene **153** in excellent yield. This synthetic pathway was adopted for the preparation of helical 4,5-diarylphenanthrene derivatives¹⁷ with one of the structures resembles that of a spiral staircase.⁵⁰

Scheme 38. Synthesis of 11*H*-benzo[*b*]fluorene via Schmitt cyclization reaction.

2. Research Objective

We envisioned that by replacing the phenyl group of **147** with a 2-naphthyl, a 3-phenanthryl, or a 2-benzo[*c*]phenanthryl group, the synthetic sequence outlined in Scheme 38 could lead to fused aromatic systems having an extended conjugation and bearing a phenyl substituent at the most sterically hindered position to cause a helical twist.

3. Literature Survey for the Synthesis Benzo[*c*]phenanthrene and Derivatives with a Phenyl Substituent at the Most Sterically Hindered Position

4-Phenylphenanthrene (**154**) and 1-phenylbenzo[*c*]phenanthrene (**155**) could be obtained through photodehydrocyclization of the corresponding 1,4-diarylbut-1-en-3-ynes.⁵¹ For example, photocyclization of 1-(3-phenanthryl)-4-phenylbut-1-en-3-yne (**156**) was reported to produce 1-phenylbenzo[*c*]phenanthrene (**155**) in 50% yield (eq 1). 10-Phenyldibenzo[*c,g*]phenanthrene (1-phenylpentahelicene, **158**) could be obtained along with two isomers by photocyclization of 8'-phenyldi- β -naphthylethylene (**157**) (eq. 2).⁵²

4. Results and Discussion

4. 1. Synthesis of Aryl Ketones 160

The requisite aryl ketone **160a** was prepared by treatment of commercially available 2-naphthoyl chloride (**159a**) with *t*-butylcopper, prepared from *t*-butyllithium and CuBr·SMe₂ (eq 3). Similarly, aryl ketones **160b** and **160c** were prepared by converting the corresponding carboxylic acids **159b** and **159c** to the acid chlorides with thionyl chloride followed by treatment with *t*-butylcopper (eq 4). 3-Phenanthrenecarboxylic acid (**159b**) was prepared from commercially available 3-acetylphenanthrene as reported previously.⁵³

A synthetic procedure for benzo[*c*]phenanthrene-2-carboxylic acid (**159c**) involving oxidation of 2-methylbenzo[*c*]phenanthrene was reported previously.⁵⁴ An alternative synthetic sequence was used to prepare **159c** (Scheme 39). The Wittig reaction between 2-(bromomethyl)naphthalene (**161**) and methyl 4-formylbenzoate (**162**), using lithium ethoxide as the base, produced ethyl 4-[2-(2-naphthalenyl)ethenyl]benzoate (**163**) as a mixture of the *trans* and *cis* isomers (*trans*:*cis* = 5.5:4.5). A subsequent photochemical cyclization reaction⁵⁵ furnished ethyl benzo[*c*]phenanthrene-2-carboxylate (**164**), which then was hydrolyzed to give **159c**.

Scheme 39. Synthesis of benzo[*c*]phenanthrene-2-carboxylic acid through photocyclization.

4. 2. Synthesis of Indeno-Fused Phenanthrene **167** and Related Derivatives

The use of **160a-c** for condensation with **46** furnished propargylic alcohols **165a-c**, which were reduced with triethylsilane in the presence of trifluoroacetic acid to afford the benzannulated enediynes **166a-c** (Table 1). Treatment of **166a-c** with potassium *t*-butoxide under refluxing toluene converted them to the indeno-fused phenanthrene **167a**, benzo[*c*]phenanthrene **167b**, and dibenzo[*c,g*]phenanthrene ([5]helicene) **167c**, respectively,

with a phenyl substituent at the most sterically hindered position in a single operation. The parent 4-phenylphenanthrene (**154**),⁵¹ 1-phenylbenzo[*c*]phenanthrene (**155**),⁵¹ and 10-phenyldibenzo[*c,g*]phenanthrene (1-phenylpentahelicene),⁵² and related compounds^{51,52,56} were prepared previously by photodehydrocyclization reactions.

Table 1. Synthesis of Phenanthrene 167a, Benzo[*c*]phenanthrene 167b, and Dibenzo[*c,g*]phenanthrene 167c

propargylic alcohols and benzannulated enediynes	phenanthrenes 167
<p>165a: R = OH, 96% 166a: R = H, 98%</p>	<p>167a, 89%</p>
<p>165b: R = OH, 94% 166b: R = H, 98%</p>	<p>167b, 83%</p>
<p>165c: R = OH, 87% 166c: R = H, 89%</p>	<p>167c, 78%</p>

4. 3. Products of [2 + 2] Cycloaddition Reaction

Minor amounts of **168b** (ca. 2%) and **168c** (ca. 12%), derived from the intramolecular [2 + 2] cycloaddition reactions of the corresponding benzannulated

enyne–allene precursors, were also produced as observed previously.^{16b,50}

4. 4. Structure Analysis of **167**

It is worth noting that the intramolecular radical–radical coupling reaction of the biradical derived from **166a** involved only the α -position of the naphthyl ring to produce **167a** preferentially. Attaching the β -position to form an indeno-fused anthracene derivative did not appear to occur. The higher reactivity of the α -position than the β -position of naphthalene in homolytic addition may be responsible for the regioselectivity.⁵⁷ A similar preference could also account for the formation of the angularly fused **167b** and **167c**.

Recorded on a 600 MHz NMR spectrometer, the ^1H NMR signal of the two hydrogens on the five-membered ring of **167a** in CDCl_3 appeared as a singlet at δ 4.45. This observation is consistent with the planar geometry of the indeno[2,1-*b*]phenanthrene ring system of **167a** with the phenyl substituent oriented essentially perpendicular to the phenanthrene ring as observed in the X-ray structure (Figure 3).

Figure 3. ORTEP drawing of the crystal structure of **167a**.

Interestingly, the ^1H NMR signals of the methylene hydrogens of **167b** in CDCl_3 , also recorded on a 600 MHz NMR spectrometer at 25 °C, exhibited as an AB quartet at δ 4.55 and 4.34 with a coupling constant of 20.7 Hz, indicating that the indeno-fused benzo[*c*]phenanthrene ring system with the phenyl substituent at the most sterically hindered position is nonplanar, and the rate of racemization is relatively slow on the NMR time scale. As a result, the methylene hydrogens are diastereotopic, exhibiting a large geminal coupling constant. The helical nature of the structures of several 1-phenylbenzo[*c*]phenanthrene derivatives was established by temperature-dependent NMR studies earlier.^{51b} The rate of racemization with the phenyl group moving from one side of the helical twist to the other side was determined to be ca. 16 kcal/mol. The well resolved AB quartet of the ^1H NMR signals of the methylene hydrogens of **167b** also provided an opportunity to determine the activation barrier of racemization by temperature-dependent NMR studies. However, the AB signals of **167b** in 1,1,2,2-tetrachloroethane-*d*₂, recorded on a 270 MHz NMR spectrometer, remained well separated and exhibited essentially no line broadening at 125 °C, indicating that the rate of the helix inversion is relatively slow on the NMR time scale. The $\Delta G^\ddagger_{\text{rac}}$ of **167b** is estimated to be at least 19.4 kcal/mol on the basis of the AB signals at δ 4.60 and 4.39 ($\delta_{\text{A}} - \delta_{\text{B}} = 56.6$ Hz) with a coupling constant of 20.7 Hz at 125 °C. The higher energy barrier for racemization than those of earlier cases may be attributed to the buttressing effect of the fused indeno group and the *t*-butyl substituent in **167b** as observed previously in the related systems.^{17, 51}

The ^1H NMR spectrum of **167b** in CDCl_3 recorded on a 600 MHz NMR spectrometer at 25 °C also showed four broad humps at δ 8.01, 7.33, 6.72, and 6.07. At –20 °C, the signals at δ 8.01 and 6.07 became doublets and the signals at δ 7.33 and 6.72 became triplets, attributable to the *ortho* and *meta* hydrogens on the phenyl substituent, respectively. The fact that four separate signals were observed suggests that rotation around the carbon–carbon single bond attaching the phenyl substituent to the benzo[*c*]phenanthrene ring system is restricted on the NMR time scale. The signals of the *ortho* hydrogens coalesced at ca. 60 °C and the signals of the *meta* hydrogens coalesced at ca. 50 °C, corresponding to a rotational barrier of ca. 14.5 kcal/mol, which is slightly higher than the

rotational barriers of ca. 13 kcal/mol of several other 1-phenylbenzo[*c*]phenanthrene derivatives reported earlier.^{51b}

Compared to **167b**, the structural distortion of **167c** with an additional fused benzene ring could be expected to be even more profound. The X-ray structure of **167c** (Figure 4) showed that the indeno-fused dibenzo[*c,g*]phenanthrene ([5]helicene) skeleton is severely twisted to minimize unfavorable van der Waal's contact with the π electrons of the phenyl substituent at the most sterically hindered position. The acute dihedral angle between the mean planes of the benzene ring bearing the phenyl substituent and the benzene ring at the other end of the [5]helicene system is pronounced 58.4° from planarity. The phenyl substituent is oriented at a 60.6° angle from the mean plane of the benzene ring where it is attached.

As in **167b**, the AB quartet of the methylene hydrogens of **167c** in 1,1,2,2-tetrachloroethane-*d*₂ at δ 4.63 and 4.35 ($\delta_A - \delta_B = 77.8$ Hz, $J = 21.1$ Hz), recorded on a 270 MHz NMR spectrometer, remained well separated and exhibited essentially no line broadening at 125 °C, corresponding to a $\Delta G^\ddagger_{\text{rac}}$ of at least 19.3 kcal/mol. The ¹H NMR signals of the *ortho* hydrogens on the phenyl substituent appeared as doublets at δ 6.43 and 5.75, whereas those of the *meta* hydrogens appeared as overlapping triplets at δ 6.56 and 6.54. The coalescence temperature of the *ortho* hydrogens was determined to be at 100 °C, corresponding to a higher rotational barrier of 17.5 kcal/mol than the rotational barrier of 14.5 kcal/mol of **167b**.

Figure 4. Perspective view of the molecular structure of **167c** with the thermal ellipsoids scaled to enclose 30% probability.

5. Conclusions

The indeno-fused phenanthrene **167a**, benzo[*c*]phenanthrene **167b**, and dibenzo[*c,g*]phenanthrene **167c**, bearing a phenyl substituent at the most sterically hindered position were readily synthesized from the benzannulated enediynyl propargylic alcohols **165a-c**. The fused aromatic ring systems of **167b** and **167c** possess a helical twist and the rotation of the phenyl substituent is restricted. The X-ray structure of **167c** allowed direct measurement of the extent of distortion from planarity.

Chapter V

Synthesis of Helical Derivatives of Indenofluorene via Schmittel Cyclization Reaction of Benzannulated Enyne–Allenes

1. Introduction

Biradicals generated from Schmittel cyclization reaction of benzannulated enyne–allenes provide many opportunities for subsequent synthetic applications to give formal Diels–Alder adducts.^{14,15} For example, as reported earlier we adopted an efficient synthetic pathway outlined in Scheme 40 for the synthesis of indeno-fused benzo[*c*]phenanthrene **167a**. Condensation between lithium acetylide **46** and aryl ketone **160a** furnished propargylic alcohol **165a**, which was then reduced with triethylsilane in the presence of trifluoroacetic acid to give the benzannulated enediyne **166a**. Treatment of **166a** with potassium *t*-butoxide in refluxing toluene then produced **167a** by a sequence of cascade reactions. The transformation from **166a** to **167a** involved initially a prototropic rearrangement to form the benzannulated enyne–allene **168**. A subsequent Schmittel cyclization reaction produced biradical **169** followed by an intramolecular radical–radical coupling reaction leading to the formal Diels–Alder adduct **170**, which in turn underwent tautomerization to give **167a**.

Scheme 40. Synthesis of phenanthrene **167a** via the Schmittel cyclization reaction.

2. Research Objective

We envisioned that by replacing **46** with tetraacetylene **171a**, the synthetic sequence outlined in Scheme 40 could lead to the derivatives of indenofluorene through double formal

intramolecular Diels–Alder reactions.

3. Literature Survey for the Synthesis of the Derivatives of Indenofluorene

Indenofluorene was first synthesized by Nierenstein and Webster in 1945 as a minor product called *ellagene* by distillation of ellagic acid with zinc dust.⁵⁸ Double Friedel–Crafts cyclization reactions were employed as a key step for the synthesis of derivatives of indenofluorene.⁵⁹

4. Results and Discussion

4.1. Synthesis of 179a, 182a and 185

The use of tetraacetylene **171a** for the condensation reaction with aryl ketone **147** furnished propargylic alcohol **172a**, which was reduced with triethylsilane in the presence of trifluoroacetic acid to afford tetraacetylenic hydrocarbon **173a**. Treatment of **173a** with potassium *t*-butoxide in refluxing toluene efficiently furnished **179a** through double formal Diels–Alder reactions (Scheme 41).

Scheme 41. Synthesis of phenanthrene **179a** via the Schmitt cyclization reactions.

By replacing the phenyl group of **147** with a 2-naphthyl, or a 3-phenanthryl group, the synthetic sequence outlined in Scheme 41 led to the fused aromatic systems **182a** and **185**, respectively, with more extended conjugations.

Table 2. Synthesis of 182a, 185

aryl ketone	propargylic alcohol and enediyne	product
<p>160a</p>	<p>180a, R = OH, 74% 181a, R = H, 85%</p>	<p>182a, 72%</p>
<p>160b</p>	<p>183, R = OH, 73% 184, R = H, 84%</p>	<p>185, 70%</p>

4. 2. Structure Analysis of 179a, 182a and 185

It is worth noting that the intramolecular radical–radical coupling reaction of the biradical derived from **181a** involved only the α -position of the naphthyl ring to produce **182a** preferentially as observed earlier. The higher reactivity of the α -position than the β -position of the naphthyl ring in homolytic addition may be responsible for the

regioselectivity.⁵⁷ A similar preference could also account for the formation of **185**.

Recorded on a 600 MHz NMR spectrometer, the ¹H NMR signal of the methylene hydrogens on the five-membered rings of **179a** in CDCl₃ appeared as a singlet at δ 4.52, indicating that the rate of racemization is faster than the NMR time scale. As a result, the methylene hydrogens were observed as a singlet. Similarly, the singlet at δ 4.46 of the methylene hydrogens on the five-membered rings of **182a** also indicates a rapid rate of racemization.

However, the distorted structure with a helical twist in **185** was manifested with a set of AB quartet at δ 4.53 and 4.44 from the diastereotopic methylene hydrogens on the five-membered rings, as observed earlier in the structurally related the indeno-fused benzo[*c*]phenanthrene ring system of **167b** with a phenyl substituent at the most sterically hindered position.

4. 3. An Alternative Synthetic Pathway to Helical Structure

The distorted structure in the conjugated indenofluorene ring system could also be produced by an alternative approach. It could be envisaged that by replacing the two phenyl substituents of **179a** and **182a** with two longer 4-(*tert*-octyl)phenyl groups (*tert*-octyl = 1,1,3,3-tetramethylbutyl), unfavorable van der Waal's contact between the two longer substituents would be produced. As a result, the indenofluorene ring system had to adopt a helical conformation to minimize the steric repulsion. By replacing phenyl substituents with 4-(*tert*-octyl)phenyl groups, the synthetic sequence in Scheme 41 could lead to **179b** and **182b** (Table 3).

4. 4. Structure Analysis of **179b** and **182b**

As expected, steric hindrance between the two longer 4-(*tert*-octyl)phenyl groups causes a helical twist in **179b** and **182b**, also manifested each with AB quartet with a large coupling constant .

Table 3. Synthesis of 179b and 182b

aryl ketone	tetraacetylene	propargylic alcohol and enediyne	product
<p>147</p>	<p>171b, Ar = 4-(<i>tert</i>-octyl)phenyl</p>	<p>172b, R = OH, 47% 173b, R = H, 85%</p>	<p>179b, 73%</p>
<p>160a</p>	<p>171b, Ar = 4-(<i>tert</i>-octyl)phenyl</p>	<p>180b, R = OH, 46% 181b, R = H, 78%</p>	<p>182b, 70%</p>

4. 5. Synthesis of Tetraacetylenes 171

Tetraacetylene **171a** was prepared by two Sonogashira reactions between 1,5-dibromo-2,4-diiodobenzene (**186**)⁶⁰ and phenylacetylene **187a** to afford **188a**. Two bromo to iodo exchanges followed by cross-coupling reactions with (trimethylsilyl)acetylene produced **189a**, which was desilylated to afford **171a**. Tetraacetylene **171b** was likewise synthesized (Scheme 42).

Scheme 42. Synthesis of tetraacetylenes **171a** and **171b**.

5. Conclusions

Several derivatives of indenofluorene ring system were efficiently synthesized via double formal Diels–Alder reactions. Two different synthetic approaches for the helical structures were developed.

Chapter VI

Studies of Helical Molecules: Efficient Synthesis of Overcrowded Molecules of Diindeno-Fused 1,12-Diphenylbenzo[*c*]phenanthrene and 1,14-Diphenyldibenzo[*c,g*]phenanthrene

1. Introduction

1,12-Disubstituted benzo[*c*]phenanthrenes **190** and analogs were known as overcrowded molecules.⁶¹ Because of steric hindrance, the aromatic system of the 1,12-disubstituted benzo[*c*]phenanthrenes is distorted and the two substituents are bent out of the plane of the aromatic rings. X-ray structure analysis shows that 1,12-dimethylbenzo[*c*]phenanthrene (**190a**) is nonplanar.⁶² Further evidence of nonplanarity was provided by resolution of 1,12-dimethylbenzo[*c*]phenanthrenes-5-acetic acid (**190b**).⁶³ The optical stability of the molecule is high, with racemization occurring only at ca. 250 °C.

Figure 4. Examples of Overcrowded Molecules

2. Research Objective

We envisioned that replacing the methyl groups with sterically more demanding phenyl groups in the overcrowded fjord region could lead to even more distorted structures.

3. Literature Survey for the Synthesis of Overcrowded Molecules

Several synthetic methods for 1,12-dimethylbenzo[*c*]phenanthrenes **190**, 1,14-disubstituted dibenzo[*c,g*]phenanthrenes **191**, and related compounds have been reported,^{61,63,64} including intramolecular Friedel–Crafts cyclization reactions followed by aromatization (Scheme 43)^{64a} and photochemically induced dehydrocyclization of stilbenes (Scheme 44).^{64f}

Scheme 43. Synthesis of 1,12-dimethylbenzo[*c*]phenanthrene.

Scheme 44. Synthesis of 14,15-diphenyldibenzo[*f,j*]picene.

We recently reported¹⁷ the use of the Schmitt cyclization reaction of the benzannulated enyne–allenes **59** for the synthesis of 4,5-diarylphenanthrenes **60** (Scheme 13). Our continued interest in nonplanar polycyclic aromatic compounds led us to apply this method for the synthesis of 1,12-diphenylbenzo[*c*]phenanthrene **204a** and 1,14-diphenyldibenzo[*c,g*]phenanthrene **204b**.

4. Results and Discussion

4. 1. Synthesis of Overcrowded Molecules 204

Aryl ketone **196a** was obtained by converting the corresponding carboxylic acid **195a**⁶⁵ to the acid chloride with thionyl chloride followed by treatment with *t*-butylcopper, prepared from *t*-butyllithium and CuBr·SMe₂ (Scheme 45). Condensation between diketone **196a** and the lithium acetylide **46** furnished the benzannulated enediynyl propargylic alcohol **197a** as an essentially 1:1 mixture of diastereomers. Treatment of **197a** with triethylsilane in the presence of trifluoroacetic acid produced tetraacetylenic hydrocarbon **198a** also as an essentially 1:1 mixture of diastereomers. On exposure to potassium *tert*-butoxide under refluxing toluene for 3 h, hydrocarbon **198a** was transformed to 1,12-diphenylbenzo[*c*]phenanthrene **204a**. The transformation from **198a** to **204a** presumably involved a cascade of reactions including an initial prototropic rearrangement to form the benzannulated

enyne–allene **199** followed by two Schmitt cyclization reactions and intramolecular radical–radical coupling reactions to form the formal Diels–Alder adduct **203**, and subsequently, after prototropic rearrangements, **204a**.

Conditions: (i) SOCl_2 , reflux. (ii) $\text{CuBr}\cdot\text{SMe}_2$, $t\text{-BuLi}$, -50°C . (iii) Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$. (iv) $\text{KO-}t\text{-Bu}$, refluxing toluene.

Scheme 45. Synthesis of 1,12-diphenylbenzo[*c*]phenanthrene **204a**.

The synthetic sequence outlined in Scheme 45 was also adopted to convert 3,6-phenanthrene dicarboxylic acid (**195b**)⁶⁶ to 1,14-diphenyldibenzo[*c,g*]phenanthrene **204b** (Table 4). Compared to the observation^{64f} that only trace amount (<1%) **191d** having a similar structure was obtained by photocyclization of diarylethylene (Scheme 44), the synthetic pathway for **204b** provides a viable alternative for the preparation of highly congested 1,14-diphenyldibenzo[*c,g*]phenanthrenes.

Table 4. Synthesis of 204b

carboxylic acid and aryl ketone	propargylic alcohol and enediyne	product
195b : R = OH 196b : R = <i>t</i> -Bu, 43%	197b : R = OH, 91% 198b : R = H, 83%	204b , 47%

4.2. Structure Analysis of 204a and 204b

It is worth noting that the intramolecular radical–radical coupling reactions derived from **200** and **202** prefer the α -position of the naphthyl ring to produce **204a** instead of the sterically less congested β -position. A similar preference could also account for the formation of the angularly fused **204b**, as observed in previous cases.¹⁷ The higher reactivity of the α -position than the β -position of naphthalene and phenanthrene in homolytic addition may be responsible for the regioselectivity.⁵⁷

The structure of **204a** was unequivocally established by X-ray structure analysis. The ORTEP drawing of **204a** is given in Figure 5 to illustrate the severity of structural distortion. Due to two phenyl substituents in the highly congested fjord region, the acute dihedral angle between the mean planes of the two benzene rings bearing the phenyl substituent is pronounced 59.9° from planarity, which indicates an even more remarkable structure distortion, compared to the acute dihedral angle of benzo[*c*]phenanthrene at 27°.⁶⁷

The ¹H NMR spectrum of **204a** in CDCl₃ exhibited a set of AB quartet at δ 4.09 and 4.26 (J = 20.4 Hz) from the diastereotopic methylene hydrogens on the five-membered rings, manifesting the presence of a helical twist.

The upfield-shift signal at δ 5.71 (doublet) was attributable to the inner *ortho* hydrogens on the phenyl substituents, indicating that each of the phenyl substituents is essentially parallel to the benzene ring at the other end of the central aromatic system. Such

an orientation places the inner *ortho* hydrogens in the shielding region of the induced aromatic ring current, but puts the outer *ortho* hydrogens in the deshielding region with a downfield signal at δ 7.89. Such an orientation was also manifested by an upfield signal at δ 6.31 (doublet), attributable to the two aromatic hydrogens closest to the phenyl substituents as observed in previous case¹⁷.

The fact that two distinct signals were observed for the *ortho* hydrogens suggests that rotation of the phenyl groups is restricted on the NMR time scale. The signals of the *ortho* hydrogens observed at δ 7.89 and 5.71 coalesced at ca. 120 °C, corresponding to a rotational barrier of ca. 17.6 kcal/mol.

Figure 5. ORTEP drawing of the crystal structure of **204a** with hydrogen atoms omitted for clarity.

The distorted structure of **204b** was also indicated by an AB pattern on the ¹H NMR spectrum from the diastereotopic methylene hydrogens on the five-membered rings and conformed by X-ray structure analysis (Figure 6). The X-ray structure of **204b** showed that the acute dihedral angle between the mean planes of the two benzene rings bearing the phenyl substitutes is 57.8 °, smaller than that of **204a**, still much larger than the value of 30° for [5]helicene.⁶⁸

The ¹H NMR spectrum of **204b** in CDCl₃ recorded on a 600 MHz NMR spectrometer at 25 °C showed two broad humps at δ 6.50 and 5.58, attributable to the *ortho*

hydrogens on the phenyl substituents. The coalescence temperature for the *ortho* hydrogens is 75 °C, corresponding to a rotation barrier of 16.3 kcal/mol, which is lower than that of **204a**. The observations of **204b** with a smaller acute dihedral angle and a lower rotation barrier of the phenyl substituents than those of **204a** suggests that **204b** is less strained, since **204b** has a larger skeletal framework between the interfering phenyl substituents over which to distribute the distortion created by the phenyl overcrowding.

Figure 6. ORTEP drawing of the crystal structure of **204b**
with hydrogen atoms omitted for clarity.

5. Conclusions

The diindeno-fused benzo[*c*]phenanthrene **204a** and dibenzo[*c,g*]phenanthrene **204b**, bearing two phenyl substituents at the overcrowded region, were readily synthesized via the Schmitt cyclization reaction of the corresponding benzannulated enyne–allenes **198a** and **198b** respectively. The structures of **204a** and **204b** with a helical twist were established by X-ray structure analysis and the rotation of the phenyl substituents is restricted.

Chapter VII

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, toluene and *p*-xylene were distilled over CaH₂ prior to use. Melting points were uncorrected. ¹H (270 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.0) as internal standards unless otherwise indicated. IR spectra were taken on Perkin-Elmer LX10-8704 Spectrum One FT-IR spectrometer. Mass spectra and high resolution mass spectra were obtained on Hewlett Packard 5970B GC/MSD instrument at 70 eV, VG 7070 by DEI, VG-ZAB by FAB and DE-STR by MALDI.

n-Butyllithium (2.5 M) in hexanes, *t*-butyllithium (1.7 M) in pentane, lithium diisopropylamide (LDA, 2.0 M) in THF/*n*-heptane, CuBr·SMe₂, triethylsilane, trifluoroacetic acid, potassium *t*-butoxide (1.0 M) in 2-methyl-2-propanol, potassium *t*-butoxide, 2-methyl-2-propanol, triethylamine, phenylacetylene, (trimethylsilyl)acetylene, Pd(PPh₃)₂Cl₂, copper(I) iodide, 2,2-dimethylpropiophenone (**147**), 2-naphthynyl chloride (**159a**), 3-acetylphenanthrene, 2-(bromomethyl)naphthalene (**161**), triphenylphosphine, and methyl 4-formylbenzoate (**162**) were purchased from chemical suppliers and were used as received.

1-Ethynyl-2-(phenylethynyl)benzene (**46**)¹⁷, 2,2-dimethyl-1,3-indandione (**111**)³⁴, 3-phenanthrenecarboxylic acid (**159b**)⁵³, 1,5-dibromo-2,4-diiodobenzene (**186**)⁶⁰, 1-ethynyl-4-(1,1,3,3-tetramethylbutyl)benzene (**187b**)³³, 2,7-naphthalenedicarboxylic acid (**195a**), 3,6-phenanthrenedicarboxylic acid (**195b**)⁶⁶ were prepared according to the reported procedures.

Propargylic Diols 112. To a solution of 1-ethynyl-2-(phenylethynyl)benzene (0.368 g, 1.82 mmol) in 10 mL THF was added 0.73 mL of a 2.5 M solution of *n*-butyllithium (1.82 mmol) at 0 °C. The reaction mixture was then allowed to warm to rt. After 30 min, a solution of 2,2-dimethyl-1,3-indandione (**111**, 0.138 g, 0.792 mmol) in 10 mL THF was added via cannula. After an additional 12 h of stirring at rt, the reaction mixture was quenched with 10 mL of water and extracted with diethyl ether. The organic layer was separated, washed with

water, dried over sodium sulfate, and concentrated to furnish a light yellow residue. The residue was purified by flash column chromatography (silica gel/50% methylene chloride in hexanes) to afford *trans*-**112a** (0.233 g, 51%) and *cis*-**112b** (0.040 g, 9%) as white solids. *trans*-Diol **112a**: mp 63–65 °C; IR 3440, 2217, 755 cm⁻¹; ¹H NMR δ 7.68–7.65 (4 H, m), 7.56–7.48 (4 H, m), 7.46–7.41 (4 H, m), 7.35–7.23 (10 H, m), 2.71 (2 H, s), 1.42 (6 H, s); ¹³C NMR δ 143.6, 132.2, 132.0, 131.7, 129.6, 128.4, 128.3, 128.2, 127.9, 125.8, 124.6, 124.3, 122.9, 93.4, 87.9, 86.5, 80.2, 57.4, 20.1; *cis*-Diol **112b**: mp 59–61 °C; IR 3423, 755 cm⁻¹; ¹H NMR δ 7.78–7.74 (4 H, m), 7.60–7.53 (4 H, m), 7.45–7.41 (4 H, m), 7.35–7.19 (10 H, m), 3.18 (2 H, s), 1.52 (3 H, s), 1.29 (3 H, s); ¹³C NMR δ 144.6, 132.4, 132.1, 131.7, 129.7, 128.41, 128.38, 128.3, 127.9, 126.1, 124.8, 124.7, 122.9, 93.4, 90.9, 88.0, 85.9, 81.8, 56.3, 25.8, 15.7.

4H-Cyclopenta[def]phenanthrene 116. To *trans*-**7** (0.208 g, 0.361 mmol) in 10 mL of THF at 0 °C was added via cannula a solution of thionyl chloride (0.215 g, 1.803 mmol) and anhydrous pyridine (0.285 g, 3.61 mmol) in 5 mL of THF. The reaction mixture was allowed to warm to rt. After an additional 8 h, 10 mL of water was introduced, and the reaction mixture was extracted with 20 mL of methylene chloride. The combined organic extracts were washed with water, dried over sodium sulfate, and concentrated to furnish the crude dichloride **115**. To a flask containing AIBN (0.0059 g, 0.0361 mmol) were added a solution of the crude **115** in 20 mL of benzene and tributyltin hydride (0.29 mL, 1.02 mmol). The reaction mixture was heated under reflux for 18 h. After the reaction mixture was allowed to cool to rt, 10 mL of a 10% aqueous potassium fluoride solution was introduced. The mixture was stirred for an additional 2 h and filtered. The organic layer was separated, washed with water, dried over sodium sulfate, and concentrated to give a brown solid residue. The residue was purified by flash column chromatography (silica gel/50% methylene chloride in hexanes) to afford **116** (0.084 g, 43%) as a yellow solid: compound becomes black without melting at 289 °C; IR 1599, 1459, 1402, 747, 700 cm⁻¹; ¹H NMR δ 7.66–7.48 (12 H, m), 7.41 (2 H, s), 7.25 (2 H, t, *J* = 7.3 Hz), 7.07 (2 H, t, *J* = 7.5 Hz), 6.74 (2 H, d, *J* = 7.7 Hz), 4.33 (4 H, s), 2.02 (6 H, s); ¹³C NMR δ 145.9, 143.8, 142.1, 139.2, 138.6, 134.9, 134.7, 131.8, 130.1, 128.9, 127.6, 126.9, 126.5, 126.4, 124.9, 123.7, 123.4, 51.1, 33.8, 23.3; MS *m/z* 546 (M⁺),

531, 516; HRMS calcd for $C_{43}H_{30}$ (M^+) 546.2348, found 546.2367.

Benzo[*c*]phenanthrene-2-carboxylic acid (159c). A suspension of 0.324 g of **164** (1.08 mmol) and 1.00 g of sodium hydroxide in 20 mL of ethanol and 20 mL of water was heated under reflux for 3 h. The solution was concentrated to reduce the volume of the solution to ca. 15 mL and then extracted with 20 mL of diethyl ether. The aqueous layer was acidified with a 10% aqueous hydrochloric acid solution to produce a white precipitate. The white precipitate was filtered and then washed with a 1 M aqueous hydrochloric acid solution, water, and hexanes. The product was pumped to dryness in vacuo to afford 0.282 g of **159c** (1.03 mmol, 96%) as a white solid: IR 3300–2500 (br), 1686 cm^{-1} ; 1H NMR δ (600 MHz, $CDCl_3$) 9.99 (1 H, s), 9.12 (1 H, d, $J = 8.4$ Hz), 8.30 (1 H, d, $J = 7.8$ Hz), 8.11 (1 H, d, $J = 8.4$ Hz), 8.07 (1 H, d, $J = 7.8$ Hz), 7.99–7.95 (3 H, m), 7.86 (1 H, d, $J = 8.4$ Hz), 7.81 (1 H, t, $J = 7.5$ Hz), 7.70 (1 H, t, $J = 7.5$ Hz); ^{13}C NMR (600 MHz, 1% DMSO- d_6 in $CDCl_3$) δ 170.6, 136.3, 133.7, 131.27, 131.23, 130.1, 129.60, 129.57, 128.7, 128.6, 128.18, 128.05, 127.9, 126.98, 126.92, 126.90, 126.6, 126.3, 125.9.

Aryl Ketone 160a. The following procedure is representative for the preparation of the aryl ketones. To a suspension of 1.36 g of $CuBr \cdot SMe_2$ (6.63 mmol) in 40 mL of THF was added 3.9 mL of a 1.7 M solution of *t*-butyllithium (6.63 mmol) in pentane at $-50^\circ C$. After 30 min of stirring, a solution of 1.05 g of 2-naphthyl chloride (**159a**, 5.53 mmol) in 15 mL of THF was introduced dropwise via cannula. After an additional 4 h at $-50^\circ C$, the reaction mixture was allowed to warm to room temperature and treated with 20 mL of a saturated aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 1.17 g of **160a** (5.53 mmol, 100%) as a white solid: mp $54-56^\circ C$; IR 1670, 1164, 1122, 760 cm^{-1} ; 1H NMR δ 8.23 (1 H, s), 7.94–7.76 (4 H, m), 7.60–7.50 (2 H, m), 1.43 (9 H, s); ^{13}C NMR δ 209.0, 135.7, 134.2, 132.3, 129.1, 128.4, 127.7, 127.6, 126.6, 124.8, 44.3, 28.2; MS m/z 212 (M^+), 155, 127.

Aryl Ketone 160b. To a flask containing 0.500 g (2.25 mmol) of 3-phenanthrenecarboxylic

acid (**159b**) was introduced 39 mL of thionyl chloride. The reaction mixture was heated under reflux for 12 h. The excess thionyl chloride was removed in vacuo to furnish the crude 3-phenanthrenecarbonyl chloride. The same procedure was then repeated as described for **160a** except that 0.562 g of CuBr·SMe₂ (2.71 mmol) and 1.6 mL of a 1.7 M solution of *t*-butyllithium (2.71 mmol) in pentane were used to afford 0.558 g of **160b** (2.13 mmol, 95%) as an orange solid: mp 57–59 °C; IR 1667, 842 cm⁻¹; ¹H NMR δ 9.13 (1 H, s), 8.64 (1 H, d, *J* = 7.9 Hz), 7.93 (1 H, dd, *J* = 8.2, 1.4 Hz), 7.76 (2 H, t, *J* = 8.7 Hz), 7.67–7.51 (4 H, m), 1.50 (9 H, s); ¹³C NMR δ 209.0, 136.2, 133.4, 132.2, 130.5, 129.6, 128.85, 128.78, 128.1, 127.09, 127.03, 126.2, 125.6, 123.2, 122.6, 44.4, 28.3; MS *m/z* 262 (M⁺), 205, 177.

Aryl Ketone 160c. The same procedure was repeated as described for **160b** except that 0.264 g (0.97 mmol) of benzo[*c*]phenanthrene-2-carboxylic acid (**159c**) was heated with 17 mL of thionyl chloride under reflux for 12 h to furnish the crude benzo[*c*]phenanthrene-2-carbonyl chloride. The acid chloride was treated with *t*-butylcopper, prepared from 0.241 g of CuBr·SMe₂ (1.16 mmol) and 0.68 mL of a 1.7 M solution of *t*-butyllithium (1.16 mmol) in pentane, to afford 0.193 g of **160c** (0.62 mmol, 64%) as an orange solid: mp 68–70 °C; IR 1668, 848 cm⁻¹; ¹H NMR δ 9.57 (1 H, s), 9.03 (1 H, d, *J* = 8.4 Hz), 8.07–7.97 (3 H, m), 7.94 (1 H, d, *J* = 8.4 Hz), 7.90 (2 H, s), 7.84 (1 H, d, *J* = 8.6 Hz), 7.77–7.63 (2 H, m), 1.49 (9 H, s); ¹³C NMR δ 208.8, 135.4, 134.6, 133.6, 131.2, 129.9, 129.2, 128.73, 128.66, 128.5, 128.2, 127.9, 127.7, 126.8, 126.7, 126.5, 126.2, 125.1, 44.2, 28.2; MS *m/z* 255 (M⁺), 226, 57.

Ethyl 4-[2-(2-Naphthalenyl)ethynyl]benzoate (163). A suspension of 1.44 g of 2-(bromomethyl)naphthalene (**161**, 6.25 mmol) and 1.64 g of triphenylphosphine (6.25 mmol) in 15 mL of *N,N*-dimethylformamide was heated at 150 °C for 30 min. After the solution was cooled to rt, 1.03 g of methyl 4-formylbenzoate (**162**, 6.25 mmol) and lithium ethoxide, prepared from treatment of 10 mL of ethanol with 5.6 mL of a 2.5 M solution of *n*-butyllithium (14.0 mmol) in hexanes, were added. The resulting suspension was stirred at rt for 3.5 h. The reaction mixture was then diluted with 30 mL of diethyl ether and washed successively with 30 mL of a 10% aqueous hydrochloric acid solution, brine, and water. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by

flash column chromatography (silica gel/50% methylene chloride in hexanes) afforded 1.51 g of **163** (5.0 mmol, 80%, a mixture of the *trans* and *cis* isomers; *trans*:*cis* = 5.5:4.5) as a white solid: ^1H NMR δ 8.07 (1 H, d, J = 8.2 Hz), 7.94–7.59 (6 H, m), 7.53–7.43 (2 H, m), 7.38 (0.55 H, d, J = 16.3 Hz), 7.36–7.29 (2 H, m), 7.25 (0.55 H, d, J = 16.3 Hz), 6.87 (0.45 H, d, J = 12.1 Hz), 6.70 (0.45 H, d, J = 12.1 Hz), 4.41 (1.1 H, q, J = 7.2 Hz), 4.37 (0.9 H, q, J = 7.2 Hz), 1.43 (1.7 H, t, J = 7.2 Hz), 1.38 (1.3 H, t, J = 7.2 Hz); ^{13}C NMR δ 166.4, 141.9, 141.7, 134.2, 133.6, 133.3, 133.2, 132.6, 132.1, 131.1, 130.0, 129.51, 129.45, 129.2, 129.0, 128.9, 128.4, 128.13, 128.07, 127.9, 127.8, 127.7, 127.6, 127.3, 126.6, 126.4, 126.24, 126.19, 126.1, 123.3, 60.9, 14.3.

Ethyl Benzo[*c*]phenanthrene-2-carboxylate (164). A solution of 0.245 g of **163** (0.811 mmol), 0.204 g of iodine (1.27 mmol), and 8.5 mL of propylene oxide (120 mmol) in 1.5 L of benzene was photolyzed for 72 h in a Rayonet photochemical apparatus equipped with sixteen of the 254-nm mercury lamps. The reaction mixture was then concentrated to reduce the volume of the reaction mixture to 100 mL. The concentrated solution was washed with a 15% aqueous sodium thiosulfate solution, brine, and water. The organic layer was separated, dried over sodium sulfate, and concentrated. Four separate runs of similar scales followed by purification of the resulting adducts by flash column chromatography (silica gel/5% diethyl ether in hexanes) converted 0.984 g (3.26 mmol) of **163** to 0.728 g (2.41 mmol, 74%) of **164** as a white solid: IR 1710, 1268 cm^{-1} ; ^1H NMR δ 9.89 (1 H, s), 9.11 (1 H, d, J = 8.4 Hz), 8.23 (1 H, dd, J = 8.4, 1.5 Hz), 8.06–8.01 (2 H, m), 7.95–7.89 (3 H, m), 7.81 (1 H, d, J = 8.4 Hz), 7.77 (1 H, td, J = 8.4, 1.5 Hz), 7.67 (1 H, t, J = 6.7 Hz), 4.51 (2 H, q, J = 7.2 Hz), 1.49 (3 H, t, J = 7.2 Hz); ^{13}C NMR δ 167.0, 135.8, 133.6, 131.1, 130.5, 130.0, 129.4, 129.2, 128.6, 128.5, 128.0, 127.86, 127.80, 127.7, 126.8, 126.6, 126.5, 126.2, 125.5, 61.1, 14.4.

Propargylic Alcohol 165a. The following procedure is representative for the preparation of the propargylic alcohols. A solution of 0.264 g of **160a** (1.25 mmol) in 20 mL of THF was introduced via cannula to the solution of **46** in 10 mL of THF, prepared from 0.302 g of 1-ethynyl-2-(phenylethynyl)benzene (1.50 mmol) and 0.60 mL of a 2.5 M solution of *n*-butyllithium (1.50 mmol) in hexanes at 0 °C with 30 min of stirring, then the reaction mixture was allowed to warm to rt. After an additional 2 h, 20 mL of water was introduced,

and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 0.496 g of **165a** (1.20 mmol, 96%) as a white solid: IR 3574, 1494 cm^{-1} ; ^1H NMR δ 8.25 (1 H, d, J = 1.2 Hz), 7.96 (1 H, dd, J = 8.7, 1.7 Hz), 7.83–7.81 (2 H, m), 7.71 (1 H, d, J = 8.9 Hz), 7.63–7.56 (2 H, m), 7.50–7.40 (4 H, m), 7.36–7.17 (5 H, m), 2.65 (1 H, s), 1.20 (9 H, s); ^{13}C NMR δ 139.7, 132.6, 132.4, 132.21, 132.15, 131.6, 128.38, 128.34, 128.2, 127.9, 127.3, 126.5, 126.4, 126.2, 125.9, 125.8, 125.0, 122.9, 96.2, 93.3, 88.2, 84.7, 79.6, 40.0, 25.6.

Propargylic Alcohol 165b. The same procedure was repeated as described for **165a** except that 0.558 g of **160b** (2.13 mmol) was treated with the solution of **46** in 20 mL of THF, prepared from 0.516 g of 1-ethynyl-2-(phenylethynyl)benzene (2.56 mmol) and 1.0 mL of a 2.5 M solution of *n*-butyllithium (2.5 mmol) in hexanes, to afford 0.931 g of **165b** (2.01 mmol, 94%) as a white solid: IR 3546, 2213, 753 cm^{-1} ; ^1H NMR δ 9.32 (1 H, s), 8.96 (1 H, d, J = 7.7 Hz), 8.25 (1 H, d, J = 8.2 Hz), 7.99 (1 H, d, J = 6.9 Hz), 7.90–7.70 (7 H, m), 7.60 (2 H, d, J = 7.4 Hz), 7.44–7.28 (5 H, m), 3.17 (1 H, s), 1.44 (9 H, s); ^{13}C NMR δ 140.3, 132.14, 132.10, 131.9, 131.5, 131.1, 130.4, 129.1, 128.4, 128.2, 128.03, 127.98, 127.86, 127.0, 126.9, 126.7, 126.4, 126.3, 125.8, 124.9, 122.75, 122.68, 121.4, 96.4, 93.4, 88.3, 84.8, 79.8, 39.9, 25.6.

Propargylic Alcohol 165c. The same procedure was repeated as described for **165a** except that 0.102 g of **160c** (0.33 mmol) was treated with the solution of **46** in 10 mL of THF, prepared from 0.079 g of 1-ethynyl-2-(phenylethynyl)benzene (0.39 mmol) and 0.16 mL of a 2.5 M solution of *n*-butyllithium in hexanes, to afford 0.146 g of **165c** (0.28 mmol, 87%) as a white solid: IR 3556, 2217, 730 cm^{-1} ; ^1H NMR δ 9.58 (1 H, s), 9.23 (1 H, d, J = 8.4 Hz), 8.09 (1 H, dd, J = 8.4, 1.7 Hz), 8.01 (1 H, d, J = 7.9 Hz), 7.95–7.82 (5 H, m), 7.67–7.61 (2 H, m), 7.57 (1 H, t, J = 7.4 Hz), 7.44–7.32 (5 H, m), 7.28–7.12 (3 H, m), 2.74 (1 H, s), 1.24 (9 H, s); ^{13}C NMR δ 140.1, 133.4, 132.7, 132.3, 132.1, 131.5, 131.1, 130.2, 129.1, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 127.07, 126.96, 126.91, 126.7, 126.2, 126.1, 125.9, 125.8, 125.1, 122.7, 96.5, 93.4, 88.3, 84.9, 80.0, 40.2, 25.7.

Benzannulated Eneidyne 166a. The following procedure is representative for the

preparation of the benzannulated enediynes. To a solution of 0.494 g of **165a** (1.19 mmol) and 0.208 g of triethylsilane (1.79 mmol) in 20 mL of methylene chloride was added 0.37 mL of trifluoroacetic acid (0.543 g, 4.77 mmol). After 10 min of stirring at rt, a solution of 0.322 g of sodium carbonate (3.04 mmol) in 15 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes) afforded 0.466 g of **166a** (1.17 mmol, 98%) as a yellow solid: mp 90–92 °C; IR 2215, 1494, 783 cm^{-1} ; ^1H NMR δ 7.97 (1 H, s), 7.90–7.82 (2 H, m), 7.81–7.72 (2 H, m), 7.69–7.61 (2 H, m), 7.54–7.46 (4 H, m), 7.38–7.31 (3 H, m), 7.24 (2 H, t, $J = 7.3$ Hz), 4.01 (1 H, s), 1.21 (9 H, s); ^{13}C NMR δ 136.8, 133.0, 132.4, 132.10, 132.04, 131.6, 128.3, 128.14, 128.07, 127.8, 127.45, 127.38, 127.0, 126.3, 125.8, 125.7, 125.5, 123.2, 95.6, 92.9, 88.6, 82.7, 50.8, 35.8, 27.9; MS m/z 398 (M^+), 355, 270.

Benzannulated Enediyne 166b. The same procedure was repeated as described for **166a** except that 0.114 g of **165b** (0.25 mmol) was treated with 0.043 g of triethylsilane (0.37 mmol) and 0.8 mL of trifluoroacetic acid (0.99 mmol) in 10 mL methylene chloride to afford 0.107 g of **166b** (0.24 mmol, 98%) as a yellow solid: IR 2214, 1493, 842, 756 cm^{-1} ; ^1H NMR δ 8.90 (2 H, m), 8.04–7.97 (1 H, m), 7.94–7.81 (4 H, m), 7.77–7.69 (4 H, m), 7.55 (2 H, d, $J = 6.9$ Hz), 7.44–7.22 (5 H, m), 4.18 (1 H, s), 1.35 (9 H, s); ^{13}C NMR δ 137.6, 132.1, 132.0, 131.6, 130.8, 130.2, 129.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.4, 126.53, 126.50, 126.4, 126.2, 125.7, 123.5, 123.1, 122.6, 95.7, 93.0, 88.6, 82.8, 51.1, 35.7, 27.9; MS m/z 448 (M^+), 391, 207.

Benzannulated Enediyne 166c. The same procedure was repeated as described for **166a** except that 0.140 g of **165c** (0.27 mmol) was treated with 0.048 g of triethylsilane (0.41 mmol) and 0.90 mL of trifluoroacetic acid (1.08 mmol) in 10 mL methylene chloride to afford 0.121 g of **166c** (0.24 mmol, 89%) as a yellow solid: IR 2217, 844 cm^{-1} ; ^1H NMR δ 9.23–9.17 (2 H, m), 8.01 (1 H, $J = 7.9$ Hz), 7.93–7.75 (6 H, m), 7.63–7.54 (3 H, m), 7.45 (1 H, tm, $J = 7.8, 1.2$ Hz), 7.36–7.27 (4 H, m), 7.21 (1 H, m), 7.16–7.08 (2 H, m), 4.06 (1 H, s), 1.17 (9 H, s); ^{13}C NMR δ 137.4, 133.4, 132.4, 132.2, 132.0, 131.5, 131.0, 130.3, 129.7,

128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.0, 126.7, 126.5, 126.3, 126.1, 125.7, 123.1, 95.8, 93.0, 88.6, 82.9, 51.2, 36.0, 27.9; MS m/z 498 (M^+), 441.

7-(1,1-Dimethylethyl)-13-phenyl-8*H*-indeno[2,1-*b*]phenanthrene (167a). The following procedure is representative for the preparation of phenanthrenes **167**. To a solution of 0.182 g of **166a** (0.46 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere were added 0.50 mL of a 1.0 M solution of potassium *t*-butoxide (0.50 mmol) in 2-methyl-2-propanol and 0.35 mL of 2-methyl-2-propanol (3.65 mmol). The reaction mixture was then heated under reflux for 3 h. After the reaction mixture was allowed to cool to rt, 10 mL of water and 20 mL of methylene chloride were introduced, and then the organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes) afforded 0.163 g of **167a** (0.41 mmol, 89%) as a yellow solid: mp 156–157 °C; IR 1440, 1364 cm^{-1} ; ^1H NMR δ (600 MHz, CDCl_3) 8.41 (1 H, d, $J = 9.6$ Hz), 7.78 (1 H, d, $J = 7.8$ Hz), 7.66 (1 H, d, $J = 8.4$ Hz), 7.61–7.58 (4 H, m), 7.50 (1 H, d, $J = 7.2$ Hz), 7.46–7.42 (2 H, m), 7.37 (1 H, t, $J = 7.5$ Hz), 7.18 (1 H, t, $J = 7.5$ Hz), 6.99 (1 H, tm, $J = 8.1, 1.2$ Hz), 6.92 (1 H, t, $J = 7.8$ Hz), 5.99 (1 H, d, $J = 7.8$ Hz), 4.45 (2 H, s), 1.90 (9 H, s); ^{13}C NMR δ (150 MHz, CDCl_3) 144.2, 143.3, 141.8, 141.1, 139.9, 138.8, 134.0, 132.5, 131.5, 131.3, 130.4, 130.2, 129.9, 129.1, 127.7, 127.2, 126.5, 126.1, 126.0, 125.4, 123.9, 123.80, 123.78, 123.5, 40.3, 38.5, 34.1; m/z 398 (M^+), 383, 341. HRMS calcd for $\text{C}_{31}\text{H}_{26}$ 398.2035, found 398.2043. Recrystallization of **167a** from CH_2Cl_2 /hexanes produced a crystal suitable for X-ray structure analysis.

9-(1,1-Dimethylethyl)-15-phenyl-10*H*-benz[*c*]indeno[1,2-*h*]phenanthrene (167b). The same procedure was repeated as described for **167a** except that a solution of 0.280 g of **166b** (0.63 mmol) in 10 mL of anhydrous toluene was treated with 0.077 g of potassium *t*-butoxide (0.69 mmol) and 0.48 mL of 2-methyl-2-propanol (5.00 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.232 g of **167b** (0.52 mmol, 83%) as a yellow solid: mp 169–171 °C; IR 1366, 831 cm^{-1} ; ^1H NMR δ (600 MHz, CDCl_3 , –20 °C) 8.34 (1 H, d, $J = 8.4$ Hz), 8.01 (1 H, d, $J = 7.8$ Hz), 7.84 (1 H, d, $J = 7.8$ Hz), 7.76 (1 H, t, $J = 8.4$ Hz), 7.75 (1 H, t, $J = 8.4$ Hz), 7.62 (1 H, d, $J = 7.8$ Hz), 7.55 (1 H, d, $J = 8.4$ Hz), 7.52 (1 H, d, $J = 7.8$ Hz), 7.33 (1 H, t, $J = 7.5$ Hz), 7.18 (1 H, t, $J = 7.2$ Hz), 7.16 (1 H, t, $J =$

7.2 Hz), 7.02 (1 H, t, $J = 7.5$ Hz), 6.97 (1 H, t, $J = 7.2$ Hz), 6.88 (1 H, t, $J = 7.2$ Hz), 6.72 (1 H, t, $J = 7.8$ Hz), 6.27 (1 H, d, $J = 8.4$ Hz), 6.07 (1 H, d, $J = 7.8$ Hz), 4.545 (1 H, d, $J = 21.6$ Hz), 4.331 (1 H, d, $J = 21.0$ Hz), 1.84 (9 H, s); ^{13}C NMR δ (150 MHz, CDCl_3 , 25 °C) 144.4, 140.9, 140.7, 140.6, 139.0, 138.6, 134.6, 133.2, 131.5, 130.9, 130.6, 130.4, 130.1, 128.0, 127.7, 127.1, 126.8, 126.5, 126.0, 125.9, 125.5, 124.8, 124.4, 124.3, 124.2, 123.9, 122.3, 40.0, 38.2, 33.5; MS m/z 448 (M^+), 433, 391. HRMS calcd for $\text{C}_{35}\text{H}_{28}$ 448.2191, found 448.2193.

The chemical shift of the AB quartet was calculated according to the equation: $\delta_a = [(v_1 + v_4) + \{(v_1 - v_4)(v_2 - v_3)\}^{1/2}]/2$;

In addition to **167b**, the formation of a minor amount (ca. 2%) of the intramolecular [2 + 2] cycloaddition adduct **168b** was also detected with characteristic ^1H NMR signals (600 MHz, CDCl_3) at δ 8.84 (1 H, s), 8.40 (1 H, d, $J = 9.0$ Hz), 8.12 (2 H, d, $J = 8.4$ Hz), 7.84 (1 H, d, $J = 7.8$ Hz), 6.49 (1 H, s, vinylic), and 1.29 (9 H, s) and a ^{13}C NMR signal (150 MHz, CDCl_3) at δ 76.1 attributable to the sp^3 carbon on the four-membered ring as observed previously in similar systems.¹⁷

Indeno-Fused Dibenzo[*c,g*]phenanthrene 167c. The same procedure was repeated as described for **167a** except that a solution of 0.120 g of **166c** (0.24 mmol) in 10 mL of anhydrous toluene was treated with 0.030 g of potassium *t*-butoxide (0.26 mmol) and 0.18 mL of 2-methyl-2-propanol (1.92 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.094 g of **167c** (0.19 mmol, 78%) as a yellow solid: mp >250 °C; IR 1366, 839 cm^{-1} ; ^1H NMR δ (600 MHz, CDCl_3) 8.42 (1 H, d, $J = 8.4$ Hz), 7.85 (1 H, d, $J = 8.4$ Hz), 7.81 (1 H, d, $J = 7.8$ Hz), 7.76 (1 H, d, $J = 8.4$ Hz), 7.618 (1 H, d, $J = 6.0$ Hz), 7.605 (1 H, d, $J = 9$ Hz), 7.52 (1 H, d, $J = 8.4$ Hz), 7.45 (1 H, d, $J = 7.8$ Hz), 7.40 (1 H, d, $J = 8.4$ Hz), 7.32 (1 H, td, $J = 7.5, 1.2$ Hz), 7.12 (1 H, ddd, $J = 7.8, 6.6, 1.2$ Hz), 7.08 (1 H, td, $J = 7.8, 0.8$ Hz), 6.73 (2 H, t, $J = 7.5$ Hz), 6.558 (1 H, t, $J = 8.4$ Hz), 6.546 (1 H, t, $J = 7.8$ Hz), 6.42 (1 H, d, $J = 7.8$ Hz), 6.04 (1 H, d, $J = 8.4$ Hz), 5.76 (1 H, d, $J = 7.8$ Hz), 4.58 (1 H, d, $J = 21.0$ Hz), 4.28 (1 H, d, $J = 21.0$ Hz), 1.97 (9 H, s); ^{13}C NMR δ (150 MHz, CDCl_3) 144.3, 141.0, 140.8, 139.3, 139.2, 138.3, 134.5, 132.7, 132.0, 131.8, 131.5, 131.4, 131.3, 129.5, 129.22, 129.18, 127.7, 127.0, 126.8, 126.6, 126.5, 126.4, 126.0, 125.74, 125.70, 125.67,

125.59, 125.45, 125.3, 125.04, 125.03, 123.82, 123.80, 122.1, 40.1, 38.3, 33.8. MS m/z 498 (M^+), 441, 363. HRMS calcd for $C_{39}H_{30}$ 498.2348, found 498.2351. Recrystallization of **167c** from CH_2Cl_2 /hexanes produced a crystal suitable for X-ray structure analysis.

In addition to **167c**, the formation of a minor amount (ca. 12%) of the intramolecular [2 + 2] cycloaddition adduct **168c** was also detected with characteristic 1H NMR signals (600 MHz, $CDCl_3$) at δ 9.28 (1 H, s), 8.88 (1 H, d, J = 8.4 Hz), 8.12 (2 H, d, J = 8.4 Hz), 7.99 (1 H, d, J = 7.8 Hz), 6.51 (1 H, s, vinylic), and 1.27 (9 H, s) and a ^{13}C NMR signal (150 MHz, $CDCl_3$) at δ 76.3 attributable to the sp^3 carbon on the four-membered ring as observed previously in similar systems.¹⁷

1,5-Dibromo-2,4-bis(phenylethynyl)benzene (188a). The following procedure is representative for the preparation of the 1,5-dibromo-2,4-bis(arylethynyl)benzenes. To a flask containing 0.051 g of dichlorobis(triphenylphosphine)palladium (0.072 mmol) and 0.092 g of CuI (0.048 mmol) was added via cannula a solution of 0.296 g of 1,5-dibromo-2,4-diiodo-

-benzene (**186**, 0.61 mmol) in 20 mL of triethylamine followed by a solution of 0.124 g of phenylacetylene (**187a**, 1.22 mmol) in 10 mL of triethylamine. The resulting mixture was heated at 70 °C. After 1 h, the mixture was allowed to cool to rt and concentrated. A saturated aqueous ammonium chloride solution (20 mL) was then added. After filtration, the filtrate was extracted with hexanes. The combined organic layers were washed with water, dried over Na_2SO_4 , and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 0.220 g (0.50 mmol, 83%) of **188a** as a yellow solid: IR 2247, 1457 cm^{-1} ; 1H NMR δ 7.89 (1 H, s), 7.73 (1 H, s), 7.60–7.56 (4 H, m), 7.41–7.36 (6 H, m); ^{13}C NMR δ 136.5, 135.7, 131.7, 129.0, 128.4, 125.3, 124.8, 122.4, 95.3, 86.6.

1,5-Dibromo-2,4-bis[[4-(1,1,3,3-tetramethylbutyl)phenyl]ethynyl]benzene (188b). The same procedure was repeated as described for **188a** except that 0.080 g of dichlorobis(triphenylphosphine)palladium (0.11 mmol) and 0.014 g of CuI (0.076 mmol) were treated with a solution of 0.926 g of 1,5-dibromo-2,4-diiodobenzene (**186**, 1.87 mmol) in 40 mL of triethylamine and a solution of 0.812 g of 1-ethynyl-4-(1,1,3,3-tetramethylbutyl)

-benzene (**187b**, 3.79 mmol) in 20 mL of triethylamine to afford 0.862 g of **188b** (1.31 mmol, 69%) as a yellow solid: IR 2214, 1508, 1454, 831 cm^{-1} ; ^1H NMR δ 7.88 (1 H, s), 7.70 (1 H, s), 7.49 (4 H, d, $J = 8.7$, Hz), 7.38 (4 H, d, $J = 8.7$, Hz), 1.76 (4 H, s), 1.37 (12 H, s), 0.73 (18 H, s); ^{13}C NMR δ 151.5, 136.3, 135.6, 131.2, 126.3, 124.95, 124.91, 119.1, 95.7, 86.1, 56.7, 38.8, 32.3, 31.8, 31.4.

1,5-Bis(trimethylsilylethynyl)-2,4-bis(phenylethynyl)benzene (189a). The following procedure is representative for the preparation of the tetraacetylenes. A 2.5 M solution of *n*-butyllithium (3.7 mL, 9.36 mmol) in hexanes was added dropwise to a solution of 1.70 g of **188a** (3.90 mmol) in diethyl ether (20 mL) at -78°C . After 2 h of stirring at -78°C , 2.38 g of I_2 (9.36 mmol) in 40 mL of diethyl ether was added via cannula at -78°C and the mixture was then allowed to warm to rt. After 12 h, 40 mL of a 5% aqueous solution of sodium thiosulfate was added, and the organic layer was separated, washed with water, dried with sodium sulfate, and concentrated to furnish crude 1,5-diiodo-2,4-bis(phenylethynyl)benzene as a yellow solid. It was used for the next step without further purification. To a flask containing 0.164 g of dichlorobis(triphenylphosphine)palladium (0.234 mmol) and 0.045 g of CuI (0.234 mmol) were added via cannula a solution of the crude product of 1,5-diiodo-2,4-bis(phenylethynyl)benzene in 30 mL of triethylamine followed by a solution of 0.919 g of (trimethylsilyl)acetylene in 15 mL of triethylamine. The resulting mixture was heated at 45°C . After 3 h, the mixture was allowed to cool to rt and concentrated. A saturated aqueous ammonium chloride solution (20 mL) was then added. After filtration, the filtrate was extracted with diethyl ether. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 1.05 g (2.24 mmol, 57%) of **189a** as a yellow solid: IR 2218, 2254, 1496, 1250 cm^{-1} ; ^1H NMR δ 7.68 (1 H, s), 7.66 (1 H, s), 7.57–7.53 (4 H, m), 7.37–7.35 (6 H, m); ^{13}C NMR δ 136.0, 134.7, 131.8, 128.7, 128.4, 125.7, 124.9, 122.9, 102.3, 100.8, 95.4, 87.3, -0.1 .

1,5-Bis(trimethylsilylethynyl)-2,4-bis[[4-(1,1,3,3-tetramethylbutyl)phenyl]ethynyl]-benzene (189b). The same procedure was repeated as described for **189a** except that 0.689 g of **188b** (1.04 mmol) was treated with a 2.5 M solution of *n*-butyllithium (2.0 mL, 3.13

mmol) in hexanes and a solution of 0.795 g of I₂ (3.13 mmol) in 30 mL of diethyl ether followed by 0.044 g of dichlorobis(triphenylphosphine)palladium (0.063 mmol) and 0.012 g of CuI (0.062 mmol) and then a solution of 0.246 g of (trimethylsilyl)acetylene in 15 mL of triethylamine to afford 0.362 g of **189b** (0.52 mmol, 50%) as a white solid: IR 2151, 1511, 1250 cm⁻¹; ¹H NMR δ 7.65 (2 H, s), 7.46 (4 H, d, *J* = 8.4, Hz), 7.36 (4 H, d, *J* = 8.4, Hz), 1.75 (4 H, s), 1.37 (12 H, s), 0.71 (18 H, s), 0.26 (18 H, s); ¹³C NMR δ 151.2, 136.0, 134.5, 131.3, 126.2, 126.0, 124.6, 119.6, 102.4, 100.6, 95.8, 86.8, 56.8, 38.8, 32.4, 31.8, 31.4, -0.1.

1,5-Diethynyl-2,4-bis(phenylethynyl)benzene (171a). The following procedure is representative for the preparation of the 1,5-diethynyl-2,4-bis(arylethynyl)benzenes. To 0.762 g of **189a** (1.63 mmol) in 40 mL of diethyl ether were added 40 mL of methanol and 25 mL of a 10% aqueous solution of sodium hydroxide. After 30 min stirring at rt, the organic solvents were removed in vacuo. Water (30 mL) and diethyl ether (50 mL) were then added. The organic layer was separated, washed with 2 M solution of aqueous hydrochloric acid and water, dried over sodium sulfate₄, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 0.515 g (1.58 mmol, 93%) of **171a** as a yellow solid: IR 3289, 2212, 1598, 1496 cm⁻¹; ¹H NMR δ 7.72 (1 H, s), 7.69 (1 H, s), 7.59–7.56 (4 H, m), 7.39–7.36 (6 H, m); ¹³C NMR δ 136.4, 134.8, 131.8, 128.9, 128.4, 126.5, 123.9, 122.6, 95.7, 86.8, 83.0, 81.0.

1,5-Diethynyl-2,4-bis[[4-(1,1,3,3-tetramethylbutyl)phenyl]ethynyl]benzene (171b). The same procedure was repeated as described for **171a** except that 0.376 g of **189b** (0.54 mmol) in 20 mL of diethyl ether was treated with 15 mL of methanol and 15 mL of a 10% aqueous solution of sodium hydroxide to afford 0.289 g (0.53 mmol, 97%) of **171b** as a yellow solid: IR 3302, 2211, 1511, 1478 cm⁻¹; ¹H NMR δ 7.69 (1 H, s), 7.67 (1 H, s), 7.48 (4 H, d, *J* = 8.4, Hz), 7.38 (4 H, *J* = 8.4, Hz), 3.44 (2 H, s), 1.76 (4 H, s), 1.40 (12 H, s), 0.73 (18 H, s); ¹³C NMR δ 151.5, 136.4, 134.6, 131.4, 126.7, 126.3, 123.6, 119.4, 96.1, 86.3, 82.8, 81.2, 56.8, 38.8, 32.4, 31.8, 31.4.

Propargylic Alcohol 172a. The same procedure was repeated as described for **165a** except that 0.126 g of 2,2-dimethylpropiophenone (**147**, 0.78 mmol) was treated with the lithium acetylide, prepared from 0.127 g of tetraacetylene **171a** (0.39 mmol) and 0.49 mL of a 2.0 M

solution of lithium diisopropylamide (0.98 mmol) in THF/*n*-heptane, to afford 0.220 g of **172a** (0.34 mmol, 87%) as a white solid: IR 3371, 2212, 1598, 1498 cm^{-1} ; ^1H NMR δ 7.75 (1H, s), 7.74–7.71 (4 H, m), 7.63 (1 H, s), 7.47–7.43 (4 H, m), 7.36–7.31 (6 H, m), 7.28–7.24 (6 H, m), 2.42 (2 H, s), 1.09 (18 H, s); ^{13}C NMR δ 141.7, 135.67, 135.61, 131.8, 128.7, 128.3, 127.7, 127.4, 127.1, 125.5, 124.5, 122.6, 98.3, 95.1, 87.3, 83.6, 79.6, 39.8, 25.6.

Propargylic Alcohol 172b. The same procedure was repeated as described for **165a** except that 0.123 g of 2,2-dimethylpropiophenone (**147**, 0.76 mmol) was treated with the lithium acetylide, prepared from 0.209 g of tetraacetylene **171b** (0.38 mmol) and 0.48 mL of a 2.0 M solution of lithium diisopropylamide (0.96 mmol) in THF/*n*-heptane, to afford 0.156 g of **172b** (0.18 mmol, 47%) as a white solid: IR 3540, 2210, 1483, 833 cm^{-1} ; ^1H NMR δ 7.74 (2 H, d, J = 6.2 Hz), 7.73 (2 H, d, J = 6.2 Hz), 7.72 (1 H, s), 7.62 (1 H, s), 7.39 (4 H, d, J = 8.7 Hz), 7.33 (4 H, d, J = 8.7 Hz), 7.26–7.23 (6 H, m), 2.45 (2 H, s), 1.76 (4 H, s), 1.38 (12 H, s), 1.09 (18 H, s), 0.73 (18 H, s); ^{13}C NMR δ 151.2, 141.8, 135.6, 135.5, 131.3, 127.7, 127.3, 127.1, 126.2, 125.8, 124.2, 119.3, 98.0, 95.4, 86.8, 83.7, 79.6, 56.8, 39.8, 38.7, 32.4, 31.8, 31.4, 25.6.

Propargylic Alcohol 180a. The same procedure was repeated as described for **165a** except that 0.134 g of 2,2-dimethyl-1-(2-naphthalenyl)-1-propanone (**160a**, 0.63 mmol) was treated with the lithium acetylide, prepared from 0.103 g of tetraacetylene **171a** (0.31 mmol) and 0.40 mL of a 2.0 M solution of lithium diisopropylamide (0.80 mmol) in THF/*n*-heptane, to afford 0.176 g of **180a** (0.24 mmol, 74%) as a white solid: IR 3354, 1599, 1498 cm^{-1} ; ^1H NMR δ 8.18 (2 H, s), 7.88 (2 H, dd, J = 8.6, 1.7 Hz), 7.81–7.78 (4 H, m), 7.69 (2 H, d, J = 8.6, Hz), 7.68 (1 H, s), 7.50–7.41 (4 H, m), 7.37–7.34 (5 H, m), 7.29 (1 H, s), 7.17 (4 H, t, J = 7.6 Hz), 2.60 (2 H, s), 1.16 (18 H, s); ^{13}C NMR δ 139.4, 135.7, 135.6, 132.7, 132.4, 131.7, 128.7, 128.4, 128.2, 127.4, 126.5, 126.4, 126.1, 126.0, 125.9, 125.7, 124.5, 122.5, 98.2, 95.2, 87.3, 83.8, 79.7, 40.1, 25.7.

Propargylic Alcohol 180b. The same procedure was repeated as described for **165a** except that 0.051 g of 2,2-dimethyl-1-(2-naphthalenyl)-1-propanone (**160a**, 0.24 mmol) was treated with the lithium acetylide, prepared from 0.066 g of tetraacetylene **171b** (0.12 mmol) and 0.15 mL of a 2.0 M solution of lithium diisopropylamide (0.30 mmol) in THF/*n*-heptane, to

afford 0.054 g of **180b** (0.06 mmol, 46%) as a white solid: IR 3352, 2210, 1511, 1483 cm^{-1} ; ^1H NMR δ 8.21 (2 H, s), 7.91 (2 H, dd, $J = 8.7, 1.7$ Hz), 7.84–7.79 (4 H, m), 7.75 (1 H, s), 7.72 (2 H, d, $J = 8.7$ Hz), 7.67 (1 H, s), 7.50–7.42 (4 H, m), 7.22 (4 H, d, $J = 8.7$ Hz), 7.13 (4 H, d, $J = 8.7$ Hz), 2.62 (2 H, s), 1.71 (4 H, s), 1.32 (12 H, s), 1.16 (18 H, s), 0.71 (18 H, s); ^{13}C NMR δ 151.2, 139.6, 135.7, 135.4, 132.7, 132.5, 131.2, 128.5, 127.4, 126.6, 126.4, 126.3, 126.1, 126.0, 125.9, 124.2, 119.2, 98.0, 95.6, 86.8, 83.9, 79.7, 56.7, 40.1, 38.7, 32.3, 31.8, 31.4, 31.3, 25.7.

Propargylic Alcohol 183. The same procedure was repeated as described for **179a** except that 0.445 g of 2,2-dimethyl-1-(3-phenanthryl)-1-propanone (**160b**, 1.70 mmol) was treated with the lithium acetylide, prepared from 0.277 g of tetraacetylene **171a** (0.85 mmol) and 1.1 mL of a 2.0 M solution of lithium diisopropylamide (2.20 mmol) in THF/*n*-heptane, to afford 0.526 g of **183** (0.62 mmol, 73%) as a white solid: IR 3546, 2210, 1498 cm^{-1} ; ^1H NMR δ 9.06 (2 H, s), 8.77–8.74 (2 H, m), 8.01 (2 H, dd, $J = 8.4, 1.5$ Hz), 7.89–7.86 (2 H, m), 7.81 (1 H, s), 7.75–7.68 (7 H, m), 7.60–7.55 (4 H, m), 7.34 (4 H, d, $J = 7.4$ Hz), 7.24–7.21 (2 H, m), 7.12 (4 H, t, $J = 7.7$ Hz), 2.76 (2 H, s), 1.21 (18 H, s); ^{13}C NMR δ 140.1, 135.76, 135.71, 132.1, 131.7, 131.2, 130.5, 129.2, 128.6, 128.5, 128.1, 127.2, 127.0, 126.6, 126.54, 126.50, 126.4, 125.8, 124.5, 122.7, 122.4, 121.4, 98.4, 95.4, 87.3, 83.9, 80.0, 40.0, 25.7.

Tetraacetylenic Hydrocarbon 173a. The same procedure was repeated as described for **166a** except that 0.190 g of **172a** (0.29 mmol) was treated with 0.102 g of triethylsilane (0.87 mmol) and 0.18 mL of trifluoroacetic acid (0.266 g, 2.33 mmol) in 15 mL methylene chloride to afford 0.155 g of **173a** (0.25 mmol, 85%) as a yellow solid: IR 2221, 1599, 1497 cm^{-1} ; ^1H NMR δ 7.73 (1 H, s), 7.57 (1 H, s), 7.45–7.40 (8 H, m), 7.35–7.31 (6 H, m), 7.25–7.21 (6 H, m), 3.72 (2 H, s), 1.07 (18 H, s); ^{13}C NMR δ 138.9, 135.55, 135.50, 131.7, 129.7, 128.5, 128.2, 127.6, 126.7, 125.7, 124.7, 122.9, 97.6, 94.3, 87.7, 81.7, 50.7, 35.5, 27.8.

Tetraacetylenic Hydrocarbon 173b. The same procedure was repeated as described for **166a** except that 0.111 g of **172b** (0.13 mmol) was treated with 0.044 g of triethylsilane (0.38 mmol) and 0.08 mL of trifluoroacetic acid (1.01 mmol) in 10 mL of methylene chloride to afford 0.092 g of **173b** (0.11 mmol, 85%) as a yellow solid: IR 2214, 1365, 833

cm⁻¹; ¹H NMR δ 7.69 (1 H, s), 7.53 (1 H, s), 7.42 (2 H, d, J = 7.7 Hz), 7.41 (2 H, d, J = 7.7 Hz), 7.35 (4 H, d, J = 8.7 Hz), 7.31 (4 H, d, J = 8.7 Hz), 7.23–7.20 (6 H, m), 3.70 (2 H, s), 1.76 (4 H, s), 1.37 (12 H, s), 1.04 (18 H, s), 0.72 (18 H, s); ¹³C NMR δ 150.9, 139.0, 135.5, 135.4, 131.2, 129.8, 127.6, 126.6, 126.1, 125.4, 124.9, 119.7, 97.3, 94.6, 87.2, 81.8, 56.8, 50.7, 38.7, 35.5, 32.4, 31.8, 31.4, 27.8.

Tetraacetylenic Hydrocarbon 181a. The same procedure was repeated as described for **166a** except that 0.151 g of **180a** (0.20 mmol) was treated with 0.070 g of triethylsilane (0.60 mmol) and 0.13 mL of trifluoroacetic acid (1.61 mmol) in 10 mL of methylene chloride to afford 0.129 g of **181a** (0.18 mmol, 85%) as a yellow solid: IR 2253, 1459 cm⁻¹; ¹H NMR δ 7.85 (2 H, s), 7.83–7.73 (6 H, m), 7.70 (2 H, s), 7.64–7.61 (3 H, m), 7.49–7.42 (4 H, m), 7.34–7.25 (7 H, m), 7.14 (4 H, t, J = 7.7 Hz), 3.92 (2 H, s), 1.14 (18 H, s); ¹³C NMR δ 136.6, 135.6, 135.5, 133.0, 132.4, 131.7, 128.4, 128.13, 128.09, 127.9, 127.5, 127.1, 125.8, 125.6, 125.5, 124.8, 122.8, 97.6, 94.4, 87.7, 81.9, 50.9, 35.9, 27.9.

Tetraacetylenic Hydrocarbon 181b. The same procedure was repeated as described for **166a** except that 0.053 g of **180b** (0.05 mmol) was treated with 0.019 g of triethylsilane (0.16 mmol) and 0.03 mL of trifluoroacetic acid (0.43 mmol) in 5 mL of methylene chloride to afford 0.040 g of **181b** (0.04 mmol, 78%) as a yellow solid: IR 2212, 1510, 1476 cm⁻¹; ¹H NMR δ 7.85 (1 H, s), 7.83–7.75 (6 H, m), 7.71 (2 H, s), 7.64 (2 H, dd, J = 8.4, 1.2 Hz), 7.60 (1 H, s), 7.47–7.44 (4 H, m), 7.15 (4 H, d, J = 8.2 Hz), 7.07 (4 H, d, J = 8.2 Hz), 1.70 (4 H, s), 1.32 (12 H, s), 1.13 (18 H, s), 0.71 (18 H, s); ¹³C NMR δ 150.8, 136.8, 135.4, 135.2, 133.0, 132.5, 131.2, 128.4, 128.1, 127.9, 127.5, 127.2, 126.0, 125.8, 125.6, 125.3, 125.1, 119.5, 97.2, 94.8, 87.2, 82.1, 56.7, 50.9, 38.6, 35.8, 32.3, 31.7, 31.4, 27.9.

Tetraacetylenic Hydrocarbon 184. The same procedure was repeated as described for **166a** except that 0.513 g of **183** (0.60 mmol) was treated with 0.210 g of triethylsilane (1.81 mmol) and 0.39 mL of trifluoroacetic acid (4.82 mmol) in 20 mL of methylene chloride to afford 0.414 g of **184** (0.51 mmol, 84%) as a yellow solid: IR 2224, 1498 cm⁻¹; ¹H NMR δ 8.70–8.67 (4 H, m), 7.89–7.85 (2 H, m), 7.76 (1 H, s), 7.72–7.70 (8 H, m), 7.64 (1 H, s), 7.58–7.54 (4 H, m), 7.30–7.27 (4 H, m), 7.19 (2 H, dd, J = 7.4, 1.5 Hz), 7.08 (4 H, td, J = 7.7, 2.5 Hz), 4.01 (2 H, s), 1.14 (18 H, s); ¹³C NMR δ 137.4, 135.6, 132.1, 131.6, 130.9, 130.2,

129.7, 128.5, 128.4, 128.0, 127.9, 126.6, 126.53, 126.46, 125.6, 124.9, 123.5, 122.73, 122.65, 97.6, 94.4, 87.7, 82.1, 51.3, 35.8, 27.9.

179a. The same procedure was repeated as described for **167a** except that a solution of 0.076 g of **173a** (0.12 mmol) in 10 mL of anhydrous toluene was treated with 0.25 mL of a 1.0 M solution of potassium *t*-butoxide (0.25 mmol) in 2-methyl-2-propanol and 0.18 mL of 2-methyl-2-propanol (1.93 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.059 g of **179a** (0.09 mmol, 78%) as a yellow solid: IR 1367, 761 cm^{-1} ; ^1H NMR δ 8.54 (2 H, d, $J = 8.4$ Hz), 7.63 (1 H, s), 7.41 (2 H, t, $J = 7.2$ Hz), 7.36–7.34 (6 H, m), 7.30 (2 H, d, $J = 8.4$ Hz), 7.20 (2 H, t, $J = 7.2$ Hz), 7.06 (4 H, d, $J = 7.8$ Hz), 6.65 (1 H, s), 4.52 (4 H, s), 1.89 (18 H, s); ^{13}C NMR δ 144.1, 140.3, 138.7, 138.5, 138.1, 137.7, 134.7, 132.5, 131.2, 130.3, 129.3, 127.7, 127.2, 127.0, 123.9, 123.1, 120.1, 119.4, 40.0, 38.8, 34.3; MS m/z 618 (M^+), 561; HRMS calcd for $\text{C}_{48}\text{H}_{42}$ 618.3281, found 618.3295.

179b. The same procedure was repeated as described for **167a** except that a solution of 0.024 g of **173b** (0.03 mmol) in 10 mL of anhydrous *p*-xylene was treated with 0.03 mL of a 1.0 M solution of potassium *t*-butoxide (0.03 mmol) in 2-methyl-2-propanol and 0.02 mL of 2-methyl-2-propanol (0.16 mmol) and then the resulting mixture was heated under reflux for 5 h to afford 0.017 g of **179b** (0.02 mmol, 73%) as a yellow solid: IR 1466, 1365, 908 cm^{-1} ; ^1H NMR δ 8.53 (2 H, d, $J = 9.0$ Hz), 7.59 (1 H, s), 7.55 (2 H, d, $J = 7.8$ Hz, at -25°C), 7.40 (2 H, dd, $J = 8.4, 1.2$ Hz), 7.34 (2 H, td, $J = 7.6, 1.2$ Hz), 7.21 (2 H, d, $J = 7.8$ Hz, at -25°C), 7.17 (2 H, t, $J = 7.6$ Hz), 7.08 (2 H, d, $J = 7.8$ Hz, at -25°C), 6.85 (1 H, s), 6.70 (2 H, d, $J = 7.8$ Hz, at -25°C), 4.58 (2 H, d, $J = 21.6$ Hz), 4.44 (2 H, d, $J = 21.6$ Hz), 1.88 (18 H, s), AB pattern for CH_2 , 1.72 (6 H, s), 1.45 (6 H, s), 0.77 (18 H, s); MS m/z 842 (M^+); HRMS calcd for $\text{C}_{64}\text{H}_{74}$ 842.5785, found 842.5751.

182a. The same procedure was repeated as described for **167a** except that a solution of 0.209 g of **181a** (0.29 mmol) in 10 mL of anhydrous toluene was treated with 0.61 mL of a 1.0 M solution of potassium *t*-butoxide (0.61 mmol) in 2-methyl-2-propanol and 0.43 mL of 2-methyl-2-propanol (4.64 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.150 g of **182a** (0.21 mmol, 72%) as a yellow solid: IR 1459, 822, 699 cm^{-1} ; ^1H NMR δ 8.24 (2 H, d, $J = 9.6$ Hz), 7.69 (2 H, d, $J = 7.8$ Hz), 7.68 (1 H, s), 7.47 (2 H, d, $J =$

9.0 Hz), 7.21 (2 H, t, $J = 7.8$ Hz), 7.17 (4 H, t, $J = 8.4$ Hz), 6.99 (4 H, d, $J = 8.4$ Hz), 6.74 (2 H, t, $J = 8.4$ Hz), 6.58 (2 H, d, $J = 7.8$ Hz), 6.44 (1 H, s), 4.47 (4 H, s), 1.83 (18 H, s); ^{13}C NMR δ 143.6, 140.7, 140.4, 139.2, 139.0, 138.7, 132.9, 132.4, 131.3, 131.0, 130.7, 130.3, 129.2, 127.3, 126.4, 125.7, 125.1, 122.8, 39.9, 38.5, 34.0; MS m/z 718 (M^+), 551; HRMS calcd for $\text{C}_{56}\text{H}_{46}$ 718.3594, found 718.3594.

182b. The same procedure was repeated as described for **167a** except that a solution of 0.024 g of **181b** (0.03 mmol) in 10 mL of anhydrous *p*-xylene was treated with 0.03 mL of a 1.0 M solution of potassium *t*-butoxide (0.03 mmol) in 2-methyl-2-propanol and 0.02 mL of 2-methyl-2-propanol (0.16 mmol) and then the resulting mixture was heated under reflux for 5 h to afford 0.017 g of **182b** (0.02 mmol, 73%) as a yellow solid: IR 1459, 699 cm^{-1} ; ^1H NMR δ 8.25 (2 H, d, $J = 9.6$ Hz), 7.69 (2 H, d, $J = 7.8$ Hz), 7.64 (1 H, s), 7.48 (2 H, d, $J = 9.6$ Hz), 7.29 (2 H, d, $J = 8.4$ Hz), 6.93 (2 H, q, $J = 8.4$ Hz), 6.72 (2 H, qd, $J = 9.6, 1.2$ Hz), 6.64 (1 H, s), 4.45 (2 H, d, $J = 21.6$ Hz), 4.42 (2 H, d, $J = 21.6$ Hz), AB pattern for CH_2 , 1.83 (18 H, s), 1.50 (6 H, s), 1.28 (6 H, s), 0.85 (18 H, s); MS m/z 942 (M^+); HRMS calcd for $\text{C}_{72}\text{H}_{78}$ 942.6098, found 942.6150.

185. The same procedure was repeated as described for **167a** except that a solution of 0.155 g of **184** (0.19 mmol) in 10 mL of anhydrous toluene was treated with 0.40 mL of a 1.0 M solution of potassium *t*-butoxide (0.40 mmol) in 2-methyl-2-propanol and 0.15 mL of 2-methyl-2-propanol (3.03 mmol) and then the resulting mixture was heated under reflux for 3.5 h to afford 0.109 g of **185** (0.13 mmol, 70%) as a yellow solid: IR 1365, 829 cm^{-1} ; ^1H NMR δ 8.26 (2 H, d, $J = 9.0$ Hz), 7.72 (2 H, d, $J = 7.2$ Hz, -20°C), 7.71 (1 H, s), 7.68 (2 H, d, $J = 7.7$ Hz), 7.67 (2 H, $J = 9.0$ Hz), 7.48 (2 H, d, $J = 7.2$ Hz), 7.47 (2 H, d, $J = 9.0$ Hz), 7.18 (2 H, d, $J = 8.4$ Hz), 6.94 (2 H, td, $J = 7.2, 1.2$ Hz), 6.60 (2 H, t, $J = 7.2$ Hz, -20°C), 6.57 (2 H, td, $J = 7.8, 1.2$ Hz), 6.40 (1 H, s), 6.35 (2 H, t, $J = 7.8$ Hz), 6.13 (2 H, t, $J = 7.2$ Hz, -20°C), 5.71 (2 H, d, $J = 7.2$ Hz, -20°C), 4.48 (4 H, q, $J = 21.0$ Hz), 1.84 (18 H, s); ^{13}C NMR δ 143.7, 139.3, 138.98, 138.89, 138.4, 138.1, 133.4, 132.8, 130.5, 130.3, 130.20, 130.17, 130.1, 127.5, 126.9, 125.6, 125.3, 124.6, 124.0, 123.8, 121.8, 120.8, 119.4, 39.6, 38.2, 33.6; MS m/z 818 (M^+), 761, 650; HRMS calcd for $\text{C}_{64}\text{H}_{50}$ 818.3907, found 818.3916.

Aryl Ketone 196a. The same procedure was repeated as described for **160b** except that

0.999 g (4.62 mmol) of 2,7-naphthalenedicarboxylic acid (**195a**) was heated with 40 mL of thionyl chloride under reflux for 12 h to furnish the crude 2,7-naphthalenedicarbonyl chloride. The acid chloride was treated with *t*-butylcopper, prepared from 2.09 g of CuBr·SMe₂ (10.1 mmol) and 6.0 mL of a 1.7 M solution of *t*-butyllithium (10.2 mmol) in pentane, to afford 0.945 g of **196a** (3.19 mmol, 69%) as a white solid: IR 1671, 1477, 851 cm⁻¹; ¹H NMR δ 8.27 (2 H, s), 7.88 (2 H, d, *J* = 8.7 Hz), 7.85 (2 H, d, *J* = 8.7 Hz); ¹³C NMR δ 208.7, 136.5, 135.0, 131.3, 129.4, 127.6, 126.6, 44.4, 28.1; MS *m/z* 212 (M⁺), 155, 127.

Aryl Ketone 196b. The same procedure was repeated as described for **160b** except that 0.149 g (0.56 mmol) of 3,6-phenanthrenedicarboxylic acid (**195b**) was heated with 17 mL of thionyl chloride under reflux for 12 h to furnish the crude 3,6-phenanthrenedicarbonyl chloride. The acid chloride was treated with *t*-butylcopper, prepared from 0.254 g of CuBr·SMe₂ (1.23 mmol) and 0.73 mL of a 1.7 M solution of *t*-butyllithium (1.23 mmol) in pentane, to afford 0.083 g of **196b** (0.24 mmol, 43%) as an orange solid: IR 1669, 1770, 852 cm⁻¹; ¹H NMR δ 9.05 (2 H, s), 7.95 (2 H, dd, *J* = 8.4, 1.5 Hz), 7.88 (2 H, d, *J* = 8.2 Hz), 7.79 (2 H, s), 1.47 (18 H, s); ¹³C NMR δ 208.8, 136.6, 133.4, 129.7, 128.3, 128.0, 125.8, 122.9, 44.3, 28.2.

Propargylic Alcohol 197a. The same procedure was repeated as described for **165a** except that 0.498 g of **196a** (1.68 mmol) was treated with lithium acetylide **46** prepared from 0.748 g of 1-ethynyl-2-(phenylethynyl)benzene (3.70 mmol) and 1.5 mL of a 2.5 M solution of *n*-butyllithium (3.70 mmol) in hexanes, to afford 1.12 g of **197a** (1.58 mmol, 95% yield, 1:1 mixture of diastereomers) as a white solid: Diastereomer **1**: IR 3545, 1477, 848 cm⁻¹; ¹H NMR δ 8.28 (2 H, s), 8.00 (2 H, d, *J* = 8.7 Hz), 7.70 (2 H, d, *J* = 8.7 Hz), 7.66–7.59 (4 H, m), 7.43–7.15 (14 H, m), 2.68 (2H, s), 1.24 (18 H, s); ¹³C NMR δ 139.8, 132.2, 132.1, 131.8, 131.6, 128.3, 128.1, 127.9, 126.9, 126.5, 125.8, 125.0, 122.8, 96.3, 93.3, 88.3, 84.7, 79.6, 39.9, 25.6. Diastereomer **2**: IR 3568, 2250, 1477, 848 cm⁻¹; ¹H NMR δ 8.21 (2 H, s), 7.89 (2 H, dd, *J* = 8.9, 1.7 Hz), 7.65 (2 H, d, *J* = 8.7 Hz), 7.59 (1H, d, *J* = 2.0, Hz), 7.56 (2 H, m), 7.53 (1H, d, *J* = 2.0, Hz), 7.37–7.11 (14 H, m), 2.50 (2H, s), 1.11 (18 H, s); ¹³C NMR δ 139.9, 132.2, 132.1, 131.9, 131.6, 128.2, 128.1, 127.9, 127.1, 126.4, 125.9, 125.1, 122.9, 96.3, 93.3, 88.2, 84.7, 79.6, 40.0, 25.7.

Propargylic Alcohol 197b. The same procedure was repeated as described for **165a** except that 0.102 g of **196b** (0.33 mmol) was treated with lithium acetylide **46** prepared from 0.079 g of 1-ethynyl-2-(phenylethynyl)benzene (0.39 mmol) and 0.16 mL of a 2.5 M solution of *n*-butyllithium in hexanes, to afford 1.12 g of **197a** (1.58 mmol, 95% yield, 1:1 mixture of diastereomers) as a white solid: Diastereomer **1**: IR 3540, 3452, 2249, 2215, 1494, 754 cm⁻¹; ¹H NMR δ 9.13 (2 H, d, *J* = 1 Hz), 8.02 (2 H, d, *J* = 8.4 Hz), 7.71 (2 H, d, *J* = 9.4 Hz), 7.70 (2 H, s), 7.59–7.55 (4 H, m), 7.41–7.38 (4 H, m), 7.33–7.30 (4 H, m), 7.23–7.16 (4 H, m), 2.72 (2H, s), 1.13 (18 H, s); ¹³C NMR δ 140.4, 132.3, 132.1, 131.6, 131.3, 129.4, 128.3, 128.1, 128.0, 127.1, 126.7, 126.5, 125.8, 125.0, 122.9, 121.4, 96.3, 93.2, 88.3, 84.9, 79.9, 39.9, 25.6. Diastereomer **2**: IR 3548, 2248, 2216, 1494, 754; ¹H NMR δ 9.14 (2 H, s), 8.06 (2 H, dd, *J* = 8.1, 1.2 Hz), 7.71 (2 H, d, *J* = 8.2 Hz), 7.70 (2H, s), 7.62–7.58 (4 H, m), 7.43–7.40 (4H, m), 7.35–7.30 (4 H, m), 7.29–7.16 (2 H, m), 2.68 (2H, s), 1.18 (18 H, s); ¹³C NMR δ 140.5, 132.3, 132.1, 131.6, 131.3, 129.4, 128.3, 128.1, 127.9, 127.1, 127.0, 126.5, 125.8, 125.0, 122.9, 121.2, 96.3, 93.2, 88.3, 85.0, 79.8, 39.9, 25.6.

Benzannulated Eneidyne 198a. The same procedure was repeated as described for **166a** except that 0.649 g of **197a** (0.93 mmol) was treated with 0.323 g of triethylsilane (2.78 mmol) and 0.58 mL of trifluoroacetic acid (0.845 g, 7.41 mmol) in 10 mL methylene chloride to afford 0.496 g of **198a** (0.74 mmol, 80% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2216, 1494, 845 cm⁻¹; ¹H NMR δ 7.77 (2 H, s), 7.74 (2 H, s), 7.66–7.47 (16 H, m), 7.33–7.18 (20 H, m), 7.15–7.09 (8H, m), 3.86 (2 H, s), 3.82 (2 H, s), 1.11 (18 H, s), 1.10 (18 H, s); ¹³C NMR δ 136.92, 136.87, 132.65, 132.57, 132.1, 132.0, 131.6, 131.4, 128.4, 128.15, 128.12, 128.07, 127.91, 127.86, 127.4, 126.7, 126.6, 126.3, 125.67, 125.62, 123.16, 123.12, 95.6, 92.9, 88.6, 88.5, 82.6, 82.58, 50.8, 50.7, 35.7, 27.9.

Benzannulated Eneidyne 198b. The same procedure was repeated as described for **166a** except that 0.140 g of **197b** (0.19 mmol) was treated with 0.066 g of triethylsilane (0.57 mmol) and 0.173 g of triethylsilane (1.52 mmol) in 10 mL methylene chloride to afford 0.111 g of **198b** (0.15 mmol, 83% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2217, 1493, 753 cm⁻¹; ¹H NMR δ 8.80 (2 H, s), 8.67 (2 H, s), 7.85–7.74 (8 H, m), 7.70 (4 H, s), 7.63–7.54 (10 H, m), 7.41 (10 H, m), 7.33–7.21 (12 H, m), 7.19–7.12 (8 H, m), 4.01 (2 H,

s), 4.01 (2 H, s), 1.19 (18 H, s), 1.17 (18 H, s); ^{13}C NMR δ 137.6, 137.5, 132.13, 132.09, 132.03, 131.6, 130.95, 130.91, 129.60, 129.56, 128.33, 128.30, 128.2, 128.1, 128.0, 127.88, 127.86, 127.7, 127.4, 126.2, 125.62, 125.57, 123.6, 123.5, 123.11, 123.06, 95.7, 95.6, 92.9, 92.8, 88.7, 88.5, 82.81, 82.80, 51.1, 50.9, 35.74, 35.69, 27.9.

1,12-Diphenylbenzo[*c*]phenanthrene 204a. The same procedure was repeated as described for **167a** except that a solution of 0.101 g of **198a** (0.15 mmol) in 10 mL of anhydrous toluene was treated with 0.32 mL of a 1.0 M solution of potassium *t*-butoxide (0.32 mmol) in 2-methyl-2-propanol and 0.23 mL of 2-methyl-2-propanol (2.41 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.010 g of **204a** (0.01 mmol, 10%) as a yellow solid: IR 1600, 842 cm^{-1} ; ^1H NMR δ 8.09 (2 H, d, $J = 8.7$ Hz), 7.91–7.86 (2 H, m), 7.41 (2 H, d, $J = 7.4$ Hz), 7.40 (2 H, d, $J = 8.6$ Hz), 7.08 (2H, t, $J = 7.4$ Hz), 6.98–6.95 (4H, m), 6.79 (2H, t, $J = 7.2$ Hz), 6.76 (2H, t, $J = 7.2$ Hz), 6.30 (2 H, d, $J = 8.2$ Hz), 5.70 (2 H, d, $J = 7.7$ Hz), 4.26 (2 H, d, $J = 21.0$ Hz), 4.10 (2 H, d, $J = 21.0$ Hz), 1.74 (18 H, s); ^{13}C NMR δ 144.4, 140.8, 140.3, 138.5, 137.9, 137.0, 134.9, 134.4, 131.5, 131.4, 130.8, 127.9, 126.5, 126.1, 125.9, 125.8, 125.3, 123.8, 123.0, 120.0, 39.6, 37.9, 33.2; m/z 668 (M^+), 551. HRMS calcd for $\text{C}_{52}\text{H}_{44}$ 668.3438, found 668.3433. Recrystallization of **204a** from CH_2Cl_2 /hexanes produced a crystal suitable for X-ray structure analysis.

1,14-Diphenyldibenzo[*c,g*]phenanthrene 204b. The same procedure was repeated as described for **167a** except that a solution of 0.029 g of **198b** (0.040 mmol) in 10 mL of anhydrous toluene was treated with 0.09 mL of a 1.0 M solution of potassium *t*-butoxide (0.09 mmol) in 2-methyl-2-propanol and 0.07 mL of 2-methyl-2-propanol (0.64 mmol) and then the resulting mixture was heated under reflux for 3 h to afford 0.014 g of **204b** (0.019 mmol, 47%) as a yellow solid: IR 1465, 731 cm^{-1} ; ^1H NMR δ 8.05 (2 H, d, $J = 9.2$ Hz), 7.82 (2 H, s), 7.40 (2 H, d, $J = 8.9$ Hz), 7.36 (2 H, d, $J = 7.4$ Hz), 6.99 (4 H, m), 6.81 (4 H, m), 6.64 (2 H, t, $J = 7.4$ Hz), 6.20 (4 H, d, $J = 6.9$ Hz, at 85 $^\circ\text{C}$), 5.19 (2 H, d, $J = 8.2$ Hz), 4.45 (2 H, d, $J = 20.0$ Hz), 4.22 (2 H, d, $J = 20.0$ Hz), 1.91 (18 H, s); m/z 718 (M^+), 661. HRMS calcd for $\text{C}_{56}\text{H}_{46}$ 718.3594, found 718.3561. Recrystallization of **204b** from CH_2Cl_2 /hexanes produced a crystal suitable for X-ray structure analysis.

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167c

179a

179b: Ar = 4-(tert-octyl)phenyl

197b: Diastereomer 1