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**Synthesis of Bowl-shaped Polycyclic Aromatic Compounds and
Homo-bi-dentate 4,5-Diarylphenanthrene Ligands**

Daehwan Kim

**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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**Morgantown, West Virginia
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**Keyword: Schmitt cyclization, enyne–allenes, bowl-shaped polycyclic aromatic
hydrocarbons, C₂-symmetrical homo-bi-dentate ligands**

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ABSTRACT

Synthesis of Bowl-shaped Polycyclic Aromatic Compounds and Homo-bi-dentate 4,5-Diarylphenanthrene Ligands

Daehwan Kim

A new synthetic pathway leading to buckybowls was developed via cascade cyclization reactions of benzannulated enyne-allenes. The convergent assembly of the benzannulated enediynyl propargylic alcohols and the efficient cascade cyclizations of the resulting enyne-allenes leading to polycyclic aromatic dibromides for subsequent palladium-catalyzed intramolecular arylation reactions are the key features of this synthetic pathway. Three new buckybowls with their structures confirmed by X-ray structure analyses were thus synthesized.

Polycyclic aromatic hydrocarbon bearing ten fused ring system was successfully synthesized by using diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene prepared from the thionyl chloride-induced cascade cyclization reactions of the corresponding enediynyl propargylic alcohols. Direct tandem Knoevenagel condensation and hydrogenation efficiently furnished the diketones as precursors of propargylic diols for cascade cyclizations. Only five steps were involved in producing aromatic dibromides or diiodides as precursors for the buckybowls containing more than 44 carbons of C₆₀.

The synthetic pathway to the twisted polycyclic aromatic hydrocarbons bearing 4,5-diphenylphenanthrene moiety via the Schmitt reaction was successfully adopted for the synthesis of C₂-symmetrical homo-bi-dentate ligands. Demethylation followed by derivatization with camphorsulfonyl group could convert enantiomers of 4,5-di(4-methoxyphenyl)phenanthrene derivatives to the corresponding diastereomers, which are separable on silica column chromatography. Similarly, 4,5-di-(4-aminophenyl)phenanthrene was likewise synthesized.

Dedicated to
My parents and my daughter, Sarah D. Kim

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Part I

Cyclization Reactions of Enyne–Allenenes

1. Introduction

A touring scientist collected a rock at Waco, Texas and brought it to his laboratory to find fungi or bacteria living inside in 1987. He discovered a compound inside this rock, called calicheamicin (**1**) which is normally derived from organism, *Micromonospora echinospora* ssp *calichensis* and was proved to be over 1000 times more potent than adriamycin, an old chemotherapy drug.¹ However, it is too toxic to be used directly as a medicine, although calicheamicin is extremely active against tumor and cancer cells, which can bind to DNA, cleave it into pieces, and finally cause cell death.

1.1. Structure of enediynes

The molecular architecture of calicheamicin (**1**) had aroused a great deal of interest due to its unique enediyne structure and intricate modes of action as well as exceptional antitumor and antibiotic activity.²

Figure 1. Structure of calicheamicin.

Their enediyne structures, characterized by two acetylenic groups conjugated to a double bond, fall into two categories: nine- or ten-membered ring core structure.³

1.1.1. Eneidyne with a 9-membered ring core structure

Actually, the first elucidated structure of enediyne came from neocarzinostatin(NCS) chromophore which contains a nine-membered ring core, bicycle[7.3.0] structure.⁴ There had been a rapid escalation in the discovery of biologically active natural products containing enediyne: neocarzinostatin(NCS),⁵⁻⁷ C-1027,⁸ maduropeptin,⁹ N1999A2,¹⁰ actinoxanthin,¹¹ largomycin,¹² auromomycin,¹³ and sporamycin.¹⁴

2. neocarzinostatin(NCS), 3. kedarcidin, 4. C1027, 5. maduropeptin, 6. N1999A2

Figure 2. Structures of enediynes containing a nine-membered ring core.

The relatively unstable nine-membered enediynes appear to be the most potent anticancer agents ever discovered, which is caused by the cyclization of the enediyne group via highly reactive 1,4-biradical intermediate triggering single- and double-stranded DNA lesion.¹⁵ The key transformation of the natural enediyne system into a diradical benzenoid species is based on the Bergman cycloaromatization, reported in the early 70th by Masamune and Bergman.¹⁶ Although the classical Bergman thermal cycloaromatization occurs only above 200 °C, the steric strain due to the inclusion of enediyne in a nine-membered ring may

decrease the activation energy to allow cyclization to occur at 37 °C.¹⁷ The proposed mechanism shown in Scheme 1 is that stereospecific nucleophilic attack at C12 of the NCS chromophore **7** triggers the rearrangement of the ring skeleton, followed by the ring opening of the epoxide and the formation of cumulene **8**, a very strained intermediate due to its rigidity, which then generates biradical **9** through rapid cycloaromatization.¹⁸

Scheme 1. Mechanism of action of neocarzinostatin chromophore containing a nine-membered ring core.¹⁹

1.1.2. Endiynes with a ten-membered ring core structure

Esperamicin containing an unprecedented ten-membered enediyne, was first discovered in 1985, which received much attention from a number of researchers, largely in the hope of finding new class of antitumor antibiotics. Most of naturally occurring enediynes contain a more stable ten-membered ring and in rare cases contain a nine-membered ring.²⁰ Esperamicin **11**, namenamicin **10**, and dynemicin **13** were previously reported and the most

recent family member was shishijimicin **12** reported in 2003.²¹ Although the mode of action of the ten-membered core is similar to that of the nine-membered enediyne, a relative unspecific mode of action causes side effects associated with its toxicity.²¹

10. Namenamicin, **11.** esperamicin, **12.** shishijimicin, **13.** dynemicin

Figure 3. Structures of enediynes containing a ten-membered ring core.

The proposed mechanism suggested that nucleophilic attack on the allyl trisulfide group of **14** cleaves the S-S bond and forms a new S-S bond, a thiolate **15**, followed by cycloaromatization and biradical formation.²²

Scheme 2. Mechanism of action of shishijimicin containing a ten-membered core.³

1.2. Research orientation to enediynes

Initial main focuses on enediynes were total synthesis of the naturally occurring endiynes and simple model compounds bearing an endiynes structure, with similar antitumor and antibiotic activities. The relation between biradical cycloaromatization protocols and radical cyclizations has also been extensively studied.²³ Organic chemists have explored the thermal cycloaromatization of enyne-allenes by C^2 - C^7 (Myers-Saito) cyclization or C^2 - C^6 (Schmittel) cyclization to furnish polycyclic aromatic systems. In addition, theoretical organic chemists have studied extensively the energetics of many modes of cyclization to demonstrate details on newly formed rings.²⁴

1.3. Bergman cyclization of the enediyne system

Generally, Sondheimer *et al.* is regarded as the first group to synthesize the cyclization product related to enediyne chemistry in 1966. The proposed mechanism of this cyclization is that the 11-membered ring of the bicyclic hydrocarbon **18** could generate a fused ring system by transferring hydride ion from methoxide under reflux in dimethyl sulfoxide and with potassium hydroxide in methanol.²⁵

Scheme 3. Cyclization reported by Sondheimer.

A similar reaction was attempted by Masamune in 1971 who accidentally obtained anthracene (**22**) from diacetylene compound **20**, although Bergman firstly reported his detailed mechanism on the cycloaromatization of enediynes. Masamune supposed the intermediate

might be compound **21**, but did not provide any proper mechanism regarding the unexpected cyclization.²⁶

Scheme 4. Observed cyclization by Masamune.

In 1972, Bergman formulated the cycloaromatization of enediynes by heating deuterium labeled *cis*-3-hexene-1,5-diyne (**23a**) at 200 °C. After 5 min, NMR showed deuteriums evenly distributed among acetylenic and vinyl positions (**23a** and **23c**). He inferred that the free radicals of 1,4-dehydrobenzene **23b** are the only intermediate capable of removing hydrogens from hydrocarbon.

Scheme 5. Thermal rearrangements of *cis*-3-hexene-1,5-diyne via 1,4-dehydrobenzene.

However, this labeling study with NMR did not provide any information regarding an intermediate or transition state. In order to confirm his inference, he pyrolyzed *cis*-3-hexene-1,5-diyne (**24**) in carbon tetrachloride, which generated *p*-dichlorobenzene. The observed products through this reaction were benzene, *p*-dichlorobenzene, and benzyl alcohol depending on the solvents used. This pioneering work of Bergman on enediyne cyclization had not gain much attention until the structures of calicheamicin and esperamicin, two potent antitumor antibiotics, were elucidated. Bergman then reported that their enediyne system could trigger biradical aromatization responsible for DNA cleavage. These two novel substances containing an enediyne structure prompted organic chemists to synthesize unique

unsaturated structures which could be cyclized.²⁷

Scheme 6. Confirmation of biradical intermediate.

1.4. Various cyclizations: Moore Cyclization, Myers Cyclization, Schmittel

Cyclization, and Myers-Saito Cyclization

Figure 4. Moore²⁹: Enyne-Ketenes, Bergman³⁰: Ene-Diynes, Myers³¹: Enyne-Cumulenes, Myers-Saito³²: Enyne-Allenenes, and Schmittel³³: Enyne-Allenenes.²⁸

1.4.1. Moore Cyclization: Enyne-Ketenes

The Moore cyclization of enyne-ketenes is also a type of biradical cyclization reactions such as Bergman reaction of enediynes. Before the remarkable discovery of Myers-Saito cyclization, Moore had already found a similar cyclization mode from enyne-ketenes. However, the Moore cyclization did not receive as much attention as the Bergman or Myers-Saito cyclization because it did not show antitumor antibiotic activities as those of enediynes and enyne-allenes.²⁸ Moore *et al.* reported the C²-C⁷ and the C²-C⁶ cyclizations of enyne-ketenes giving rise to quinones **29**, **30** or cyclopentenenedione **32**, and their derivatives. 4-Alkynylcyclobutenones **26** and **27** generated the ketene **28** via ring opening under thermolysis, which then underwent ring closure with an intramolecular transfer of the substituent E (proton, trimethylsilyl, or allyl) from oxygen to carbon.³⁴ Surprisingly, he suggested that the phenyl group of the alkynyl moiety might redirect the cyclization reaction toward the formation of a 5-membered ring, since the phenyl group or the alkynyl group might be able to stabilize the adjacent radical ion on C7.

Scheme 7. Moore cyclization; C²-C⁷ and C²-C⁶ cyclizations of enyne-ketenes.

1.4.2. Myers-Saito (C²-C⁷) Cyclization: Enyne-Allenes

In 1989, Myers and Saito groups reported independently that enyne-allene system containing 1,2,4-heptatrien-6-yne (**33**) underwent thermal cyclization reaction via biradical formation.

Scheme 8. Myers-Saito Cyclization: C^2-C^7 cyclization of enyne-allene.

At that time, mechanistic studies of the antitumor agents, neocarzinostatin, calicheamicin, and esperamicin were ongoing to identify essential features triggering their antibiotic activities. It was a generally accepted idea that the cyclic enediyne system abstracts hydrogen atoms from the DNA backbone via reactive benzenoid biradicals. This proposal prompted many groups to participate in the design of a simplified enediyne system to mimic the mode of action of the antitumor agents.³⁵ Myers group provided supporting evidence that the cyclization reaction occurs via biradical intermediate by using various solvent systems as summarized in Scheme 9.³⁶ Saito *et al.* and Myers *et al.* reported that the enyne-allene system could produce a biradical at lower temperature than that of the Bergman cyclization reaction. The Arrhenius activation barrier of the enyne-allene system was measured to be 21-23 kcal/mol lower than that of the enediyne system.³⁷

Scheme 9. Evidence of cyclization reaction via biradical intermediate.

Saito group postulated the distance between C1 and C6 for enyne-allene cyclization is close enough to trigger spontaneous cyclization at lower temperature than that of the Bergman cyclization which occurs at more than 130 °C.^{35a} They designed a simple enyne-allenyl phosphonate **36** to demonstrate the cyclization generates a biradical intermediate capable of DNA cleavage activity at ambient temperature.

Scheme 10. Saito group's approach for cyclization of enyne-allene.

1.4.3. Schmittel (C²-C⁶) Cyclization: Enyne-Allenenes

In 1995, Schmittel and co-workers discovered a complete switch from Myers-Saito (C²-C⁷) cyclization to Schmittel (C²-C⁶) cyclization, which was a remarkable discovery further extending the synthetic potentials of thermal enyne-allene reactions.³⁸ The Schmittel group unexpectedly discovered the novel C²-C⁶ cyclization by replacing the terminal hydrogen atom with an aryl group (**40**, R¹ = *p*-tol), which generated **41b** and **42b** in the presence of 1,4-cyclohexadiene. They suggested that the aryl group could stabilize the formation of an adjacent vinyl radical in **41a** and **41b**, leading to either a formal Diels-Alder adduct or an ene product.

Scheme 11. Mechanism of switch from $C^2\text{-}C^7$ cyclization to $C^2\text{-}C^6$ cyclization.

1.4.4. Various effects on Myers-Saito ($C^2\text{-}C^7$) and Schmittel ($C^2\text{-}C^6$) cyclization

Since Gillman *et al.*³⁹ and Rodriguez *et al.*⁴⁰ discovered a similar new $C^2\text{-}C^6$ reaction by placing the sterically bulky TMS group at acetylenic terminus, various effects for switching from Myers-Saito to Schmittel cyclization have been elucidated. This switch is attributed to substituent effects of aryl substituents on the acetylene terminus, ring strain caused by ring size, benzannulation and oxy-anion substitution, and steric effects exerted by bulky substituents especially at the alkyne terminus or on the allene.⁴¹

The ring strain generated by cyclopentene ring resulted in the switch from the $C^2\text{-}C^6$ cyclization to $C^2\text{-}C^7$ cyclization despite the presence of a phenyl substituent (**44**) at the alkyne terminus.⁴²

Scheme 12. Thermolysis of enyne-allenes with a central five-membered ring.

Surprisingly, this phenomenon had already been observed in our group without mentioning the ring strain effect generated by the five-membered ring.⁴³

Scheme 13. C²-C⁷ cyclization generated by ring strain.

Scheme 14 below shows that a bulky group (**50**) at the alkyne terminus destabilized the C²-C⁷ transition state due to steric congestion between the bulky group and newly formed benzene ring. Simply changing H to the methyl group at the inner position of allene (**52a** and **52b**) destabilizes the resulting enyne-allene. The enyne-allene product **53b** is not stable at room temperature, undergoing thermal C²-C⁶ cyclization directly to produce **54**.⁴³

Scheme 14. C²-C⁷ and C²-C⁶ cyclization affected by substituents.

Brunette and Lipton investigated the electronic role of the oxyanion substituent. The substitution led to rapid cyclization at ambient temperature or even subambient temperatures.⁴⁴ The acceleration of the C²-C⁶ cyclization by oxyanion was presumed to arise from the stabilization of biradicaloid transition state which has the same origin as the well known

acceleration of the Oxy-Cope rearrangement.⁴⁵

Scheme 15. Acceleration of cyclization by oxyanion substituent.

1.4.5. Heteroaromatic compounds via C²-C⁶ cyclization

Interestingly, our group and Schmittel's group reported the biradical forming reactions involving other heteroatoms in 1998, which was an unexplored area at that time, by substituting a carbon with a nitrogen or an oxygen on the enyne-allene frameworks.⁴⁶ Valuable heteroaromatic compounds which are potential DNA-intercalating agents have been synthesized in our group by converting carbons (A, B, C, D, and E) to nitrogens or by placing a variety of heteroatom-containing substituents at the allenic terminus. The first heterocyclic system was synthesized from enyne-ketenimines (B=nitrogen, C=carbon),⁴⁶ enyne-carbodiimides (B=nitrogen, C=nitrogen),⁴⁷ and enyne-isocyanates (B=oxygen, C=nitrogen)⁴⁸ via biradical intermediates **60**. The substitution of the alkynyl group with the isoelectronic nitrile group (D=nitrogen, E=carbon)⁴⁹ or the nitrile group (D=carbon, E=nitrogen)⁵⁰ produced the corresponding 11*H* indeno[1,2-*b*]quinoline-related compounds and substituted ABCD ring cores of the camptothecin family of alkaloids, respectively.

Scheme 16. Heteroaromatic compounds via C²-C⁶ cyclization.

1.4.6. The concerted or the biradical mechanism of the enyne-allene reaction

Scheme 17. The concerted or the biradical mechanism of the enyne-allene reaction.

Although the postulated formation of biradical intermediate in the naturally occurring endiynes and enyne-cumulene antitumor antibiotics had been proposed, examples in many literatures could be reconciled with concerted ene or Diels-Alder reaction. Most of the mechanistic and theoretical evidences are in favor of the stepwise biradical intermediate of the C^2 - C^6 thermal cycloaromatization, supporting a fulvenyl biradical mechanism.⁵¹ Most convincing and direct result for the postulated stepwise biradical intermediate of C^2 - C^6 cyclization is that the fulvene biradical intermediate could be trapped by hydrogen atom transfer. When enyne-allene **64** was heated for 18 h in 1,4-cyclohexadiene, the benzofulvene derivatives, 7% of (*Z*)-**65** and 4% of (*E*)-**65** were obtained along with 3% of the C^2 - C^7 product **66**.⁵²

Scheme 18. Evidence of the biradical intermediate, benzofulvene of the C^2 - C^6 cyclization.

Another significant evidence for a stepwise mechanism was supported by the

activation barriers of the formation **69** which would be expected to require much higher energy than that of **68** because the sterically hindered bulky mesityl group slows down the rate of cyclization reaction. However, the activation energy of **68** and **69** from **67** are almost the same by 25.9 kcal/mol and 26.3 kcal/mol, respectively.⁵³

Scheme 19. Evidence for a stepwise mechanism: mesityl group doesn't affect activation energy.

Another evidence for this reaction is that the rate of the cyclization of enyne-allene system was not affected by the solvent change from nonpolar solvent (benzene) to polar solvent (DMSO) which excludes a zwitterionic intermediate.^{54b} The experimental evidence of the kinetic isotope effects (KIE) also supported a stepwise biradical mechanism of enyne-allenes. KIE⁵⁴ is a powerful method to observe the reaction rate change. When an atom in one of the reactants is replaced by one of its isotopes, significant reaction rate change could be observed at the bond-breaking or the bond-forming step. Larger than two of KIE ($=k_{\text{H}}/k_{\text{D}}$) represents a hydrogen transfer is the rate determining step, which is taken as an evidence for concerted mechanism. On the basis of experimental data of KIE = 1.17, Schmittel concluded that the stepwise biradical mechanism is more predominant than the concerted ene reaction mechanism that Engels inferred through computational investigation.⁵⁵

Scheme 20. Kinetic isotope effect (KIE) experiment by Schmittel.

1.5. Literature survey on the preparation of enyne-allenes or enyne-cumulenes

As mentioned earlier, the most widely used methodology for the synthesis of enyne-allenes was [2,3]-sigmatropic rearrangement of enediynyl propargylic alcohols **74**, which was adopted by Saito,⁵⁶ Nicolaou,⁵⁷ Grissom⁵⁸ and Schmittel^{59a,c} for the synthesis of a variety of allenyl phosphonates or phosphine oxides.

Scheme 21. Enyne-allenes via [2,3]-sigmatropic rearrangement of enediynyl propargylic alcohols.

First conjugated enyne-cumulene system was synthesized by Hirama group who expected cross-conjugated dienediynyl **77** to undergo a vinylogous propargylic rearrangement. The dimethyl substituents on C11 prevented direct S_N2 reaction and thermolysis of the desired vinylogous S_N2 product **78** led to the Bergman type cyclization via biradical intermediate **79** and **80** in deoxygenated 1,4-cyclohexadiene at 80 °C.⁶⁰

Scheme 22. First conjugated enyne-cumulene system by the Hirama group.

Transition-metal catalyzed coupling reactions have been employed for the synthesis of a variety of enyne-allenes. Gillman group⁶¹ synthesized an enyne-allene ester through the Pd-catalyzed coupling reaction between arylzinc halides **83** and 2-halo-allene carboxylates **84** at room temperature. Heating silyl derivative **85** in chlorobenzene in the presence of 1,4-cyclohexadiene produced the tricyclic product **86** through a [2+2] cycloaddition reaction.⁶¹

Scheme 23. Enyne-allenes via transition metal-catalyzed coupling reactions.

Enyne-allene **88** could be easily prepared from **87** through a 1,3-prototropic rearrangement under basic conditions (Scheme 24).⁶² The enediyne-sulfone underwent base-catalyzed conversion to enyne-allene-sulfone **88**, which then underwent the Myers cyclization reaction leading to **90**.

Scheme 24. Enyne-allene via prototropic rearrangement under a basic condition.

Enyne-allenes could also be prepared via double olefination using titanium-substituted ylides. This synthetic methodology was reported by the Finn group.⁶³ The cycloaromatization rate and the product selectivity by changing the steric and electronic properties of the substituents R₁ and R₂ were investigated extensively.⁶³

Scheme 25. Synthesis of benzannulated enyne–allenes **93** via titanium-substituted ylides.

Recently, the Toste group envisioned a mechanism involving sequential rearrangements by transition-metal activation of alkynes. The metal was coordinated to the acetylene adjacent to propargylic ester, which then generated enyne-allene **98** via a [3,3]-sigmatropic rearrangement. The remaining alkyne might also be activated by this metal, allowing the final Myers-Saito cyclization through the 6-endo-dig addition of the allenyl acetate.⁶⁴

Scheme 26. Synthesis of the benzannulated enyne–allenes **98** via the metal-activated [3,3]-sigmatropic rearrangement.

Part II

Synthesis of Bowl-Shaped Polycyclic Aromatic Hydrocarbons via Palladium-Catalyzed Intramolecular Arylation Reactions

1. Introduction

The synthesis of buckybowls, usually referred to as bowl-shaped polycyclic aromatic hydrocarbons on the surface of buckminsterfullerene, or fullerene fragments, has evoked intense research activity in recent years due to their useful applications for nanotechnology, electronics, optics, and other fields of materials science. Discoverers of fullerene C_{60} , H. W. Kroto, R. F. Curl and R. E. Smalley, were awarded the Nobel prize in chemistry for the year 1996.^{65a} Buckminsterfullerene, C_{60} the smallest fullerene, is composed of twenty hexagonal rings and twelve pentagonal rings. The shape of the molecule prevents it from being planar.^{65b}

Figure 5. Various bowl-shaped polycyclic aromatic hydrocarbons.

Although fullerene C_{60} was discovered in 1985, corannulene (**102**), the smallest bowl-shaped polycyclic aromatic hydrocarbon, was synthesized by Barth and Lawton in 1966.⁶⁶ This pioneering synthesis of seventeen steps could not ignite extensive studies on bowl-shaped polycyclic aromatic hydrocarbons because of its lengthy synthetic pathway.

Scheme 27. Synthesis of Corannulene by Barth and Lawton.

However, this non-pyrolytic work for the synthesis of corannulene became a noteworthy landmark 30 years later, when Siiders and Siegel synthesized several curved molecules by a titanium-promoted reductive coupling strategy, followed by dehydrogenation of dimethyltetrahydrocorannulene with DDQ.⁶⁷

Scheme 28. Siiders and Siegel's approach for the synthesis of corannulene.

2. Literature survey on the synthesis of bowl-shaped polycyclic aromatic hydrocarbons

In 1991, Scott reported a short route to synthesize corannulene by using flash vacuum pyrolysis (FVP) from commercially available starting material, which opened a new era and inspired many groups to participate in this field. Flash vacuum pyrolysis (FVP) uses very low pressures of 10^{-3} mm or less, high temperatures in the range of 500-1100 °C, short contact times in the order of milliseconds, and short distance for short time of flight before analysis or collection.⁶⁸ Scott employed the FVP method for the synthesis of various bowl-shaped compounds. The investigation was inspired by the reports of R.F.C. Brown that terminal

acetylene **105** and vinylidene **106** are in equilibrium via 1,2-hydrogen shift under FVP conditions.⁶⁹

Scheme 29. Equilibrium of terminal acetylene and vinylidene under FVP condition.

The synthesis of corannulene illustrated below shows that 7,10-diethynylfluoranthene (**107**) was cyclized to form corannulene (**102**) under FVP conditions via two vinylidene moieties which were trapped by insertions into nearby C-H bonds.⁷⁰

Scheme 30. Synthesis of corannulene via two vinylidene moieties.

Since Scott's pioneering work, many curved molecules have been synthesized by the FVP method. Recently, Scott *et al.* reported the first rational synthesis of C₆₀ via the pyrolytic method.^{75a} However, the FVP method is problematic due to the limitation of relatively small scale runs, very low yields, a lack of functional group tolerance, and the potential for thermal rearrangements of the molecular framework.^{75b} Accordingly, many organic chemists are interested in finding nonpyrolytic methods for the synthesis of bowl-shaped PAHs.^{76a} “The first production of C₆₀ by physicists adopting not-so-rational methods was so embarrassing to the synthetic chemists that many synthetic chemistry groups were set out to achieve the synthesis of C₆₀ by rational means.”^{76b}

Scheme 31. Curved molecules prepared by the FVP method.⁷¹⁻⁷⁴

As introduced earlier, corannulene synthesis in a solution-phase was reported by Siegel and co-workers in 1996. 2,6-Dimethylcorannulene (**104**) was synthesized from diketone **116** by condensation with 4-heptanone to produce cyclopentanone carbinol **117**, which was brominated to form tetrabromide **103**. The reductive coupling strategy using $\text{TiCl}_3/\text{LiAlH}_4$ or $\text{VCl}_3/\text{LiAlH}_4$ was employed for internal cyclization of **103**.⁶⁷

Scheme 32. Corannulene synthesis reported by Siegel.

In 1999, the Rabideau group improved the yield up to 70-75% by using benzylic dibromide **119**, instead of benzylic monobromide **103**.⁷⁷ They used 8.8 equivalent of NBS in refluxing benzene with a catalytic amount of dibenzoyl peroxide under sun lamp irradiation to produce **119**.

Scheme 33. Improved corannulene synthesis reported by Rabideau.

In 2000, Sygula and his collaborators reported an inexpensive and convenient synthetic route to 1,2,5,6-tetrabromocorannulene (**120**) in 83% yield, in which they used a small amount of NaOH in aqueous dioxane to promote ring closures. Compared to this route (Scheme 34), the previous synthetic sequence reported by Siegel required strict oxygen- and moisture-free conditions and 2 to 4 days of reaction time.⁷⁸

Scheme 34. A simple corannulene synthesis reported by Sygula.

Another powerful catalytic method was employed in 2000 by the Scott group to produce strained fullerene fragments. The procedure employed intramolecular palladium-catalyzed aryl-aryl coupling reactions, which involved mild reaction conditions, allowed wide functional group tolerance, and the possibility for scaling-up.^{75b}

Scheme 35. Corannulene synthesis via palladium-catalyzed aryl-aryl coupling reactions.

3. Research Objective

Our group reported an efficient route to 5-phenyl-11*H*-benzo[*b*]fluorenes (**131**) involving condensation between benzannulated enediynes and aryl ketones to produce benzannulated enediynyl propargylic alcohols followed by reduction to trigger a sequence of tandem cyclization reactions.¹⁴ Lithium acetylide **125** and 2,2-dimethylpropiophenone (**124**) were condensed to furnish propargylic alcohol **126**, which was then reduced with triethylsilane and trifluoroacetic acid to furnish the benzannulated enediyne **127**. Enediyne **127** was treated with potassium *t*-butoxide under refluxing toluene leading to **131** via a sequence of cascade reactions. Benzannulated enyne-allene **128** was formed initially which then underwent a Schmitt cyclization reaction to give **129**, which then underwent a radical-radical coupling to give **130** and then **131**.

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

We have adopted this synthetic sequence to furnish the corresponding 5-(2,6-dibromophenyl)-11*H*-benzo[*b*]fluorene (**132**), the precursor for the subsequent palladium-catalyzed intramolecular arylation reactions, leading to buckybowls.

Scheme 39. Synthetic route for buckybowl.

Different type of buckybowls could be prepared by changing ketones at the beginning of the synthetic sequences.

4. Results and Discussions

The requisite (2,6-dibromophenyl)ethyne (**134**) was prepared by the Sonogashira coupling reaction between 1,3-dibromo-2-iodobenzene and (trimethylsilyl)ethyne, followed by desilylation as reported previously.⁸¹ A second Sonogashira reaction between **134** and 1-(2-iodophenyl)-2-(trimethylsilyl)ethyne (**135**) then led to **136**,⁸² which was readily desilylated to afford the benzannulated enediyne **137** as shown in Scheme 40. Condensation between **137** and pivalophenone **122** then produced enediynyl propargylic alcohol **138**. Treatment of **138** with triethylsilane in the presence of trifluoroacetic acid then afforded **139**. On exposure to potassium *tert*-butoxide in refluxing toluene for twelve hours, **139** was converted to 5-(2,6-dibromophenyl)-10-(1,1-dimethylethyl)-11*H*-benzo[*b*]fluorene (**132**) in a single operation. The transformation from **139** to **140** presumably proceeded through an initial 1,3-protropic rearrangement to form the corresponding benzannulated enyne–allene **140**. A Schmitt cyclization reaction^{33ab} to generate biradical **141** for an intramolecular radical–radical coupling to afford, in situ, **142** followed by a second prototropic rearrangement to regain aromaticity then furnished **132** as proposed previously.^{51g}

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Scheme 41. Synthesis of buckybowls via palladium-catalyzed aryl-aryl coupling reaction.

The X-ray structure of **133** indicates the presence of a significant curvature. Compared to **111**, the structure of **133** appears to be less strained with one less ring due to the absence of three sp^2 -carbons in the southeastern corner.

Figure 6. ORTEP drawings of the crystal structure of **133**.

The pyramidalization angle, defined as $\Theta_{\sigma\pi} - 90$ using the π -orbital axis vector analysis (POAV1),⁸⁴ of the central ethylene carbon atoms of **111** was reported to be 9.0° , whereas the pyramidalization angle of the four carbon atoms attached to the central double bond was determined to be 6.7° (Figure 7).⁸⁵ The POAV1 angles of these carbon atoms are clearly larger than those of the corresponding carbon atoms of **133** based on the geometry obtained from the X-ray analysis.

Figure 7. POAV1 pyramidalization angles ($\Theta_{\sigma\pi} - 90$) of **111** and **133**.

The ^1H NMR signal of the diastereotopic methylene hydrogens of **133** occurs as a singlet at δ 4.75 ppm. Barring accidental isochrony, this observation suggests a rapid bowl-to-bowl inversion on the NMR time scale at room temperature, reminiscent of what was observed previously in substituted corannulene derivatives.⁸⁶ Similarly, by using aryl ketones **144a** and **144b**^{51g} for condensation with the lithium acetylide of **137**, benzannulated enediynyl propargylic alcohols **145a** and **145b** were obtained, respectively. Reduction with triethylsilane in the presence of trifluoroacetic acid then gave benzannulated enediynes **146a** and **146b**. Treatment of **146a** and **146b** with potassium *tert*-butoxide in refluxing toluene for 12 h then furnished **147a** and **147b**, respectively. The palladium-catalyzed intramolecular arylation reactions of **147a** produced buckybowl **148a** and the monocyclized hydrocarbon **149a**.

Figure 8. Synthesis of bowl-shaped PAHs **148** from ketone **144**.

The X-ray structure of **148a** also indicates the presence of a significant curvature. Similarly, buckybowl **148b** along with the monocyclized hydrocarbon **149b** were likewise produced from **147b**. The structure of **148b** was also confirmed by X-ray structure analysis (Figure 8). The presence of an additional five-membered ring in **148b** appears to cause its structure to be more strained than those of **133** and **148a**. As a result, the transformation from **147b** to **148b** is less efficient, and the yield of **148b** was lowered to 11% along with 23% of the mono-closed product **149b**.

Figure 9. ORTEP drawing of the crystal structure of **148b**.

Based on the geometry obtained from the X-ray analysis, one of the central carbon atoms of **148b** has a POAV1 angle of 10.3° (Figure 9), which is larger than those of **111** and corresponds to 88% of that found for C_{60} with all carbon atoms having a POAV1 angle of 11.64° . In addition, one of the four carbon atoms attached to the central double bond of **148b** has a POAV1 angle of 9.2° , which is also larger than those of the corresponding carbon atoms of **111**.

Figure 10. POAV1 pyramidalization angles of **148a** and **148b**.

It was reported that, unlike corannulene, dihydrocyclopentacorannulene with an additional five-membered ring "locked" the bowl configuration, preventing a rapid bowl-to-bowl inversion process.⁸⁷ However, no such effect was observed for **148b** with the two sets of the methylene hydrogens appeared as two sharp singlets at δ 4.41 and 3.29 and the two groups of methyl hydrogens appeared as a sharp singlet at δ 1.63 at 25°C . At -33°C , the methylene signals, recorded on a 600-MHz NMR spectrometer, became two broad humps

ranging from ca. δ 4.6 to 4.2 and from ca. δ 3.4 to 3.1, and the methyl signal also appeared as a broad peak ranging from ca. δ 1.8 to 1.5. Further broadening but without the appearance of distinct signals for the diastereotopic hydrogens was observed at -40 °C, suggesting relatively fast bowl-to-bowl inversion on the NMR time scale even at -40 °C.

5. Conclusion

A new synthetic route to buckybowl was developed. The convergent assembly of the benzannulated enediynyl propargylic alcohols and the efficient cascade cyclizations of the resulting enyne-allenes leading to polycyclic aromatic dibromides for subsequent palladium-catalyzed intramolecular arylation reactions are the key features of this synthetic pathway. The use of benzannulated enediynyl propargylic alcohols to form the corresponding aromatic dibromides represents a new approach to the preparation of buckybowl precursors. Three new buckybowl with their structures confirmed by X-ray structure analyses were thus synthesized.

Part III

Synthesis of C₂-Symmetrical homo-bi-dentate Ligands bearing a 4,5-Diarylphenanthrene Moiety

1. Introduction

Development of effective catalytic asymmetric reactions promoted by chiral synthetic catalysts is an important area of research.⁸⁸ W. Marckwald provided a definition of asymmetric reaction as “Asymmetric syntheses are those reactions which produce optically active substances from symmetrically constituted compounds, with intermediate use of optically active materials.”⁸⁹ The progress of this research area has seen rapid advance in recent years in using organometallic catalysts, enzymes, and chiral auxiliaries to promote asymmetric synthesis.⁹⁰ One of the most widely used chiral ligands for catalytic asymmetric reactions is BINOL **149a**, (1,1'-binaphthyl-2,2'-diol), which was first synthesized as a racemate in 1873 with the absolute configuration established in 1979.⁹¹

In 1979, Noyori demonstrated the extremely high stereoselectivity (99%) of carbonyl group reduction by a binaphthol-modified aluminum hydride reagent.⁹² Takaya and Noyori then reported that the Rh and Ru complexes of BINAP **149b**, (2,2'-bis(diphenylphosphine)-1,1'-binaphthyl), are excellent complexed chiral ligands for the asymmetric hydrogenation of olefins and carbonyl compounds.⁹³ The success of BINAP complexes of ruthenium, rhodium, and palladium stimulated the development of a wide variety of C₂-symmetrical homo-bi-dentate ligands and non-C₂-symmetrical hetero-bi-dentate ligands.

C₂-symmetrical homo-bi-dentate ligands

149a: BINOL

149b: BINAP

149c: BINAM

non-C₂-symmetrical hetero-bi-dentate ligands

150a: MOP

150b: NOBIN

150c: MAP

BINAP (2,2'-bis(Diphenylphosphino)-1,1'-binaphthyl) **BINAM** (1,1'-Binaphthalene-2,2'-diamine)
MOP (2-(Diphenylphosphino)-2-methoxy-1,1'-binaphthyl) **NOBIN** (2-Amino-2-hydroxy-1,1'-binaphthyl)
MAP (2-Dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl)

Figure 11. A variety of C₂-symmetrical bidentate ligands.

2. Research Objective

4,5-Disubstituted phenanthrenes have a helical twist imposed by the two substituents bent out of the plane of the aromatic rings. The angle of 4,5-dimethylphenanthrene **151** between the outer ring planes is 27.9°, and its enantiomers were separated by chiral column.⁹⁴

Figure 12. 4,5-Disubstituted phenanthrenes.

Dr. Hongbin Li in our group synthesized the twisted PAH bearing 4,5-diphenylph-

enanthrene moiety via C²-C⁶ cyclization reaction of the benzannulated enyne-allenes. He demonstrated that the C²-C⁶ cyclization reaction could be used for the synthesis of 4,5-diarylphenanthrenes (**157**).^{47c} The synthetic sequence involves the condensation of 2 equiv of the lithium acetylide **153** with **154** to form the propargylic alcohols **155**. The reduction of **155** with triethylsilane in the presence of trifluoroacetic acid gave rise to the tetraacetylenic hydrocarbons **156**. Treatment of **156** with potassium *tert*-butoxide in refluxing toluene at 110 °C then furnished 4,5-diarylphenanthrenes **157**.

Scheme 41. Synthesis of 4,5-diarylphenanthrenes.

The most attractive feature of this cyclization reaction was the fact that uniquely twisted polycyclic aromatic hydrocarbon was formed in just a few steps. X-ray crystal structure (Figure 13) of **157a** from two different perspectives showed that the structure is severely twisted due to nonbonding steric interactions of phenyl groups which are oriented essentially parallel to each other. There is a 46.1° twist between the mean planes of the outer rings of the phenanthrene system.

Figure 13. ORTEP drawings of 4,5-diarylphenanthrene **157a**.^{47c}

Based on Dr. Li's discovery, we have further pursued the use of properly functionalized **157** as C_2 -symmetrical homo-bi-dentate ligands or chiral auxiliaries for enantioselective reduction or oxidation reactions. We envisioned that replacing the phenyl groups with phenol or aniline group could lead to the formation of C_2 -symmetrical homo-bi-dentate 4,5-diarylphenanthrene containing the necessary functional groups for metal coordination resembling those of BINOL, and related derivatives (Figure 14).

Figure 14. 4,5-Diarylphenanthrene bearing helical twisted phenolic groups.

3. Results

3.1. Synthesis of a diindeno-fused 4,5-diarylphenanthrene containing phenolic groups

The synthetic sequence outlined in Scheme 42 illustrates the synthesis of twisted dianisole **163**. Condensation between 1-ethynyl-2-iodobenzene (**158**) and diketone **154** produced the propargylic alcohol **159**. Treatment of **159** with triethylsilane in the presence of trifluoroacetic acid afforded diiodide **160**. The Sonogashira coupling reaction between 4-ethynylanisole (**161**) and diiodide **160** produced the tetraacetylenic compound **162** which

served as the precursor of the corresponding benzannulated enyne-allene. On exposure to potassium *tert*-butoxide in refluxing toluene for twelve hours, **162** was converted to 4,5-di(4-methoxyphenyl)phenanthrene **163** in 42% yield via the cascade cyclization reactions of the corresponding benzannulated enyne-allene.

Scheme 42. Synthesis of *rac*-**163** containing a 4,5-di(4-methoxyphenyl)phenanthrene substructure.

The ORTEP drawing of **163** viewing along the axis perpendicular to the phenanthrene ring is given in Figure 15 to show a severe structural distortion. As expected, the two anisole substituents are twisted away from each other.

Figure 15. ORTEP drawing of the crystal structure of **163**.

The BBr₃-mediated deprotection of the methoxy groups in compound **163** gave rise to the *rac*-diphenolic product **164**.

Scheme 43. Demethylation of 4,5-di(*p*-methoxyphenyl)phenanthrene.

3.2. Resolution of 4,5-diarylphenanthrene containing phenolic groups

3.2.1. Literature survey for resolution

The resolution of *rac*-BINOL by chemical methods and the selective synthesis of (*R*)- or (*S*)-BINOL have been extensively studied. The classical method for the chemical resolution of *rac*-BINOL involved separation of diastereomers derivatized with additional chiral compounds. The chemical resolution of *rac*-BINOL was first achieved by the synthesis of cyclic binaphthyl phosphoric acids, which were successfully resolved as cinchonine salts.⁹⁷

Scheme 44. Resolution of BINOL with cinchonine salts.

The resolution of *rac*-BINOL was also achieved by Hu and De Lucchi's groups independently, who employed the case of phosphoramidates derived from optically active phenethylamines. It was possible to achieve 100% ee by using the three amines depicted in Scheme 45.⁹⁸

Scheme 45. Resolution of BINOL using phosphoramidates derivatization.

In 1995, Fabbri *et al.* reported that (-)-menthyl chloroformate-derivatized BINOL could be chromatographically separated. After then, two more chiral acyl chlorides, camphor sulfonyl chloride (**172**) and neomenthylthioacetic acid chloride (**173**), were employed for the resolution of *rac*-BINOL. This resolution method has been widely used due to their convenience and low cost.⁹⁹

Figure 16. Chiral acyl chlorides for the resolution of BINOL.

Resolution with camphor sulfonyl chloride (**172**) is a facile, inexpensive, and useful method for a simple two-step resolution of *rac*-BINOL in 80-95% yield.^{99(a)} Based on the result reported by the Chow's group (Scheme 46),^{99(a)} we envisioned that our *rac*-biphenolic

product **164** could be chromatographically resolved through its derivatization with camphor sulfonyl group. Diastereomeric bis-(*S*)-camphorsulfonates **174** could be separated on silica gel column by using a hexane-diethyl ether mixture as eluent.

Scheme 46. Separation of *rac*-BINOL substituted with camphorsulfonyl group.

3.2.2. Results of resolution

Demethylation followed by derivatization with camphorsulfonyl group converted enantiomers of 4,5-di(4-methoxyphenyl)phenanthrene (*rac*-**163**) to the corresponding (*S*)-camphorsulfonate diastereomers **175**. We separated **P-175** and **M-175** on silica gel column chromatography and confirmed their separation on the base of ^1H NMR spectra obtained in a 270 MHz NMR spectrometer.

Scheme 47. Preparation and separation of camphorsulfonate derivatives.

As shown in Figure 17, respective ^1H NMR spectra show the two diastereomers were clearly separated on silica gel column chromatography with high diastereomeric purity. Before column chromatography, the NMR signals of the methylene hydrogens on the five-membered rings exhibited two set of AB quartet signals in the upfield-shift portions of the signals overlap with each other. However, after column chromatography, the separated derivatives exhibit only one set of the AB quartet signals. In addition, the two doublets at δ 6.1 and 6.2, attributable to the two aromatic hydrogens closest to the phenyl substituents, also showed clean separation after column chromatography. However, the singlets attributable to the two hydrogens on the central benzene ring have identical chemical shift at δ 7.8. Another set of AB quartets attributable to the methylene groups ($-\text{CH}_2\text{SO}_2-$) were observed at δ 3.9 (2 H, d, $J = 15.0$ Hz) and 3.2 (2 H, d, $J = 15.0$ Hz) and 3.8 (2 H, d, $J = 15.0$ Hz) and 3.2 (2H, d, $J = 15.0$ Hz), respectively.

(a) Diastereomers derivatized with camphorsulfonyl group

(b) Separated Diastereomer

(c) Separated Diastereomer

Figure 17. ^1H NMR spectra of camphorsulfonates **175**.

Based on our previous experience, the methylene hydrogens on the five-membered ring of **163** are very acidic and can be easily oxidized to keto group under basic conditions. In order to prevent oxidation of the methylene hydrogens, attempts were made to try to replace them with methyl groups by treatment with potassium *t*-butoxide for methylation with iodomethane to furnish the corresponding tetra-methylated compound **176'**. However, the X-ray of the product (Figure 18) shows that instead of tetra-methylation, the trans-di-methylated adduct **176** was obtained in 91% yield. Further methylation to produce **176'** was unsuccessful.

Figure 18. ORTEP drawing of the crystal structure of the di-methylated **176**.

Scheme 48. Methylation of **163** and resolution of **177**.

The camphorsulfonate **178** was synthesized from **177** and then resolved with the same method shown in Scheme 47. As shown in Figure 19, the well resolved ^1H NMR signals of the AB patterns between δ 3.8 and 3.1, attributable to the hydrogens adjacent to the sulfonyl group. The two aromatic hydrogens closest to the phenolic substituents at δ 6.3 are partly overlapped.

(a) Methylated diastereomers derivatized with camphorsulfonyl group

(b) Separated methylated diastereomer

Figure 19. ^1H NMR spectra of camphorsulfonates **178**.

The camphorsulfonyl moiety in **175** was readily removed by treatment with aqueous sodium hydroxide solution at 40 °C to regenerate the optically pure parent **P**- and **M**-**164**. **P-164** and **M-164** enantiomers exhibited large specific rotations of $[\alpha]_{\text{D}}^{25} = -904 \pm 6^\circ$ (c 1, CH_2Cl_2) and $[\alpha]_{\text{D}}^{25} = +904 \pm 6^\circ$ (c 1, CH_2Cl_2).

Scheme 49. Hydrolysis of bis-camphor sulfonate **175**.

3.3. Low stability of diphenol-substituted phenanthrene

The methylated product **176** was unstable under acidic conditions. The product decomposed on standing and the NMR spectrum showed such decomposition. Several small peaks, marked with arrows, were observed adjacent to the original peaks. These small peaks became bigger and bigger and finally only broad peaks were observed.

Figure 20. NMR spectrum of decomposition of compound **176**.

Dr. Yonghong Yang of our group observed that the *tert*-butyl groups were easily removed from the aromatic ring via retro Friedel-Craft alkylation reaction on exposure to proton or a Lewis acid.¹⁰⁰ This might be one of the reasons for the phenolic product to be unstable, when exposed to even mild acidic conditions.

Scheme 50. Cleavage of the *tert*-butyl group under acidic condition.

The other potential origin of low stability might come from protonation followed by a facile intramolecular electrophilic aromatic substitution reaction, which was observed for the transformation of 1-phenylbenzo[*a*]anthracene to dibenzo[*a,l*]pyrene (**180**).¹⁰¹

Scheme 51. Intramolecular electrophilic aromatic substitution.

Dr. Yonghong Yang of our group also observed a similar transformation from **182** to **187**, which proceeded via protonation followed by an intramolecular electrophilic aromatic substitution reaction involving the phenyl substituent to form **185**, followed by deprotonation to give **186**.¹⁰⁰

Scheme 52. Dr. Yang's observation of protonation and intramolecular electrophilic aromatic substitution reaction.

In my case, the hydroxyl groups on the phenolic substituents could stabilize the carbocation intermediate and thus greatly facilitates the intramolecular electrophilic aromatic substitution reaction.

Scheme 53. Intramolecular electrophilic aromatic substitution and resonance structures.

Various unidentified factors might contribute to the decomposition of the cyclized products. Even crystallized compounds of high purity decomposed gradually even under an inert atmosphere at below 0 °C.

3.4. C₂-Symmetrical homo-bi-dentate 4,5-diarylphenanthrene ligands containing ortho- and meta-substituents

A series of products bearing ortho- or meta-phenolic group have also been synthesized using the same synthetic strategy, beginning with the Sonogashira coupling between 3-ethynylanisole (**192**) or 2-ethynylanisole, and diiodide **160**, as shown in Schemes 54 and 55.

The meta-anisole product **195** also decomposed on standing and totally decomposed on attempts for demethylation by treatment with boron tribromide. The dimethylated meta-anisole product of **196** also slowly decomposed on standing. Methylation of the benzofluorene moiety appears to slow down the rate of decomposition as observed in the para-anisole product.

Scheme 54. Synthesis of 4,5-diarylphenanthrene containing meta-anisole moieties **196**.

Interestingly, the ortho-anisole product **198** was obtained as a mixture of three isomers not separable by flash column chromatography. The *t*-butyl groups of the mixture gave three peaks at around δ 1.8 on the ^1H NMR spectrum with a ratio of 55 : 38 : 7. Presumably, the restricted rotation of the anisole groups is responsible for giving rises to these rotational isomers.

Scheme 55. Synthesis of 4,5-diortho-anisolic phenanthrene **198**.

The methylene hydrogen signals at δ 4.00-4.45 also show three sets of AB quartets with the same germinal coupling constant of 21.0 Hz.

Figure 21. ^1H NMR Spectrum of three sets of AB quartet from methylene hydrogens of **198**.

3.5. Para-aniline substituted C₂-symmetrical homo-bi-dentate product

Aniline groups were also employed to produce helical 4,5-diarylphenanthrene derivative **201** resembling BINAM, which could show high stability at elevated temperatures and under strong basic and acidic conditions. The palladium-catalyzed (Sonogashira) coupling of terminal acetylene **199** with diaryl iodide **160** afforded **200**. The cascade cyclization reactions of **200** produced 4,5-di(4-aminophenyl)phenanthrene **201**. The resulting enantiomers could be separated on column chromatography by converting **201** to the corresponding diastereomeric sulfonamides **202** by treatment with camphor sulfonyl chloride and triethylamine. The solvent system used for the separation of diastereomers on silica gel chromatography was 40% diethyl ether in hexanes.

Scheme 56. Synthesis of a ligand containing 4-aminophenyl moiety.

Interestingly, compared to para-anisole-substituted phenanthrene, the diastereomeric sulfonamides **202** showed different chemical shift patterns especially in the aromatic region and between δ 4.5 and 3.5 of methylene hydrogens (Figure 22). One set of AB pattern

attributable to the methylene hydrogens, occurred as a doublet at δ 4.38 (Figure 22b) ($J = 21$ Hz) and 4.45 (Figure 22c) ($J = 21$ Hz), whereas the other set occurred as a doublet at δ 4.12 (Figure 22b) ($J = 21.0$ Hz) and as an overlapping signal at δ 4.20-4.09 (Figure 22c).

(a) Diastereomeric sulfonamides

(b) Separated diastereomeric sulfonamide

(c) Separated diastereomeric sulfonamide

Figure 22. ^1H NMR spectra of diastereomeric sulfonamide.

After chromatographic separation, attempts were made to remove the camphorsulfonyl groups in **202** to produce the optically pure M- or P-enantiomer. A few methods were employed to remove the camphorsulfonyl group from very stable sulfonamide.¹⁰² Several reports in the literature described detosylation from the arylation products using samarium iodide. However, this method failed in our case.¹⁰² Treatment of sulfonamide **202** with aqueous sodium hydroxide in refluxing THF for 12 h showed no

reaction. All attempts to remove the sulfonyl group from sulfonamide **202** failed.

Scheme 57. Hydrolysis of biscamphor sulfonamide **202**.

4. Conclusion

The synthetic strategy for the twisted polycyclic aromatic hydrocarbon bearing 4,5-diarylphenanthrene moiety was successfully adopted for the synthesis of C₂-symmetrical homo-bi-dentate ligands. Demethylation of cyclization product followed by derivatization with camphor sulfonyl group converted the racemic mixture of 4,5-di(4-methoxyphenyl)phenanthrenes to the corresponding diastereomers, which could be separated on silica gel column chromatography. However, the resolved diphenolic compound could not be used as a ligand due to its low stability. A 4,5-diarylphenanthrene derivative containing 4-aminophenyl substituents were likewise synthesized and its camphorsulfonamide derivatives were separated by silica gel column chromatography.

Part IV

Attempted Synthesis of an Indeno-Fused Corannulene via Cascade

Cyclizations of Benzannulated Enyne-Allenes

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) generated from the cyclization of benzannulated enyne-allenes provided many opportunities for various synthetic applications. Recently, bowl-shaped compound, pentaindenocorannulene ($C_{50}H_{20}$) **203** was synthesized via non-pyrolytic method by the Scott's group.^{84d} We are interested in the synthesis of **204** and **205** using the cascade cyclization reaction of benzannulated enyne-allenes.

Scheme 58. The structures of pentaindenocorannulene and PAHs **204** and **205**.

The synthetic sequence for bowl-shaped compounds mentioned in Part II was also employed for this investigation. In an earlier work of our research group, Dr. Yonghong Yang firstly reported the synthesis of PAHs via enyne-allenes derived from an Ireland-Claisen rearrangement.²⁴ Dr. Yang's approach is outlined in Scheme 59. The propargylic acetate **207** was obtained by condensation between the lithium acetylide **124** and 9-fluorenone (**206**). Treatment of **207** with LDA, followed by trapping with *tert*-butyldimethylsilyl chloride (TBDMSCl) then furnished the silyl ketene acetal. A subsequent Ireland-Claisen rearrangement then furnished the corresponding benzannulated enyne-allene. A subsequent

Schmitt cyclization then led to the silyl ester **212**, in which hydrolysis produced carboxylic acid **213** in 57% yield.²⁴

Scheme 59. Synthesis of a PAH containing carboxylic acid via Ireland-Claisen rearrangement.

Conversion of **213** to the corresponding acid chloride with thionyl chloride followed by an intramolecular acylation reaction promoted by aluminum chloride produced the polycyclic aromatic ketone **214** in 88% yield.

Scheme 60. Intramolecular acylation with thionyl chloride and aluminum chloride.

Dr. Han of our group also tried to synthesize a precursor of tetraindenocorannulene via cascade cyclization reaction of enyne-allenes. It was envisioned that ketone **215** could be used as a potential precursor of **216** leading to **217** containing a corannulene unit.

Scheme 61. Han's approach for the synthesis of a PAH containing a corannulene unit.

Han's approach is outlined in Scheme 62. Condensation between diketone **218** and 2 equiv of **219** led to propargylic diols **220** which were treated with thionyl chloride to give the diindeno-fused *4H*-cyclopenta[*def*]phenanthrene **215**. The reaction involved two cascade cyclization sequences. The reduction of the crude product with tributyltin hydride gives **215** in 44% overall yield from the *trans*-diol **220a**. It is worth noting that four new rings were constructed in a single operation at room temperature, making the pathway is very efficient route for the construction of polycyclic aromatic structures. Ketone **215** was then treated with dimethyl malonate in the presence of TiCl₄ and pyridine to give diester **221** in 51% yield. The diester was reduced with LiEt₃BH and then converted to dichloride **223** with thionyl chloride in 45% yield. However, attempts for ring closure to give **216** were unsuccessful.

Scheme 62. Synthesis of *4H*-cyclopenta[*def*]phenanthrene.

Previous research of Ms. Parbin of our group demonstrated that small polycyclic aromatic hydrocarbons could be synthesized via simple intramolecular S_N2 reactions. In her work, condensation of **224** with the lithium acetylide **124** furnished the propargylic alcohol

225 in 75% yield. Reduction of propargylic alcohol **225** with triethylsilane in the presence of trifluoroacetic acid produced hydrocarbon **226** in 80% yield. Treatment of **226** with potassium *t*-butoxide in refluxing toluene produced alkene **227** in a single operation.¹⁰⁴ Hydroboration of alkene **226** with disiamylborane followed by iodination in the presence of sodium hydroxide led to alkyl iodide **228** in 65% yield. Treatment of alkyl iodide **228** with potassium *t*-butoxide in THF at 40 °C furnished the polycyclic aromatic hydrocarbon **229** in 60% yield. Parbin's approach involved incorporating less strained sp³-hybridized carbons into the PAH skeleton.

Scheme 63. Parbin's approach to synthesize all fused ring.

2. Research objective

Based on our previous discovery about the synthesis of double-cyclized hydrocarbon via S_Ni' reaction promoted by thionyl chloride, we were interested in further exploring its application for the synthesis of fused ring system. We were also interested in exploring the synthesis of corannulene derivative **230** by introducing sp³-hybridized carbons into its skeleton. We envisioned that tandem Knoevenagel/hydrogenation reaction could furnish valuable diketones leading to potential precursors for pentaindenocorannulene (**203**) or tetraindenocorannulene.

Scheme 64. Retrosynthetic sequence for the synthesis of corannulene derivative **230**.

3. Results and Discussion

3.1. Synthesis of all fused polycyclic aromatic hydrocarbons containing corannulene moiety

A synthetic design leading to bowl-shaped PAH is outlined in Scheme 65. The synthetic sequence began with **233** for tandem Knoevenagel condensation and Hydrogenation. The amino acid L-proline catalyzed-Knoevenagel condensation of 1,3-dimethoxyacetone (**233**) with 1,3-indanedinone (**238**) to furnish the olefin, which was reduced with Hantzsch ester^{105a} to produce the hydrogenated product **234** in 82% yield.^{105b} Methylation was carried out with potassium *t*-butoxide and iodomethane to give the methylated 1,3-indandione **232** in 78% yield. Condensation with the lithium acetylide followed by cyclization with thionyl chloride and reduction with tributyltin hydride then furnished **236** in 40% overall yield. Compound **236** was converted to diol **237** with boron tribromide. Subsequent bromination with triphenylphosphine and carbon tetrabromide gave the requisite dibromide **231**.

Scheme 65. Synthesis of a precursor for a bowl-shaped compound bearing a corannulene moiety.

Attempts were made to try to promote the two intramolecular $\text{S}_{\text{N}}2$ reactions to connect methylene carbons on five-membered rings with the carbons bearing the bromo substituents. A variety of conditions, including high temperature and more than 2 equiv of *t*-BuOK resulted in decomposition of **231**. The crude NMR spectra showed only broad peaks, and the methylene hydrogens on the five-membered ring were partially oxidized to the keto group.

Scheme 66. Attempts to produce **230** containing a partially hydrogenated corannulene unit.

Although we applied a relatively milder condition, which was the use of 2.4 equiv of base and room temperature, to produce **230**, any sign of the formation of the mono-closed

product as well as double-closed product was not observed in the ring closing step. Attempt to use sodium hydride and catalytic amount of *tert*-butanol, was also unsuccessful.

3.2. Fused polycyclic aromatic hydrocarbons via intramolecular alkylation

A modified strategy was used to gain access to fused ring systems. In **241**, one additional carbon was added to end of the two alkyl halide substituents, which could reduce the ring strain in the final ring-closed product. A retrosynthetic analysis is outlined in Scheme 67. The fused polycyclic aromatic hydrocarbon **240** could be synthesized from alkyl diiodide **241** via intramolecular alkylations. Alkyl diiodide **241** could be prepared from simple ring opening of pyran **242** with iodotrimethylsilane.¹⁰⁶

Scheme 67. The retro-synthetic analysis for the preparation of fused rings.

Diketone **245** was synthesized by the one-pot Knoevenagel/hydrogenation protocol. Following the synthesis of **245**, the same procedure was employed for the synthesis of the *trans*-propargylic diol **246** for treatment with thionyl chloride and subsequent reduction with tributyltin hydride to give **242**. In order to open up the pyran ring, an excess of trimethylsilyl iodide was used to furnish diiodide **241** in 76% yield.¹⁰⁶

Scheme 68. The synthetic sequence for diiodide **241**.

Attempts to use potassium *tert*-butoxide for the intramolecular alkylation reactions were unsuccessful.

Scheme 69. First attempt to form all fused rings.

However, when **241** was treated with LDA at room temperature, 8% of the fused polycyclic aromatic hydrocarbon **240** was obtained as a minor product along with the unexpected fused unsymmetrical **247** as a major product.

Scheme 70. Intramolecular alkylations promoted by LDA.

The formation of the unexpected product **247** could arise from an intramolecular S_N2 reaction involving a 5-exo-tet pathway of **249** according to the Baldwin's rule. It is worth noting that the 5-exo-tet pathway leading to **247** resulted in the loss of aromaticity of one of the benzene rings in **248**.

Scheme 71. Mechanism for the major product **247**.

Although the products **240** and **247** could not be separated by flash column chromatography, the ^1H NMR spectrum of **247** in CDCl_3 using 1D TOCSY technique revealed the presence of the minor product **240** in 8% yield by NMR integration.

Figure 23. 1D TOCSY spectrum of compound **240**.

The structure of **247** was characterized by using a variety of NMR techniques including two-dimensional NOESY, gHSQC, and gHMBC. The stereochemistry was also assigned on the basis of one-dimensional NOSEY experiments (Figure 24).

In the NOESY spectrum of **247** (Figure 24), CH₃ protons at 1.68 ppm shows strong nOes to H₃^α proton at 2.81 ppm, H₄^α proton at 2.69 ppm, and H₆ proton at 4.12 ppm. H₃^α proton at 2.81 ppm shows strong nOes to CH₃ protons at 1.68 ppm, H₄^α proton at 2.69 ppm, and H₂^α proton at 1.63 ppm. H₆ proton at 4.12 ppm shows strong nOes to CH₃ protons at 1.68 ppm, H₅^α proton at 1.56 ppm, and H₈^α proton at 7.50 ppm. Therefore, the CH₃ group is in the same orientation with H₃ proton, and H₆ proton.

Figure 24. nOe of compound **247**.

In the NOESY spectrum of **240** (Figure 24), H₁ proton and H₇ proton at 4.27 ppm shows strong nOes to H₂^α proton and H₆^α proton at 1.35 ppm, and CH₃ protons at 1.96 ppm. CH₃ protons at 1.68 ppm shows strong nOes to H₁ proton and H₇ proton at 4.27 ppm, and H₂^α proton and H₆^α proton at 1.35 ppm. In addition, H₂^β proton and H₆^β proton at 2.61 ppm show strong nOes only to H₂^α proton and H₆^α proton at 1.35 ppm. Therefore, the CH₃ group is in the same orientation with H₁ proton, H₇ proton and H₄ proton.

Figure 25. nOe of compound **240**.

3.3. Attempted synthesis of fused polycyclic aromatic hydrocarbons via intramolecular Barbier reaction

The use of samarium(II) iodide for reductive coupling to promote intramolecular Barbier-type reaction between alkyl halides and carbonyl groups to form fused PAHs was also explored.¹⁰⁷ We have investigated SmI₂-mediated intramolecular Barbier reaction with dibromide **252** (Scheme 72). Propargylic diol **235** was converted to the corresponding diketone **250** using the cascade reaction sequence with air oxidation in the presence of sodium hydroxide. Demethylation of the methoxy groups in **250** with boron tribromide to give **251** followed by bromination with carbon tetrabromide and triphenylphosphine furnished dibromide **252** from **250** in only 23% overall yield.

Scheme 72. Synthesis of diketone **252** containing alkyl dibromide.

Diketone **254** having a longer alkyl chain on each of the alkyl chain connecting to the iodo substituent was likewise synthesized as outlined in scheme 73. Propargylic diol **246** was converted to the corresponding diketone **253**, and then treatment with trimethylsilyl iodide produced **254**.

Scheme 73. Synthesis of diketone containing alkyl iodide.

However, attempts for intramolecular condensation using Samarium-Barbier reaction were unsuccessful. The ^1H NMR spectrum of the crude reaction mixture showed broad peaks in the aromatic region.

Scheme 74. The preparation of all fused rings via Samarium-Barbier reaction.

3.4. Attempted synthesis of pentaindenocorannulene **203**

Another diketone **262** was also synthesized by the same synthetic sequence. The

retrosynthetic sequence for pentaindenocorannulene **203** is outlined in Scheme 75. It was presumed that tetraketone **264** could undergo intramolecular ring closure via McMurry coupling reactions between the keto groups. The structure of **263** has a bowl shape and bears a corannulene unit. Subsequent intramolecular arylation reactions could furnish pentaindenocorannulene **203**.

Scheme 75. Retrosynthetic analysis for the preparation of PAH **203** containing a corannulene unit.

The synthetic sequence outlined in Scheme 65 was adopted for the preparation of **262**. From the methylated diketone **260**, the propargylic diol **261** was then converted to **262** by the cascade cyclization sequence followed by air oxidation in the presence of sodium hydroxide.

Scheme 76. Synthesis of diketone **262**.

The oxidation of diketone **262** outlined in Scheme 77 was carried out via light-induced radical bromination of the benzyl positions with *N*-bromosuccinimide or bromine. After radical bromination, NMR spectrum showed many unidentified peaks in the aromatic region. All attempts to furnish dibromide **265** were unsuccessful.

Scheme 77. Attempted radical bromination of **262**.

4. Conclusion

Polycyclic aromatic hydrocarbon **240**, bearing a ten fused ring system and **247** were successfully synthesized from a diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene precursor. Direct tandem Knoevenagel/hydrogenation reaction sequence also furnished valuable diketones as potential precursors of a variety of PAHs. It is also worth noting that the cascade cyclization sequence via an enyne-allene intermediate is an efficient pathway for the construction of a variety of diverse carbon backbones as potential precursors of bowl-shaped PAHs.

Part V

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen or an argon atmosphere. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. Methylene chloride, benzene, toluene, and *p*-xylene were also distilled over calcium hydride (CaH₂) prior to use. Silica gel for flash column chromatography was purchased from chemical suppliers. 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 for those recorded on a 600-MHz NMR spectrometer (Varian VXR-600). 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/ethylbenzene, CuBr·SMe₂, triethylsilane, trifluoroacetic acid, potassium *tert*-butoxide (1.0 M) in 2-methyl-2-propanol, potassium *tert*-butoxide, 2-methyl-2-propanol, triethylamine, phenylacetylene, (trimethylsilyl)acetylene, Pd(PPh₃)₂Cl₂, copper(I) iodide, 2,2-dimethylpropiophenone (**122**), triphenylphosphine, Pd(PPh₃)₂Br₂, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), boron tribromide (1.0 M solution in

dichloromethane), methanol, ethanol, (1*S*)-(+)-10-camphorsulfonyl chloride, 1-ethynyl-3-methoxybenzene, 1-ethynyl-2-methoxybenzene, 1-ethynyl-2-iodobenzene, 4-ethynylanisole, 4-ethynylaniline, hexamethyl phosphoramidate, samarium(II) iodide, thionyl chloride, pyridine, tetrahydro-4*H*-pyran-4-one, 1,3-indanedione, L-proline, iodotrimethylsilane, methyl iodide, tri-*n*-butyltin hydride were purchased from chemical suppliers and were used as received.

(2,6-Dibromophenyl)ethyne (**134**),⁸¹ [(2-iodophenyl)ethynyl]trimethylsilane (**135**),⁸² 2,2-dimethyl-1-indanone (**144b**),^{51g} and Hantzsch ester^{105a} were prepared as reported previously.

[[2-[(2,6-Dibromophenyl)ethynyl]phenyl]ethynyl]trimethylsilane (136). To a flask containing 0.17 g of dichlorobis(triphenylphosphine)palladium (0.24 mmol) and 0.030 g of CuI (0.16 mmol) were added via cannula a solution of 1.42 g of **135** (4.74 mmol) in 20 mL of triethylamine followed by a solution of 1.23 g of **134** (4.74 mmol) in 20 mL of triethylamine. The resulting mixture was stirred vigorously for 12 h. The mixture was then filtered to remove solid particles, and the filtrate was concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 1.72 g of **136** (3.98 mmol, 84%) as a yellow liquid: R_f = 0.67 (hexanes:diethyl ether = 9:1); IR 2158, 1421 cm^{-1} ; ^1H δ 7.65–7.62 (1 H, m), 7.57 (2 H, d, J = 8.2 Hz), 7.55–7.51 (1 H, m), 7.35–7.27 (2 H, m), 7.02 (1 H, t, J = 8.2 Hz), 0.26 (9 H, s); ^{13}C δ 132.9, 132.7, 131.2, 129.7, 128.5, 128.1, 127.2, 126.4, 125.3, 125.1, 103.2, 99.0, 97.0, 90.9, 0.1; MS m/z 434/432/430 (M^+), 419/417/415.

Benzannulated Eneidyne 137. To 1.72 g of **136** (3.98 mmol) in 50 mL of diethyl ether were added 50 mL of a 10% NaOH solution and 50 mL of methanol. After 10 h at room temperature, 35 mL of 6 M HCl solution was added slowly. The organic layer was separated, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to afford 1.29 g of **137** (3.58 mmol, 90%) as a yellow solid: R_f = 0.52 (hexanes:diethyl ether = 9:1); IR 3293, 1423 cm⁻¹; ¹H δ 7.67–7.62 (1 H, m), 7.57 (2 H, d, J = 8.2 Hz), 7.55–7.52 (1 H, m), 7.38–7.28 (2 H, m), 7.02 (1 H, t, J = 8.2 Hz), 3.37 (1 H, s); ¹³C δ 132.7, 132.6, 131.3, 129.8, 128.7, 128.5, 127.1, 126.5, 125.8, 124.4, 96.6, 90.9, 82.0, 81.8; MS m/z 362/360/358 (M⁺), 281/279, 200.

α -[[2-[(2,6-Dibromophenyl)ethynyl]phenyl]ethynyl]- α -(1,1-dimethylethyl)benzene

methanol (138). To 0.567 g (1.57 mmol) of **137** in 40 mL of THF under a nitrogen atmosphere at 0 °C was added 0.887 mL of a 2.0 M solution of LDA (1.7 mmol) in THF/*n*-heptane. After 30 min of stirring, a solution of 0.255 g of pivalophenone (**122**, 1.57 mmol) in 20 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/40% diethyl ether in hexanes, R_f = 0.64) to provide 0.607 g (1.16 mmol, 74%) of **138** as a viscous yellow liquid: IR 3563, 1483 cm⁻¹; ¹H δ 7.70–7.62 (3 H, m), 7.58–7.54 (1 H, m), 7.53 (2 H, d, J = 8.2 Hz), 7.38–7.31 (2 H, m), 7.24–7.19 (3 H, m), 7.00 (1

H, t, $J = 7.9$ Hz), 2.5 (1 H, br s), 1.05 (9 H, s); ^{13}C δ 141.9, 132.5, 132.3, 131.2, 129.8, 128.6, 128.0, 127.8, 127.2, 127.1, 126.9, 126.5, 125.3, 124.9, 97.0, 96.6, 90.7, 84.3, 79.4, 39.7, 25.5.

Benzannulated Eneidyne 139. To a mixture of **138** (0.607 g, 1.16 mmol) and triethylsilane (0.405 g, 3.48 mmol) in 30 mL of methylene chloride was added 0.71 mL of trifluoroacetic acid (1.06 g, 9.28 mmol). After five min of stirring at room temperature, 0.99 g of sodium carbonate (9.3 mmol) was added followed by 20 mL of water and 50 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/20% diethyl ether in hexanes, $R_f = 0.46$) provided 0.546 g (1.08 mmol, 93%) of **139** as a yellow liquid: IR 2219, 1421 cm^{-1} ; ^1H δ 7.69–7.65 (1 H, m), 7.60–7.55 (1 H, m), 7.55 (2 H, d, $J = 7.9$ Hz), 7.47–7.18 (7 H, m), 6.99 (1 H, t, $J = 8.2$ Hz), 3.75 (1 H, s), 1.09 (9 H, s); ^{13}C δ 138.9, 132.4, 132.3, 131.1, 129.8, 129.6, 128.5, 127.5, 127.3, 126.6, 126.5, 126.4, 124.7, 97.3, 96.1, 90.3, 82.2, 50.6, 35.4, 27.7.

5-(2,6-Dibromophenyl)-10-(1,1-dimethylethyl)-11H-benzo[*b*]fluorene (132). To 0.546 g of **139** (1.08 mmol) in 30 mL of anhydrous toluene under a nitrogen atmosphere was added 1.08 mL of a 1.0 M solution of potassium *tert*-butoxide (1.08 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 12 h. After the reaction mixture was allowed to cool to room temperature, 20 mL of water and 40 mL of diethyl ether were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes, $R_f = 0.51$) to provide 0.382 g of **132** (0.755 mmol, 70%) as a yellow solid: IR 1546, 1423 cm^{-1} ; ^1H δ 8.69 (1 H, d, $J = 8.9$ Hz), 7.83 (2 H, d, $J = 8.2$ Hz), 7.65–7.17 (6 H, m), 7.08 (1 H, t, $J = 7.7$ Hz), 6.36

(1 H, d, $J = 7.9$ Hz), 4.56 (2 H, s), 1.95 (9 H, s); ^{13}C δ 144.3, 142.1, 140.7, 139.5, 137.9, 137.6, 132.4, 131.6, 131.3, 130.5, 128.3, 127.3, 126.8, 126.0, 125.5, 124.7, 124.1, 123.6, 122.0, 40.3, 38.9, 34.5; MS m/z 508/506/504 (M^+), 493/491/489, 451/449/447.

Buckybowl 133 and Hydrocarbon 143. To a flask containing 0.139 g of **132** (0.274 mmol) and 0.022 g of dibromobis(triphenylphosphine)palladium (0.0274 mmol) under a nitrogen atmosphere were added via cannula 0.409 mL of DBU (2.74 mmol) in 10 mL of DMF. The resulting mixture was stirred vigorously at 150 °C for 72 h. The reaction mixture was then allowed to cool to room temperature before 20 mL of water, 10 mL of a 2 M HCl solution, and 40 mL of diethyl ether were introduced. The organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to provide 0.035 g of **133** (0.102 mmol, 37%) and 0.015 g of **143** (0.044 mmol, 16%) as yellow solids.

133: IR 1364, 1218 cm^{-1} ; ^1H δ 8.42 (1 H, d, $J = 8.4$ Hz), 8.30 (1 H, t, $J = 3.6$ Hz), 8.24 (1 H, d, $J = 7.8$ Hz), 8.01 (1 H, d, $J = 7.2$ Hz), 7.96 (1 H, d, $J = 7.2$ Hz), 7.65–7.58 (3 H, m), 7.55 (1 H, dd, $J = 8.4, 7.2$ Hz), 4.75 (2 H, s), 1.87 (9 H, s); ^{13}C δ 147.3, 145.1, 140.0, 139.2, 138.4, 137.4, 136.7, 135.0, 131.9, 130.6, 129.3, 129.1, 128.8, 128.1, 127.6, 126.5, 123.9, 123.1, 122.4, 122.0, 45.0, 38.5, 33.6; MS m/z 344 (M^+), 329, 313, 300; HRMS calcd for $\text{C}_{27}\text{H}_{20}$ 344.1565, found 344.1552. Recrystallization from a mixture of methylene chloride and ethanol produced a single crystal suitable for X-ray structure analysis. **143:** IR 1443, 1365 cm^{-1} ; ^1H δ 8.67 (1 H, d, $J = 7.8$ Hz), 8.55 (1 H, d, $J = 7.2$ Hz), 8.47 (1 H, d, $J = 8.4$ Hz), 7.96 (1 H, d, $J = 7.2$ Hz), 7.90 (1 H, d, $J = 7.2$ Hz), 7.62 (1 H, d, $J = 7.8$ Hz), 7.56 (1 H, dd, $J = 8.7, 6.9$ Hz), 7.51–7.37 (4 H,

m), 4.54 (2 H, s), 1.90 (9 H, s); ^{13}C δ 145.2, 142.7, 140.3, 140.2, 139.9, 139.7, 138.6, 137.3, 134.8, 128.0, 127.8, 127.3, 126.9, 126.6, 125.3, 124.5, 124.4, 124.2, 121.0, 118.1, 40.3, 39.0, 35.0; MS m/z 346 (M⁺), 331, 313, 289; HRMS calcd for C₂₇H₂₂ 346.1721, found 346.1720. The structure of **143** was tentative assigned based on the assumption that the first cyclopalladation reaction of **143** occurred preferentially with the naphthyl moiety of **143** producing a five-membered ring as reported previously.¹¹⁰ The resulting brominated fluoranthene intermediate could undergo either a second cyclopalladation reaction to produce **133** or a reductive debromination reaction to give **143**. Analysis of the crude reaction mixture by GC/MS before purification by silica gel chromatography also suggests the presence of small amount of **131**.

1-[[2-[(2,6-Dibromophenyl)ethynyl]phenyl]ethynyl]-1,2,3,4-tetrahydro-2,2-dimethyl-1-naphthalenol (145a). The same procedure was repeated as described for **138** except that 0.557 g (1.55 mmol) of **137** and 0.270 g (1.55 mmol) of **144a** were used to afford **145a** (0.572 g, 1.07 mmol, 69%) as a viscous yellow liquid: IR 3569, 1422 cm⁻¹; ^1H δ 8.01 (1 H, d, J = 7.7 Hz), 7.67–7.62 (1 H, m), 7.56 (2 H, d, J = 8.2 Hz) 7.54–7.50 (1 H, m), 7.36–7.32 (2 H, m), 7.18–6.99 (4 H, m), 2.90–2.75 (2 H, m), 2.45 (1 H, s), 2.11–1.95 (1 H, m), 1.78–1.65 (1 H, m), 1.24 (3 H, s), 1.17 (3 H, s); ^{13}C δ 138.5, 134.9, 132.5, 132.4, 131.2, 129.8, 128.9, 128.8, 128.6, 128.0, 127.8, 127.1, 126.6, 126.2, 125.3, 124.9, 97.0, 95.6, 90.6, 84.9, 75.2, 37.7, 31.1, 25.8, 23.8.

Benzannulated Eneidyne 146a. The same procedure was repeated as described for **139** except that 0.572 g (1.07 mmol) of **145a** was used to afford **146a** (0.493 g, 0.952 mmol, 89%)

as a viscous yellow liquid: IR 2220, 1422 cm^{-1} ; ^1H δ 7.70–7.62 (2 H, m), 7.56 (2 H, d, J = 8.2 Hz), 7.53–7.48 (1 H, m), 7.35–7.27 (2 H, m), 7.14–6.99 (4 H, m), 3.80 (1 H, s), 3.02–2.72 (2 H, m), 1.82 (1 H, ddd, J = 13.3, 6.2, 4.7 Hz), 1.60 (1 H, ddd, J = 13.4, 8.3, 6.4 Hz), 1.19 (3 H, s), 1.08 (3 H, s); ^{13}C δ 135.3, 134.9, 132.5, 132.4, 131.2, 129.7, 129.6, 128.62, 128.56, 127.4, 126.6, 126.5, 126.3, 125.8, 124.8, 97.5, 95.4, 90.3, 82.7, 44.7, 35.2, 33.3, 29.2, 26.2, 22.6.

7-(2,6-Dibromophenyl)-1,2,3,12-tetrahydro-1,1-dimethylindeno[2,1-*a*]phenalene (147a).

The same procedure was repeated as described for **132** except that 0.493 g (0.952 mmol) of **146a** was used to afford **147a** (0.326 g, 0.629 mmol, 66%) as a yellow solid: IR 1365, 1217 cm^{-1} ; ^1H δ 7.81 (2 H, d, J = 8.2 Hz), 7.56 (1 H, d, J = 7.4 Hz), 7.35–7.19 (5 H, m), 7.08 (1 H, t, J = 7.4 Hz), 6.38 (1 H, d, J = 7.9 Hz), 4.37 (2 H, s), 3.22 (2 H, t, J = 6.5 Hz), 2.07 (2 H, t, J = 6.4 Hz), 1.65 (6 H, s); ^{13}C δ 144.2, 140.9, 140.1, 140.0, 137.8, 136.7, 136.0, 132.4, 131.4, 130.7, 130.4, 129.2, 127.3, 126.9, 126.1, 125.0, 124.5, 124.3, 122.8, 122.1, 40.1 38.7, 36.1, 28.9, 28.1.

Buckybowl 148a and Hydrocarbon 149a. The same procedure was repeated as described for **133** and **143** except that 0.194 g (0.374 mmol) of **147a** was used to afford **148a** (0.056 g, 0.157 mmol, 42%) and **149a** (0.028 g, 0.078 mmol, 21%) as yellow solids. **23a**: IR 1363, 1217 cm^{-1} ; ^1H δ (600 MHz) 8.28 (1 H, d, J = 7.8 Hz), 8.20 (1 H, d, J = 7.2 Hz), 7.96 (1 H, d, J = 7.2 Hz), 7.89 (1 H, d, J = 7.2 Hz), 7.61–7.58 (3 H, m), 7.31 (1 H, d, J = 6.6 Hz), 4.60 (2 H, s), 3.20 (2 H, t, J = 6 Hz), 2.17 (2 H, t, J = 5.4 Hz), 1.53 (6 H, s); ^{13}C δ (600 MHz) 145.6, 144.6, 141.3, 140.4, 140.2, 138.7, 138.0, 137.2, 136.1, 135.3, 131.3, 131.0, 129.8, 129.5, 127.9, 127.4, 125.0, 123.3, 122.7, 122.5, 122.2, 41.8, 40.0, 35.5, 28.3, 25.9; MS m/z 356 (M^+), 341, 326; HRMS calcd for

C₂₈H₂₀ 356.1565, found 356.1562. Recrystallization from a mixture of methylene chloride and ethanol produced a single crystal suitable for X-ray structure analysis. **149a**: IR 1365, 1218 cm⁻¹; ¹H δ 8.70 (1 H, d, *J* = 7.7 Hz), 8.55 (1 H, d, *J* = 7.2 Hz), 7.97 (1 H, d, *J* = 6.7 Hz), 7.87 (1 H, d, *J* = 6.9 Hz), 7.67 (1 H, d, *J* = 7.2), 7.54 (1 H, t, *J* = 7.2 Hz), 7.48–7.34 (4 H, m), 4.37 (2 H, s), 3.21 (2 H, t, *J* = 6.2 Hz), 2.10 (2 H, t, *J* = 6.4 Hz), 1.62 (6 H, s); ¹³C δ 145.1, 140.6, 140.29, 140.25, 139.9, 139.2, 138.8, 136.7, 134.4, 133.1, 129.0, 127.9, 126.8, 126.6, 125.9, 124.9, 124.6, 124.5, 120.8, 118.9, 41.7, 38.5, 35.6, 28.2, 26.7; MS *m/z* 358 (M⁺), 343.

1-[[2-[(2,6-Dibromophenyl)ethynyl]phenyl]ethynyl]-2,3-dihydro-2,2-dimethyl-1*H*-inden-1-ol (145b). The same procedure was repeated as described for **138** except that 0.706 g (1.96 mmol) of **137** and 0.314 g (1.96 mmol) of **144b** were used to afford **145b** (0.661 g, 1.27 mmol, 65%) as a viscous yellow liquid: IR 3561, 1422 cm⁻¹; ¹H δ 7.68–7.58 (2 H, m), 7.55 (2 H, d, *J* = 8.2 Hz), 7.53–7.50 (1 H, m), 7.35–7.30 (2 H, m), 7.23–7.20 (2 H, m), 7.09 (1 H, t, *J* = 7.2 Hz), 7.01 (1 H, t, *J* = 7.9 Hz), 3.00 (1 H, d, *J* = 15.2 Hz), 2.65 (1 H, d, *J* = 15.1 Hz), 2.32 (1 H, s), 1.28 (3 H, s), 1.17 (3 H, s); ¹³C δ 145.3, 142.5, 132.6, 132.5, 131.2, 129.8, 128.7, 128.6, 128.1, 127.1, 126.6, 126.5, 125.2, 125.1, 124.9, 124.2, 97.0, 93.0, 90.8, 85.4, 81.7, 49.0, 44.4, 26.3, 21.4.

Benzannulated Eneidyne 146b. The same procedure was repeated as described for **139** except that 0.661 g (1.27 mmol) of **145b** was used to afford **146b** (0.570 g, 1.13 mmol, 89%) as a viscous yellow liquid: IR 1423, 1217 cm⁻¹; ¹H δ 7.67–7.63 (1 H, m), 7.55 (2 H, d, *J* = 8.2 Hz), 7.54–7.49 (1 H, m), 7.44 (1 H, d, *J* = 7.2 Hz), 7.35–7.27 (2 H, m), 7.18–7.06 (3 H, m), 7.01 (1 H, t, *J* = 8.2 Hz), 4.03 (1 H, s), 2.81 (1 H, d, *J* = 15.3 Hz), 2.71 (1 H, d, *J* = 15.3 Hz), 1.33 (3 H,

s), 1.11 (3 H, s); ^{13}C δ 142.9, 142.1, 132.6, 132.5, 131.2, 129.6, 128.6, 127.5, 127.4, 126.9, 126.6, 126.5, 126.4, 125.0, 124.8, 124.6, 97.5, 93.2, 90.5, 83.0, 49.2, 46.6, 45.7, 27.4, 24.3.

6-(2,6-Dibromophenyl)-2,11-dihydro-1,1-dimethyl-1*H*-indeno[1,7-*ab*]fluorine (147b).

The same procedure was repeated as described for **132** except that 0.570 g (1.13 mmol) of **146b** was used to afford **147b** (0.353 g, 0.70 mmol, 62%) as a yellow solid: IR 1423, 1217 cm^{-1} ; ^1H δ 7.82 (2 H, d, $J = 7.9$ Hz), 7.57 (1 H, d, $J = 7.3$ Hz), 7.41 (1 H, t, $J = 7.2$ Hz), 7.32–7.24 (3 H, m), 7.14–7.08 (2 H, m), 6.56 (1 H, d, $J = 7.9$ Hz), 4.20 (2 H, s), 3.38 (2 H, s), 1.67 (6 H, s); ^{13}C δ 148.3, 144.3, 143.3, 141.0, 140.0, 136.8, 133.0, 132.3, 130.4, 129.0, 128.2, 127.7, 127.2, 127.0, 126.0, 125.3, 125.1, 122.2, 120.0, 119.4, 48.5, 44.5, 33.9, 28.1.

Buckybowl 148b and Hydrocarbon 149b. The same procedure was repeated as described for **133** and **143** except that 0.205 g (0.407 mmol) of **147b** was used to afford **148b** (0.015 g, 0.045 mmol, 11%) and **149b** (0.032 g, 0.094 mmol, 23%) as yellow solids. **148b**: IR 1365, 1217 cm^{-1} ; ^1H δ 8.24 (1 H, dd, $J = 6.6, 2.5$ Hz), 8.15 (1 H, d, $J = 7.8$ Hz), 7.90 (1 H, d, $J = 7.2$ Hz), 7.79 (1 H, d, $J = 7.8$ Hz), 7.59–7.50 (3 H, m), 7.20 (1 H, d, $J = 7.2$ Hz), 4.41 (2 H, s), 3.29 (2 H, s), 1.63 (6 H, s); ^{13}C δ 154.4, 147.6, 145.5, 145.3, 142.7, 141.2, 140.4, 139.5, 139.2, 138.5, 136.7, 135.8, 131.9, 130.5, 127.7, 127.1, 125.5, 123.0, 122.3, 122.2, 121.9, 49.6, 47.3, 38.2, 29.1; MS m/z 342 (M^+), 327, 312; HRMS calcd for $\text{C}_{27}\text{H}_{18}$ 342.1409, found 342.1411.

Recrystallization from a mixture of methylene chloride and ethanol produced a single crystal suitable for X-ray structure analysis.

149b: IR 1448, 1365, 1217 cm^{-1} ; ^1H δ 8.68 (1 H, d, $J = 7.8$ Hz), 8.54 (1 H, d, $J = 10.2$ Hz), 8.03 (1 H, d, $J = 7.2$ Hz), 7.96 (1 H, d, $J = 7.2$ Hz), 7.70–7.40 (6 H, m), 4.24 (2 H, s), 3.47 (2 H, s), 1.68 (6 H, s); MS m/z 344 (M^+), 329.

Propargylic diols 159. To a solution of 1-ethynyl-2-iodo-benzene (4.10 g, 0.0180 mol) in 150 mL THF under a nitrogen atmosphere was added 10.8 mL of a 2.0 M solution of LDA in THF/heptane/ethylbenzene (0.0216 mol) at 0 °C. After 30 min, a solution of diketone (**154**, 2.22 g, 9.00 mmol) in 30 mL THF was added via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 12 h of stirring at room temperature, the reaction mixture was quenched with 50 mL of distilled water. THF layer was separated and water layer was extracted with diethyl ether twice. Organic layers were combined, dried over sodium sulfate, and concentrated until 20 mL of dark sticky black residue remain. This residue could not be purified by flash column chromatography due to its low solubility. When 50 mL of THF and 200 mL of hexanes were added to the black residue, a yellow solid was formed. This yellow solid **159** was collected by filtration. Filtrate and a dark black solid remained on the surface of glassware were combined, and concentrated to dryness. To this dry residue were added 50 mL of THF and 200 mL of hexane. After 12 h in the ice bath, a pale yellow solid was formed on the surface of glassware. This pale yellow solid **159** was also collected and combined with yellow solid: IR 3460, 2955, 2208 cm^{-1} ; ^1H NMR δ 7.86–7.84 (2 H, d, $J = 7.2$), 7.71 (4 H, s), 7.47 (2 H, dd, $J = 7.8$ and 1.5), 7.30 (2 H, t, $J = 7.4$), 7.01 (2 H, td, $J = 7.9$ and 1.5), 2.43 (2H, s), 1.12 (18 H, s); ^{13}C NMR δ 140.9, 138.7, 133.1, 129.5, 127.7, 126.6, 100.3, 96.0, 87.6, 79.5, 39.9, 25.6.

Diiodide 160. To a flask containing dry pale yellow solid **159** were added 100 mL of methylene chloride, 3.19 g of triethylsilane (27.0 mmol), and 5.35 mL of trifluoroacetic acid (8.21 g, 72.0 mmol). After 24 h of stirring at room temperature, a solution of 4.46 g of sodium carbonate (36.0 mmol) in 100 mL of water was introduced, and extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate, and concentrated. To the concentrated residue was added 50 mL of diethyl ether. White solid was formed and collected by filtration. Collected solid **160** was washed with diethyl ether twice. Combined filtrate was concentrated, and purified by flash column chromatography (silica gel/40% diethyl ether in hexanes). White solid and column-purified product were combined to afford 1.88 g of **160** (7.65 mmol, 85%): IR 2955, 2353 cm^{-1} ; ^1H NMR δ 7.84 (2 H, d, $J = 7.9$), 7.44 (2H, dd, $J = 7.7$ and 1.5), 7.39 (4H, s), 7.27 (2H, t, $J = 7.4$), 6.96 (2H, t, $J = 7.7$), 3.68 (2 H, s), 1.08 (18 H, s); ^{13}C NMR δ 137.4, 132.5, 132.0, 129.0, 128.4, 127.2, 124.5, 95.9, 82.8, 82.0, 80.7, 50.2, 35.5, 27.8.

Tetraacetylenic Hydrocarbon 162. To a flask containing 2.48 g of diacetylenic hydrocarbon (**160**, 3.70 mmol) were added 0.260 g of dichlorobis(triphenylphosphine)palladium (7.40 mmol), 0.473 g of CuI (2.48 mmol), and 100 mL of triethylamine. After 30 min of nitrogen flush, a solution of 1.47 g of 4-ethynylanisole (**161**, 11.1 mmol) in 10 mL of triethylamine was added. The resulting mixture was heated at 60 °C for 12 h under a nitrogen atmosphere. After heating, the reaction mixture was allowed to cool to room temperature and was filtered to remove solid particles. Rinse the solid particles with 100 mL of diethyl ether. The combined filtrate was concentrated and was purified by flash column chromatography (silica gel/40%

diethyl ether in hexanes). This dark sticky product **162** contained byproduct, 1,4-di(*p*-anisol)butadiyne which could not be separated on silica gel column chromatography.

4,5-Di(4-methoxyphenyl)phenanthrene 163. To a solution of **162** in 50 mL of anhydrous toluene under a nitrogen atmosphere was added 5.00 mL of a 1.0 M solution of potassium *t*-butoxide (5.00 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 12 h. After the reaction mixture was allowed to cool to room temperature, 50 mL of water and 50 mL of diethyl ether were introduced, and then the organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 1.01 g of **163** (1.55 mmol, 42%) as a yellow solid: ^1H NMR δ 7.81 (2 H, s), 7.40 (2 H, d, $J = 7.7$ Hz), 7.06 (2 H, t, $J = 7.4$ Hz), 6.78 (2 H, t, $J = 7.7$ Hz), 6.58 (4 H, d, $J = 8.9$ Hz), 6.45 (4 H, d, $J = 8.7$ Hz), 6.34 (2 H, d, $J = 8.2$ Hz), 4.38 (2 H, d, $J = 22$ Hz), 4.14 (2 H, d, $J = 22$ Hz), 3.79 (6 H, s), 1.80 (18 H, s); ^{13}C NMR δ 158.4, 144.2, 141.2, 139.0, 138.8, 137.2, 134.6, 131.9, 131.8, 131.7, 126.0, 125.3, 123.7, 122.8, 122.0, 55.1, 37.8, 33.4; Recrystallization of **163** from CH_2Cl_2 /ethanol produced a crystal suitable for X-ray structure analysis.

4,5-Diphenolicphenanthrene 164. To a solution of 4,5-diarylphenanthrene **163** (2.55 g, 3.76 mmol) in dry CH_2Cl_2 kept in -78°C was added 11.3 mL of boron tribromide (1.0 M) under stirring. After stirring for 1 h at -78°C , the solution was allowed to reach 0°C and stirred for 4 h. The resulting solution was warmed to room temperature and stirred for 2 more hours. The solution was cooled to 0°C again and transferred via cannula to the stirring saturated sodium bicarbonate solution at 0°C . The reaction mixture was thoroughly extracted with diethyl ether.

The combined extracts were dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/ from 20% diethyl ether in hexanes to 80% diethyl ether in hexanes) afforded 1.01 g of **164** (1.96 mmol, 52%) as a yellow solid. This compound was not stable on standing: ^1H NMR δ 7.80 (2 H, s), 7.39 (2 H, d, $J = 7.2$ Hz), 7.06 (2 H, t, $J = 7.2$ Hz), 6.78 (2 H, t, $J = 7.4$ Hz), 6.54-6.37 (10 H, m), 5.00 (2 H, s), 4.38 (2 H, d, $J = 21$ Hz), 4.14 (2 H, d, $J = 21$ Hz), 1.80 (18 H, s); This compound decomposed easily, which resulted in line broadening in NMR spectra.

Camphorsulfonate 175. To a solution of 0.532 g of **164** (0.776 mmol) in 30 mL of dry dichloromethane at 0 °C were added dry triethylamine (2.33 mmol), and 0.502 g of (1*S*)-camphor-10-sulfonyl chloride (2.00 mmol). The mixture was warmed to room temperature and stirred for 3 h. 50 mL of water was added, and the reaction mixture was extracted with dichloromethane. The combined extracts were washed with saturated NaCl solution, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/40% diethyl ether in hexanes) afforded 0.535 g of **175** (1.96 mmol, 62%) as a yellow solid. In order to separate diastereomeric (*S*)-camphorsulfonates **175**, 50 cm of long silica gel column was prepared, and 30% diethyl ether in hexanes was used as eluent to give diastereomerically pure **P-175** and **M-175**.

Separated diastereomer **P-175** or **M-175**: ^1H NMR δ 7.84 (2 H, s), 7.38 (2 H, d, $J = 7.2$ Hz), 7.09-7.02 (6 H, m), 6.74 (2 H, t, $J = 8.4$ Hz), 6.63 (4 H, d, $J = 8.7$ Hz), 6.07 (2 H, d, $J = 7.7$ Hz), 4.41 (2 H, d, $J = 21$ Hz), 4.14 (2 H, d, $J = 21$ Hz), 3.86 (2 H, d, $J = 15$ Hz), 3.21 (2 H, d, $J = 15$ Hz), 2.53-2.32 (4 H, m), 2.10-2.04 (4 H, m), 1.94 (2 H, d, $J = 19$ Hz), 1.81 (18 H, s), 1.75-1.69

(2H, m), 1.46-1.40 (2H, m), 1.07 (6 H, s), 0.77 (6 H, s); ^{13}C NMR δ 214.0, 148.2, 144.2, 140.6, 140.2, 139.8, 138.4, 137.6, 133.3, 131.9, 130.7, 126.3, 125.5, 123.8, 122.8, 122.0, 58.1, 47.8, 47.6, 42.7, 42.4, 39.9, 37.8, 33.3, 33.1, 26.8, 25.0, 19.8, 19.4.

Separated diastereomer **M-175** or **P-175**: ^1H NMR δ 7.84 (2 H, s), 7.38 (2 H, d, $J = 7.4$ Hz), 7.07-7.02 (6 H, m), 6.75 (2 H, t, $J = 7.2$ Hz), 6.61 (4 H, d, $J = 8.7$ Hz), 6.14 (2 H, d, $J = 8.4$ Hz), 4.43 (2 H, d, $J = 21$ Hz), 4.14 (2 H, d, $J = 21$ Hz), 3.77 (2 H, d, $J = 15$ Hz), 3.21 (2 H, d, $J = 15$ Hz), 2.49-2.32 (4 H, m), 2.14-2.07 (4 H, m), 1.89 (2 H, d, $J = 19$ Hz), 1.81 (18 H, s), 1.75-1.66 (2H, m), 1.51-1.39 (2H, m), 1.15 (6 H, s), 0.86 (6 H, s); ^{13}C NMR δ 214.0, 148.2, 144.4, 140.5, 140.2, 139.8, 138.3, 137.4, 133.2, 131.9, 130.9, 126.3, 125.5, 123.8, 122.8, 122.1, 58.1, 47.7, 47.4, 42.9, 42.3, 39.9, 37.8, 33.3, 28.9, 26.8, 24.9, 19.9, 19.5.

Hydrolyzed 4,5-diphenolicphenanthrene 164. To a 0.226 g of **175** (0.209 mmol) in methanol (20 mL) was added an aqueous solution of sodium hydroxide (2 M, 5 mL). The resulting mixture was stirred at 60 °C until TLC indicated the completion of hydrolysis. After the solution was cooled to room temperature, solvent was evaporated. The residue was extracted with dichloromethane, and evaporated to give the optically pure parent **164** as a yellow solid. Purification by flash column chromatography (silica gel/50% diethyl ether in hexanes) afforded 0.0558 g of **164** (0.0857 mmol, 41%).

Methylated 4,5-di(4-methoxyphenyl)phenanthrene 176. To a flask containing 0.327 g of **163** (0.482 mmol) in 30 mL of dry THF was added 1.50 mL of a 1.0 M solution of potassium *t*-butoxide (1.50 mmol) in 2-methyl-2-propanol. The color of the reaction mixture turned to black. After 30 min's stirring, 0.60 g of iodomethane (4.14 mmol) was introduced via syringe,

and the reaction mixture was stirred for 24 h. The color of the reaction mixture turned to white, which indicated the completion of this reaction. After 20 mL of water and 40 mL of diethyl ether were introduced, organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography to afford 0.298 g of **176** (0.439 mmol, 91%) as a yellow solid (silica gel/20% diethyl ether in hexanes): ^1H NMR δ 7.97 (2 H, s), 7.32 (2 H, d, $J = 7.4$ Hz), 7.04 (2 H, t, $J = 7.4$ Hz), 6.76 (2 H, t, $J = 7.9$ Hz), 6.53-6.43 (10 H, m), 4.71 (2 H, q, $J = 6.7$ Hz), 3.74 (6 H, s), 1.87 (18 H, s), 1.59 (6 H, d, 6.7 Hz); ^{13}C NMR δ 158.6, 151.1, 147.1, 139.4, 137.5, 135.0, 134.9, 134.0, 133.9, 131.3, 131.0, 126.0, 125.3, 123.1, 122.9, 122.4, 112.5, 55.1, 44.2, 38.1, 34.5, 27.2; Recrystallization of **176** from CH_2Cl_2 /ethanol produced a crystal suitable for X-ray structure analysis.

Methylated 4,5-diphenolicphenanthrene 177. The same procedure was repeated as described for **164** except that 0.109 g of methylated 4,5-di(4-methoxyphenyl)phenanthrene **176** (0.154 mmol) was treated with 0.326 mL of 1 M boron tribromide to afford 0.0506 g of **177** (0.074 mmol, 48%) as a yellow solid: ^1H NMR δ 7.97 (2 H, s), 7.32 (2 H, d, $J = 7.2$ Hz), 7.04 (2 H, t, $J = 7.4$ Hz), 6.77 (2 H, t, $J = 7.9$ Hz), 6.61-6.43 (10 H, m), 4.71 (2 H, q, 6.7 Hz), 4.55 (2 H, s), 1.86 (18 H, s), 1.59 (6 H, d, 6.7 Hz); ^{13}C NMR δ 154.5, 151.0, 147.1, 139.3, 137.6, 135.0, 134.8, 134.1, 133.9, 131.6, 131.0, 126.1, 125.3, 123.1, 122.9, 122.4, 114.1, 44.2, 38.1, 34.5, 27.2.

4,5-Di(3-methoxyphenyl)phenanthrene 195. The same procedure was repeated as described for **163** except that 6.34 g of diiodide **160** (9.45 mmol) and 3.75 g of 3-ethynylanisole (**192**) (28.4 mmol) were treated with 0.66 g of dichlorobis(triphenylphosphine) palladium (0.94

mmol) and 0.33 g of CuI (1.73 mmol), and 100 mL of triethylamine. For cyclization step, 14.0 mL of a 1.0 M solution of potassium *t*-butoxide (14.0 mmol) in 2-methyl-2-propanol was used. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 3.02 g of **195** (1.55 mmol, 37%) as a yellow solid.

Methylated 4,5-di(3-methoxyphenyl)phenanthrene 196. Methylation step was repeated as described for **176** except that 1.48 g of **195** (2.18 mmol), 5.0 mL of a 1.0 M solution of potassium *t*-butoxide (5.00 mmol) in 2-methyl-2-propanol, and 1.20 g of iodomethane (8.28 mmol) were introduced in sequence to furnish 0.298 g of **196** (0.439 mmol, 91%) as a yellow solid (silica gel/20% diethyl ether in hexanes): ^1H NMR δ 7.97 (2 H, s), 7.32 (2 H, d, $J = 7.4$ Hz), 7.04 (2 H, t, $J = 7.4$ Hz), 6.76 (2 H, t, $J = 7.9$ Hz), 6.53-6.43 (10 H, m), 4.71 (2 H, q, $J = 6.7$ Hz), 3.74 (6 H, s), 1.87 (18 H, s), 1.59 (6 H, d, 6.7 Hz); ^{13}C NMR δ 158.4, 151.1, 147.0, 139.4, 139.0, 138.0, 135.5, 134.9, 134.0, 131.1, 128.0, 126.2, 125.6, 125.3, 123.4, 122.5, 122.4, 116.5, 144.0, 54.7, 44.2, 38.1, 34.5, 27.2.

4,5-Di(2-methoxyphenyl)phenanthrene 198. The same procedure was repeated as described for **163** except that 2.88 g of diiodide **160** (4.30 mmol) and 1.70 g of 2-ethynylanisole (12.9 mmol) were treated with 0.33 g of dichlorobis(triphenylphosphine)palladium (0.47 mmol) and 0.17 g of CuI (0.87 mmol), and 100 mL of triethylamine. For cyclization step, 13.0 mL of a 1.0 M solution of potassium *t*-butoxide (13.0 mmol) in 2-methyl-2-propanol was used. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 1.08 g of **198** (1.59 mmol, 37%) as a yellow solid. Generated three isomers could not be separated on silica gel column chromatography: ^1H NMR δ 7.81, 7.80 (2 H, s, s), 7.37, 7.36

(2 H, d, d, $J = 7.4$ Hz), 7.24–7.11 (2 H, m), 7.07–6.99 (2 H, m), 6.83–6.68 (2 H, m), 6.67–6.50 (4 H, m), 6.47–6.40 (2 H, m), 6.26, 6.09, 6.04, 5.75 (2 H, d, d, d, d, $J = 8.2$ Hz), 4.37, 4.34 (2 H, d, d, $J = 21$ Hz), 4.12, 4.11, 4.09 (2H, d, d, d, $J = 21$ Hz), 3.12, 3.09, 3.07 (6 H, s, s, s), 1.82, 1.80, 1.78 (18 H, s, s, s); ^{13}C NMR δ 159.1, 156.1, 155.3, 144.2, 144.1, 143.3, 142.2, 141.5, 141.4, 139.4, 139.1, 139.0, 138.9, 138.7, 138.5, 137.7, 137.2, 136.8, 136.1, 135.2, 134.6, 134.0, 133.2, 132.2, 131.9, 131.3, 131.2, 131.0, 130.4, 130.0, 129.0, 128.7, 128.2, 128.1, 128.0, 127.2, 125.7, 125.3, 123.5, 123.3, 123.2, 122.2, 122.0, 121.8, 121.7, 121.1, 120.9, 119.5, 111.0, 110.5, 110.3, 54.8, 54.6, 54.0, 39.9, 39.8, 37.9, 37.8, 37.7, 33.6, 33.5, 33.4.

4,5-Di(4-aminophenyl)phenanthrene 201. The same procedure was repeated as described for **162** except that 6.22 g of **160** (9.28 mmol) and 2.18 g of 4-ethynylaniline **199** (18.6 mmol) were treated with 0.66 g of dichlorobis(triphenylphosphine)palladium (0.94 mmol) and 0.33 g of CuI (1.74 mmol), and 100 mL of triethylamine. For cyclization step, 23.0 mL of a 1.0 M solution of potassium *t*-butoxide (23.0 mmol) in 2-methyl-2-propanol was used. Purification by flash column chromatography (silica gel/50% diethyl ether in hexanes to 100% ether) afforded 1.32 g of **201** (1.59 mmol, 22%) as a yellow solid: IR 3368, 2949, 2214 cm^{-1} ; ^1H NMR δ 7.80 (2 H, s), 7.40 (2 H, d, $J = 7.2$ Hz), 7.07 (2 H, t, $J = 7.2$ Hz), 6.82 (2 H, t, $J = 7.4$ Hz), 6.56 (2 H, d, $J = 7.9$ Hz), 6.41 (8 H, s), 4.38 (2 H, d, $J = 21$ Hz), 4.15 (2 H, d, $J = 21$ Hz), 3.80 (4 H, s), 1.81 (18 H, s); ^{13}C NMR δ 144.8, 144.1, 141.5, 139.1, 138.7, 137.0, 135.4, 131.7, 129.7, 125.8, 125.3, 123.5, 123.8, 123.1, 114.8, 37.7, 33.4, 33.3.

Sulfonamide 202. The same procedure was repeated as described for **175** except that 1.22 g of **201** (1.87 mmol) was treated with dry triethylamine (5.61 mmol) and 1.20 g of

(1*S*)-camphor-10-sulfonyl chloride (5.61 mmol) to afford 1.86 g of **202** (1.68 mmol, 90%) as a yellow solid. The same separation method was employed to give diastereomerically pure **M-202** and **P-202** except for the use of 40% diethyl ether in hexanes as eluent.

Diastereomer **P-202** or **M-202**: ^1H NMR δ 7.85 (2 H, s), 7.33 (2 H, d, $J = 7.4$ Hz), 7.17 (4 H, d, $J = 8.7$ Hz), 7.02 (2 H, t, $J = 7.4$ Hz), 6.80 (2 H, t, $J = 7.7$ Hz), 6.72 (2 H, d, $J = 7.2$ Hz), 6.62 (2 H, d, $J = 7.2$ Hz), 6.29 (2 H, d, $J = 8.2$ Hz), 4.45 (2 H, d, $J = 21$ Hz), 4.12 (2 H, d, $J = 21$ Hz), 4.00-3.62 (4 H, m), 2.46-2.22 (4 H, m), 2.14-1.95 (4 H, m), 1.83 (18 H, s), 1.40-1.38 (2 H, m), 1.25-1.24 (2 H, m), 1.50-1.32 (2 H, m), 1.15 (6 H, s), 0.90 (6 H, s); ^{13}C NMR δ 219.0, 144.5, 140.9, 140.3, 140.1, 140.0, 137.1, 135.6, 133.5, 132.3, 131.8, 131.3, 131.1, 130.2, 126.2, 125.7, 123.4, 123.1, 122.1, 59.1, 58.9, 53.0, 52.2, 47.9, 47.4, 42.9, 42.7, 42.4, 42.3, 39.8, 37.9, 33.4, 26.9, 25.1, 20.3, 20.1, 19.7.

Diastereomer **P-202** or **M-202**: ^1H NMR δ 7.86 (2 H, s), 7.54 (2 H, d, $J = 8.9$ Hz), 7.17 (4 H, d, $J = 7.2$ Hz), 7.20 (2 H, d, $J = 7.9$ Hz), 6.99 (2 H, t, $J = 7.7$ Hz), 6.73-6.68 (6 H, m), 6.02 (2 H, d, $J = 8.2$ Hz), 4.38 (2 H, d, $J = 21$ Hz), 4.20-4.09 (4 H, m), 3.76 (2 H, d, $J = 14$ Hz), 3.60 (2 H, d, $J = 15$ Hz), 2.50-2.31 (4 H, m), 2.13-1.86 (4 H, m), 1.81 (18 H, s), 1.96-1.86 (2 H, m), 1.69-1.62 (2 H, m), 1.40-1.29 (2 H, m), 1.14 (6 H, s), 0.88 (6 H, s); ^{13}C NMR δ 219.0, 144.5, 140.9, 140.3, 140.1, 140.0, 137.1, 135.6, 133.5, 132.3, 131.8, 131.3, 131.1, 130.2, 126.2, 125.7, 123.4, 123.1, 122.1, 59.0, 58.9, 53.0, 52.3, 47.9, 47.4, 42.9, 42.7, 42.4, 42.3, 39.8, 37.9, 33.4, 26.9, 25.1, 20.4, 20.2, 19.7.

2-(1,3-Dimethoxypropyl)-1,3-indandione (234). In an ordinary glassware equipped with a magnetic stirring bar, 15 mL of DMSO was added to 1.70 g of 1,3-dimethoxyacetone (15.0

mmol), 2.19 g of 1,3-indandione (15.0 mmol) and 3.81 g of Hantzsch ester (15.0 mmol). 0.35 g of L-proline (3.00 mmol) was then added and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was directly loaded onto a silica gel column without work-up, and 3.05 g of yellowish green liquid (12.3 mmol, 82%) was obtained by silica gel column chromatography (silica gel/20% diethyl ether in hexanes, R_f = 0.48 (hexanes:diethyl ether = 4:6)): IR 2928, 2354, 1709 cm^{-1} ; ^1H NMR δ 7.96-7.77 (m, 4 H, indanyl aromatic H), 3.48 (4 H, d, J = 7.2 Hz), 3.14 (1 H, d, J = 2.7 Hz), 3.09 (6 H, s), 3.03 (1 H, m); ^{13}C NMR δ 199.8, 142.3, 134.9, 122.7, 71.0, 58.5, 52.1, 39.6; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4$ (MH^+) 249.11214, found 249.11213.

2-Methyl-2-(1,3-dimethoxypropyl)-1,3-indandione (232). To a flask containing 2.08 g of **234** (8.39 mmol) in 20 mL of THF under a nitrogen atmosphere was added 16.0 mL of 1.0 M solution of potassium *t*-butoxide (16.0 mmol) in 2-methyl-2-propanol. After 30 min of stirring, 4.64 g of iodomethane (32.0 mmol) was introduced via syringe, and the reaction mixture was stirred for 48 h. 20 mL of water and 40 mL of diethyl ether were introduced, and organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (15% diethyl ether in hexanes, R_f = 0.41 (hexanes:diethyl ether = 4:6)) to furnish 1.72 g of yellowish green liquid (6.54 mmol, 78%): IR 2925, 2340, 1706 cm^{-1} ; ^1H NMR δ 7.97 – 7.79 (m, 4 H, indanyl aromatic H), 3.55 (2 H, dd, J = 9.9 and 5.4 Hz), 3.43 (2 H, dd, J = 9.8 and 6.7 Hz), 3.01 (6 H, s), 2.53 (1 H, m), 1.32 (3 H, s); ^{13}C NMR δ 203.3, 140.9, 135.1, 123.0, 70.1, 58.4, 53.3, 44.7, 18.5; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$ (MH^+) 263.12779, found 263.12773.

Propargylic diols 235. To a flask containing 4.11 g of 1-(2-ethynylphenyl)-2-phenylethyne (20.0 mmol) in 50 mL of THF under a nitrogen atmosphere at 0 °C was added 12.5 mL of 1.6 M solution of *n*-butyl lithium. After 30 min of stirring, a solution of 1.49 g of **232** (5.69 mmol) in 20 mL of THF was introduced via cannula, and the reaction mixture was allowed to cool to room temperature. After additional 5 h, 50 mL of water was added, and then the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/70% diethyl ether in hexanes, R_f = 0.37 (hexanes:diethyl ether = 4:6) to furnish 3.54 g of sticky brown liquid (5.29 mmol, 93%): IR 3493, 2927, 2355 cm^{-1} ; ^1H NMR δ 7.75 (1 H, d, J = 7.4 Hz), 7.60-7.38 (6 H, m), 7.35-7.18 (15 H, m), 5.09 (1 H, s), 4.81 (1 H, s), 4.13 (1 H, dd, J = 9.5 and 5.7 Hz), 3.59-3.50 (2 H, m), 3.39 (3 H, s), 3.31 (3 H, s), 3.33-3.29 (2 H, m), 1.15 (3 H, s); ^{13}C NMR δ 143.7, 142.6, 132.2, 132.2, 132.0, 131.8, 131.7, 129.8, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 125.6, 125.2, 125.2, 123.7, 123.1, 122.9, 96.1, 94.2, 93.1, 93.0, 88.2, 88.1, 87.7, 84.5, 81.0, 79.4, 72.0, 61.1, 59.0, 58.3, 40.6, 15.0; HRMS calcd for $\text{C}_{47}\text{H}_{38}\text{O}_4$ (MH^+) 667.28429, found 667.28676.

Dimethoxy compound 236. To 1.20 g of *trans*-diol **235** (1.80 mmol) in 50 mL of THF at 0 °C was added via cannula a solution of thionyl chloride (1.04 g, 8.74 mmol) and anhydrous pyridine (1.38 g, 17.4 mmol) in 20 mL of THF. The reaction mixture was allowed to warm to room temperature. After an additional 8 h, reaction mixture was cooled down to 0 °C, and transferred via cannula to 50 mL of stirring ice water. The reaction mixture was extracted with 50 mL of benzene. The combined organic extracts were washed with water, dried over sodium

sulfate, and concentrated to furnish the crude dichloride. To a flask containing AIBN (0.0327 g, 0.200 mmol) were added the crude in 40 mL of benzene and tributyltin hydride (1.51 mL, 5.30 mmol). The reaction mixture was heated under reflux for 18 h under oxygen free condition. After the reaction mixture was allowed to cool to room temperature, 30 mL of a 10% aqueous potassium fluoride solution was introduced. The mixture was stirred for an additional 5 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/30% diethyl ether in hexanes, R_f = 0.58 (hexanes: diethyl ether = 4:6)) to afford 0.46 g of **236** (0.72 mmol, 40%) as a yellow solid of which the solubility in diethyl ether was quite low: IR 3059, 2927, 2345 cm^{-1} ; ^1H NMR δ 7.64-7.54 (10 H, m), 7.46-7.43 (2 H, m), 7.39 (2 H, s), 7.26 (2 H, t, J = 7.2 Hz), 7.07 (2 H, t, J = 7.4 Hz), 6.70 (2 H, d, J = 7.9 Hz), 4.36 (2 H, d, J = 23.0 Hz), 4.30 (2 H, d, J = 23.2 Hz), 3.56 (2 H, dd, J = 4.7 and 5.2 Hz), 3.38 (2 H, dd, J = 6.7 and 9.5 Hz), 3.25 (1 H, m), 3.21 (6 H, s), 2.05 (3 H, s); ^{13}C NMR δ 144.6, 143.7, 141.9, 139.3, 138.6, 135.5, 135.5, 132.1, 130.1, 130.1, 128.9, 127.7, 126.9, 126.5, 126.5, 126.5, 124.8, 123.6, 123.4, 72.4, 58.7, 56.6, 46.3, 35.3, 20.2; HRMS calcd for $\text{C}_{47}\text{H}_{38}\text{O}_2$ (MH^+) 634.28720, found 634.28603.

Dibromide 231. To a flask containing **236** (0.15 g, 0.24 mmol) in 50 mL of dry CH_2Cl_2 kept in -78°C was added 0.58 mL of boron tribromide (1.0 M). After stirring for 5 h at -78°C , the solution was allowed to reach 0°C and stirring for 8 h. The resulting solution was warmed to room temperature and stirred for more than 2 h. The solution was cooled to 0°C again and transferred via cannula to the stirring saturated sodium bicarbonate solution at 0°C . The

reaction mixture was thoroughly extracted with diethyl ether. The combined extracts were dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/from 50% diethyl ether in hexanes to 100% acetone) afforded a yellow sticky liquid **237**. To a flask containing alcohol **237** were added 0.19 g of triphenylphosphine (0.72 mmol), 0.24 g of carbon tetrabromide (0.72 mmol), and 30 mL of dry dichloromethane. The reaction mixture was stirred at room temperature for 48 h. After the reaction mixture was concentrated, the residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes, R_f = 0.75 (hexanes:diethyl ether = 6.5:3.5)) to afford 0.060 g of **231** (0.082 mmol, 34%) as a yellow solid: IR 3057, 2926, 2247 cm^{-1} ; ^1H NMR δ 7.64-7.56 (10 H, m), 7.43-7.41 (2 H, m), 7.39 (2 H, s), 7.26 (2 H, t, J = 7.4 Hz), 7.06 (2 H, t, J = 7.4 Hz), 6.70 (2 H, d, J = 7.9 Hz), 4.34 (2 H, d, J = 21.0 Hz), 4.24 (2 H, d, J = 22.0 Hz), 3.93-3.90 (2 H, m), 3.58-3.56 (3 H, m), 2.13 (3 H, s); ^{13}C NMR δ 143.1, 142.6, 141.7, 139.6, 138.3, 135.5, 132.9, 130.1, 129.9, 129.0, 129.0, 127.8, 127.2, 126.8, 126.7, 124.8, 123.9, 123.6, 58.3, 50.6, 35.4, 33.2, 20.7; HRMS calcd for $\text{C}_{45}\text{H}_{32}\text{Br}_2$ 759.05288, found 759.05558.

2-Tetrahydropyranyl-1,3-indandione (244). The same procedure was repeated as described for **234** except 0.50 g of tetrahydro-4H-pyran-4-one (5.00 mmol), 0.73 g of 1,3-Indandione (5.00 mmol), 1.27 g of Hantzsch ester (5.00 mmol), and 0.12 g of L-proline (1.00 mmol) were used to furnish **244**. 0.921 g of yellow solid product (4.00 mmol, 80%) was obtained by silica gel column chromatography (20% diethyl ether in hexanes, R_f = 0.43 (hexanes:diethyl ether = 4:6)): IR 2956, 2105, 1705 cm^{-1} ; ^1H NMR δ 7.99-7.83 (m, 4 H, indanyl aromatic H), 3.94 (2 H, dd, J = 7.2 and 3.7 Hz), 3.36 (2 H, td, J = 11.9 and 2.0 Hz), 2.90 (1 H, d, J = 3.9 Hz), 2.51-2.40

(1 H, m), 1.92-1.77 (2 H, m), 1.51-1.46 (2 H, d, $J = 12.6$ Hz); ^{13}C NMR δ 200.4, 142.7, 135.7, 123.0, 67.9, 57.5, 36.1, 29.5; HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$ (MH^+) 231.10157, found 231.10158.

2-Methyl-2-tetrahydropyranyl-1,3-indandione (245). The same procedure was repeated as described for **232** except that 0.16 g (0.69 mmol) of **244** in 20 mL of THF, 1.40 mL of a 1.0 M solution of potassium *t*-butoxide (1.40 mmol) in 2-methyl-2-propanol, and 0.20 g of iodomethane (1.38 mmol) were used to furnish **245**. The residue was purified by flash column chromatography (silica gel/15% diethyl ether in hexanes, $R_f = 0.57$ (hexanes:diethyl ether = 4:6)) to give 0.13 g of yellow solid product (0.54 mmol, 78%): IR 2933, 2338, 1703 cm^{-1} ; ^1H NMR δ 7.98-7.83 (m, 4 H, indanyl aromatic H), 3.92 (2 H, dd, $J = 10.9$ and 4.0 Hz), 3.29 (2 H, td, $J = 11.9$ and 2.5 Hz), 2.15-2.03 (1 H, m), 1.64-1.43 (4 H, m), 1.28 (3 H, s); ^{13}C NMR δ 204.2, 141.4, 135.8, 123.0, 67.9, 55.8, 41.0, 27.8, 16.4; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ (MH^+) 245.11722, found 245.11726.

Propargylic diols 246. The same procedure was repeated as described for **235** except that 1.12 g of 1-(2-ethynylphenyl)-2-phenylethyne (5.60 mmol) in 50 mL of THF, 3.50 mL of 1.6 M solution of *n*-butyl lithium, and 0.35 g of **245** (1.43 mmol) in 20 mL of THF were used to furnish **246**. The residue was purified by flash column chromatography (silica gel/70% diethyl ether in hexanes, $R_f = 0.40$ (hexanes:diethyl ether = 4:6) to give 0.825 g of **246** (1.27 mmol, 89%): IR 3343, 2956, 2248 cm^{-1} ; ^1H NMR δ 7.73 (1 H, d, $J = 7.4$ Hz), 7.58-7.50 (4 H, m), 7.43-7.23 (16 H, m), 7.15 (1 H, td, $J = 7.4$ and 1.0 Hz), 3.92 (1 H, dd, $J = 10.9$ and 3.5 Hz), 3.83 (1 H, dd, $J = 10.9$ and 3.7 Hz), 3.49 (1 H, t, $J = 10.2$ Hz), 3.30 (1 H, t, $J = 11.6$ Hz), 3.05-3.01 (1 H, m), 2.27 (1 H, d, $J = 13.6$ Hz), 2.05 (1 H, d, $J = 11.9$ Hz), 1.81-1.61 (2 H, m), 1.17 (3 H,

s); ^{13}C NMR δ 144.3, 143.2, 132.2, 132.1, 132.0, 131.8, 131.6, 130.1, 129.4, 128.5, 128.4, 128.3, 127.9, 125.7, 125.6, 124.9, 124.7, 124.2, 123.5, 122.9, 122.6, 94.3, 93.4, 93.1, 88.0, 87.6, 86.4, 80.2, 79.8, 68.4, 68.3, 61.7, 38.0, 28.9, 28.3; HRMS calcd for $\text{C}_{47}\text{H}_{36}\text{O}_3$ (MH^+) 649.27372, found 649.27404.

Tetrahydropyranyl compound 242. The same procedure was repeated as described for **236** except that 1.30 g of *trans*-diol **246** (2.00 mmol) in 50 mL of THF, a solution of thionyl chloride (1.19 g, 9.99 mmol) and anhydrous pyridine (1.58 g, 20.0 mmol) in 20 mL of THF were used to furnish the crude dichloride. AIBN (0.0327 g, 0.200 mmol), tributyltin hydride (1.61 mL, 5.65 mmol) were added to the crude dichloride. The reaction mixture was heated under reflux for 18 h. The residue was purified by flash column chromatography (silica gel/30% diethyl ether in hexanes, R_f = 0.77 (hexanes:diethyl ether = 4:6)) to afford 0.493 g of **242** (0.80 mmol, 40%) as a yellow solid: IR 3057, 2929, 2244 cm^{-1} ; ^1H NMR δ 7.65-7.52 (10 H, m), 7.45-7.41 (2 H, m), 7.38 (2 H, s), 7.25 (2 H, td, J = 7.4 and 1.0 Hz), 7.06 (2 H, t, J = 7.4 Hz), 6.70 (2 H, d, J = 7.9 Hz), 4.40 (2 H, d, J = 21.8 Hz), 4.30 (2 H, d, J = 21.8 Hz), 3.93 (2 H, d, J = 11.1 Hz), 3.38 (2 H, t, J = 9.4 Hz), 2.83-2.73 (1 H, m), 2.06 (3 H, s), 1.67-1.46 (4 H, m); ^{13}C NMR δ 144.1, 143.5, 141.9, 139.3, 138.6, 136.0, 135.5, 132.2, 130.1, 130.0, 129.0, 128.9, 127.7, 126.9, 126.6, 126.5, 124.7, 123.7, 123.5, 68.7, 59.1, 44.4, 35.7, 29.9, 18.8; HRMS calcd for $\text{C}_{47}\text{H}_{36}\text{O}$ (MH^+) 617.28389, found 617.27951.

Diiodide 241. To a flask containing 0.424 g of **242** (0.688 mmol) in 50 mL of wet chloroform was added excess amount of iodotrimethylsilane. The flask of the reaction mixture was tightly closed and heated up to 70 $^\circ\text{C}$ for 3 days. After the reaction mixture was allowed to cool to

room temperature, 20 mL of saturated sodium thiosulfate solution was introduced, and extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes, R_f = 0.77 (hexanes:diethyl ether = 6.5:3.5)) to furnish 0.447 g of **241** (0.523 mmol, 76%): IR 3057, 2969, 2367 cm^{-1} ; ^1H NMR δ 7.63-7.54 (10 H, m), 7.43-7.42 (2 H, m), 7.39 (2 H, s), 7.25 (2 H, td, J = 7.4 and 1.0 Hz), 7.06 (2 H, t, J = 7.2 Hz), 6.70 (2 H, d, J = 8.4 Hz), 4.44 (2 H, d, J = 21.0 Hz), 4.32 (2 H, d, J = 21.6 Hz), 3.16-3.08 (4 H, m), 2.94-2.90 (1 H, m), 2.30 (2 H, m), 2.02 (3 H, s), 1.84-1.78 (2 H, m); ^{13}C NMR δ 144.1, 143.5, 141.8, 139.5, 138.4, 135.6, 135.5, 132.5, 130.1, 130.0, 129.0, 129.0, 127.8, 127.1, 126.6, 126.6, 124.8, 123.8, 123.5, 58.7, 46.6, 36.9, 35.8, 20.3, 6.55; HRMS calcd for $\text{C}_{47}\text{H}_{36}\text{I}_2$ (MH^+) 855.09791, found 855.09358.

Polycyclic Aromatic Hydrocarbon 240 and 247. To a flask containing 0.161 g of **241** (0.188 mmol) in THF (50 mL) was added 1.8 M solution of LDA (0.451 mmol) in THF/*n*-heptane. The reaction mixture was stirred at room temperature for 8 h, and quenched with water. The reaction mixture was extracted with diethyl ether, and dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.87 (hexanes:diethyl ether = 8:2)) to provide the polycyclic aromatic hydrocarbon **240** and **247** (60.10 mg, 0.0978 mmol) as an orange red solid in 8% and 44%, respectively: IR 3062, 2923, 2023 cm^{-1} ; **247**: ^1H NMR δ 7.58-7.46 (10 H, m), 7.42-7.38 (1 H, m), 7.264-7.23 (2 H, m), 7.19 (1 H, d, J = 8.4 Hz), 7.10 (1 H, t, J = 7.8 Hz), 7.04 (1 H, t, J = 7.8 Hz), 7.02 (1 H, d, J = 9.0 Hz), 6.84 (1 H, s), 6.78 (1 H, t, J = 7.2 Hz), 6.72 (1 H, d, J = 7.8 Hz),

6.40 (1 H, d, $J = 7.2$ Hz), 4.12 (1 H, d, $J = 12.0$ Hz), 2.82-2.81 (1 H, m), 2.69 (1 H, t, $J = 13.2$ Hz), 2.46-2.44 (1 H, m), 2.39-2.36 (1 H, m), 2.22-2.17 (2 H, m), 1.71-1.66 (1 H, m), 1.68 (3 H, s), 1.30-1.27 (2 H, m); ^{13}C NMR δ 151.3, 148.6, 147.5, 145.6, 143.2, 141.7, 140.4, 139.4, 139.1, 138.2, 137.1, 136.1, 134.8, 134.3, 130.5, 130.4, 129.9, 129.5, 128.9, 128.8, 128.1, 127.6, 127.5, 127.2, 127.0, 126.9, 125.3, 124.8, 124.3, 123.8, 123.6, 123.2, 121.9, 120.2, 64.4, 61.2, 50.7, 47.9, 46.8, 29.3, 28.6, 27.2, 20.0.

Dimethoxy diketone 250. To a solution of the crude product of the dichloride (prepared from *trans*-diol **235** (3.02 g, 4.51 mol)) in 200 mL of THF was added 24 mL of 2 N sodium hydroxide aqueous solution at 0 °C. The resulting mixture was stirred while a stream of air bubbled into the solution for 24 h at room temperature. The reaction mixture was concentrated in vacuum and then extracted with methylene chloride. The organic layer was washed with saturated NH_4Cl and water, dried over sodium sulfate, and concentrated. The residue was purified by flash chromatography (silica gel/30% diethyl ether in hexanes, $R_f = 0.57$ (hexanes: diethyl ether = 6.5:3.5)) to afford 1.26 g of **250** (1.89 mmol, 42% yield) as a yellow solid. IR 3058, 2920, 2247, 1702 cm^{-1} ; ^1H NMR δ 7.71 (2 H, d, $J = 7.2$ Hz), 7.63-7.56 (6 H, m), 7.50 (2 H, d, $J = 7.2$), 7.42-7.41 (2 H, m), 7.38 (2 H, s), 7.21 (2 H, t, $J = 7.2$), 7.16 (2 H, t, $J = 7.2$), 6.42 (2 H, d, $J = 7.2$ Hz), 3.70 (2 H, dd, $J = 10.2$ and 4.8 Hz), 3.64-3.60 (1H, m), 3.40 (2 H, dd, $J = 10.2$ and 6.6 Hz), 2.98 (6 H, s), 2.40 (3 H, s); ^{13}C NMR δ 193.0, 151.7, 145.5, 139.4, 138.7, 136.8, 135.9, 134.4, 132.8, 131.5, 129.7, 129.7, 129.3, 129.2, 128.5, 128.4, 128.1, 126.9, 124.0, 123.7, 71.4, 58.5, 58.3, 46.5, 18.5; HRMS calcd for $\text{C}_{47}\text{H}_{34}\text{O}_4$ (MH^+) 663.25299, found 663.25179.

Dibromoketone 252. The same procedure was repeated as described for **231** except that 0.645 g of **250** (0.973 mmol) was used to afford 0.223 g of **252** (0.352 mmol, 23% yield) as a yellow green solid (R_f = 0.59, (hexanes:diethyl ether = 6.5:3.5)): IR 2976, 2201, 1703 cm^{-1} ; ^1H NMR δ 7.72 (2 H, d, J = 7.2 Hz), 7.64-7.58 (6 H, m), 7.53 (2 H, d, J = 6.6 Hz), 7.41-7.39 (2 H, m), 7.41 (2 H, s), 7.23 (2 H, t, J = 7.2 Hz), 7.18 (2 H, t, J = 7.2 Hz), 6.43 (2 H, d, J = 7.2 Hz), 4.28 (2 H, dd, J = 10.8 and 3.6 Hz), 4.04-4.01 (1 H, m), 3.48 (2 H, dd, J = 10.8 and 6.6 Hz), 2.40 (3 H, s); ^{13}C NMR δ 193.1, 149.1, 145.4, 139.7, 138.6, 136.4, 135.5, 134.8, 133.7, 132.0, 129.8, 129.5, 129.4, 129.3, 128.7, 128.6, 128.6, 127.4, 124.2, 123.8, 59.8, 48.6, 34.7, 19.0; HRMS calcd for $\text{C}_{45}\text{H}_{28}\text{Br}_2\text{O}_2$ (MH^+) 759.05288, found 759.05558.

Diketone 253. The same procedure was repeated as described for **250** except that the crude product of the dichloride **246** (prepared from trans-diol (1.30 g, 2.00 mmol)) in 100 mL of THF and 8 mL of 2 N sodium hydroxide aqueous solution was used to furnish 0.619 g of **253** (0.960 mmol, 48% yield) as a yellow green solid (R_f = 0.67 (hexanes:diethyl ether = 4:6)): IR 2948, 2346, 1707 cm^{-1} ; ^1H NMR δ 7.71 (2 H, dd, 7.9 and 1.2 Hz), 7.64-7.48 (8 H, m), 7.43-7.40 (2 H, m), 7.38 (2 H, s), 7.22 (2 H, dd, J = 6.9 and 1.0 Hz), 7.17 (2 H, td, J = 7.4 and 1.5 Hz), 6.41 (2 H, d, J = 6.9 Hz), 3.85 (2 H, dd, J = 11.4 and 3.7 Hz), 3.35 (2 H, t, J = 10.9 Hz), 3.23-3.14 (1 H, m), 2.45 (3 H, s), 1.61 (2 H, t, J = 11.4 Hz), 1.37-1.22 (2 H, m); ^{13}C NMR δ 193.1, 150.9, 145.3, 139.7, 138.9, 136.6, 135.8, 134.6, 133.0, 131.5, 129.7, 129.6, 129.3, 129.3, 128.6, 128.5, 127.2, 124.0, 123.7, 68.5, 61.6, 44.1, 29.9, 17.1; HRMS calcd for $\text{C}_{47}\text{H}_{32}\text{O}_3$ (MH^+) 645.24242, found 645.24283.

Diiododiketone 254. The same procedure was repeated as described for **252** except that 0.201 g of **253** (3.12 mmol) was reacted for 10 days to afford 1.87 g of **254** (2.12 mmol, 68%) as a yellow solid (R_f = 0.63, (hexanes:diethyl ether = 6.5:3.5)): IR 3061, 2927, 2355, 1705 cm^{-1} ; ^1H NMR δ 7.75 (2 H, d, J = 6.6 Hz), 7.66-7.51 (8 H, m), 7.41-7.38 (2 H, m), 7.40 (2 H, s), 7.23 (2 H, td, J = 7.8 and 1.2 Hz), 7.17 (2 H, td, J = 7.8 and 1.2 Hz), 6.42 (2 H, d, J = 7.2 Hz), 3.25-3.12 (5 H, m), 2.43-2.37 (2 H, m), 2.35 (3 H, s), 1.70-1.57 (2 H, m); ^{13}C NMR δ 192.8, 150.5, 145.3, 139.8, 138.5, 136.5, 135.7, 134.6, 133.3, 131.8, 129.7, 129.6, 129.3, 129.3, 128.7, 128.5, 128.5, 127.3, 124.2, 123.8, 61.1, 47.9, 36.5, 18.4, 6.0; HRMS calcd for $\text{C}_{47}\text{H}_{32}\text{I}_2\text{O}_2$ (MH^+) 883.05644, found 883.05545.

2-(Indan-2-yl)-1,3-indandione 259. The same procedure was repeated as described for **234** except that 1.32 g of 2-indanone (10.0 mmol), 1.46 g of 1,3-indandione (10.0 mmol), 2.53 g of Hantzsch ester (10.0 mmol), and 0.23 g of L-proline (3.00 mmol) were used to furnish **259**. Pale black solid product was obtained by column chromatography 2.10 g of **259** (8.00 mmol, 80% yield) (silica gel/20% diethyl ether in hexanes, R_f = 0.42, (hexanes:diethyl ether = 7:3)): IR 2980 , 2357 , 1705 cm^{-1} ; ^1H NMR δ 8.01-7.84 (m, 4 H, indanyl aromatic H), 7.20-7.11 (4 H, m), 3.22-2.99 (6 H, m); ^{13}C NMR δ 200.4, 142.5, 142.2, 135.7, 126.4, 124.3, 123.2, 55.5, 39.6, 36.4.

2-Methyl-2-(indan-2-yl)-1,3-indandione 260. The same procedure was repeated as described for **234** except that 0.989 g of **259** (3.77 mmol) in 30 mL of THF and 5.00 mL of a 1.0 M solution of potassium *t*-butoxide (5.00 mmol) in 2-methyl-2-propanol, and 2.00 g of iodomethane (13.8 mmol) were used to furnish **260**. The residue was purified by flash column

chromatography (silica gel/15% diethyl ether in hexanes, R_f = 0.49 (hexanes:diethyl ether = 7:3)) to give 0.817 g of **260** (2.98 mmol, 79% yield): IR 3061, 2353, 1740 cm^{-1} ; ^1H NMR δ 8.01-7.83 (m, 4 H, indanyl aromatic H), 7.13-7.06 (4H, m), 3.02-2.79 (5 H, m), 1.42 (3 H, s); ^{13}C NMR δ 204.2, 142.0, 141.2, 135.8, 126.3, 124.2, 123.3, 54.5, 45.4, 34.2, 17.5; HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$ (MH^+) 277.12231, found 277.12224.

Propargylic diols 261. The same procedure was repeated as described for **235** except that 3.04 g of 1-(2-ethynylphenyl)-2-phenylethyne (15.2 mmol) in 50 mL of THF, 9.48 mL of 1.6 M solution of *n*-butyl lithium, and a solution of 1.37 g of **260** (4.98 mmol) in 20 mL of THF were used to furnish **261**. The residue was purified by flash column chromatography (silica gel/70% diethyl ether in hexanes, R_f = 0.32 (hexanes:diethyl ether = 4:6)) to give 2.72 g of **261** (4.08 mmol, 82% yield): IR 3535, 3063, 2935, 2344 cm^{-1} ; ^1H NMR δ 7.74 (1 H, d, J = 7.4 Hz), 7.61-7.45 (6 H, m), 7.38-7.28 (14 H, m), 7.23-7.06 (5 H, m), 3.98-3.84 (1 H, m), 3.40-3.07 (5 H, m), 2.60 (2 H, s), 1.21 (3 H, s); ^{13}C NMR δ 144.3, 143.4, 143.3, 143.1, 132.2, 132.0, 131.8, 131.7, 130.1, 129.4, 128.5, 128.3, 128.2, 128.0, 127.9, 125.9, 125.8, 125.6, 125.0, 124.9, 125.0, 124.9, 124.5, 124.2, 124.1, 123.6, 122.9, 122.7, 94.5, 93.4, 93.2, 93.0, 88.1, 87.6, 85.8, 81.0, 80.0, 61.3, 59.6, 51.9, 41.8, 34.7, 34.6.

Indanyldiketone 262. The same procedure was repeated as described for **250** except that the crude product of the dichloride **261** in 100 mL of THF and 8 mL of 2 N sodium hydroxide aqueous solution was used to furnish 0.379 g of **262** (0.560 mmol, 28% yield) as a yellow solid (R_f = 0.65 (hexanes:diethyl ether = 7:3)); IR 3061, 2236, 1716 cm^{-1} ; ^1H NMR δ 7.69 (2 H, d, J = 7.2 Hz), 7.63-7.58 (6 H, m), 7.50 (2 H, d, J = 7.2 Hz), 7.41 (2 H, s), 7.41 (2 H, m), 7.21-7.13

(4 H, indanyl aromatic H) , 6.98-6.93 (4 H, m), 6.39 (2 H, d, $J = 7.8$ Hz), 4.17-4.11 (1 H, m), 2.88 (2 H, dd, $J = 15.0$ and 7.2 Hz), 3.40 (2 H, dd, $J = 15.6$ and 11.4 Hz), 2.60 (3 H, s); ^{13}C NMR δ 193.1, 150.9, 145.3, 143.2, 139.7, 138.6, 136.7, 135.8, 134.5, 133.0, 131.7, 129.7, 129.6, 129.3, 129.3, 128.6, 128.5, 127.2, 125.8, 124.0, 123.7, 60.6, 49.2, 35.8, 18.7; HRMS calcd for $\text{C}_{51}\text{H}_{32}\text{O}_2$ (MH^+) 677.24751, found 677.24696.

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Figure 26. ORTEP drawing of the crystal structure of **Buckybowl 148a**.

Figure 27. ORTEP drawing of the crystal structure of **4,5-diphenolicphenanthrene 177**.

Figure 28. ORTEP drawing of the crystal structure of **Dibromoketone 252**.

Figure 29. ORTEP drawing of the crystal structure of **Diiodoketone 254**.

133

148a

175-Diastereomers

M-175 or P-175

M-175 or P-175

M-175 or P-175

rac-176

rac-198

rac-201

rac-201

M-202 or P-202

235

236

236

231

242

241

186

240

247

¹H NMR Spectra of
247 (aliphatic region)

¹H NMR Spectra of
247 (aromatic region)

gHMQC spectra of 247

NOESY spectra of 247

¹D TOCSY Spectra of
247 (aromatic region)

DPFGSE NOE spectra of
247 (aliphatic region)

DPFGSE NOE spectra of
247 (aromatic region)

DEPT spectra of 247

¹D TOCSY Spectrum of **240**

DPFGSE NOE spectrum of **240**

250

250

252

202

252

253

254

254

259

259

260

261

262

262