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Yonghong Yang
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**Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes and Development of New
Synthetic Strategies for Novel Polycyclic Aromatic Compounds**

Yonghong Yang

**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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ABSTRACT

Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes and Development of New Synthetic Strategies for Novel Polycyclic Aromatic Compounds

Yonghong Yang

The cascade radical cyclization of benzannulated enyne–allene generated in situ from enediynyl propargylic alcohols promoted by thionyl chloride via an S_Ni' reaction provides an efficient synthetic pathway to 11*H*-benzo[*b*]fluoren-11-ols and related compounds. The simplicity of the synthetic sequence and the mildness of the reaction condition make this cascade reaction sequence useful for the construction of polycyclic aromatic compounds. Interestingly, when this strategy was employed for the systems having two benzannulated enyne–allene units, it was quite unexpected that the reaction sequence led to the formation of highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes involving an unusual cleavage of a benzene ring, and spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes] along with other polycyclic aromatic compounds. Conceivably, the transformation from the precursors having two benzannulated enyne–allene units to the novel polycyclic compounds involves a C^2 – C^6 cyclization reaction followed by a radical–radical coupling reaction and a tautomerization to give the formal Diels–Alder adducts or the [2 + 2] cycloaddition adducts.

The Ireland–Claisen rearrangement of the benzannulated enediynyl propargylic acetates was successfully adopted for the synthesis of the corresponding benzannulated enyne–allenenes in situ for the subsequent Schmittel cyclization to generate benzofulvene biradicals for cascade radical cyclizations. The mildness of the reaction conditions and the ready availability of a variety of silyl ketene acetal make this synthetic pathway quite attractive. Several polycyclic aromatic derivatives of benzo[*ghi*]fluoranthene and 11*H*-benzo[*b*]fluorene were thus produced from the corresponding enediynyl propargylic acetates in a single operation.

The Wagner–Meerwein rearrangement of fluorenylmethanols derived from 15,16-diaryl-diindeno[2,1-*b*:1',2'-*h*]phenanthrenes was successfully adopted for the synthesis of helical 17,18-diaryl-dibenzo[*a,o*]pentaphenes involving the carbocation-promoted ring expansion and aromatization. Two of the 17,18-diaryl-dibenzo[*a,o*]pentaphenes were employed for the subsequent intramolecular Friedel–Crafts arylation reactions involving phenyl or 4-biphenyl substituents at the 17 & 18 positions, producing several butterfly-shaped compounds having two planes of symmetry and a C_2 symmetry in the case of the phenyl substituent and having only a C_2 symmetry in the case of the 4-biphenyl substituent. They possess very interesting structural features.

DEDICATED TO

my husband, Shengqiao Li, and my parents

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CHAPTER I

Prelude

1. Introduction

A novel class of antitumor antibiotic natural products, including calicheamicins (**1**),¹ dynemicin (**2**),² esperamicins (**3**),³ kedarcidin chromophore (**4**),⁴ C-1027 chromophore (**5**),⁵ and neocarzinostatin chromophore (**6**),⁶ derived from bacterial sources in the latter half of the 1980s (Figure 1), and two new marine natural products, such as namenamicin (**7**)⁷ and shishijimicins (**8A–D**)⁸ reported in 1996 and 2003 respectively (Figure 2), have attracted a great deal of interest in chemical, biochemical, and medical research. This discovery marked the beginning of an exciting era in basic research toward new and potentially useful chemotherapeutic agents. Because of unprecedented and highly unusual molecular architecture containing a cyclic enediyne or related systems, fascinating mode of action, and excellent biological activities, these antitumor antibiotics have been widely investigated.⁹

Chemically, much research is focused mainly on the total synthesis of the natural enediynes and on the preparation of simple model compounds with analogous antitumor and antibiotic activity. Furthermore, the connection of biradical cycloaromatization protocols and subsequent radical cyclizations provides an exquisite approach to polycyclic ring systems.¹⁰ The thermal cycloaromatization of enediynes by the Bergman cyclization to afford reactive biradicals has been extensively investigated.^{9,11} Moreover, extensive investigations have also been focused on the thermal cycloaromatization of enyne–allenes by C²–C⁷ (Myers–Saito) cyclization¹¹ or C²–C⁶ (Schmittel) cyclization,¹² and enyne–ketenes by the Moore cyclization.¹¹ In addition, these systems also attract considerable attention of the physical organic and theoretical chemists.^{9a}

Figure 1. Structures of naturally occurring antitumor antibiotics from bacterial sources.

Figure 2. Structures of naturally occurring antitumor antibiotics from marine sources.

2. Biological Activities and DNA–Cleavage Mechanism of Eneidyne Antitumor Antibiotics

The natural enediyne antitumor antibiotics are one class of the most potent antitumor and antibacterial agents known. All of the naturally occurring enediynes are highly cytotoxic.⁹ Moreover, shishijimicin (**8A**) is almost 10 times more reactive than namenamicin (**7**).⁸

The biological activity of these naturally occurring enediynes is attributed to their ability to cleave DNA irreversibly. Generally, selective DNA cleavage by the naturally occurring enediynes occurs in the following four steps:^{9b}

- a. Recognizing and binding to the minor groove of DNA by a specific structural feature.
- b. Activation of the cyclic enediyne toward the Bergman cyclization.
- c. Bergman cyclization to produce 1,4-didehydroarene biradicals.
- d. Abstraction of hydrogen atoms from the backbone of DNA by the 1,4-didehydroarene biradicals leading to DNA cleavage and cell death.

The following proposed mechanism accounts for their damaging action on DNA.¹ Specifically, Calicheamicin γ_1^I (**1**) binds to the minor groove of double helical DNA via oligosaccharide which is thought to be the molecule's main recognition and binding moiety. A nucleophile attacks the central sulfur atom of the trisulfide group, followed by intramolecularly attacking the α,β -unsaturated ketone to form intermediate **9**. A facile Bergman cyclization reaction affords the 1,4-didehydrobenzenoid biradical **10**. This highly reactive biradical abstracts two hydrogen atoms from the backbone of DNA double strand to generate DNA radical, which proceeds to react with molecular oxygen leading to DNA cleavage and cell death, and an aromatic compound **11** (Scheme 1).

A similar mechanism was proposed to account for the action of NCS chromophore (**6**) by Myers.¹³ The DNA damage is initiated by stereospecific nucleophilic attack at C12, followed by

rearrangement of the ring skeleton with epoxide opening and formation of a cumulene as a labile intermediate **12**. A rapid Myers–Saito cyclization leads to biradical **13**, followed by extraction of two hydrogen atoms from DNA resulting in the formation of **14** and DNA cleavage (Scheme 2).

Scheme 1. Mechanism of DNA cleavage by **1**.

Scheme 2. Mechanism of DNA cleavage by **6**, RSH = thionucleophile, Ar = naphthyl substituent.

3. Cyclization Reaction of Enediynes via Bergman Cyclization

The chemistry of enediynes could date back to 1966. Sondheimer reported the reaction from **15** to **17** and proposed a cyclization mechanism via an ionic intermediate **16** (Scheme 3).¹⁴

Scheme 3. Cyclization of **15** reported by Sondheimer.

In 1971, Masamune *et al.* reported the reaction of converting two cyclic enediynes **18** to the benzenoid systems **19**, but without proposing the reaction via a biradical intermediate (Scheme 4).¹⁵

Scheme 4. Cyclization of enediyne observed by Masamune, Ms = mesyl.

In 1972, Bergman published his detailed study on the cycloaromatization of enediynes.¹⁶ He first proposed 1,4-didehydrobenzene biradical as a key intermediate for the cyclization reaction of enediynes. As a good indirect evidence of the Bergman cyclization via a biradical intermediate, when **20** was heated in solution, the observed products were benzene or its derivative **22** via the biradical intermediate **21**, depending on the solvents used (Scheme 5).¹⁷

Scheme 5. The Bergman cyclization of **20** in a variety of solvents.

The reactivity of (*Z*)-enediynes in the Bergman cyclization is affected by the following important factors including: 1) the *cd* distance, which is the distance between the two terminal acetylenic carbon atoms; 2) the difference in strain energy between the enediyne and the transition state; 3) the concentration of the trapping agent; and 4) substituent effects. Several studies related to these effects on the reactivity of enediynes toward the Bergman cyclization were published.^{9b}

Based on Nicolaou *et al.*'s model study on 10-membered cyclic, strain-free enediyne systems, the upper limit of *cd* distance required for the Bergman cyclization at a measurable rate at ambient temperature is 3.2–3.3 Å.¹⁸ These pioneering studies show that the 10-membered cyclic enediynes are optimal for the Bergman cyclization. The relationship of the reactivity of enediynes with *cd* distance is summarized in Table 1.

Magnus and Snyder, using different methods, found independently that the critical factor determining the reactivity of strained enediynes is not the *cd* distance but the difference in strain energy between the enediyne and the transition state leading to the biradical intermediate.^{9c} Scheme 6 outlines the result of Magnus.²⁰ They found that **23B** is more reactive.

Scheme 6. The Bergman cyclization observed by Magnus.

Semmelhack *et al.* reported the dependence of the Bergman cyclization rate on the concentration of trapping agents. They found that the reactivity of **25** to produce **26** depends on the concentration of 1,4-cyclohexadiene (1,4-CHD) (Scheme 7).²¹

Scheme 7. The rate of Bergman cyclization observed by Semmelhack.

Table 1. Calculated *cd* Distance and Stabilities of Conjugated Enediynes

Entry	Compound	Ring Size	<i>cd</i> Distance [Å]	Stability	Ref.
1		9	2.84	unknown compound	19a
2		10	3.25	$t_{1/2} = 18$ h at 37 °C	19a
3		10	3.20	$t_{1/2} = 11.8$ h at 37 °C	19b
4		10	3.03	cyclized at 25 °C	19c
5		10	3.01	cyclized < 25 °C	15
6		10	2.99	cyclized < 25 °C	15
7		11	3.61	stable at 25 °C	19a
8		12	3.77	stable at 25 °C	19d
9		-	4.12	stable at 25 °C; $t_{1/2} = 30$ s at 200 °C	16a
10		-	3.94	stable at 25 °C; $k_{obs} = 6.4 \times 10^{-4} \text{ s}^{-1}$ at 156 °C	19e

Although complete systematic effects of substituents on the reactivity of enediynes were not reported, this reactivity seemed to be sensitive to both electronic and steric effects of substituents.^{9b} Generally, cyclic enediynes containing benzo or quinone in the ene portion are more reactive than acyclic enediynes. Furthermore, the enediynes containing quinone are much

more reactive (Table 2).^{21b} Alabugin *et al.* found that the Bergman cyclization of aromatic enediynes is sensitive to ortho substitution as a result of a combination of electronic, steric, and electrostatic effects.²² Benzannulated enediynes with ortho substituents, such as CH₃, NH₂, and OH, have high activation energy; the large decrease in the activation energy upon protonation has been discovered, which is important because cancer cells are more acidic than normal cells. This discovery provides possibilities for DNA–cleavage drug design.

Table 2. Effects of Substituents on the Reactivity of Ene-diynes

Compd.	$t_{1/2}$ (h)	T (°C)
>168	120
24	84
88	40

To explore the potential of using simple enediynes as DNA-cleavage drug, some research interests extended to develop the convenient method to suppress or activate cyclization. Turro and Nicolaou *et al.* first reported the photo-induced cyclization of an enediyne as a mild alternative to thermolysis, which could avoid high temperature to activate the Bergman cyclization (Scheme 8).^{23a} A similar mechanism to that of thermal cyclization was proposed. The more extensive investigation of the photochemically activated Bergman cyclization was reported by Funk *et al.*^{23b} and Zaleski *et al.*^{23c}

Scheme 8. Photo-induced Bergman cyclization, R = *n*-Pr.

The remarkable reactivity of the enediynes has facilitated efforts toward the exploitation of the 1,4-didehydroarene biradical intermediate for therapeutic applications. The capacity of initiating and controlling the reactivity of enediynes is important for the realization of such goals. Transition metals were reported to both stabilize and activate enediynes toward thermally initiated Bergman cyclization, depending on two common factors: the conformational flexibility of the enediyne ligand coordinated to the metal ion and the specific geometry of the chelated metalloenediyne complex.^{23c} Buchwald *et al.* reported a controlled acceleration and inhibition of the Bergman cyclization by metal chlorides.²⁴ The enediyne-based biphenylphosphine **30**, upon coordination to palladium or platinum dichloride, underwent a Bergman cyclization at a greatly enhanced rate at relatively low temperature (Scheme 9).

Scheme 9. The Bergman cyclization accelerated by metal chlorides.

Since this pioneering work, more examples of metal-assisted thermal enediyne cyclization have been reported to demonstrate the utility of transition metals for controlling enediyne cyclization.²⁵ Investigation of several metal ions, such as Cu(I), Cu(II), Ni(II), Pd(II), Pt(II), Ru, and Mg²⁺, provides both theoretical and practical advances in the ability to control the Bergman cyclization.²⁶ Zaleski *et al.* reported that enediyne ligands could be activated by using Mg²⁺ salts, a biologically prevalent and innocuous metal ion.^{26c} They found that compound **32** would cyclize at 100 °C, but was stable at room temperature. However, as a result of decreasing

cd distance and coordination effect, complex **33** could cyclize at room temperature (Scheme 10).^{26c}

Scheme 10. The Bergman cyclization accelerated by Mg²⁺.

4. Cyclization Reaction of Enyne–Allenes

4.1. Myers–Saito (C²–C⁷) Cyclization

In the investigation of conjugated unsaturated structures that could cyclize via biradical intermediates at mild conditions and possess promising DNA-cleaving activity, Myers²⁷ and Saito's²⁸ group reported a new variant of the Bergman type cyclization with the parent system (*Z*)-1,2,4-heptatrien-6-yne (**35**) (Scheme 11) in 1989, respectively. This cycloaromatization was recognized as Myers–Saito cyclization, also termed as the C²–C⁷ cyclization, which proceeds via $\alpha,3$ -didehydrotoluene biradical (**36**) leading to toluene (**37**) upon hydrogen atom abstraction. As evidence of the cyclization via a biradical mechanism, thermolysis of acyclic enyne–allene **35** in various solvents was studied. The result is summarized in Figure 3. Moreover, Myers found the reaction is a first-order reaction with the following activation parameters: $\Delta H^\ddagger = 21.8 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = -11.6 \pm 1.5$ cal K⁻¹mol⁻¹ ($E_a = 22.5$ kcal/mol, $\log A = 10.7$). Although the Bergman cyclization and the Myers–Saito cyclization are related, the ground state of **36** is most likely a σ, π -biradical, whereas that of **21** is almost constrained as a σ, σ -biradical, and the former

is more stable. In addition, the *cd* distance of enyne–allenes is shorter than that of enediynes. Therefore, the Myers–Saito cyclization is more facile and strongly exothermic ($\Delta H \approx -15 \pm 3$ kcal/mol), whereas the Bergman cyclization is modestly endothermic ($\Delta H \approx 14$ kcal/mol).

Scheme 11. The Myers-Saito cyclization.

Figure 3. Products of thermolysis of (*Z*)-1,2,4-heptatrien-6-yne (**35**) in various solvents.

Saito *et al.* demonstrated the chemistry of the C^2 – C^7 cyclization and the DNA cleavage activity based on a series of simple model molecules, which were readily constructed and cyclized at body temperature with DNA cleavage activities (Scheme 12).²⁸ The intriguing possibilities of developing analogs of antitumor antibiotics based on enyne–allene system might be realized by further modification of the structures.

Scheme 12. The Myers-Saito cyclization observed by Saito *et al.*

4.2. Schmittle (C²–C⁶) Cyclization

With the extensive investigation of thermal cyclization of enyne–allenes, most of them result in the formation of six-membered rings through the C²–C⁷ pathway. However, in 1995, Schmittle *et al.* reported their surprising discovery that some of the masked enyne–allene model systems exhibit a novel thermal cyclization model via the C²–C⁶ pathway by replacing the hydrogen at the acetylene terminus with an aryl group or a sterically bulky group (R = *t*Bu or TMS).¹² The proposed mechanism of the switch from the C²–C⁷ to the novel C²–C⁶ cyclization is outlined in Scheme 13.²⁹ This novel C²–C⁶ cyclization involves a very short-lived benzofulvene biradical intermediate **51** (lifetime < 10^{–8} s). The aryl group could stabilize the vinyl radical, therefore this stabilizing effect favors the formation of biradical **51** over biradical **49**. Moreover, the steric effect is more significant in the biradical intermediate of C²–C⁷ cyclization than the benzofulvene biradical of C²–C⁶ cyclization.^{29f} As a result, with R¹ = H, the thermal cyclization leads to the Myers–Saito cycloaromatization product **50** in the presence of 1,4-cyclohexadiene (1,4-CHD), whereas with R¹ = *p*Tol, the thermal cyclization leads to the formal ene product **52** or the formal Diels–Alder product **53d** and **54c** depending on the nature of the group R².

Although all attempts to trap the postulated biradical intermediate were unsuccessful, the stepwise mechanism is based on the following evidence:^{10,29a} 1) The activation barriers for the formal ene and the Diels–Alder reaction are very similar. In addition, the activation barriers for the enyne–allenes with different aryl substitutes are almost identical. If the mechanism were a concerted reaction, the activation energy of **48d** would be much higher than that of **48c**. Moreover, there was no example of mesitylene analogs undergoing the Diels–Alder reaction leading to cycloadducts across a mesitylene ring even under extreme conditions. 2) Polarity of

the solvents such as mesitylene, benzene, and DMSO, does not affect the reaction rate of the cyclization. 3) The similar DNA cleavage activity as the biradical intermediate of the Myers–Saito cyclization was demonstrated by the formation of the open circular DNA.^{29f,g} 4) Theoretical calculation studies also support the biradical mechanism with the formation of the biradical intermediate being the rate-determining step.³⁰

4.3. Construction of Polycyclic Ring Systems via Cycloaromatization of Enyne–Allenenes

The current research on the thermal biradical cyclization of enediynes, enyne–cumulenes, and enyne–allenenes is not only focused on the synthesis of model compounds with similar analogous antitumor antibiotic activity as the natural enediynes, but also on employing the high potential of the cycloaromatization reaction for the construction of polycyclic ring systems.

In addition to the theoretical and mechanistic study of the Myers–Saito and the Schmittle cyclization reactions, the Myers–Saito and the Schmittle cyclizations were employed to construct

novel ring systems. If an aryl group is placed at the allenic terminus, the enyne–allene could undergo the C^2 – C^6 cyclization producing a fulvene/benzofulvene biradical followed by a rapid intramolecular radical–radical coupling reaction leading to the formal Diels–Alder product (Scheme 14).³¹

Scheme 14. Application of the C^2 – C^6 cyclization to construct novel ring systems.

Dr. Hai-Ren Zhang developed a new synthetic pathway to generate the chlorosubstituted benzannulated enyne–allenes in situ via a S_Ni' reaction promoted by thionyl chloride. The subsequent rapid cascade radical cyclization and tautomerization lead to novel polycyclic ring systems.³² This pathway was adopted for the synthesis of a $C_{44}H_{26}$ hydrocarbon (Scheme 15)^{32a} and other polycyclic aromatic hydrocarbons.

Scheme 15. Synthesis of a $C_{44}H_{26}$ hydrocarbon via benzannulated enyne-allene.

Dr. Hongbin Li developed a new synthetic pathway to the benzannulated enyne-allenes without a chloro-substituent, followed by similar cyclization and tautomerization leading to the corresponding polycyclic aromatic hydrocarbons directly (Scheme 16).^{32b} This strategy was adopted for the preparation of twisted 4,5-diarylphenanthrenes (Scheme 17),³³ polycyclic hydrocarbons,^{32b} and helical hydrocarbons.³⁴

Scheme 16. A new synthetic pathway to the benzannulated enyne-allene and polycyclic hydrocarbon.

Scheme 17. Synthesis of 4,5-diarylphenanthrenes via benzannulated enyne-allenes.

The Gillmann group^{35a} and Rodriguez group^{35b} reported their discovery of a potential stepwise biradical process for the formal [2 + 2] cyclization reaction (Scheme 18).^{35a}

Scheme 18. Gillmann's observation of formal [2 + 2] cycloaddition.

Lipton *et al.* reported a new type of benzannulated enyne–allene that could cyclize at a faster rate via oxyanion than nearly all known examples leading to new polycyclic compounds (Scheme 19).³⁶ The C²–C⁶ cyclizations were promoted by methyllithium at –20 °C.

Scheme 19. Lipton's result of the enyne-allene cyclization via oxyanion.

In addition to the polycyclic hydrocarbons, some heterocyclic compounds were prepared via the cycloaromatization. Shibuya's group reported their discovery of pH dependent cycloaromatization of enediyne model compounds via enyne–allene intermediates leading to heterocyclic products promoted by trifluoroacetic acid (Scheme 20).³⁷

Scheme 20. Cycloaromatization catalyzed by trifluoroacetic acid.

4.4. Cyclization Reaction of Hetero Enyne–Allenenes and Their Applications to the Synthesis of Novel Heterocyclic Ring Systems

In addition to the thermal cyclization of carbon enyne–allenes, the thermal cyclization of hetero enyne–allenes has also attracted considerable interests. The synthetic applications of the biradical intermediates could be further expanded if the CH_n groups in the enyne–allene system are replaced by heteroatoms.³⁸ Indeed, enyne–ketenes (A = carbon, B = oxygen) were reported to undergo the C²–C⁷ and the C²–C⁶ cyclizations by Moore *et al.* (Scheme 21)³⁹ leading to quinones or its derivatives; this reaction was termed as the Moore cyclization. By placing a

phenyl group at the acetylenic terminus, the cyclizations are directed mainly toward the C²–C⁶ cyclization pathway instead of the C²–C⁷ cyclization route.

Scheme 21. Enyne-ketene cyclization via a Moore cyclization pathway.

Schmittel *et al.* reported their results concerning the cyclization of enyne–ketenimines (A = N, B = CR'R'') and enyne–carbodiimides (A = N, B = NR') and their synthetic potentials.⁴⁰ These systems undergo the C²–C⁷ and the C²–C⁶ cyclizations as a function of substituents at the acetylenic terminus. With an aryl group, the reaction follows the C²–C⁶ cyclization pathway, whereas with a hydrogen atom, the reaction follows the C²–C⁷ cyclization pathway (Scheme 22).

Scheme 22. C²–C⁷ and C²–C⁶ cyclization of hetero enyne-allenes.

Our group developed new methods of generating enyne–ketenimines and enyne–carbodiimides via the aza-Wittig reaction. Moreover, these new synthetic methods were adopted for the synthesis of several novel heterocyclic ring systems with structures similar to

those of the naturally occurring ellipticine and its derivatives and other more complex structures by modification of R', R'', or benzo moiety.⁴¹

In conclusion, the thermal cyclization of enyne-allenes and hetero enyne-allenes provides many opportunities for the construction of a variety of novel polycyclic ring systems including hydrocarbons and heterocyclic compounds. This strategy is one of the most convenient pathways to construct complex ring systems in a single operation.

5. Literature Survey on the Synthetic Methodologies for the Preparation of Benzannulated Enyne-Allenenes and Acyclic Enyne-Allenenes

To further investigate the cyclization reaction of enyne-allenes, several synthetic methods were developed to prepare enyne-allenes with diverse structural features.

Enyne-allenes can be obtained by using the [2,3] sigmatropic rearrangement of propargylic phosphite or phosphinite to form allenyl phosphonate or phosphine oxide; this scheme was first reported by Sevin *et al.* in 1967.⁴² This synthetic method was adopted by Saito,²⁸ Nicolaou,⁴³ Grissom,⁴⁴ and Schmitt²⁹ for the preparation of enyne-allenes. For example, Nicolaou *et al.* reported that propargylic alcohol **102** was treated with chlorodiphenylphosphine in methylene chloride at -78 °C in the presence of triethylamine to produce allenyl phosphine oxide **104** in good yield (Scheme 23).

Scheme 23. Synthesis of enyne-allenes via [2,3] sigmatropic rearrangement by Nicolaou.

Grissom *et al.* reported a synthetic pathway to enyne-allenes via thermolysis of propargyl vinyl ethers to promote the [3,3] sigmatropic Claisen rearrangement at 150 °C.^{44,45}

They also discovered that the corresponding Lewis acid-catalyzed [3,3] sigmatropic Claisen rearrangement promoted by AgBF_4 for the preparation of the benzannulated enyne-allenes could be carried out at room temperature (Scheme 24).⁴⁴

Scheme 24. Grissom's Approach to Benzannulated enyne-allenes.

Enyne-allenes could also be synthesized via base-catalyzed isomerization of enediyne sulfones.⁴⁶ An example is outlined in Scheme 25.^{46c} When enediyne sulfone **109** was treated with triethylamine in benzene and 1,4-cyclohexadiene at 37 °C, the enyne-allene cyclization product **112** was isolated in 76% yield.

Scheme 25. Benzannulated enyne-allenes via base-catalyzed isomerization.

Dr. Finn's group developed a convenient methodology for the assembly of allene compounds from two aldehyde units and a doubly oxophilic "carbon atom" synthon.⁴⁷ However,

enyne-allenes were prepared in low to moderate yield by employing the doubly oxophilic ylide reagent prepared *in situ* from $\text{TiCl}_2(\text{OiPr})_2$, $(\text{Me}_2\text{N})_3\text{P}=\text{CH}_2$, and $\text{NaN}(\text{SiMe}_3)_2$ (Scheme 26).

Scheme 26. Finn's approach to benzannulated enyne-allenes.

Dr. Gillmann's group reported that the thermolabile enyne-allene esters could be prepared by a Pd-catalyzed cross-coupling reaction between arylzinc halides and 2-haloallene carboxylates in moderate yield.^{35a,48} This is a mild reaction process to generate enyne-allenes. The specific examples are outlined in Scheme 27.

(a) *n*-BuLi, THF, -90 °C, 10 min; ZnCl_2 , -90 °C to -20 °C; (b) *n*-BuLi, THF, -90 °C, 10 min; $\text{B}(\text{OCH}_3)_3$ (1.3 equiv.), -90 to 0 °C; (c) Coupling of **117a**: $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) or $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5 mol%), AsPh_3 (40 mol%), **118a** or **118b**, THF, rt; (d) coupling of **117b**: $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5 mol%), AsPh_3 (40 mol%), 1 M aq. Ag_2O (4 equiv.), **118b**, THF, 0 °C to rt, 2 h

Scheme 27. Gillmann's approach to benzannulated enyne-allenes.

Dr. Cunico's group developed a method for *in situ* formation of an enyne-allene based on their earlier findings of a facile elimination-trimethylsilyl (TMS) group migration within the propargylic framework of structures similar to **121**.⁴⁹ The reaction sequences are outlined in Scheme 28 with all steps giving good yields.

Scheme 28. Cunico's approach to benzannulated enyne-allenes.

Dr. Schmittel's group developed a method for substituted enyne-allenes by the process outlined in Scheme 29.^{29e} The formation of enyne-allenes could be understood assuming a migration of the carbonyl group.

Scheme 29. Schmittel's approach to benzannulated enyne-allenes.

Dr. Schmittel's group also developed the preparation of enyne-allenes via the Pd-catalyzed addition of arylzinc chloride and cuprate addition to propargylic acetates (Scheme 30).^{29g}

Scheme 30. Schmittel's approach to benzannulated enyne-allenes.

Our group developed several convenient procedures for the synthesis of enyne-allenes.⁵⁰ One method involves bromoboration of 1-alkynes with BBr₃ producing alkenyl boronic esters, followed by subsequent Pd(0)-catalyzed cross-coupling with acetylenic zinc chlorides and iodination and a second Pd(0)-catalyzed reaction with allenic zinc chlorides (Scheme 31).^{50a}

Dr. Lipton's group reported that the oxygen-substituted enyne-allenes could be prepared by treating the acetylenic ketones with cuprates and trapping the resultant enolates with acetic anhydride in good yield (Scheme 32).³⁶

Inanaga *et al.* reported that the allenes **147** could be produced from propargylic acetates by treatment of **143** with a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$, 2-propanol, and SmI_2 -THF. The reaction sequence with its mechanism is outlined in Scheme 33.⁵¹

CHAPTER II

Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes. Unusual Cleavage of a Benzene Ring Leading to Twisted 1,1'-Dialkyl-9,9'-bifluorenylidenes and Spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes].

1. Introduction

Our research group recently reported the use of thionyl chloride to induce an S_NI' reaction of the benzannulated enediynyl propargylic alcohol **149**, derived from condensation between 9-fluorenone and the lithium acetylide **60** (Scheme 34).^{32b} This scheme provided a convenient pathway to produce in situ the benzannulated enyne–allene **151**. A subsequent C²–C⁶ cyclization reaction (Schmittel cyclization) then generated the biradical **152**, which in turn underwent an intramolecular radical–radical coupling to give the formal Diels–Alder adduct **153**. Tautomerization followed by hydrolysis then afforded **155** in 74% yield. Although the transformation from **151** to **153** could also be regarded as a concerted Diels–Alder reaction, the mechanistic,^{12,29a,c,31} theoretical,^{30a–f} and DNA-cleaving^{29g} studies suggest a two-step biradical pathway. Interestingly, in addition to **155**, a minor amount of the [2 + 2] cycloaddition adduct **156** (12%) as a derivative of spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] was also isolated. This synthetic strategy was adopted for the synthesis of a C₄₄H₂₆ hydrocarbon **69** having a carbon framework represented on the surface of C₆₀.^{32a} Furthermore, by employing a system containing two units of the benzannulated enyne–allene moiety, three highly twisted 4,5-diarylphenanthrenes **78a–c** were obtained.³³

Scheme 34. Polycyclic compounds via a $\text{C}^2\text{-C}^6$ cyclization and subsequent reactions.

2. Research Objective

Based on our previous discovery about the formation of chlorinated benzannulated enyne-allenes via a S_{Ni}' reaction promoted by thionyl chloride and subsequent $\text{C}^2\text{-C}^6$ cyclization,³² we were interested in further exploring the use of molecules having two benzannulated enyne-allene units for the synthesis of polycyclic aromatic compounds. We envisioned the use of the following molecules to achieve this objective (Scheme 35). If these reactions follow the normal cyclization pathway, **158** could be produced. However, it was quite unexpected that this strategy led to the formation of highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes and other polycyclic compounds. Moreover, we were also interested in using the synthetic pathway developed for benzannulated enyne-allenes without a chloro substituent^{32b,33} for the preparation of polycyclic aromatic compounds via usual cyclization pathway.

Scheme 35. Expected polycyclic compounds from diol **157**.

3. Literature Survey for the 9,9'-Bifluorenylidenes

Because of overcrowding, the two fluorenylidene fragments of 9,9'-bifluorenylidenes are severely twisted.⁵² The crystal structure of the parent compound **159a** shows a twist angle of ca. 42° while the more crowded 1,1'-disubstituted 9,9'-bifluorenylidene **159b** exhibits a higher twist angle of ca. 52°. ^{52a} Remarkable twist angles of 55° and 66° were recently reported for the octachlorobifluorenylidene **160** and the perchlorobifluorenylidene **161**, respectively (Figure 4).^{52b} The reported synthetic methods for 9,9'-bifluorenylidenes generally involve coupling of two fluorenyl fragments.⁵²

Figure 4. Some examples of twisted 9,9'-bifluorenylidenes.

4. Results and Discussion

4.1. Unusual Cascade Cyclizations of Dipropyl Substituted Propargylic Diol

The diketone **164** was synthesized by treatment of **162**⁵³ with 4-octyne to form **163** followed by two intramolecular acylation reactions (Scheme 36). Condensation between **164**

and 2 equiv of **60** then provided the benzannulated enediynyl propargylic alcohol **157a** as a mixture of the trans and cis isomers (isomer ratio = 2:1). Upon treatment with thionyl chloride, four products, including the 1,1'-dipropyl-9,9'-bifluorenylidene **165**, the polycyclic compounds **166** and **167**, and the spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] **168** as a mixture of the trans and cis isomers (trans:cis = 5:1), were isolated. The structures of **165**, **167**, and the trans isomer of **168** were established by X-ray structure analysis.

Scheme 36. Unusual cascade cyclizations of **157a** leading to **165** and other polycyclic compounds.

The formation of the products **165**, **166**, and **167** was unexpected. Apparently in the case of **165**, the intramolecular radical–radical coupling of the initially formed biradical **170** involved the central benzene ring having the two propyl substituents to form **171** (Scheme 37). It was originally anticipated that such a coupling would occur on one of the peripheral benzene rings, which is sterically less crowded. However, molecular modeling suggests that this pathway suffers from nonbonded steric interactions between the chloro substituent and the neighboring

propyl group on the central benzene ring. The effect of such a steric interaction in dictating the course of the reaction was observed previously.^{32b} A second formal intramolecular Diels–Alder reaction, again promoted by thionyl chloride, then led to **172**. Cleavage of the bond connecting the two carbons having the propyl substituent then gave the valence tautomer **173a**, which could also be regarded as a resonance structure of **173b** having a carbon–carbon single bond joining the two central five-membered rings. Rotation of the carbon–carbon bond joining the two central five-membered rings then gave the trans isomer **174**. The temperature-dependent NMR studies have also shown that the rotational barriers of the cis-trans isomerization of several sterically congested 1,1'-disubstituted 9,9'-bifluorenylidenes are relatively low, allowing rapid interconversion to occur at ambient temperature.⁵⁴ Oxidation of **174**, presumably by oxygen, followed by hydrolysis then produced **165**. The X-ray crystal structure reveals that it has a twist angle of 45.2° for the carbon–carbon double bond connecting the two bifluorenylidene fragments (Figure 5a,b). This carbon–carbon double bond has a bond length of 1.380 Å, unusually long for a carbon–carbon double bond indicating a partial diradical character for the bond.

Scheme 37. Mechanism of unusual cyclization leading to **165**.

It is worth noting that transformation from **157a** to **165** involves a rare occurrence of cleavage of a benzene ring. However, the loss of the resonance energy is more than compensated for with the eventual formation of two new benzene rings in **165**.

Figure 5a. ORTEP drawing of the crystal structure of the 1,1'-dipropyl-9,9'-bifluorenylidene **165** with hydrogen atoms omitted for clarity.

The chlorosulfite **175**, derived from **171**, could also undergo a different S_N1 reaction involving the carbon–carbon double bond substituted with a propyl group to produce the chloride **166** (Scheme 38). The structure of **166** was tentatively assigned on the basis of the MS and ^1H NMR spectra. It was observed by ^1H NMR that the majority of **166** in the crude reaction mixture was converted to **167** after purification by silica gel column chromatography. Presumably, a 1,2-migration of the propyl group to the adjacent carbon having a chloro substituent occurred to give **176**, which upon hydrolysis then produced **167**.

Two intramolecular [2 + 2] cycloaddition reactions with the two chlorinated allenes derived from **157a** could account for the formation of **168** as a mixture of the trans and cis isomers. A single crystal of the trans isomer suitable for X-ray structure analysis was obtained.

Scheme 38. Mechanism of unusual cyclization leading to **166** and **167**.

4.2. Unusual Cascade Cyclizations of Dimethyl Substituted Propargylic Diol

The diketone **179** was likewise synthesized by two intramolecular acylation reactions of **178**, derived from condensation between **162** and 1,4-dichloro-2-butyne to form **177** followed by reduction with tributyltin hydride (Scheme 39). Treatment of **179** with two equiv of **60** then afforded the diol **157b** also as a mixture of the trans and cis isomers (isomer ratio = 2:1). On exposure to thionyl chloride, **157b** was also transformed to the 1,1'-dimethyl-9,9'-bifluorenylidene **180** and the polycyclic compounds **181** and **182**. The structure of **181** was tentatively assigned on the basis of the MS and ^1H NMR spectra. Compared to the case of **157a**, elimination of a molecule of hydrogen chloride from **181** to form **182** appears to occur more readily than 1,2-migration of the adjacent methyl group. The structure of **182** was established by X-ray structure analysis. The [2 + 2] cycloaddition adduct was not detected in this case.

Scheme 39. Unusual cascade cyclizations of **157b** leading to **180** and other polycyclic compounds.

4.3. Cascade Cyclizations of Benzannulated Propargylic Diol

Condensation between **162** and benzyne,⁵⁵ generated in situ from anthranilic acid, eventually led to the diketone **184** and subsequently the diol **157c** as a mixture of the trans and cis isomers (isomer ratio = 3:1) (Scheme 40). Treatment of **157c** with 2 equiv of thionyl chloride produced the [2 + 2] cycloaddition adduct **185** as a mixture of the trans and cis isomers (trans:cis = 3:1). In addition, the alcohol **186** as a mixture of the trans and cis isomers (isomer ratio = 2:1) and the ketone **187** were also isolated. The structure of the trans isomer of **185** was established by X-ray structure analysis. Unlike the cases of **157a** and **157b**, the formation of **186** and **187** indicated that the intramolecular radical–radical coupling reaction involved one of the peripheral benzene rings. Apparently, the central naphthyl ring with its higher resonance energy is more resistant to being attacked at the ring junction because such an attack would result in the loss of the entire naphthyl aromaticity. The reaction pathway leading to the alcohol **186** is similar to the one described for **155**. It was previously observed that treatment of the chloride **154** and other analogous compounds with NaOH under air produced the corresponding ketones in excellent yields.⁵⁶ A similar reaction could likewise give rise to the ketone **187**.

Scheme 40. Cascade cyclizations of **157c** leading to polycyclic compounds.

4.4. Other Attempts to Synthesize Polycyclic Aromatic Compounds

Scheme 41 outlines attempts to synthesize polycyclic aromatic hydrocarbon **189** via cascade radical cyclization of the molecules having two units of benzannulated enyne-allenes without a chloro substituent.^{32b} Treatment of **157b** with trifluoroacetic acid in the presence of triethylsilane at low temperature afforded the tetraacetylenic hydrocarbon **188b** as a 2:1 mixture of diastereomers. On exposure to potassium *tert*-butoxide under refluxing toluene at 110 °C, the reaction mixture turned into dark pink color immediately. The ¹H NMR spectrum of the crude reaction mixture showed only broad peaks in the aromatic region, indicating that the starting material decomposed or polymerized. Treatment of **188b** with weaker bases, such as basic aluminum oxide, triethylamine, basic aluminum oxide in the presence of 1,4-CHD, at 0 °C to room temperature gave similar results. However, treatment of **157c** with trifluoroacetic acid in the presence of triethylsilane at low temperature gave a dark-colored solid. The ¹H NMR spectrum of the crude reaction mixture showed only broad peaks in the aromatic region, indicating that the starting diol **157c** decomposed or polymerized.

Scheme 41. Attempt to synthesize compound **189** via the new synthetic pathway.

Scheme 42 outlines a study to generate enyne-allenes in situ from crude propargylic acetate promoted by $\text{Pd(PPh}_3)_4$, 2-propanol and SmI_2 -THF, followed by cascade radical cyclization leading to polycyclic hydrocarbons in a single operation.⁵¹ Condensation between 9-fluorenone and the lithium acetylide **60** as reported previously furnished the corresponding alkoxide,^{32b} which was captured by acetic anhydride to afford the propargylic acetate **190**. Upon treatment of the reaction mixture with $\text{Pd(PPh}_3)_4$, SmI_2 -THF, and 2-propanol, polycyclic hydrocarbon **191** was isolated. The structure was established by ^1H NMR and ^{13}C NMR.

Scheme 42. Polycyclic hydrocarbon **191** from **190**.

Scheme 43 outlines a similar reaction sequence starting from compound **184**. Condensation between **184** and 2 equiv of **60** or its derivative **192** furnished the corresponding alkoxide, which was captured with acetic anhydride leading to propargylic acetate. Upon treatment of the reaction mixture of **193a** with $\text{Pd(PPh}_3)_4$, SmI_2 -THF, and 2-propanol, a black solid with low solubility in CDCl_3 was obtained. The ^1H NMR spectrum of the crude reaction mixture showed only broad peaks in the aromatic region, indicating that the starting material decomposed or polymerized. To improve the solubility of final product, **200** as a precursor of **192** with a long aliphatic chain was synthesized (Scheme 44).⁵⁷ A similar result of unidentifiable products was obtained by treatment of the reaction mixture of **193b** with $\text{Pd(PPh}_3)_4$, SmI_2 -THF, and 2-propanol.

Scheme 43. Attempt to synthesize polycyclic compounds **189c** and **189d**.

Scheme 44. Synthesis of **200** as a precursor of **192**.

5. Conclusions

The transformations from **157a** and **157b** to the highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes **165** and **180**, respectively, represent a novel synthetic pathway to these highly twisted compounds. The cascade sequence involves an unusual cleavage of a benzene ring. Alternatively, the intramolecular [2 + 2] cycloaddition reactions of the benzannulated enyne-allenes lead to the spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes] **168** and **185–187**. They are also structurally interesting compounds. Several approaches to prepare polycyclic aromatic compounds **158a–c** and **189b–d** via usual cascade radical cyclization of the molecules having two units of benzannulated enyne-allenes with or without a chloro substituent were explored.

CHAPTER III

Polycyclic Aromatic Compounds via Radical Cyclizations of Benzannulated Enyne–Allenes Derived from Ireland–Claisen Rearrangement

1. Introduction

Biradicals generated from cyclization of (Z)-1,2,4-heptatrien-6-ynes (enyne–allenes) and the benzannulated analogues under mild thermal conditions provide many opportunities for subsequent synthetic applications.^{9,11} Cyclization of the enyne–allene **201** could proceed either via the C²–C⁷ pathway (Myers–Saito cyclization) to form the α ,3-didehydrotoluene/naphthalene biradical **202**^{27a,b,28} or via the C²–C⁶ pathway (Schmittel cyclization) to produce the fulvene/benzofulvene biradical **203** (Scheme 45).^{10,12,29a,c,f, 40b} The enyne–allenes bearing an aryl substituent or a sterically demanding group, such as the *tert*-butyl group or the trimethylsilyl group, at the alkynyl terminus favor the Schmittel cyclization pathway.

Scheme 45. C²–C⁶ and C²–C⁷ cyclizations.

One of the synthetic methods that have been used to prepare in situ the benzannulated enyne–allenes for the subsequent Myers–Saito cyclization reaction involves producing the allenic moiety via thermolysis of propargyl vinyl ethers to promote the [3,3] sigmatropic Claisen rearrangement at 150 °C.⁴⁴ The corresponding Lewis-acid catalyzed [3,3] sigmatropic Claisen rearrangement promoted by AgBF₄ was also successfully adopted for the preparation of the benzannulated enyne–allenes at 25 °C.⁴⁴

The silyl ketene acetals of propargylic acetates have also been reported to undergo facile Ireland–Claisen rearrangement to produce, after hydrolysis, the corresponding allenyl acetic

acids.⁵⁸ Specifically, the propargylic acetate **204** was treated with lithium diisopropylamide (LDA) followed by trapping the resulting enolate with trimethylsilyl chloride to form the silyl ketene acetal **205** at $-78\text{ }^{\circ}\text{C}$ (Scheme 46). Upon warming the reaction mixture to $40\text{ }^{\circ}\text{C}$, the Ireland–Claisen rearrangement occurred to produce the silyl ester **206**, which after hydrolysis furnished the allenyl acetic acid **207** in 50% overall yield.

Scheme 46. Allenyl acetic acid **207** via Ireland-Claisen rearrangement.

The discovery and subsequent investigation of the chemistry of buckminsterfullerene (C_{60}) have attracted a great deal of interest in bowl-shaped polycyclic aromatic hydrocarbons. As the smallest fullerene fragment, corannulene has received renewed attention.⁵⁹ Recently, development of new synthetic methods for corannulene and related compounds has attracted considerable attention.⁶⁰

2. Research Objective

The mildness of the reaction condition and the ready availability of a variety of silyl ketene acetals make the transformation of Ireland–Claisen rearrangement well suited for the preparation of thermally labile enyne–allenes and the benzannulated analogues. However, this reaction sequence did not appear to have been adopted for the synthesis of enyne–allenes. We envisioned that this transformation could be employed to develop a new synthetic strategy to produce in situ the benzannulated enyne–allenes for radical cyclizations leading to polycyclic aromatic compounds. Secondly, we were also interested in exploring the possibility of employing the new polycyclic aromatic compounds to synthesize corannulene and its derivatives via a non-pyrolytic pathway.

3. Literature Survey for the Synthesis of Benzo[ghi]fluoranthene, Corannulene and Related Compounds, and Synthetic Pathway for Ring Contraction

3.1. Synthesis of Benzo[ghi]fluoranthene and Related Compounds

In 1966 and 1971, Barth and Lawton first reported their synthetic approach toward benzo[ghi]fluoranthene, corannulene, and related compounds, which mainly involved intramolecular Friedel–Crafts reactions and an acyloin closure promoted by sodium in inert solvent.⁶¹ Crombie *et al.* reported an alternative route to benzo[ghi]fluoranthene via two intramolecular Friedel–Crafts reactions to construct two six-membered rings.⁶² In 1999, Cho *et al.* reported an alternative pathway to benzo[ghi]fluoranthene (Scheme 47).⁶³

Scheme 47. Cho's approach to **212**.

Studt *et al.* reported a synthetic pathway to benzo[ghi]fluoranthene catalyzed by Pt/C at 400°C (Scheme 48).⁶⁴

Scheme 48. Studt's approach to **212**.

Benzo[ghi]fluoranthene was also prepared via flash vacuum pyrolysis (FVP). Scheme 49 outlines the pyrolytic routes to benzo[ghi]fluoranthene from a variety of starting materials.⁶⁵

Scheme 49. The syntheses of **212** from a variety of starting materials via FVP.

3.2. Synthesis of Corannulene and Related Compounds

Corannulene was first synthesized by Barth and Lawton in 1966 by a 17-step process.⁶¹ This C_{20} carbon framework, representing the polar cap of buckminsterfullerene (C_{60}), has attracted renewed interest in the development of efficient pathways for its synthesis. Several attempts to improve the synthesis were unsuccessful⁶⁶ until Scott *et al.* first successfully applied flash vacuum pyrolysis methodology to the ring-forming step leading to corannulene in 1991.^{59a}

3.2.1. Synthesis of Corannulene via Flash Vacuum Pyrolysis (FVP)

Scott *et al.* reported a readily accessible process to corannulene **221** via FVP (Scheme 50).⁵⁹

Scheme 50. The first synthesis of corannulene **221** via FVP.

During the past several years, several syntheses of corannulene **221** and related bowl-shaped compounds via FVP were reported (Scheme 51).⁶⁰ In these syntheses, the central five-membered ring is pre-formed and two six-membered aromatic rings are formed via the key FVP process.

Scheme 51. The syntheses of **221** from a variety of starting materials via FVP.

Mehta *et al.* reported an alternative approach to corannulene **221** by employing simple starting materials and basic reactions, and generating a five- and a six-membered ring via FVP step (Scheme 52).^{60h,67}

Although FVP method is successful for the synthesis of several buckybowls in moderate to low yield,^{68a} it suffers from a few disadvantages, such as low yields for larger, nonvolatile systems; difficulties to scale up; and a lack of functional group tolerance.^{68b}

Reagents and yield: a. K_2CO_3 , THF, 18-crown-6, 65%; b. $h\nu$, C_6H_6 , I_2 , propylene oxide, 2 h, 35%; c. NBS, CCl_4 , AIBN, 75%; d. $(Bu_4N)_2Cr_2O_7$, $CHCl_3$, 60%; e. $ClCH_2PPh_3^+Cl^-$, $t-BuO^+K^+$, 2 h, 60%; f. $ClCH_2PPh_3^+Cl^-$, $t-BuO^+K^+$, 0.5 h, 70%; g. (i) CH_3MgI , THF, 0.5 h, 80%; (ii) PCC, DCM, 2 h, 60%; h. PCl_5 , C_6H_6 , 40%; i. LDA, THF, TMSCl, 60%; j. FVP, 1200 °C, 0.5 torr, N_2 flow.

Scheme 52. Mehta's approach to corannulene **221** via FVP.

3.2.2. Synthesis of Corannulene and Related Compounds via Non-pyrolytic Pathway

In 1996, Siegel *et al.* first reported that the corannulene derivatives could be prepared via non-pyrolytic pathway involving the formation of the two rim bonds via reductive coupling with $TiCl_3/LiAlH_4$ or $VCl_3/LiAlH_4$ (Scheme 53).⁶⁹ This method was adopted for synthesis of more complex corannulene derivatives.⁷⁰

Conditions: a. 4-heptanone, KOH; b. norbornadiene, acetic anhydride (49%, 2 steps); c. NBS, benzoylperoxide, hv (quantitative); d. TiCl_3 , LiAlH_4 (33%); e. DDQ, (55%).

Scheme 53. Siegel's non-pyrolytic pathway to **243**.

In 2000, Rabideau *et al.* reported an inexpensive, convenient synthesis of corannulene and its derivatives in over 80% yield and mild conditions where reaction mixtures were refluxed for 15 min in aqueous dioxane containing NaOH (Scheme 54).⁷¹

Scheme 54. Rabideau's improved approach to **221** via non-pyrolytic pathway.

Scott *et al.* developed a new route to dibenzo[*a,g*]corannulene by intramolecular palladium-catalyzed arylation reactions (Scheme 55).^{72, 68a}

Scheme 55. Scott's approach to **249** via non-pyrolytic pathway.

Rabidau *et al.* recently discovered that the formation of the two rim bonds could be promoted by nickel-mediated intramolecular coupling of benzyl and benzyldiene bromides (Scheme 56).^{68b,73}

Conditions: a. (i) acetic anhydride, H_2SO_4 , 1 h, rt; (ii) dimethyl acetylene dicarboxylate, 2 h reflux, (75–80%); b. CCl_4 , NBS, benzoylperoxide, hv, 2 h, reflux (quantitative); c. DMF, Ni powder, 12 h, 80–90 °C (60%).

Scheme 56. Rabideau's approach to **253** catalyzed by $\text{Ni}(0)$.

3.3. Synthetic Pathway for Ring Contraction

3.3.1. Ring Contraction via Lead(IV) Acetate

Taylor *et al.* reported an oxidative rearrangement of alkyl aryl ketone under mild conditions by using thallium(III) nitrate leading to corresponding methyl arylacetate in good yield. This method was adopted for ring contraction.⁷⁴ Following this report, a ring contraction method using lead(IV) acetate in the presence of boron trifluoride and methanol appeared.⁷⁵ A specific example including the reaction mechanism is outlined in Scheme 57.^{75a}

Scheme 57. Ring contraction catalyzed by $\text{Pb}(\text{OAc})_4$.

A ring contraction of aliphatic cycloketones was reported by Myrboh, which was carried out in the presence of perchloric acid, triethyl orthoformate, and lead(IV) acetate (Scheme 58).⁷⁶

Scheme 58. Ring contraction of aliphatic cycloketones catalyzed by $\text{Pb}(\text{OAc})_4$.

3.3.2. Ring Contraction via Wolff Rearrangement

Ring contraction via Wolff rearrangement of diazo ketones has been applied to the synthesis of several highly strained ring systems.⁷⁷ It is successful in the construction of the 4- and 5-membered rings (Scheme 59).^{77a} Generally, the synthesis of diazo ketones involved the reaction sequence of the preparation of formyl derivatives followed by treatment with tosyl or mesyl azide.^{77a,e,f,78} An alternative synthetic pathway to diazo ketones involved a two-step reaction sequence using isoamyl nitrite and chloramine (Scheme 60).^{77c,d, 79}

Scheme 59. Ring contraction via Wolff rearrangement.

Scheme 60. An alternative pathway to the diazo ketone and ring contraction.

4. Results and Discussion

4.1. Polycyclic Aromatic Carboxylic Acids via Ireland–Claisen Rearrangement

Condensation between 9-fluorenone and the lithium acetylide **60**³³ as reported previously furnished the corresponding alkoxide,^{32b} which was captured by acetic anhydride to afford the propargylic acetate **190** (Scheme 61). Treatment of **190** with LDA at $-78\text{ }^{\circ}\text{C}$ followed by trapping the resulting enolate with *tert*-butyldimethylsilyl chloride (TBDMSCl) then gave the silyl ketene acetal **269**.⁸⁰ A series of reactions then occurred upon warming the reaction mixture to $45\text{ }^{\circ}\text{C}$, including an Ireland–Claisen rearrangement to form the benzannulated enyne–allene **270** followed by a Schmitt cyclization to generate the benzofulvene biradical **271**. An intramolecular radical–radical coupling then produced the formal Diels–Alder adduct **272**, which

in turn underwent a prototropic rearrangement to give the silyl ester **273** and, after hydrolysis, the carboxylic acid **274** in 57% overall yield from **190** in a single operation. The cascade transformation from **270** to **273** is reminiscent of what was observed previously in a chlorinated enyne–allene system derived from condensation between 9-fluorenone and **60** to form the corresponding propargylic alcohol followed by treatment of the propargylic alcohol with thionyl chloride.^{32b}

Scheme 61. Synthesis of **274** via Ireland-Claisen rearrangement.

The diaryl ketone **275**,⁸¹ readily obtained by oxidation of the corresponding hydrocarbon, 4*H*-cyclopenta[*def*]phenanthrene,⁸² was also selected for condensation with **60** leading to the propargylic acetate **279** in 81% yield (Table 3). The acetate **279** was converted to the carboxylic acid **283**⁸³ via the tandem sequence of Ireland–Claisen rearrangement and Schmitt cyclization. Similarly, the use of the diaryl ketone **276**,^{59a,84} benzophenone (**277**), and dibenzosuberone (**278**)

led to the carboxylic acids **284**, **285**, and **286**, respectively. As a result of lower stability of **282**, the carboxylic acid **286** was produced in low yield. It is worth noting that the structures of **283** and **284** contain a benzo[*ghi*]fluoranthene unit and a dihydrobenzo[*ghi*]fluoranthene unit, respectively. Several synthetic methods for benzo[*ghi*]fluoranthene and related derivatives have been reported.^{59,60,61,62,63} One of these derivatives was used in the first synthesis of the bowl-shaped corannulene.⁵⁹

Table 3. Synthesis of Polycyclic Aromatic Carboxylic Acids from Diaryl Ketones

diaryl ketone	propargylic acetate	carboxylic acid
<p>275</p>	<p>279, 81%</p>	<p>283, 70%</p>
<p>276</p>	<p>280^a</p>	<p>284, 37%^b</p>
<p>277</p>	<p>281^a</p>	<p>285, 53%^b</p>
<p>278</p>	<p>282^a</p>	<p>286, 10%^b</p>

^a The crude product was used for the next step without isolation.

^b Overall yield from the diaryl ketone.

4.2. Synthesis of Polycyclic Ketone via Friedel–Crafts Reaction and Attempts to Synthesize Corannulene Derivatives

The pendent carboxylic acid group in **274** also provided the opportunity for an intramolecular acylation reaction. Conversion of **274** to the corresponding acid chloride with thionyl chloride followed by an aluminum chloride-promoted intramolecular acylation reaction then produced the polycyclic aromatic ketone **287** in 88% yield (eq 1). The structure of **287** was established by X-ray structure analysis.

The acid **283** was also readily converted to the acid chloride **288** with thionyl chloride (Scheme 62). However, attempts to promote the intramolecular acylation reaction of **288** using aluminum chloride as a catalyst to form **289** were unsuccessful. The ^1H NMR spectrum of the crude reaction mixture showed only very broad peaks in the aromatic region indicating that intermolecular acylation occurred to give polymerized adducts. It was envisioned that **289** could serve as a precursor for ring contraction^{74,75a,77a} to form **290** having an indeno-fused dihydrocorannulene moiety. The acid chloride of **284** was also used for the acylation reaction in the hope that the intermolecular reaction could be avoided. Unfortunately, such an attempt was also unsuccessful. Treatment of **284** with concentrated sulfuric acid at room temperature for 12 h resulted in the recovery of unreacted **284**. On the other hand, the aryl ketone **291**⁸⁵ was readily obtained from **285** in 70% yield (eq 2).

Scheme 62. Attempt to synthesize **289** by acylation reaction.

4.3. [4 + 2] versus [2 + 2] Cyclization

With the propargylic acetate **293**, derived from 2,2-dimethylpropiophenone (**292**), the 1*H*-cyclobut[*a*]indenyl acetic acid **296** was obtained as the predominant product along with ca. 1% of the 11*H*-benzo[*b*]fluorenyl acetic acid **297** (Scheme 63). Conceivably, the initially formed benzannulated enyne–allene **294** underwent a [2 + 2] cycloaddition reaction preferentially, perhaps also via the biradical **295**, to produce **296**. The low propensity for **295** to undergo the radical–radical coupling reaction involving a double bond of the phenyl substituent to produce the formal Diels–Alder adduct leading to **297** may be attributed to the emergence of the nonbonded steric interactions between the silyl ester group and the *tert*-butyl group depicted in **295** along the pathway toward **297**. Such a change of the reaction pathway was also observed previously in the chlorinated enyne–allene system.^{32b}

Scheme 63. [2 + 2] cyclization of **293** via Ireland-Claisen rearrangement.

As in the case of the chlorinated enyne–allene system, the use of the ketone **298**⁸⁶ having the keto group incorporated in the six-membered ring to prepare the propargylic acetate **300** for the cascade transformation appears to reduce the nonbonded steric interactions along the pathway leading to the Diels–Alder adduct (Scheme 64). As a result, the [2 + 2] cycloaddition adduct **302** and the Diels–Alder adduct **303** were produced in essentially equal amounts. In the case of **301**, prepared from **299**⁸⁷ having a five-membered ring, the effect was particularly dramatic and resulted in the formation of the Diels–Alder adduct **305** predominantly.

Scheme 64. [4 + 2] vs [2 + 2] cyclization.

4.4. Attempts for Ring Contraction

4.4.1. Attempts for Ring Contraction Catalyzed by $\text{Pb}(\text{OAc})_4$

Scheme 65 outlines an attempt for ring contraction to form **307** using $\text{Pb}(\text{OAc})_4$.^{75a} First, the reaction was carried out in benzene. The starting material **287** was recovered due to the very low solubility of **287**. To increase the solubility of **287**, the reaction was performed in a mixture of methylene chloride and benzene. It was quite unexpected that compound **306** was produced in 37% yield. The structure of **306** was established by X-ray structure analysis. The reaction mechanism is not clear at the present time.

Scheme 65. Attempt to form **307** via ring contraction catalyzed by $\text{Pb}(\text{OAc})_4$.

Scheme 66 outlines an alternative attempt for ring contraction. Compound **309** was produced successfully from benzosuberone by using the method reported previously for the ring contraction of aliphatic cycloketones.^{76a} When the same reaction condition was employed for compound **287**, compound **310** was isolated, and part of starting material was recovered. The structure of **310** was established by X-ray structure analysis.

Scheme 66. Model compound study and the second attempt to form **307**.

4.4.2. Attempts for Ring Contraction via Wolff Rearrangement

Scheme 67 outlines an attempt for ring contraction via Wolff rearrangement. We were able to successfully carry out the ring contraction of **311** via the general reaction sequences of Wolff rearrangement as reported previously.^{77a} However, compound **310** was again isolated using two different procedures for the preparation of the diazo ketone followed by ring contraction. Treatment of **287** with NaH, MeOH, and methyl formate furnished **310** instead of the corresponding formyl derivatives. Attempts to produce the diazo ketone via a one-pot procedure resulted in **310** as well.

Scheme 67. Model compound study of Wolff rearrangement and attempt to prepare the diazo ketone.

Scheme 68 outlines an alternative pathway to prepare the diazo ketone⁷⁹ for the following Wolff rearrangement. It was also unsuccessful.

Scheme 68. An alternative attempt to prepare the diazo ketone.

5. Conclusions

The Ireland–Claisen rearrangement of the propargylic acetates was successfully adopted for the synthesis of the benzannulated enyne–allenes in situ for the subsequent Schmitt cyclization to generate benzofulvene biradicals for a cascade sequence of reactions. Several polycyclic aromatic derivatives of benzo[*ghi*]fluoranthene and 11*H*-benzo[*b*]fluorene were thus produced. In several cases, the [2 + 2] cycloaddition reaction of the benzannulated enyne–allenes also occurred leading to the corresponding 1*H*-cyclobut[*a*]indenyl acetic acids. While several attempts for ring contraction of compound **287** and intramolecular acylation of polycyclic aromatic carboxylic acids **283** and **284** were unsuccessful, many other potential Lewis-acid catalysts other than AlCl_3 are available for intramolecular acylation reactions, and will be used in future studies. The highly efficient pathway outlined in Scheme 61 & eq 1 holds great promise for the synthesis of a wide variety of polycyclic aromatic compounds.

CHAPTER IV

Polycyclic Compounds via Wagner–Meerwein Rearrangement of Fluorenylmethanols and Intramolecular Friedel–Crafts Arylation Reactions

1. Introduction

Screw structures or helices are encountered frequently in nature. In addition to the helical molecules in biochemistry including nucleic acids, proteins, and polysaccharides, more and more unnatural helical molecules, such as helical alkenes, phenanthrenes, helicenes, and ariliphatic helices, have been reported.^{88a,b} Among the unnatural helices, helicenes, as helical compounds consisting of ortho-fused aromatic rings, were regarded as little more than an academic curiosity for many years.⁸⁸ Helicenes have received great attention recently, because of their unique properties associated with their inherent chirality due to their nonplanar structures.⁸⁹ [n]Helicenes were considered potentially useful for asymmetric catalysts,⁹⁰ asymmetric molecular recognition,⁹¹ liquid crystals,⁹² novel optical materials, owing to the extraordinary optical and electronic properties,⁹³ self-assembling components,⁹⁴ and molecular devices.⁹⁵ Figure 6 displays some examples of phenanthrenes, helicenes and related compounds having unique properties. 4,5-Disubstituted phenanthrenes **316** have inherently helical chirality because of steric hindrance.⁹⁶ An enantiopure [6]carbohelicene **317** was used successfully for catalyzing enantioselective synthesis of pyrimidyl alkanol.^{90a} Phosphine **318** as a chiral ligand was prepared and employed as a catalyst for enantioselective hydrogenation.^{90b,c} Compounds **319** and **320** classified as heterohelicene and helicenequinone, respectively, were found to possess nonlinear optical property.^{93a,c,d} In addition, **320** could also serve as the precursor for other novel materials, such as liquid crystal, conjugated ladder polymer, and helicene fibers.⁹²

Compound **321**, a [*P*]helicene, binds to DNA strongly and forms more stable complex than the corresponding [*M*]helicene.^{91a} Due to their unique properties and potential applications as novel materials, development of efficient methods for the synthesis of phenanthrenes and helicenes in large scale and in good enantioselectivity has attracted considerable attention.^{88e}

Figure 6. Examples of phenanthrenes and helicenes.

2. Research Objective

Our research Group recently developed a new synthetic method for polycyclic aromatic hydrocarbons by employing the C^2-C^6 cyclization reaction of the benzannulated enyne-allenes. This procedure was successfully adopted for the synthesis of 4,5-diarylphenanthrenes **78** having a helical twist due to steric interactions.³³ We were also interested in converting the two benzannulated 5-membered rings of **78** to 6-membered rings via a ring expansion reaction. We envisioned that the ring expansion and aromatization could be achieved using Wagner–Meerwein rearrangement of the corresponding fluorenylmethanols.⁹⁷ Scheme 69 displays a simple example with its reaction mechanism.

Scheme 69. Wagner-Meerwein rearrangement.

3. Literature Survey for the Synthesis of Helical Compounds, Such as Phenanthrenes and Helicenes etc.

3.1. Synthesis of Phenanthrenes and Related Compounds

Several synthetic strategies for 4,5-dimethylphenanthrenes and related compounds have been reported, including ozonolysis of pyrene,⁹⁸ intramolecular cyclization of 2,2'-bis(halomethyl)-6,6'-dimethylbiphenyls by treatment with sodium amide in liquid ammonia,⁹⁹ photochemically induced dehydrocyclization of corresponding stilbenes using I_2/O_2 as dehydrogenation agent,¹⁰⁰ and desulfurization of phenanthrene derivatives formed by Diels–Alder reaction, containing two fused thiophene rings.¹⁰¹ Among these methods, photocyclization has been widely employed to synthesize a variety of phenanthrenes with different substituents.^{96d,e,100,102} An example is shown in Scheme 70.^{100d} The disadvantage of this method is that a highly dilute condition is required to obtain reasonable yield.

Scheme 70. Synthesis of phenanthrenes via photodehydrocyclization.

Several new approaches to the skeletons of phenanthrene appeared recently, including radical cyclization, intramolecular or intermolecular aryne cycloaddition, and palladium catalyzed co-trimerization of benzyne with alkynes.¹⁰³

3.2. Synthesis of Helicenes and Related Compounds

The classical and widely used method for synthesis of helicenes involved the oxidative photocyclization of stilbene-type precursors.^{88,90b,c,104} This traditional method suffered from its fundamental drawbacks, such as highly dilute solution and low functional group tolerance.¹⁰⁵

Several new methods were developed to provide useful alternatives for the synthesis of helicene type skeletons and for material applications.^{88e}

Katz *et al.* first reported their pioneering work for the synthesis of racemic helicene bisquinones through the Diels–Alder reaction.¹⁰⁵ Scheme 71 demonstrates the pathway leading to helical quinone **333**.

Scheme 71. Katz's approach to helicene quinones via nonphotochemical route.

In 1999, Gingras *et al.* reported a five-step synthesis of [7]helicenes by using “carbenoid coupling” strategy.¹⁰⁶ Scheme 72 outlines the step-wise transformations from biphenanthrol to [7]helicene **337**.

Harrowven *et al.* reported a new route to [5]helicenes via a tin-mediated, nonreducing tandem radical cyclization.¹⁰⁷ This short and simple protocol furnished a series of different substituted [5]helicenes in moderate yields.^{107b} An example is described in Scheme 73.

Scheme 72. Gingras's approach to a [7]helicene by carbenoid coupling.

Scheme 73. Harrowven's approach to a [5]helicene via tandem radical cyclization.

In 2002, Stará *et al.* reported a new paradigm for the nonphotochemical synthesis of tetrahydrohelicenes/helicenes based on a key intramolecular [2 + 2 + 2] cycloisomerization of aromatic triynes/cis,cis-dienetriynes catalyzed by Co(I) or Ni(0).¹⁰⁸ This protocol reflected the art of organic synthesis for exploiting the atom-economic isomerization.^{108a} Different substituted [5], [6], and [7] helicenes were produced in good yields (60 to 83%) under very mild conditions. Scheme 74 demonstrates an example of the key reaction.

The first double helicene having a pentahelicene and a heptahelicene was synthesized recently by Guitián *et al.*¹⁰⁹ A new palladium-catalyzed cyclotrimerization of arynes was involved in this synthesis (Scheme 75).

Scheme 74. Stara's approach to a [6]helicene via nickel(0)-catalyzed [2 + 2 + 2] cycloisomerization.

Scheme 75. Guitian's approach to a double helicene via Pd(0)-catalyzed cyclotrimerization of aryne.

A major challenge in helicene chemistry is the development of efficient methods for synthesis of individual enantiomers with high enantioselectivity.^{88e} The classic methods of obtaining helicenes in nonracemic form generally involved separation of the racemic mixture via HPLC using chiral column,^{90b,c,106a,110} or resolving agents.^{90f,g,111} Carreño reported the first enantioselective synthesis of 7,8-dihydro[5]helicenequinones via Diels–Alder reactions.¹¹² Scheme 76 shows the synthetic route, and the dihydrohelicene quinones could be obtained with >90% ee.

A different asymmetric approach to conjugated helicenes was developed by Karikomi *et al.*¹¹³ The chiral [5]helicenes **360** were synthesized by an aromatic oxy-cope rearrangement, followed by reduction, hydrolysis, dehydration, and aromatization (Scheme 77).

Scheme 76. Carreno's approach to enantiopure dihydro-[5]helicenequinones.

Scheme 77. Karikomi's approach to chiral [5]helicenes via an aromatic oxy-Cope rearrangement.

Synthesis of nonracemic [7]helicenes via Friedel–Crafts diacylation of phenanthrenes was reported by Katz *et al.*^{114a} They also developed the method for functionalization of [6]- and [7]helicenes at their most sterically hindered positions.^{114b}

Some other helical compounds, such as oligothiophene,¹¹⁵ and angular [n]phenylene¹¹⁶ etc. were prepared by iteration, and cobalt-catalyzed double cycloisomerization respectively. Schemes 78 and 79 outline the synthetic sequences for these two new helical compounds.

phosphorus pentoxide under refluxing *p*-xylene at 138 °C for 2 h, the fluorenylmethanol **370** was transformed to the symmetric dibenz[*a,j*]anthracene **371** in 88% yield.⁹⁷

Scheme 80. Ring expansion via Wagner-Meerwein rearrangement.

Conceivably, the transformation from **370** to **371** involved the initial formation of carbocation **372**, followed by ring expansion via a carbocation rearrangement, and an aromatization by deprotonation to form **374** (Scheme 81).^{97a} It was interesting that the *tert*-butyl group was cleaved from the aromatic ring via a reversal of the Friedel–Crafts alkylation reaction on exposure to proton or Lewis acids.¹¹⁸ This was observed previously and served as a useful group-directing method by occasionally introducing the *tert*-butyl group into an aromatic ring, in turn directing the placement of other substituents, and then removing the *tert*-butyl group.

Scheme 81. Proposed mechanism leading to **371**.

4.2. Synthesis of Helical Compound 377 and Polycyclic Compounds 378 and 379

Based on the above simple model study in Scheme 80, Scheme 82 demonstrates the transformation from **78a** to three different polycyclic compounds. Similarly, the preparation of diol **376** from **78a** involved deprotonation and condensation with paraformaldehyde to give **376** as a mixture of three isomers (isomer ratio = 22:12:1) in good yield. On exposure to phosphorus pentoxide in *p*-xylene at variable temperature and reaction time, three polycyclic compounds **377**, **378**, and **379** were isolated. If the reaction mixture was heated at 110 °C for 15 minutes, the helical 17,18-diphenyl-dibenzo[*a,o*]pentaphene **377** was produced. If the reaction mixture was heated under refluxing for 1.5 h, the asymmetric compound **378** was produced. If the reaction mixture was heated under refluxing for 12 h, the symmetric butterfly-shaped compound **379** was obtained. We also discovered that compounds **377** and **378** could convert to **379** just by changing reaction time. The formation of **378** and **379** was very unexpected.

Scheme 82. Synthetic pathway leading to polycyclic compounds **377**, **378**, and **379**.

The structures of compounds **377–379** were elucidated with high resolution mass spectroscopy and ^1H and ^{13}C NMR spectroscopy, also by the product of a subsequence reaction. The molecular ions with correct exact mass were detected. The ^1H NMR spectra showed the right numbers of signals and pattern of multiplicity consistent with the assigned structures. The partial chemical shift assignments for **377**, **378**, and **379** are included in Scheme 82. Compound **377** as a symmetric aromatic compound exhibited two singlets at δ 8.03 and 7.44, respectively, attributable to the four aromatic hydrogens on the benzene rings with a phenyl substituent and the central benzene ring. The upfield shift aromatic signals at δ 6.51 and 6.62, attributable to the two aromatic hydrogen atoms closest to the phenyl substituents, indicate that the phenyl substituents are oriented perpendicular to the main aromatic system.

It is interesting to note that the asymmetric nature of **378** was manifested with a set of signals from the diastereotopic methylene hydrogens on the six-membered ring. An AB pattern at δ 4.83 and 4.77 with a large geminal coupling constant of 23.0 Hz was observed. However, compound **379** has several symmetrical elements, including two planes of symmetry and a C_2 symmetry, and exhibits very simple ^1H NMR signals, having 4 hydrogen atoms at δ 4.42 as singlet, 2 hydrogen atoms at δ 6.85 as singlet, and only eight hydrogen atoms for phenyl substituents. This indicates the phenyl substituents are no longer mono substituted. Instead, 1,2-disubstituted benzene bridges are produced. The ^{13}C NMR spectrum of **379** showed two signals in the aliphatic region for the sp^3 carbons. On exposure of compound **379** to DDQ under refluxing benzene, diketone **380** was produced (eq 3). The structure of diketone **380** was established by X-ray structure analysis. The reaction mechanism to account for the formation of **379** is outlined in Scheme 83.

Scheme 83. Proposed mechanism leading to **378** and **379**.

The transformation from diol **376** to **378** and **379** occurred with an initial Wagner–Meerwein rearrangement and a reversal of the Friedel–Crafts alkylation reaction to form **377**. Subsequent intramolecular Friedel–Crafts arylation involved one of the benzene rings having the phenyl substituent. Initially, one of the double bonds was protonated to form the carbocation **381/382**. The other pendant phenyl substituent was close enough to attack **382** to form **383**, which then underwent deprotonation to furnish **378**. A repeat of the Friedel–Crafts arylation reaction of **378** led to the symmetric compound **379**.

The 4,5-di(4-biphenyl)phenanthrene **78b** was also selected for condensation with paraformaldehyde leading to diol **385a** in 77% yield as a mixture of two isomers (isomer ratio = 1:1.2). In this case, one of the minor isomers as presenting in diol **376** was not detected in the crude reaction mixture by ^1H NMR. The diol **385a** was converted to helical compound **386a**

and compound **387** having a C_2 symmetry, involving Wagner–Meerwein rearrangement and intramolecular Friedel–Crafts arylation (Scheme 84). In **387**, an AB pattern at δ 4.46 and 4.43 with a large geminal coupling constant of 21.9 Hz was observed on a 600 MHz NMR spectrometer. However, the use of diol **385b** produced from the newly synthesized 4,5-di(1-naphthyl)phenanthrene **384**¹¹⁹ under similar conditions only led to the helical compound **386b** as a mixture of three isomers (isomer ratio = 7:2:1). This is attributed to the asymmetric 1-naphthyl substituents oriented in syn, and anti fashion. In the case of anti isomers, two sets of NMR signals were observed due to the possibilities of two different orientations of the 1-naphthyl substituents. It was originally anticipated that the formation of the butterfly-shaped compound with a C_2 symmetry could occur. However, molecular modeling suggests that this pathway suffers from nonbonded steric interactions between the naphthyl group and the peripheral benzene rings. The ¹H NMR spectrum of the crude reaction mixture showed only broad peaks in the benzene rings. The ¹H NMR spectrum of the crude reaction mixture showed only broad peaks in the aromatic region, indicating that the starting diol **385b** decomposed or polymerized.

Scheme 84. Synthesis of polycyclic compounds **386** and **387**.

4.3. Synthesis of 4,5-Di(1-naphthyl)phenanthrene **384** and the Linear Isomer **392**

The synthetic sequence for **384**, depicted in Scheme 84, is outlined in Scheme 85. Lithiation of the diacetylene **388** with *n*-butyllithium followed by condensation with diketone **389** afforded the propargylic diol **390** as an essentially 1:1 mixture of diastereomers in excellent yield.³³ Treatment of **390** with triethylsilane in the presence of trifluoroacetic acid furnished the tetraacetylenic hydrocarbon **391** in excellent yield also essentially as a 1:1 mixture of diastereomers. On exposure to potassium *tert*-butoxide under refluxing toluene for 4 h, the hydrocarbon **391** was transformed to the 4,5-di(1-naphthyl)phenanthrene **384** as a mixture of three diastereomers (isomer ratio = 4.1:1.7:1), the linear isomer **392**, along with ca. 1% of **393** detected in the crude reaction mixture before purification by ¹H NMR.

Scheme 85. Synthesis of 4,5-di(1-naphthyl)phenanthrenes via benzannulated enyne-allenes.

Conceivably, the transformation from **391** to **384** involved an initial prototropic isomerization to form the benzannulated enyne–allenes **394** (Scheme 86). A subsequent C²–C⁶ cyclization generated the biradical **395**, which in turn underwent an intramolecular radical–radical coupling to give **396**. Although the transformation from **394** to **396** could also be regarded as a Diels–Alder reaction, mechanistic and DNA-cleavage studies of analogous systems supported a two-step biradical pathway.^{29a,g,30a} A second formal Diels–Alder reaction of **396** produced **398** which gave 4,5-di(1-naphthyl)phenanthrene **384** after two subsequent tautomerizations. The similar transformation from **391** to **384** was observed in the previous case.³³ The regioselectivity for the α carbon could attribute to the higher reactivity of the α - than that of β - position of naphthalene in homolytic addition.

Scheme 86. Proposed mechanism leading to **384**.

The formation of **392** indicates that the rate of transformation from **396** to **398** is competitive with that of the tautomerization of **396** to **399** (Scheme 87). A rapid initial tautomerization could lead to the formation of **399**, followed by C²–C⁶ cyclization generating biradical **400**. Subsequent radical–radical coupling and tautomerization could lead to the linearly fused isomer **392** as a result of reducing nonbonded steric interactions in the step of the

intramolecular radical–radical coupling. The formation of the linearly fused isomer from this pathway was not observed previously.³³ Presumably, the nonbonded steric interactions are more severe in **384** as compared to those in **78**.

Scheme 87. Proposed mechanism leading to **392**.

The formation of **393** involved the direct coupling of the radical center depicted in **397** leading to [2 + 2] cycloaddition adduct having a 1*H*-cyclobut[*a*]indene moiety. Similar examples of the intramolecular [2 + 2] cycloaddition reaction of the benzannulated enyne–allene systems leading to 1*H*-cyclobut[*a*]indenes were observed and reported previously.^{35a,32b}

The structure of the major isomer of **384** was unequivocally established by the X-ray structure analysis. The ORTEP drawing of major isomer of **384** is given in Figure 7. As expected, the two naphthyl substituents are bent away from each other and are essentially perpendicular to the diindino-fused phenanthrene ring system. In addition, the two 1-naphthyl substituents are oriented essentially parallel to each other and are pointing in the same direction in the case of the syn isomer. Because of the presence of a helical twist in the diindino-fused phenanthrene system and slow rotations of the naphthyl groups, two diastereomers are possible for the anti isomers with the two 1-naphthyl rings pointing toward opposite direction.

Figure 7. ORTEP drawing of the crystal structure of the syn isomer of **384**.

4.4. Synthesis of Diacetylene **388**

The diacetylene **388** used for the preparation of **384** in Scheme 85 was prepared from 1-bromo-2-iodobenzene via two consecutive Sonogashira coupling reactions with 1-ethynynaphthalene and (trimethylsilyl)acetylene followed by desilylation as described previously (Scheme 88).³³ The second coupling reaction was significantly improved in yield and reaction conditions by converting bromide **402** to iodide **403**.

Scheme 88. Synthesis of a new diacetylene **388**.

4.5. Cyclization versus Ring Expansion

Scheme 89 illustrates the competitive reaction between cyclization and ring expansion. Treatment of compound **405**,¹²⁰ prepared from benzophenone and diacetylene **60**, with LDA and paraformaldehyde gave **406** in 86% yield. On exposure to phosphorous pentoxide under refluxing *p*-xylene for 2 h, compound **407** and **408** were isolated in 5:4 ratio. Transformation from **406** to **407** involved an intramolecular Friedel–Crafts alkylation reaction. Compound **408** was produced via a Wagner–Meerwein rearrangement of **406** followed by an aromatization. In the cases with *tert*-butyl substituent, ring expansion products were obtained as the predominant products.

Scheme 89. Cyclization versus ring expansion.

5. Conclusions

The Wagner–Meerwein rearrangement of fluorenylmethanols derived from 15,16-diaryl-diindeno[2,1-*b*:1',2'-*h*]phenanthrenes (4,5-diarylphenanthrenes) was successfully adopted for the synthesis of helical 17,18-diaryl-dibenzo[*a,o*]pentaphenes involving the carbocation-promoted ring expansion and aromatization. Two of the 17,18-diaryl-dibenzo[*a,o*]pentaphenes were employed for the subsequent intramolecular Friedel–Crafts arylation reactions involving phenyl or 4-biphenyl substituents at the 17 & 18 positions, producing several butterfly-shaped compounds having two planes of symmetry and a C_2 symmetry in the case of the phenyl substituent and having only a C_2 symmetry in the case of the 4-biphenyl substituent. They

possess very interesting structural features. This methodology exhibits great potential for the synthesis of novel polycyclic aromatic compounds with a helical twist or with a deep valley.

A new and sterically more hindered 4,5-di(1-naphthyl)phenanthrene **384**, which could exist as three rotamers and the first linear polycyclic compound **392** were also prepared involving a C²–C⁶ cyclization reaction followed by a radical–radical coupling reaction of the benzannulated enyne–allene.

CHAPTER V

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere except in the cases for the synthesis of diketones. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. Methylene chloride, benzene, toluene, and *p*-xylene were 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, 600 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.00) as internal standards. IR spectra were taken on Perkin-Elmer 1600 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, *tert*-butyllithium (1.7 M) in pentane, lithium diisopropylamide (LDA) (2.0 M) in heptane/tetrahydrofuran/ethylbenzene, potassium *tert*-butoxide (1.0 M) in 2-methyl-2-propanol, 4-octyne, 1,4-dichloro-2-butyne, benzil, dimethyl 1,3-acetonedicarboxylate, anthranilic acid, thionyl chloride, pyridine, Pd(PPh₃)₂Cl₂, copper(I) iodide, triethylamine, phenylacetylene, (trimethylsilyl)acetylene, 1-bromo-2-iodobenzene, tributyltin hydride, 2,2'-azobisisobutyronitrile (AIBN), isoamyl nitrite, and 1,2-dichloroethane, mesitylene, triethylsilane, trifluoroacetic acid, 1,4-cyclohexadiene, 9-fluorenone, acetic anhydride, tetrakis-(triphenylphosphine)-palladium (Pd(PPh₃)₄), samarium (II) iodide (0.1 M) in tetrahydrofuran, 2-propanol, trifluoromethanesulfonic anhydride, *N,N*-diisopropylethylamine, diisopropylamine, *tert*-butyldimethylsilyl chloride (1.0 M) in THF (TBDMSCl), hexamethylphosphoramide (HMPA), anhydrous aluminum chloride, benzophenone (**277**), benzosuberone (**278**), 2,2-

dimethylpropiophenone (**292**), 1-indanone, 1-tetralone, iodomethane, and 4*H*-cyclopenta[*def*]-phenanthrene,⁸² sodium hydride, sodium azide, lead (IV) acetate, boron trifluoride diethyl etherate, methyl formate, trimethyl orthoformate, perchloric acid, paraformaldehyde, phosphorus pentoxide, 2-naphthoyl chloride, terephthaloyl chloride, CuBr·SMe₂, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1-ethynylnaphthalene, and iodine were purchased from chemical suppliers and were used as received without further purification.

2,5-Dicarbomethoxy-3,4-diphenylcyclopentadienone (**162**) was prepared from dimethyl 1,3-acetonedicarboxylate and benzil according to the reported procedure.⁵³ 1-(2-Ethynylphenyl)-2-phenylethyne as the precursor of **60** was prepared as described previously from 1-bromo-2-iodobenzene, (trimethylsilyl)acetylene, and phenylacetylene.³³ Diester **183** was prepared in 96% yield from condensation between **162** and benzyne as reported previously.⁵⁵ 4*H*-Cyclopenta[*def*]-phenanthren-4-one (**275**)⁸¹ and 8,9-dihydrocyclopenta[*def*]phenanthren-4-one (**276**)^{59,84} were prepared from 4*H*-cyclopenta[*def*]phenanthrene as reported previously. 1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (**298**)⁸⁶ and 2,2-dimethyl-1-indanone (**299**)⁸⁷ were prepared from 1-tetralone and 1-indanone, respectively, according to the reported procedures. Tosyl azide was prepared from *p*-toluenesulfonyl chloride and sodium azide as reported previously.^{78a} **369** was synthesized by Yanzhong Zhang recently from *tert*-butyl 2-naphthyl ketone which was prepared from 2-naphthoyl chloride according to the reported procedure.¹²¹ The same procedures were repeated to make a large amount of **369**. 4,5-Diarylphenanthrenes **78a** and **78b** were prepared from diketone **389** derived from terephthaloyl chloride as reported previously.^{121,33}

Diester 163. A mixture of 0.174 g (0.500 mmol) of 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (**162**)⁵³ and 0.10 mL (0.68 mmol) of 4-octyne in 3 mL of mesitylene in a sealed

tube was heated to 190 °C for 12 h. The solvent was removed in vacuo. Flash column chromatography (silica gel/10% ethyl acetate in hexanes) afforded 0.109 g of **163** (0.253 mmol, 50%) as a wax-like white solid: mp 105–108 °C; IR 1728, 1200, 702 cm⁻¹; ¹H δ 7.13–7.06 (6 H, m), 7.03–6.96 (4 H, m), 3.43 (6 H, s), 2.62 (4 H, t, *J* = 8.3 Hz), 1.65 (4 H, sextet, *J* = 7.7 Hz), 1.02 (6 H, t, *J* = 7.3 Hz); ¹³C δ 170.0, 138.3, 137.0, 136.8, 136.3, 130.0, 127.3, 126.7, 51.7, 33.0, 24.9, 14.9; MS *m/z* 430 (M⁺), 415, 399, 367, 337.

Diketone 164. To a flask containing 0.088 g (0.205 mmol) of **163** was added 4 mL of concentrated sulfuric acid. The mixture was swirled periodically until the solid was dissolved in the sulfuric acid at rt. After 3 h, the reaction mixture was poured into an ice-water mixture and then was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Recrystallization of the crude yellow solid from 95% ethanol afforded 0.059 g of **164** (0.161 mmol, 79%) as bright-yellow crystals: mp 182–184 °C; IR (KBr) 1700, 757, 721 cm⁻¹; ¹H δ 8.09 (2 H, d, *J* = 7.7 Hz), 7.75 (2 H, d, *J* = 7.4 Hz), 7.59 (2 H, td, *J* = 7.5, 1.0 Hz), 7.38 (2 H, t, *J* = 7.4 Hz), 3.12 (4 H, t, *J* = 8.0 Hz), 1.55 (4 H, sextet, *J* = 7.6 Hz), 1.10 (6 H, t, *J* = 7.3 Hz); ¹³C δ 193.8, 146.0, 143.0, 136.9, 135.9, 135.4, 134.7, 129.1, 124.5, 123.5, 28.3, 24.4, 14.6; MS *m/z* 366 (M⁺), 351, 337.

Diol 157a. To a solution of 0.18 g (0.89 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne³³ in 10 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.31 mL of a 2.5 M solution of *n*-butyllithium (0.78 mmol) in hexanes. The reaction mixture was then allowed to warm to rt. After 30 min at rt, a solution of 0.099 g (0.271 mmol) of **164** in 40 mL of diethyl ether was introduced via cannula. After an additional 2 h, 5 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. Flash column chromatography

(silica gel/30% diethyl ether in hexanes) provided 0.197 g of **157a** (0.256 mmol, 94%, a mixture of the trans and cis isomers, isomer ratio = 2:1) as a soil-colored solid: mp 107–113 °C; IR 3528, 3426, 2215, 753 cm^{-1} ; ^1H δ 8.24 (2 H, d, J = 7.9 Hz), 7.85 (2 H, d, J = 7.4 Hz), 7.51–7.4 (6 H, m), 7.4–7.09 (16 H, m), 3.32–3.13 (2 H, m), 3.13–2.98 (2 H, m), 2.48 (2 H, br), 1.92–1.76 (2 H, m), 1.76–1.52 (2 H, m), 1.03 (6 H, t, J = 7.2 Hz); ^{13}C δ 148.6, 146.9, 140.9, 138.5, 132.7, 131.9, 131.8, 131.7, 129.2, 128.4, 128.1, 127.8, 125.9, 124.9, 124.5, 123.1, 93.3, 93.2, 87.9, 82.0, 75.5, 31.1, 25.0, 15.2; MS m/z 770 (M^+), 753, 736; HRMS calcd for $\text{C}_{58}\text{H}_{42}\text{O}_2$ 770.3185, found 770.3160.

Compounds 165–168. To a flask containing 0.05 mL (0.7 mmol) of thionyl chloride in 10 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.08 mL (1.0 mmol) of pyridine in 5 mL of diethyl ether via cannula. After 10 min, 0.094 g (0.122 mmol) of **157a** in 20 mL of diethyl ether was introduced slowly via cannula. After 5 h at 0 °C, the reaction mixture was allowed to warm to rt. After an additional 2 h at rt, 10 mL of water was introduced, and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) provided 0.008 g of **165** (0.010 mmol, 8%) as a pink solid, 0.0030 g of **166** (0.0037 mmol, 3%) as a dark solid, 0.026 g of **167** (0.035 mmol, 28%) as a dark brown solid, and 0.029 g of **168** (0.036 mmol, 30%, trans:cis = 5:1) as an orange solid. Compound **165**: mp 266–269 °C; IR 1701, 749 cm^{-1} ; ^1H δ 9.35 (2 H, dd, J = 7.9, 1.2 Hz), 7.93 (2 H, d, J = 7.2 Hz), 7.70–7.26 (16 H, m), 7.21 (2 H, td, J = 7.3, 1.0 Hz), 7.12 (2 H, td, J = 7.7, 1.2 Hz), 5.96 (2 H, d, J = 7.7 Hz), 3.55 (2 H, br), 2.64 (2 H, m), 1.25 (4 H, m), 0.49 (6 H, t, J = 6.8 Hz); ^{13}C δ 193.7, 149.3, 144.2, 143.7, 141.5, 141.2, 140.7, 138.6, 138.3, 137.6, 136.9, 135.6, 134.1, 130.2, 129.4, 129.1, 128.94,

128.87, 128.7, 128.2, 127.0, 126.7, 123.7, 123.5, 35.1, 25.1, 14.3; MS m/z 769 (MH^+), 768; HRMS calcd for $C_{58}H_{40}O_2$ 768.3028, found 768.3021. Recrystallization of **165** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 5). Compound **166**: IR 1447, 753, 691 cm^{-1} ; 1H δ 8.73 (1 H, d, $J = 7.2$ Hz), 8.40 (1 H, d, $J = 6.9$ Hz), 8.29 (1 H, d, $J = 7.4$ Hz), 7.85 (1 H, d, $J = 7.2$ Hz), 7.67–7.16 (19 H, m), 7.01 (1 H, t, $J = 7.5$ Hz), 6.86 (1 H, t, $J = 7.7$ Hz), 5.48 (1 H, d, $J = 7.7$ Hz), 2.32–2.22 (1 H, m), 2.2–2.0 (1 H, m), 1.8–1.4 (4 H, m), 1.12–0.96 (1 H, m), 0.9–0.8 (1 H, m), 0.69 (3 H, t, $J = 7.3$ Hz), 0.46 (3 H, t, $J = 7.1$ Hz); MS m/z 790, 771 ($M^+ - Cl$), 728. Compound **167**: mp 275–277 °C; IR (KBr) 2211, 1695, 761 cm^{-1} ; 1H δ 9.44 (1 H, dd, $J = 6.9, 1.7$ Hz), 8.64 (1 H, dd, $J = 6.9, 1.5$ Hz), 8.38 (1 H, d, $J = 7.7$ Hz), 7.78 (1 H, d, $J = 7.4$ Hz), 7.68 (1 H, d, $J = 7.2$ Hz), 7.64–7.31 (16 H, m), 7.26 (1 H, td, $J = 7.5, 1.0$ Hz), 7.17 (1 H, td, $J = 7.4, 0.7$ Hz), 7.03 (1 H, td, $J = 7.7, 1.2$ Hz), 6.96 (1 H, td, $J = 7.4, 0.7$ Hz), 5.20 (1 H, d, $J = 7.7$ Hz), 2.71 (2 H, m), 2.12 (2 H, m), 1.02 (4 H, sextet, $J = 7.9$ Hz), 0.68 (6 H, t, $J = 7.3$ Hz); ^{13}C δ 193.8, 153.3, 145.3, 145.0, 144.4, 144.3, 141.2, 140.0, 139.4, 137.2, 137.0, 136.5, 136.3, 135.2, 134.2, 132.4, 132.0, 131.8, 131.6, 130.7, 130.1, 129.1, 128.94, 128.87, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 126.9, 126.1, 125.8, 125.3, 125.0, 124.3, 123.7, 123.6, 123.1, 120.5, 118.5, 102.6, 93.7, 89.0, 88.4, 51.6, 42.5, 18.5, 14.1; MS m/z 753 (MH^+), 752, 709; HRMS calcd for $C_{58}H_{40}O$ 752.3079, found 752.3048. Recrystallization of **167** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 8). Compound **168**: mp >340 °C; IR 1640, 1424, 1196, 753 cm^{-1} ; 1H δ (trans isomer) 8.67 (2 H, d, $J = 7.7$ Hz), 7.87 (2 H, t, $J = 7.4$ Hz), 7.56–7.20 (22 H, m), 2.54 (2 H, m), 2.42 (2 H, m), 1.27 (2 H, m), 1.03 (2 H, m), 0.44 (6 H, t, $J = 7.2$ Hz); ^{13}C δ (trans isomer) 152.4, 148.8, 148.1, 145.7, 144.0, 141.1, 140.4, 139.3, 134.9, 131.9, 130.2, 129.3, 129.0, 128.5, 128.2, 127.8, 127.3, 125.0, 124.5, 123.7, 123.2, 120.0, 111.5, 65.6, 30.2, 25.2, 14.5; ^{13}C δ (cis isomer, partial) 151.9, 149.0, 145.9, 144.01,

140.97, 139.2, 135.0, 132.1, 130.0, 129.4, 128.8, 127.6, 120.1, 112.0, 65.55, 14.54; MS m/z 807 (MH^+), 763, 720; HRMS calcd for $C_{58}H_{41}Cl_2$ 807.2585, found 807.2569. Recrystallization of **168** from CH_2Cl_2 /2-propanol produced a crystal of the trans isomer suitable for X-ray structure analysis (Figure 9).

Diester 177. A mixture of 0.454 g (1.30 mmol) of **162** and 0.161 g (1.31 mmol) of 1,4-dichloro-2-butyne in 10 mL of mesitylene was heated under reflux for 72 h. The solvent was removed in vacuo. Flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 0.480 g of **177** (1.08 mmol, 83%) as a wax-like white solid: mp 150–152 °C; IR 1731, 1208, 697 cm^{-1} ; 1H δ 7.16–7.11 (6 H, m), 7.02–6.97 (4 H, m), 4.85 (4 H, s), 3.47 (6 H, s); ^{13}C δ 168.2, 140.5, 137.3, 137.2, 133.0, 129.6, 127.5, 127.4, 52.2, 39.0; MS m/z 442 (M^+), 407, 391, 375.

Diester 178. A mixture of 0.521 g (1.18 mmol) of **177**, 0.97 mL (3.60 mmol) of tributyltin hydride, and 10 mg (0.06 mmol) of AIBN in 25 mL of benzene was heated under reflux for 6 h. The reaction mixture was washed with a 10% potassium fluoride solution followed by filtration to remove the white precipitate. The filtrate was extracted with diethyl ether. The combined organic layers were washed with water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/10% diethyl ether in hexanes) afforded 0.348 g of **178** (0.93 mmol, 79%) as a wax-like white solid: mp 145–147 °C; IR 1729, 1207, 702 cm^{-1} ; 1H δ 7.12–7.07 (6 H, m), 7.03–6.97 (4 H, m), 3.47 (6 H, s), 2.32 (6 H, s); ^{13}C δ 170.0, 138.3, 136.5, 136.2, 132.7, 130.0, 127.3, 126.8, 51.8, 17.1; MS m/z 374 (M^+), 359, 343, 311.

Diketone 179. To a flask containing 0.347 g (0.93 mmol) of **178** was added 7 mL of concentrated sulfuric acid. The mixture was swirled periodically until the solid was dissolved in the sulfuric acid at rt. After 3 h, the reaction mixture was poured into an ice-water mixture and then was extracted with diethyl ether. The combined organic extracts were washed with water,

dried over magnesium sulfate, and concentrated. Recrystallization of the crude yellow solid from 95% ethanol afforded 0.184 g of **179** (0.59 mmol, 64%) as bright-yellow crystals: mp 260–263 °C; IR (KBr) 1699, 756, 714 cm^{-1} ; ^1H δ 8.02 (2 H, d, $J = 7.7$ Hz), 7.74 (2 H, d, $J = 7.4$ Hz), 7.56 (2 H, td, $J = 7.7, 1.2$ Hz), 7.37 (2 H, t, $J = 7.3$ Hz), 2.62 (6 H, s); ^{13}C δ 194.1, 142.8, 141.9, 136.3, 135.5, 135.4, 134.7, 129.1, 124.5, 123.5, 12.9; MS m/z 310 (M^+), 295, 281.

Diol 157b. To a solution of 0.264 g (1.31 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.40 mL of a 2.5 M solution of *n*-butyllithium (1.00 mmol) in hexanes. The reaction mixture was then allowed to warm to rt. After 30 min at rt, a solution of 0.123 g (0.40 mmol) of **179** in 200 mL of diethyl ether was introduced via cannula. After an additional 2 h, 5 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. Flash column chromatography (silica gel/30% diethyl ether in hexanes) provided 0.266 g of **157b** (0.37 mmol, 94%, a mixture of the trans and cis isomers, isomer ratio = 2:1) as a light brown solid: mp 125–128 °C; IR 3523, 3404, 2253, 2217 cm^{-1} ; ^1H δ 8.27 (2 H, d, $J = 7.7$ Hz), 7.85 (2 H, d, $J = 7.4$ Hz), 7.50–7.44 (6 H, m), 7.33–7.18 (16 H, m), 2.63 (6 H, s), 2.42 (2 H, s); ^{13}C δ 148.0, 146.4, 138.8, 136.1, 132.3, 131.8, 131.6, 129.3, 128.2, 127.8, 125.9, 124.8, 124.5, 123.2, 123.0, 93.2, 92.6, 87.9, 82.3, 75.3, 15.3. A minor set of ^{13}C signals due to the presence of the minor isomer was also observed.; MS m/z 714 (M^+), 697, 680; HRMS calcd for $\text{C}_{54}\text{H}_{34}\text{O}_2$ 714.2559, found 714.2548.

Compounds 180–182. To a solution of 0.130 g (0.182 mmol) of **157b** in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added a mixture of 0.05 mL (0.7 mmol) of thionyl chloride and 0.12 mL (1.5 mmol) of pyridine in 30 mL of diethyl ether slowly via cannula. The reaction mixture was allowed to warm to rt. After 6 h, 10 mL of water was introduced, and the

organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) provided 0.0065 g of **180** (0.009 mmol, 5%) as a pink solid, 0.0027 g of **181** (0.0036 mmol, 2%) as a dark solid, and 0.054 g of **182** (0.076 mmol, 42%) as a deep green solid. Compound **180**: mp 108–110 °C; IR 1705, 1598, 747 cm^{-1} ; ^1H δ 9.35 (2 H, dd, $J = 7.2, 1.5$ Hz), 7.70 (2 H, d, $J = 7.7$ Hz), 7.64–7.26 (16 H, m), 7.21 (2 H, td, $J = 7.4, 1.0$ Hz), 7.12 (2 H, td, $J = 7.4, 1.2$ Hz), 6.04 (2 H, d, $J = 7.4$ Hz), 2.27 (6 H, s); ^{13}C δ 193.9, 144.3, 143.5, 142.7, 141.6, 140.6, 140.3, 139.3, 138.9, 138.2, 137.8, 135.6, 134.1, 129.5, 129.4, 129.0, 128.8, 128.5, 128.2, 127.2, 126.9, 125.2, 123.8, 123.4, 22.6; MS m/z 712 (M^+), 419, 391; HRMS calcd for $\text{C}_{54}\text{H}_{32}\text{O}_2$ 712.2402, found 712.2388. Compound **181**: IR 1449, 756 cm^{-1} ; ^1H δ 8.70 (1 H, d, $J = 7.7$ Hz), 8.39 (1 H, d, $J = 7.9$ Hz), 8.27 (1 H, d, $J = 7.4$ Hz), 7.77 (1 H, d, $J = 7.4$ Hz), 7.70–7.23 (19 H, m), 7.00 (1 H, t, $J = 7.4$ Hz), 6.86 (1 H, t, $J = 7.9$ Hz), 5.54 (1 H, d, $J = 7.6$ Hz), 1.77 (3 H, s), 1.56 (3 H, s); MS m/z 732, 715 ($\text{M}^+ - \text{Cl}$). Compound **182**: mp >300 °C; IR (KBr) 1443, 756 cm^{-1} ; ^1H δ 8.72 (1 H, d, $J = 7.2$ Hz), 8.34 (1 H, d, $J = 7.4$ Hz), 8.23 (1 H, d, $J = 7.4$ Hz), 7.67 (1 H, d, $J = 7.4$ Hz), 7.61–7.20 (19 H, m), 7.02 (1 H, t, $J = 7.3$ Hz), 6.89 (1 H, td, $J = 7.7, 1.0$ Hz), 6.23 (1 H, s), 5.80 (1 H, d, $J = 7.9$ Hz), 5.39 (1 H, s), 1.85 (3 H, s); ^{13}C δ 148.5, 145.9, 144.7, 142.8, 142.1, 141.8, 141.4, 140.0, 138.4, 138.1, 137.1, 134.9, 133.3, 132.4, 132.3, 132.1, 132.0, 129.5, 129.4, 129.3, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 126.6, 126.3, 126.2, 126.1, 125.6, 125.5, 125.3, 125.0, 124.8, 123.1, 123.0, 121.4, 120.4, 119.1, 116.1, 101.6, 93.7, 89.2, 88.4, 48.1, 34.1; MS m/z 714 (M^+), 699. Recrystallization of **182** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 10).

Diketone 184. To a flask containing 0.660 g (1.67 mmol) of **183**⁵⁵ was added 10 mL of concentrated sulfuric acid. The mixture was swirled periodically until the solid was dissolved in the sulfuric acid at rt. After 12 h, the reaction mixture was poured into an ice-water mixture and then was extracted with a mixture of diethyl ether/THF solution. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Recrystallization of the crude yellow solid from 95% ethanol afforded 0.479 g of **184** (1.44 mmol, 87%) as red crystals: mp 247–250 °C; IR 1699, 750, 708 cm⁻¹; ¹H δ 9.01 (2 H, dd, *J* = 6.7, 3.5 Hz), 8.01 (2 H, d, *J* = 7.7 Hz), 7.72 (2 H, d, *J* = 7.2 Hz), 7.56 (2 H, td, *J* = 7.5, 1.0 Hz), 7.50 (2 H, dd, *J* = 6.7, 3.5 Hz), 7.36 (2 H, t, *J* = 7.4 Hz); ¹³C δ 194.1, 143.0, 140.0, 134.7, 134.6, 133.2, 131.2, 129.7, 129.5, 124.53, 124.49, 123.6; MS *m/z* 332 (M⁺), 304, 281.

Diol 157c. To a solution of 0.186 g (0.92 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.35 mL of a 2.5 M solution of *n*-butyllithium (0.88 mmol) in hexanes. The reaction mixture was then allowed to warm to rt. After 30 min at rt, a solution of 0.104 g (0.313 mmol) of **184** in 50 mL of THF was introduced via cannula. After an additional 2 h, 5 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. Flash column chromatography (silica gel/30% diethyl ether in hexanes) provided 0.219 g of **157c** (0.298 mmol, 95%, a mixture of the trans and cis isomers, isomer ratio = 3:1) as a soil-colored solid. Some fractions were found to contain only one of the two isomers. Isomer 1: mp 118–121 °C; IR 3391, 2215, 753 cm⁻¹; ¹H δ 8.84 (2 H, dd, *J* = 6.6, 3.3 Hz), 8.31 (2 H, d, *J* = 7.9 Hz), 7.94 (2 H, d, *J* = 7.4 Hz), 7.50–7.14 (24 H, m), 2.71 (2 H, s); ¹³C δ 148.9, 145.0, 139.1, 132.6, 132.3, 131.8, 131.7, 129.40, 129.35, 128.4, 128.3, 128.2, 127.8, 127.0, 126.1, 125.8, 124.7, 124.4, 123.5, 123.0, 93.3, 92.9, 87.9, 83.2, 75.4; MS

m/z 736 (M^+), 719, 702; HRMS calcd for $C_{56}H_{32}O_2$ 736.2402, found 736.2436. Isomer 2: mp 132–135 °C; IR 3355, 2215, 752 cm^{-1} ; 1H δ 8.84 (2 H, dd, J = 6.7, 3.2 Hz), 8.26 (2 H, d, J = 7.7 Hz), 7.92 (2 H, d, J = 7.4 Hz), 7.52–7.37 (8 H, m), 7.32–7.16 (16 H, m), 2.76 (2 H, br s); ^{13}C δ 148.7, 144.6, 139.1, 132.7, 132.4, 131.8, 131.6, 129.5, 129.4, 128.4, 128.33, 128.25, 127.7, 127.1, 126.1, 125.7, 124.7, 124.6, 123.5, 122.9, 93.5, 93.1, 87.8, 83.6, 75.3; MS m/z 736 (M^+), 719, 702.

Compounds 185–187. To a solution of 0.309 g (0.42 mmol) of **157c** in 30 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added a mixture of 0.12 mL (1.6 mmol) of thionyl chloride and 0.20 mL (2.5 mmol) of pyridine in 20 mL of diethyl ether slowly via cannula. The reaction mixture was allowed to warm to rt. After 6 h, the solvent was removed in vacuo. Water (10 mL) and methylene chloride (50 mL) were introduced, and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/30% methylene chloride in hexanes) provided 0.084 g of **185** (0.11 mmol, 26%, trans:cis = 3:1) as a green-yellow solid, 0.043 g of **186** (0.057 mmol, 14%, a mixture of the trans and cis isomers, isomer ratio = 2:1) as a yellow solid, and 0.0034 g of **187** (0.005 mmol, 1%) as a red solid. Compound **185**: mp >340 °C; IR 1637, 1425, 753 cm^{-1} ; 1H δ (trans isomer) 8.78 (2 H, d, J = 7.7 Hz), 7.96 (2 H, d, J = 7.4 Hz), 7.87 (2 H, dd, J = 6.7, 3.5 Hz), 7.62–7.48 (8 H, m), 7.44–7.33 (4 H, m), 7.19 (8 H, s), 7.13 (2 H, s), 7.08 (2 H, dd, J = 6.4, 3.2 Hz); ^{13}C δ (trans isomer) 153.1, 149.0, 148.5, 146.0, 142.8, 141.0, 139.7, 135.1, 131.7, 130.9, 130.4, 129.5, 129.0, 128.8, 128.7, 128.3, 127.7, 127.5, 126.7, 125.1, 124.4, 124.1, 123.8, 123.6, 120.3, 111.9, 65.6. A minor set of ^{13}C signals due to the presence of the cis isomer was also observed.; MS m/z 772 (M^+), 737; HRMS calcd for $C_{56}H_{30}Cl_2$ 772.1725, found 772.1766.

Recrystallization of **185** from CH₂Cl₂/2-propanol produced a crystal of the trans isomer suitable for X-ray structure analysis (Figure 11). Compound **186**: Some fractions were found to contain only one of the two isomers. Isomer 1: mp >340 °C; IR 3378, 1425, 746 cm⁻¹; ¹H δ 9.11 (1 H, d, *J* = 8.7 Hz); 8.87 (1 H, d, *J* = 6.9 Hz), 8.76 (1 H, d, *J* = 7.7 Hz), 8.03 (1 H, d, *J* = 8.7 Hz), 7.99 (1 H, d, *J* = 7.4 Hz), 7.79 (1 H, d, *J* = 7.7 Hz), 7.71–7.08 (22 H, m), 6.74 (1 H, br s), 6.52 (1 H, d, *J* = 7.9 Hz), 2.50 (1 H, br s); ¹³C δ 153.0, 149.1, 148.6, 146.1, 145.3, 142.2, 141.9, 141.2, 139.6, 139.5, 138.5, 138.1, 137.7, 136.7, 136.0, 135.4, 135.0, 134.2, 132.0, 131.5, 130.8, 130.3, 130.1, 129.6, 129.5, 129.0, 128.93, 128.8, 128.3, 128.2, 127.74, 127.66, 126.6, 126.5, 125.8, 125.2, 124.9, 124.4, 124.1, 123.7, 123.0, 120.4, 112.1, 75.6, 65.6; MS *m/z* 754 (M⁺), 737; HRMS calcd for C₅₆H₃₁ClO 754.2063, found 754.2039. Isomer 2: mp >340 °C; IR 3434, 1430, 749 cm⁻¹; ¹H δ 9.04 (1 H, d, *J* = 8.4 Hz); 8.84 (1 H, d, *J* = 6.9 Hz), 8.76 (1 H, d, *J* = 7.7 Hz), 8.00 (1 H, dd, *J* = 7.7, 1.0 Hz), 7.98 (1 H, d, *J* = 7.4 Hz), 7.77 (1 H, d, *J* = 7.4 Hz), 7.71–7.26 (16 H, m), 7.13–7.08 (6 H, m), 6.74 (1 H, d, *J* = 7.7 Hz), 6.52 (1 H, d, *J* = 7.9 Hz), 2.46 (1 H, d, *J* = 7.7 Hz); ¹³C δ 153.0, 149.1, 148.6, 146.0, 145.2, 141.9, 141.8, 141.2, 139.6, 139.5, 138.5, 138.1, 137.7, 136.6, 136.1, 135.5, 135.0, 134.1, 132.1, 131.6, 131.5, 130.7, 130.3, 130.1, 129.5, 128.99, 128.94, 128.87, 128.77, 128.3, 128.2, 128.1, 127.7, 126.62, 126.56, 126.48, 125.6, 125.2, 124.9, 124.42, 124.37, 124.1, 123.9, 123.7, 123.0, 120.4, 112.0, 75.5, 65.4; MS *m/z* 754 (M⁺), 737. Compound **187**: mp >340 °C; IR 1702, 1602, 750 cm⁻¹; ¹H δ 8.61 (2 H, dd, *J* = 7.4, 2.7 Hz), 8.29 (1 H, d, *J* = 8.7 Hz), 7.97 (1 H, d, *J* = 7.4 Hz), 7.88 (1 H, d, *J* = 8.2 Hz), 7.82 (1 H, dd, *J* = 7.7, 1.6 Hz), 7.68–7.18 (22 H, m), 6.47 (1 H, d, *J* = 6.9 Hz); ¹³C δ 192.8, 152.9, 149.1, 148.5, 146.1, 144.8, 143.9, 139.1, 138.9, 138.3, 137.7, 136.8, 136.0, 134.9, 134.7, 134.5, 132.9, 131.7, 131.6, 130.3, 130.25, 130.21, 130.03, 130.01, 129.96, 129.54, 129.45, 129.0, 128.8, 128.6, 128.5, 128.4, 127.9,

127.7, 127.1, 126.5, 125.6, 125.2, 124.4, 124.3, 124.1, 123.8, 123.3, 122.9, 120.4, 112.1, 65.4; MS m/z 752 (M^+), 705, 483, 469; HRMS calcd for $C_{56}H_{29}ClO$ 752.1907, found 752.1915.

Compound 188b. To a mixture of 0.030 g (0.042 mmol) of **157b** and 0.0502 g (0.43 mmol) of triethylsilane in 10 mL of methylene chloride under a nitrogen atmosphere at -30 to -40 °C was added 0.05 mL trifluoroacetic acid (0.074 g, 0.65 mmol). After 30 min at -30 °C, the reaction mixture was allowed to warm to room temperature. 0.77 g (7.26 mmol) sodium carbonate was added followed by 10 mL of water and 20 mL of diethyl ether. The organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/5% diethyl ether in hexanes) provided 0.025 g of **188b** (0.037 mmol, 87%, 2:1 mixture of diastereomers) as a light brown solid: mp $98-100$ °C; IR 2222, 2212, 911, 757, 732, 691 cm^{-1} ; 1H δ 8.48 (2 H, d, $J = 7.9$ Hz), 7.86 (2 H, d, $J = 7.2$ Hz), 7.52–7.43 (6 H, m), 7.35–7.12 (16 H, m), 5.14–5.06 (2 H, s), 2.59–2.49 (6 H, s).

Compound 191. To a solution of 0.422 g (2.09 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.78 mL of a 2.5 M solution of *n*-butyllithium (1.95 mmol) in hexanes. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 0.257 g (1.43 mmol) of 9-fluorenone in 30 mL of diethyl ether was introduced dropwise via cannula. After an additional 2 h at room temperature, a solution of 0.145 g (1.43 mmol) of acetic anhydride in 10 mL of diethyl ether was introduced. After an additional 4 h, to the reaction mixture, 0.033 g (0.029 mmol) of $Pd(PPh_3)_4$ and 0.086 g (1.43 mmol) of 2-propanol in 5 mL THF were added, followed by 14.3 mL of a 0.1 M solution of SmI_2 (1.43 mmol) in THF. After 12 h, a mixture of hexane and diethyl ether (4:1) was introduced to form ppt. The solid was collected by filtration

to afford 0.177 g of **191** as brown crystals: mp 227–230 °C; IR 1441, 780, 754, 733, 693 cm⁻¹; ¹H δ 8.02–7.95 (3 H, m), 7.65–7.42 (10 H, m), 7.29 (1 H, t, *J* = 7.8 Hz), 7.09 (1 H, t, *J* = 7.5 Hz), 6.71 (1 H, d, *J* = 7.9 Hz), 4.45 (2 H, s); ¹³C δ 143.8, 141.2, 140.0, 139.9, 139.0, 138.1, 137.9, 136.3, 134.0, 131.5, 131.0, 130.2, 129.7, 128.7, 127.9, 127.4, 127.23, 127.17, 126.7, 125.7, 125.1, 123.7, 123.0, 121.6, 119.6, 35.4.

Propargylic Acetate 190. The following procedure is representative for the preparation of the propargylic acetates. To a solution of 1.63 g (8.07 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 50 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 3.00 mL of a 2.5 M solution of *n*-butyllithium (7.50 mmol) in hexanes. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 1.13 g (6.27 mmol) of 9-fluorenone in 50 mL of diethyl ether was introduced dropwise via cannula. After an additional 2 h at room temperature, a solution of 0.78 g (7.64 mmol) of acetic anhydride in 50 mL of diethyl ether was introduced, and the reaction mixture was stirred for 4 h before 20 mL of water was added. The organic layer was separated, and the aqueous layer was back-extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. A mixture of hexanes and diethyl ether (3:1, 10 mL) was added to the residue, and the solution was cooled to 0 °C. A solid precipitate appeared after ca. 15 min. The solid precipitate was collected by filtration and then washed with hexanes to furnish 2.20 g of **190** (5.19 mmol, 83%) as a light brown solid: mp 120–122 °C; IR 2219, 1749, 1229, 757 cm⁻¹; ¹H δ 7.91 (2 H, d, *J* = 7.7 Hz), 7.65 (2 H, d, *J* = 7.7 Hz), 7.50 (2 H, tm, *J* = 7.4, 2 Hz), 7.40 (2 H, td, *J* = 7.4, 0.7 Hz), 7.35–7.20 (9 H, m), 2.02 (3 H, s); ¹³C δ 169.1, 144.1, 139.9, 132.5, 131.75, 131.70, 129.8, 128.41, 128.35, 128.25, 128.18, 127.8, 126.1, 126.0, 124.7,

123.1, 120.0, 93.2, 89.7, 87.8, 84.1, 79.6, 21.8; MS m/z 424 (M^+), 380, 366; HRMS calcd for $C_{31}H_{20}O_2$ 424.1463, found 424.1466.

Carboxylic Acid 274. The following procedure is representative for the preparation of the carboxylic acids. To a flask containing 1.60 mL of a 2.5 M solution of *n*-butyllithium (4.00 mmol) in hexanes under a nitrogen atmosphere at 0 °C were added 0.56 mL (4.00 mmol) of diisopropylamine and then 5 mL of THF. After 30 min at 0 °C, the reaction mixture was cooled to –78 °C. A solution of 0.85 g (2.00 mmol) of **190** in 15 mL of THF was introduced dropwise via cannula. After 30 min at –78 °C, 1 mL of HMPA and 4 mL of a 1.0 M solution of TBDMSCl (4.00 mmol) in THF were introduced. The reaction mixture was allowed to warm to room temperature slowly and then heated to 45 °C. After an additional 12 h at 45 °C, the reaction mixture was allowed to cool to room temperature, and a mixture of 10 mL of acetic acid and 3.3 mL of water was introduced. After 12 h, 20 mL of diethyl ether was added, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with water (5 × 30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/25% acetone in hexanes) provided 0.487 g of **274** (1.15 mmol, 57%) as a yellow solid: mp 258–260 °C; IR 3500–2600 (br), 1708, 756 cm^{-1} ; 1H δ 8.05 (1 H, d, J = 7.7 Hz), 8.02 (1 H, d, J = 7.7 Hz), 7.97 (1 H, d, J = 6.2 Hz), 7.68 (1 H, d, J = 7.7 Hz), 7.64–7.44 (9 H, m), 7.29 (1 H, t, J = 6.9 Hz), 7.10 (1 H, t, J = 7.4 Hz), 6.67 (1 H, d, J = 7.7 Hz), 5.18 (1 H, dd, J = 10.5, 1.4 Hz), 3.76 (1 H, dd, J = 16.6, 2.2 Hz), 2.55 (1 H, dd, J = 16.6, 10.9 Hz); ^{13}C δ 177.5, 147.3, 141.6, 140.3, 140.2, 138.6, 137.83, 137.80, 136.4, 134.2, 131.8, 130.8, 130.2, 128.83, 128.75, 128.0, 127.80, 127.77, 127.58, 127.51, 125.9, 124.6, 123.9, 123.7, 121.8, 119.8, 41.9, 38.5; MS m/z 424 (M^+), 378, 365; HRMS calcd for $C_{31}H_{20}O_2$ 424.1463, found 424.1466.

Propargylic Acetate 279. The same procedure was repeated as described for **190** except that 0.08 g (0.39 mmol) of **275** was treated with **60**, prepared from 0.140 g (0.69 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.25 mL of a 2.5 M solution of *n*-butyllithium (0.63 mmol) in hexanes at 0 °C, followed by 0.064 g (0.63 mmol) of acetic anhydride to afford 0.143 g of **279** (0.32 mmol, 81%) as a light brown solid: mp 143–145 °C; IR 2214, 1749, 1226, 756 cm⁻¹; ¹H δ 8.07–8.03 (2 H, m), 7.87–7.82 (4 H, m), 7.60–7.47 (4 H, m), 7.35–7.20 (7 H, m), 2.08 (3 H, s); ¹³C δ 169.4, 143.2, 135.7, 132.5, 131.7, 131.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 126.0, 125.8, 125.4, 124.7, 123.3, 123.0, 93.2, 89.1, 87.8, 84.7, 81.1, 21.6.

Carboxylic Acid 283. The same procedure was repeated as described for **274** except that 0.143 g (0.32 mmol) of **279** was treated with LDA, prepared from 0.26 mL of a 2.5 M solution of *n*-butyllithium (0.65 mmol) in hexanes and 0.09 mL (0.65 mmol) of diisopropylamine, followed by 0.34 mL of HMPA and 0.65 mL of a 1.0 M solution of TBDMSCl (0.65 mmol) in THF. Hydrolysis with a mixture of 2.3 mL of acetic acid and 0.8 mL water provided 0.10 g of **283** (0.22 mmol, 70%) as yellow crystals: mp 228–231 °C; IR 3500–2600 (br), 1703, 827, 750, 704 cm⁻¹; ¹H δ 8.25 (1 H, d, *J* = 6.9 Hz), 8.01 (1 H, d, *J* = 8.4 Hz), 7.97 (1 H, t, *J* = 8.2 Hz), 7.86 (1 H, d, *J* = 8.7 Hz), 7.80 (1 H, t, *J* = 7.5 Hz), 7.73 (1 H, d, *J* = 7.7 Hz), 7.67–7.52 (7 H, m), 7.30 (1 H, t, *J* = 7.9 Hz), 7.12 (1 H, t, *J* = 7.5 Hz), 6.77 (1 H, d, *J* = 7.9 Hz), 5.14 (1 H, dd, *J* = 10.9, 2.6 Hz), 3.94 (1 H, dd, *J* = 16.4, 2.6 Hz), 2.79 (1 H, dd, *J* = 16.4, 10.5 Hz); ¹³C δ 177.3, 146.7, 144.6, 141.1, 138.9, 137.8, 135.9, 135.2, 133.9, 132.7, 132.5, 131.3, 130.0, 128.9, 128.8, 128.3, 128.1, 127.9, 127.5, 127.4, 126.8, 126.7, 126.6, 125.8, 125.3, 124.78, 124.74, 124.66, 123.7, 42.2, 38.7; MS *m/z* 448 (M⁺), 402, 389; HRMS calcd for C₃₃H₂₀O₂ 448.1463, found 448.1451. Recrystallization of **283** from CH₂Cl₂/2-propanol produced a crystal suitable for X-ray structure analysis (Figure 12).

Propargylic Acetate 280. The same procedure was repeated as described for **190** except that 0.177 g (0.86 mmol) of **276** was treated with **60**, prepared from 0.19 g (0.94 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.36 mL of a 2.5 M solution of *n*-butyllithium (0.90 mmol) in hexanes, followed by 0.10 g (0.98 mmol) of acetic anhydride. A small sample of **280** was isolated as a light brown solid for structural elucidation: mp 146–148 °C; IR 2226, 1749, 1226, 756 cm⁻¹; ¹H δ 7.71 (2 H, t, *J* = 4.0 Hz), 7.55–7.50 (2 H, m), 7.41–7.23 (7 H, m), 7.17–7.12 (4 H, m), 3.21–3.02 (4 H, m), 2.07 (3 H, s); ¹³C δ 169.3, 141.8, 137.2, 132.5, 131.7, 130.5, 128.8, 128.24, 128.20, 128.1, 127.9, 127.7, 125.9, 124.8, 124.1, 123.1, 93.2, 89.4, 87.9, 84.0, 81.0, 25.6, 21.6. As in the case of **285**, the rest of the crude acetate **280** was used for the next step without further purification.

Carboxylic Acid 284. The same procedure was repeated as described for **274** except that 0.386 g (0.86 mmol) of the crude acetate **280** was treated with LDA, prepared from 0.69 mL of a 2.5 M solution of *n*-butyllithium (1.73 mmol) in hexanes and 0.24 mL (1.73 mmol) of diisopropylamine, followed by 1 mL of HMPA and 1.73 mL of a 1.0 M solution of TBDMSCl (1.73 mmol) in THF. Hydrolysis with a mixture of 5 mL of acetic acid and 3 mL of water provided 0.141 g of **284** (0.31 mmol, 37% from **276**) as a yellow solid: mp 230–233 °C; IR 3500–2600 (br), 1708, 756, 703 cm⁻¹; ¹H δ 7.79 (1 H, d, *J* = 7.4 Hz), 7.69 (1 H, d, *J* = 7.4 Hz), 7.63–7.54 (4 H, m), 7.51–7.46 (1 H, m), 7.42–7.29 (4 H, m), 7.22 (1 H, d, *J* = 7.7 Hz), 7.10 (1 H, t, *J* = 7.7 Hz), 6.72 (1 H, d, *J* = 7.9 Hz), 5.06 (1 H, dd, *J* = 10.4, 1.5 Hz), 3.83 (1 H, dd, *J* = 16.6, 2.5 Hz), 3.44–3.26, (4 H, m), 2.68 (1 H, dd, *J* = 16.6, 10.6 Hz); ¹³C δ 178.1, 146.8, 143.7, 140.8, 138.5, 138.1, 137.8, 134.6, 134.2, 133.0, 132.0, 131.1, 130.0, 129.9, 129.8, 128.9, 128.8, 128.7, 128.3, 127.9, 127.5, 126.9, 126.0, 125.8, 124.6, 123.7, 122.0, 42.0, 38.6, 26.5, 26.2; MS *m/z* 450 (M⁺), 404, 391; HRMS calcd for C₃₃H₂₂O₂ 450.1620, found 450.1615.

Carboxylic Acid 285. The following procedure is representative for the preparation of the carboxylic acids from crude propargylic acetates directly. To a solution of 0.316 g (1.56 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.62 mL of a 2.5 M solution of *n*-butyllithium (1.55 mmol) in hexanes. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 0.259 g (1.42 mmol) of benzophenone (**277**) in 20 mL of diethyl ether was introduced slowly via cannula. After an additional 2 h at room temperature, a solution of 0.158 g (1.55 mmol) of acetic anhydride in 10 mL of diethyl ether was introduced. After an additional 4 h, 20 mL of water was introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated in vacuo. The crude propargylic acetate **281** was used for the next step without further purification.

To a flask containing 1.20 mL of a 2.5 M solution of *n*-butyllithium (3.00 mmol) in hexanes under a nitrogen atmosphere at 0 °C were added 0.42 mL (3.00 mmol) of diisopropylamine and then 2 mL of THF. After 30 min at 0 °C, the reaction mixture was cooled to –78 °C. A solution of the crude propargylic acetate **281** in 15 mL of THF was introduced slowly via cannula. After 30 min at –78 °C, 0.8 mL of HMPA and 3.0 mL of a 1.0 M solution of TBDMSCl (3.0 mmol) in THF were introduced. The reaction mixture was allowed to warm to room temperature slowly and then heated at 45 °C. After an additional 12 h at 45 °C, the reaction mixture was allowed to cool to room temperature. A mixture of 10 mL of acetic acid and 3.3 mL of water was introduced. After 12 h, 20 mL of diethyl ether was introduced, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water (5 × 30 mL), dried over magnesium sulfate,

and concentrated. Flash column chromatography (silica gel/25% acetone in hexanes) provided 0.323 g of **285** (0.76 mmol, 53% from **277**) as a light yellow solid: mp 252–255 °C; IR 3500–2600 (br), 1696, 767, 703 cm^{-1} ; ^1H δ 7.72–7.35 (15 H, m), 7.20 (1 H, t, J = 7.4 Hz), 7.04 (1 H, t, J = 7.5 Hz), 6.44 (1 H, d, J = 7.7 Hz), 4.69 (1 H, dd, J = 8.9, 3.2 Hz), 2.75 (1 H, dd, J = 16.6, 3.5 Hz), 2.17 (1 H, dd, J = 16.6, 9.2 Hz); ^{13}C δ 177.2, 147.4, 141.2, 140.4, 138.9, 138.0, 136.2, 135.4, 133.34, 133.31, 131.8, 130.9, 130.1, 129.7, 129.5, 129.2, 129.1, 128.4, 127.88, 127.85, 127.6, 127.3, 126.5, 125.8, 125.52, 125.48, 124.1, 123.8, 42.5, 37.0; MS m/z 426 (M^+), 367; HRMS calcd for $\text{C}_{31}\text{H}_{22}\text{O}_2$ 426.1620, found 426.1632.

Compound 286. The same procedure was repeated as described for **285** except that 0.267 g (1.28 mmol) of benzosuberone (**278**) was treated with lithium acetylide, derived from 0.276 g (1.37 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.54 mL of a 2.5 M solution of *n*-butyllithium (1.35 mmol) in hexanes, followed by 0.140 g (1.37 mmol) of acetic anhydride to provide the crude acetate **282**. The crude acetate **282** was immediately treated with LDA, derived from 1.00 mL of a 2.5 M solution of *n*-butyllithium (2.50 mmol) in hexanes and 0.36 mL (2.57 mmol) of diisopropylamine, followed by 1.0 mL of HMPA and 2.6 mL of a 1.0 M solution of TBDMSCl (2.60 mmol) in THF. Hydrolysis with a solution of 10 mL of 10% sodium hydroxide, followed by flash column chromatography (silica gel/25% acetone in hexanes) provided 0.057 g of **286** (0.126 mmol, 10% from **278**) as a yellow solid: mp 122–125 °C; IR 1708, 780, 759, 703 cm^{-1} ; ^1H δ 7.68–7.12 (14 H, m), 7.02 (1 H, t, J = 7.4 Hz), 6.33 (1 H, d, J = 7.7 Hz), 5.07 (1 H, dd, J = 9.0, 3.3 Hz), 3.50–3.30 (3 H, m), 3.00–2.80 (1 H, m), 2.58 (1 H, dd, J = 16.3, 3.5 Hz), 2.13 (1 H, dd, J = 16.2, 9.0 Hz); ^{13}C δ 177.0, 147.2, 143.7, 143.6, 140.1, 139.5, 139.1, 137.8, 136.7, 134.5, 134.3, 134.0, 132.2, 130.5, 130.3, 129.9, 129.3, 129.1, 128.6, 127.84, 127.77, 127.5, 127.2, 126.7, 126.3, 125.3, 124.5, 123.9, 123.7, 43.9, 40.2, 36.7, 33.6.

Ketone 287. The following procedure is representative for the intramolecular acylation reaction. To a flask containing 0.25 g (0.59 mmol) of **274** under a nitrogen atmosphere was added 5.0 mL (68.5 mmol) of thionyl chloride. After 3 h at room temperature, the excess thionyl chloride was removed in vacuo to yield the crude acid chloride (IR 1794 cm^{-1}) as a light brown oil. To the solution of the crude acid chloride in 130 mL of methylene chloride at 0 °C was added 0.21 g (1.57 mmol) of anhydrous aluminum chloride. The reaction mixture was allowed to warm to room temperature slowly. After 12 h, 10 mL of a 2 M solution of hydrochloric acid was added, and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with saturated aqueous sodium bicarbonate (3 $\times$ 50 mL) and water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) furnished 0.21 g of **287** (0.52 mmol, 88%) as orange crystals: mp 323–325 °C; IR 1662, 774, 708 cm^{-1} ; ^1H δ 8.08 (1 H, d, J = 7.4 Hz), 7.97 (1 H, dd, J = 7.7, 1.5 Hz), 7.94 (1 H, d, J = 7.7 Hz), 7.63–7.43 (9 H, m), 7.33 (1 H, t, J = 7.2 Hz), 7.14 (1 H, t, J = 7.7 Hz), 6.85 (1 H, d, J = 7.7 Hz), 4.51 (1 H, d, J = 13.6 Hz), 3.64 (1 H, dd, J = 12.9, 2.5 Hz), 3.24 (1 H, dd, J = 13.6, 12.9 Hz); ^{13}C δ 199.2, 145.9, 144.0, 141.6, 139.9, 137.9, 137.2, 135.9, 134.7, 133.4, 130.7, 130.4, 130.1, 129.9, 128.9, 128.8, 128.7, 128.1, 128.0, 127.8, 127.6, 127.5, 126.9, 126.4, 126.1, 124.4, 123.8, 121.3, 44.4, 41.8; MS m/z 406 (M^+), 389, 378; HRMS calcd for $\text{C}_{31}\text{H}_{18}\text{O}$ 406.1358, found 406.1347. Recrystallization of **287** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 13).

Ketone 291. The same procedure was repeated as described for **287** except that 0.106 g (0.249 mmol) of **285** was treated with 3 mL of thionyl chloride and 0.100 g (0.749 mmol) of anhydrous aluminum chloride to afford 0.071 g of **291** (0.174 mmol, 70%) as yellow crystals: mp 239–241 °C; IR 1682, 765, 700 cm^{-1} ; ^1H δ 8.18 (1 H, dd, J = 7.9, 1.5 Hz), 7.88 (1 H, dd, J = 7.7, 1.2 Hz),

7.76 (1 H, dd, $J = 7.9, 1.0$ Hz), 7.70–7.38 (11 H, m), 7.27 (1 H, td, $J = 7.4, 1.0$ Hz), 7.08 (1 H, t, $J = 7.7$ Hz), 6.52 (1 H, d, $J = 7.9$ Hz), 4.44 (1 H, dd, $J = 13.4, 4.5$ Hz), 3.59 (1 H, dd, $J = 19.2, 4.5$ Hz), 2.69 (1 H, dd, $J = 19.2, 13.5$ Hz); ^{13}C δ 204.2, 146.2, 143.3, 140.4, 140.1, 138.5, 135.8, 134.6, 134.4, 134.3, 131.7, 130.9, 130.6, 130.1, 129.8, 129.5, 129.2, 128.0, 127.83, 127.77, 127.4, 127.1, 125.9, 125.6, 125.3, 124.0, 123.9, 52.7, 42.0; MS m/z 408 (M^+), 393, 378, 302; HRMS calcd for $\text{C}_{31}\text{H}_{20}\text{O}$ 408.1514, found 408.1527. Recrystallization of **291** from CH_2Cl_2 /hexanes produced a crystal suitable for X-ray structure analysis (Figure 14).

Carboxylic Acids 296 and 297. The same procedure was repeated as described for **285** except that 0.162 g (1.00 mmol) of **292** was treated with **60**, prepared from 0.227 g (1.12 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.44 mL of a 2.5 M solution of *n*-butyllithium (1.10 mmol) in hexanes, followed by 0.112 g (1.10 mmol) of acetic anhydride to provide the crude acetate **293** as a light brown liquid. The crude acetate **293** was treated with LDA, prepared from 0.80 mL of a 2.5 M solution of *n*-butyllithium (2.00 mmol) in hexanes and 0.28 mL (2.00 mmol) of diisopropylamine, followed by 1.2 mL of HMPA and 2.00 mL of a 1.0 M solution of TBDMSCl (2.00 mmol) in THF. Hydrolysis with a mixture of 7 mL of acetic acid and 3 mL of water provided 0.142 g of **296** (0.35 mmol, 35% from **292**) as an orange solid: mp 204–206 °C; IR 3500–2600 (br), 1707, 751, 693 cm^{-1} ; ^1H δ 7.96 (2 H, d, $J = 7.2$ Hz), 7.67 (1 H, d, $J = 7.4$ Hz), 7.55–7.10 (11 H, m), 3.85 (2 H, s), 1.22 (9 H, s); ^{13}C δ 176.5, 153.7, 151.7, 148.4, 147.5, 142.8, 135.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 127.6, 126.2, 124.0, 123.6, 120.1, 114.8, 77.2, 36.8, 33.2, 29.0; MS m/z 406 (M^+), 360, 349; HRMS calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2$ 406.1933, found 406.1915. The formation of **297** was detected in the crude reaction products with ^1H NMR signals (partial) at δ 8.57 (1 H, d, $J = 8.9$ Hz), 6.96 (1 H, t, $J = 6.7$ Hz), 6.23 (1 H, d, $J = 7.7$ Hz), 5.41 (1 H, d, $J = 11$ Hz), 3.23 (1 H, d, $J = 16$ Hz), 2.30 (1 H, dd, $J = 16, 11$ Hz).

Carboxylic Acids 302 and 303. The same procedure was repeated as described for **285** except that 0.571 g (3.28 mmol) of the ketone **298** was treated with **60**, prepared from 0.800 g (3.96 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 1.57 mL of a 2.5 M solution of *n*-butyllithium (3.93 mmol) in hexanes, followed by 0.405 g (3.96 mmol) of acetic anhydride to provide the crude acetate **300** as a light brown liquid. The crude acetate **300** was treated with LDA, prepared from 2.62 mL of a 2.5 M solution of *n*-butyllithium (6.55 mmol) in hexanes and 0.92 mL (6.55 mmol) of diisopropylamine, followed by 2.0 mL of HMPA and 6.60 mL of a 1.0 M solution of TBDMSCl (6.60 mmol) in THF. Hydrolysis with a mixture of 15 mL of acetic acid and 5 mL of water provided 0.326 g of **302** (0.78 mmol, 24% from **298**) as an orange solid and 0.326 g of **303** (0.78 mmol, 24% from **298**) as a yellow solid. **302**: mp 164–167 °C; IR 3500–2600 (br), 1702, 726 cm⁻¹; ¹H δ 7.74 (1 H, d, *J* = 7.4 Hz), 7.43–7.08 (11 H, m), 6.98 (1 H, t, *J* = 7.4 Hz), 3.43 (2 H, s), 3.12–2.98 (2 H, m), 2.04–1.93 (1 H, m), 1.85–1.76 (1 H, m), 1.13 (3 H, s), 1.03 (3 H, s); ¹³C δ 174.9, 153.0, 152.1, 148.1, 147.4, 138.4, 135.0, 134.8, 129.9, 129.4, 129.2, 128.7, 128.5, 128.4, 126.5, 126.2, 123.7, 123.6, 120.1, 113.1, 68.8, 35.3, 34.7, 31.8, 27.4, 26.2, 26.0. **303**: mp 225–228 °C; IR 3500–2600 (br), 1708, 732 cm⁻¹; ¹H δ 7.61–7.51 (4 H, m), 7.46–7.28 (5 H, m), 7.18 (1 H, td, *J* = 7.4, 0.7 Hz), 6.98 (1 H, t, *J* = 7.7 Hz), 6.25 (1 H, d, *J* = 7.7 Hz), 5.21 (1 H, dd, *J* = 10.6, 2.0 Hz), 3.57 (1 H, dd, *J* = 16.7, 2.4 Hz), 3.46 (1 H, ddd, *J* = 17.1, 11.9, 5.2 Hz), 3.12 (1 H, dt, *J* = 13.1, 4.0 Hz), 2.43 (1 H, dd, *J* = 16.6, 10.6 Hz), 2.09 (1 H, td, *J* = 12.5, 4.9 Hz), 1.94 (1 H, dt, *J* = 12.9, 4.5 Hz), 1.84 (3 H, s), 1.59 (3 H, s); ¹³C δ 177.0, 148.2, 139.8, 139.6, 139.2, 139.0, 136.6, 135.4, 134.1, 133.3, 130.2, 129.35, 129.30, 129.0, 127.7, 127.3, 127.2, 125.1, 124.9, 124.8, 124.0, 123.4, 44.2, 42.6, 40.8, 36.3, 30.7, 28.9, 27.7.

Carboxylic Acids 304 and 305. The same procedure was repeated as described for **285** except that 0.522 g (3.26 mmol) of the ketone **299** was treated with **60**, prepared from 0.806 g (3.99

mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 1.60 mL of a 2.5 M solution of *n*-butyllithium (4.00 mmol) in hexanes, followed by 0.413 g (4.00 mmol) of acetic anhydride to provide the crude acetate **301** as a light brown liquid. The crude acetate **301** was treated with LDA, prepared from 2.60 mL of a 2.5 M solution of *n*-butyllithium (6.50 mmol) in hexanes and 0.91 mL (6.49 mmol) of diisopropylamine, followed by 1.2 mL of HMPA and 6.50 mL of a 1.0 M solution of TBDMSCl (6.50 mmol) in THF. Hydrolysis with a mixture of 7 mL of acetic acid and 3 mL of water provided 0.132 g of **304** (0.327 mmol, 10% from **299**) as an orange solid and 0.662 g of **305** (1.64 mmol, 50% from **299**) as a yellow solid. **304**: mp 55–57 °C; IR 3500–2600 (br), 1708, 689 cm⁻¹; ¹H δ 7.77 (1 H, d, *J* = 7.2 Hz), 7.40–7.17 (10 H, m), 7.10–7.06 (2 H, m), 3.47 (2 H, s), 3.21 (1 H, d, *J* = 16.1 Hz), 2.99 (1 H, d, *J* = 16.1 Hz), 1.25 (3 H, s); 1.16 (3 H, s), ¹³C δ 176.3, 152.8, 152.4, 147.6, 145.8, 145.3, 141.3, 134.4, 129.6, 129.3, 128.8, 128.7, 127.9, 127.8, 126.9, 125.6, 124.9, 123.8, 123.7, 120.2, 113.6, 75.7, 47.3, 45.4, 31.9, 28.6, 24.7; MS *m/z* 404 (M⁺), 389, 359, 345, 329; HRMS calcd for C₂₉H₂₄O₂ 404.1776, found 404.1775. **305**: mp 143–146 °C; IR 3500–2600 (br), 1708, 779, 703 cm⁻¹; ¹H δ 7.63–7.47 (5 H, m), 7.40–7.35 (2 H, m), 7.30–7.24 (2 H, m), 7.20 (1 H, td, *J* = 7.4, 1.0 Hz), 7.02 (1 H, td, *J* = 7.5, 0.9 Hz), 6.52 (1 H, d, *J* = 7.9 Hz), 4.83 (1 H, dd, *J* = 10.3, 2.4 Hz), 3.57 (1 H, dd, *J* = 16.6, 2.5 Hz), 3.41 (1 H, d, *J* = 16.6 Hz), 3.31 (1 H, d, *J* = 16.6 Hz), 2.59 (1 H, dd, *J* = 16.6, 10.1 Hz), 1.76 (3 H, s), 1.65 (3 H, s); ¹³C δ 177.4, 148.1, 147.0, 142.6, 140.1, 138.64, 138.58, 137.2, 137.0, 131.5, 131.3, 130.3, 130.0, 129.1, 128.9, 127.7, 127.6, 127.29, 127.26, 124.0, 123.8, 121.6, 119.5, 49.3, 45.2, 41.4, 41.2, 30.7, 28.6; MS *m/z* 404 (M⁺), 389, 358, 345, 330, 315; HRMS calcd for C₂₉H₂₄O₂ 404.1776, found 404.1769.

Compound 306. To a flask containing 0.183 g (0.413 mmol) of lead (IV) acetate in 5 mL of benzene under a nitrogen atmosphere was added a solution of 0.070 g (0.172 mmol) of **287**, 0.8

mL (6.31 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and 1.2 mL of methanol in 20 mL of methylene chloride. The reaction mixture was heated under reflux. After 48 h, 10 mL of water was introduced and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) afforded 0.027 g of **306** (0.062 mmol, 36%) as yellow crystals: mp 214–216 °C; IR 1686, 1060, 787, 669 cm^{-1} ; ^1H δ 8.11 (1 H, dd, $J = 7.4, 0.7$ Hz), 8.01 (1 H, dd, $J = 5.9, 1.5$ Hz), 7.94 (1 H, dd, $J = 7.9, 0.7$ Hz), 7.68–7.47 (9 H, m), 7.33 (1 H, td, $J = 7.5, 1.0$ Hz), 7.15 (1 H, td, $J = 7.7, 1.0$ Hz), 6.74 (1 H, d, $J = 7.7$ Hz), 5.70 (1 H, d, $J = 10.8$ Hz), 4.56 (1 H, d, $J = 10.8$ Hz), 2.73 (3 H, s); ^{13}C δ 193.5, 143.1, 142.0, 140.0, 137.7, 137.0, 136.7, 136.5, 135.3, 134.8, 132.0, 131.6, 131.2, 130.8, 130.2, 130.1, 129.9, 129.4, 129.0, 128.8, 128.6, 128.5, 128.4, 126.7, 126.4, 126.0, 123.7, 122.0, 83.6, 68.8, 68.2, 50.5. Recrystallization of **306** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 15).

Compound 310. To a solution of 0.082 g (2.05 mmol) of sodium hydride and 1 drops of methanol in 5 mL of THF under a nitrogen atmosphere at 0 °C was added a solution of 0.022 g (0.054 mmol) of **287** and 0.1 mL of methyl formate in 20 mL of THF. The reaction mixture was then allowed to warm to room temperature. After 12 h, a solution of 0.332 g (1.69 mmol) of tosyl azide in 5 mL THF was introduced into the reaction mixture. After an additional 4 h, 5 mL of water and 30 mL of methylene chloride were introduced and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic extracts were washed with a solution of 10% NaOH and water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) afforded 0.018 g of **310** (0.045 mmol, 83%) as yellow crystals: mp 325–327 °C; IR 1695, 892,

782, 733, 708 cm^{-1} ; ^1H δ 8.43 (1 H, dd, $J = 8.2, 0.7$ Hz), 8.21 (1 H, dd, $J = 7.2, 0.7$ Hz), 8.01 (1 H, dd, $J = 6.3, 1.1$ Hz), 7.95 (1 H, d, $J = 7.2$ Hz), 7.74–7.55 (9 H, m), 7.37 (1 H, td, $J = 7.5, 1.0$ Hz), 7.26 (1 H, m), 6.90 (1 H, d, $J = 7.7$ Hz). Recrystallization of **310** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 16).

Fluorenylmethanol 370. To a solution of 0.317 g (0.796 mmol) of hydrocarbon **369** in 8 mL of THF under a nitrogen atmosphere at 0 °C was added 0.53 mL of a 2.0 M solution of LDA (1.06 mmol) in heptane/tetrahydrofuran/ethylbenzene. After 10 min at 0 °C, 0.030 g (1.00 mmol) of paraformaldehyde was transferred into the reaction mixture via a solid addition tube. The reaction mixture was then allowed to warm to room temperature. After an additional 15 min, 5 mL of saturated sodium bicarbonate solution was introduced and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 0.311 g of **370** (0.727 mmol, 91%) as a white solid: mp 207–209 °C; IR 3401 (br), 832, 750, 697 cm^{-1} ; ^1H δ 8.50 (1 H, d, $J = 9.6$ Hz), 7.79 (1 H, dd, $J = 7.9, 1.5$ Hz), 7.68–7.52 (7 H, m), 7.41–7.31 (2 H, m), 7.21 (1 H, td, $J = 7.4, 1.0$ Hz), 7.04–6.93 (2 H, m), 5.94 (1 H, d, $J = 7.9$ Hz), 5.02 (1 H, dd, $J = 7.5, 3.8$ Hz), 4.45–4.41 (1 H, m), 3.56–3.45 (1 H, m), 1.91 (9 H, s); ^{13}C δ 146.3, 143.3, 142.9, 140.8, 139.9, 139.4, 134.2, 132.8, 132.5, 131.4, 130.2, 130.0, 129.9, 128.7, 127.9, 127.6, 126.9, 126.8, 126.2, 125.6, 124.5, 124.3, 124.2, 123.6, 67.8, 51.4, 38.5, 34.6; MS m/z 429 (MH^+), 415, 355, 281, 207.

Hydrocarbon 371. To a flask containing 0.069 g (0.161 mmol) of **370** was added 0.256 g (1.80 mmol) of phosphorus pentoxide, followed by 10 mL of *p*-xylene via cannula. The reaction mixture was heated under reflux for 2 h. After the reaction mixture cooled to room temperature, 10 mL of saturated sodium bicarbonate solution was introduced and the organic layer was

separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water (3×30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/10% methylene chloride in hexanes) provided 0.050 g of **371** (0.141 mmol, 88%) as a white solid: mp 259–261 °C; IR 1443, 878, 790, 743, 696 cm⁻¹; ¹H δ 8.35 (1 H, s), 7.82 (2 H, d, *J* = 8.9 Hz), 7.79 (2 H, dd, *J* = 8.2, 1.5 Hz), 7.69 (2 H, d, *J* = 8.7 Hz), 7.66–7.58 (3 H, m), 7.52–7.48 (2 H, m), 7.39 (2 H, td, *J* = 7.9, 1.0 Hz), 7.21 (2 H, d, *J* = 8.7 Hz), 6.99 (2 H, td, *J* = 8.7, 1.7 Hz); ¹³C δ 145.4, 138.8, 134.2, 131.5, 131.3, 131.2, 130.6, 129.0, 128.4, 128.2, 128.13, 128.10, 127.8, 126.9, 125.9, 124.5; MS *m/z* 354 (M⁺), 337, 313; HRMS: calcd for C₂₈H₁₈, 354.1409; found, 354.1402.

Diol 376. The following procedure is representative for the preparation of the diols. To a solution of 0.344 g (0.557 mmol) of hydrocarbon **78a** in 60 mL of benzene and 50 mL of THF under a nitrogen atmosphere at 0 °C was added 1.80 mL of a 2.0 M solution of LDA (3.60 mmol) in heptane/tetrahydrofuran/ethylbenzene. After 20 min at 0 °C, 0.220 g (7.33 mmol) of paraformaldehyde was transferred into the reaction mixture via a solid addition tube. The reaction mixture was allowed to warm to room temperature. After an additional 30 min, 10 mL of saturated sodium bicarbonate solution was introduced and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/50% diethyl ether in hexanes) afforded 0.287 g of **376** (0.423 mmol, 76%, a mixture of three isomers, isomer ratio = 22:12:1) as an orange solid: mp 221–225 °C; IR 3412 (br), 765, 704 cm⁻¹; ¹H δ isomer 1: 7.86 (2 H, s), 7.49 (2 H, d, *J* = 7.4 Hz), 7.21–6.96 (8 H, m), 6.80 (2 H, t, *J* = 7.7 Hz), 6.53–6.50 (4 H, m), 6.27 (2 H, d, *J* = 7.9 Hz), 4.76–4.69 (2 H, m), 4.47 (2 H, d, *J* = 10.6 Hz), 3.82 (1.5 H, dd, *J* = 10.6, 6.4 Hz), 3.72 (0.5 H, dd, *J* = 10.8, 5.5 Hz), 1.85 (18 H, s); isomer 2 (partial of

signals): 8.02 (1 H, d, $J = 9.7$ Hz), 7.92 (1 H, d, $J = 9.4$ Hz), 7.47 (2 H, d, $J = 7.4$ Hz), 6.38 (1 H, d, $J = 7.4$ Hz), 6.36 (1 H, d, $J = 7.7$ Hz), 4.87 (2 H, dd, $J = 7.9, 3.7$ Hz), 4.38 (2 H, dd, $J = 10.9, 3.5$ Hz), 3.48 (1 H, dd, $J = 10.4, 8.2$ Hz), 1.90 (9 H, s), 1.88 (9 H, s); isomer 3 (partial of signals): 8.09 (2 H, s), 1.93 (9 H, s); ^{13}C δ (3 isomers) 146.7, 146.6, 140.8, 140.7, 140.6, 140.5, 140.4, 139.0, 138.8, 138.7, 138.4, 138.3, 137.4, 137.2, 135.9, 135.5, 135.4, 135.1, 135.0, 134.9, 134.8, 134.6, 133.3, 132.5, 132.2, 132.1, 131.2, 131.1, 128.2, 127.7, 127.2, 126.92, 126.88, 126.55, 126.52, 126.1, 126.0, 123.8, 123.5, 123.3, 123.0, 122.9, 122.1, 121.9, 69.5, 67.1, 67.0, 52.2, 50.6, 38.2, 37.8, 37.7, 34.5, 34.3, 34.2; MS m/z 678 (M^+), 664, 647, 605; HRMS: calcd for $\text{C}_{50}\text{H}_{46}\text{O}_2$, 678.3492; found, 678.3496.

Hydrocarbon 377. The following procedure is representative for the preparation of the hydrocarbons only via ring expansion. To a flask containing 0.0134 g of (0.0198 mmol) diol **376** was added 0.100 g (0.704 mmol) of phosphorus pentoxide, followed by 10 mL of *p*-xylene via cannula. The reaction mixture was heated at 110 °C for 10 min. After the reaction mixture cooled to room temperature, 10 mL of saturated sodium bicarbonate solution was introduced. The organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water (3×30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/10% methylene chloride in hexanes) provided 0.0076 g of **377** (0.0143 mmol, 72%) as a light yellow solid: mp 272–275 °C; IR 1437, 879, 797, 744, 697 cm^{-1} ; ^1H δ 8.03 (2 H, s), 7.71 (2 H, d, $J = 8.9$ Hz), 7.65 (2 H, d, $J = 7.7$ Hz), 7.61 (2 H, d, $J = 8.9$ Hz), 7.44 (2 H, s), 7.19 (2 H, td, $J = 7.9, 1.0$ Hz), 7.00 (2 H, tt, $J = 7.4, 1.0$ Hz), 6.81 (4 H, t, $J = 7.7$ Hz), 6.62 (2 H, td, $J = 7.8, 1.5$ Hz), 6.51 (2 H, d, $J = 8.7$ Hz), 6.40 (4 H, dd, $J = 8.0, 1.1$ Hz); ^{13}C δ 141.2, 139.3, 133.9, 132.52, 132.45, 132.3, 130.9, 128.90, 128.85,

128.2, 127.7, 127.2, 127.0, 126.4, 126.0, 125.5, 123.6, 122.8; MS m/z 530 (M^+), 453, 437, 424; HRMS: calcd for $C_{42}H_{26}$, 530.2035; found, 530.2035.

Hydrocarbon 378. To a flask containing 0.083 g (0.122 mmol) of diol **376** was added 0.310 g (2.18 mmol) of phosphorus pentoxide, followed by 15 mL of *p*-xylene via cannula. The reaction mixture was heated under reflux for 1.5 h. After the reaction mixture cooled to room temperature, 10 mL of saturated sodium bicarbonate solution was introduced and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water (3×30 mL), dried over magnesium sulfate, and concentrated. Crystallization of the crude product from hexanes provided 0.050 g of **378** (0.094 mmol, 77%) as a bright yellow solid: mp 260–262 °C; IR 1443, 873, 738, 703 cm^{-1} ; 1H δ 9.50 (1 H, dd, J = 6.4, 3.5 Hz), 8.31 (2 H, d, J = 8.2 Hz), 8.12 (1 H, s), 7.90–7.70 (6 H, m), 7.64–7.58 (3 H, m), 7.45 (1 H, d, J = 8.4 Hz), 7.36 (1 H, td, J = 7.1, 1.0 Hz), 7.31–7.22 (3 H, m), 7.06–6.92 (3 H, m), 6.61 (3 H, s), 4.83 (1 H, d, J = 22.8 Hz), 4.77 (1 H, d, J = 23.0 Hz); ^{13}C δ 149.1, 139.5, 136.1, 133.7, 133.3, 133.0, 132.4, 131.9, 131.8, 130.5, 130.4, 130.1, 129.3, 129.2, 128.72, 128.65, 128.4, 128.2, 127.9, 127.63, 127.58, 127.0, 126.9, 126.3, 126.2, 125.7, 125.6, 125.2, 125.1, 124.6, 53.4, 35.8; MS m/z 530 (M^+), 453, 435, 424; HRMS: calcd for $C_{42}H_{26}$, 530.2035; found, 530.2030.

Hydrocarbon 379. The following procedure is representative for the preparation of the butterfly-shaped hydrocarbons. To a flask containing 0.048 g (0.071 mmol) of diol **376** was added 0.496 g (3.49 mmol) of phosphorus pentoxide, followed by 20 mL of *p*-xylene via cannula. The reaction mixture was heated under reflux for 12 h. After the reaction mixture cooled to room temperature, 10 mL of saturated sodium bicarbonate solution was introduced and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The

combined organic extracts were washed with water (3×30 mL), dried over magnesium sulfate, and concentrated. Crystallization of the crude product from hexanes provided 0.033 g of **379** (0.062 mmol, 87%) as a light brown solid: mp >380 °C; IR 1455, 797, 779, 744 cm⁻¹; ¹H δ 8.02 (2 H, d, *J* = 8.2 Hz), 7.99 (2 H, d, *J* = 8.7 Hz), 7.75 (2 H, d, *J* = 8.4 Hz), 7.60 (2 H, d, *J* = 8.4 Hz), 7.49 (2 H, td, *J* = 7.7, 0.9 Hz), 7.31–7.24 (2 H, m), 6.85 (2 H, s), 6.79–6.71 (8 H, m), 4.42 (4 H, s); ¹³C δ 146.0, 141.1, 139.9, 134.8, 133.4, 132.5, 130.5, 128.8, 128.6, 128.2, 126.7, 125.6, 124.9, 124.7, 124.1, 123.7, 54.1, 33.8; MS *m/z* 530, 453, 424. HRMS: calcd for C₄₂H₂₆, 530.2035; found, 530.2025.

Diketone 380. To a flask containing 0.021 g (0.040 mmol) of hydrocarbon **379** was added 0.101 g (0.445 mmol) of DDQ, followed by 25 mL of benzene. The reaction mixture was heated under reflux for 72 h. After the reaction mixture cooled to room temperature, it was run through an aluminum oxide column, followed by diethyl ether to rinse the column. The combined organic solution was concentrated. Flash column chromatography (silica gel/10% diethyl ether in hexanes) provided 0.017 g of **380** (0.030 mmol, 75%) as a light yellow solid: mp >370 °C; IR 1654, 878, 758 cm⁻¹; ¹H δ 8.82 (2 H, d, *J* = 8.7 Hz), 8.31 (2 H, d, *J* = 8.9 Hz), 8.17 (2 H, d, *J* = 8.2 Hz), 8.12 (2 H, s), 7.88 (2 H, d, *J* = 8.7 Hz), 7.74 (2 H, td, *J* = 8.0, 1.2 Hz), 7.45 (2 H, td, *J* = 8.4, 1.2 Hz), 6.86–6.82 (4 H, m), 6.75–6.70 (4 H, m); ¹³C δ 182.6, 150.8, 143.6, 136.7, 136.5, 132.5, 131.7, 131.4, 130.3, 129.9, 129.2, 128.5, 125.79, 125.75, 125.70, 124.5, 122.9, 53.3; MS *m/z* 558 (M⁺), 529, 498, 479, 464. HRMS: calcd for C₄₂H₂₂O₂, 558.1620; found, 558.1603. Recrystallization of **380** from CH₂Cl₂/2-propanol produced a crystal suitable for X-ray structure analysis (Figure 17).

Diol 385a. The same procedure was repeated as described for **376** except that 0.094 g (0.122 mmol) of **78b** in a mixture of 30 mL of benzene and 20 mL of THF was treated with 0.50 mL of

a 2.0 M solution of LDA (1.0 mmol) in heptane/tetrahydrofuran/-ethylbenzene, followed by 0.050 g (1.67 mmol) of paraformaldehyde to afford 0.078 g of **385a** (0.094 mmol, 77%, a mixture of two isomers, isomer ratio = 1:1.2) as a bright yellow solid: mp 235–238 °C; IR 3416 (br), 906, 840, 768, 728, 696 cm^{-1} ; ^1H δ : isomer 1: 7.85 (2 H, s), 7.68–7.62 (4 H, m), 7.51–7.25 (12 H, m), 7.03 (2 H, td, $J = 7.4, 1.0$ Hz), 6.80–6.74 (2 H, m), 6.62–6.58 (4 H, m), 6.36 (2 H, d, $J = 7.9$ Hz), 4.87–4.72 (2 H, m), 4.51–4.38 (2 H, m), 3.90–3.44 (2 H, m), 1.84 (18 H, s); isomer 2 (partial of signals): 8.00 (1 H, d, $J = 9.4$ Hz), 7.90 (1 H, d, $J = 9.4$ Hz), 7.10 (2 H, t, $J = 7.4$ Hz), 6.45 (1 H, d, $J = 8.2$ Hz), 6.41 (1 H, d, $J = 8.2$ Hz), 1.88 (9 H, s), 1.87 (9 H, s); ^{13}C δ (2 isomers) 146.8, 146.6, 141.11, 141.08, 141.00, 140.8, 140.73, 140.67, 140.6, 140.5, 140.4, 139.3, 139.15, 139.08, 138.91, 138.87, 137.9, 137.7, 137.56, 137.53, 137.4, 136.1, 134.9, 134.6, 134.5, 134.3, 133.0, 132.6, 132.2, 132.0, 131.2, 131.0, 128.85, 128.76, 127.32, 127.28, 127.23, 126.8, 126.7, 126.6, 126.4, 126.2, 126.1, 126.0, 123.9, 123.6, 123.3, 123.0, 122.9, 122.8, 122.3, 122.0, 69.6, 67.1, 66.9, 52.3, 50.7, 38.3, 37.8, 37.7, 34.5, 34.3, 34.2; MS m/z 830 (M^+), 799, 681, 656. HRMS: calcd for $\text{C}_{62}\text{H}_{54}\text{O}_2$, 830.4118; found, 830.4073.

Hydrocarbon 386a. The same procedure was repeated as described for **377** except that 0.0085 g (0.0102 mmol) of **385a** and 0.100 g (0.704 mmol) of phosphorus pentoxide, followed by 10 mL of benzene at 90 °C for 15 min to afford 0.0062 g of **386a** (0.0091 mmol, 89%) as a yellow solid: mp 264–267 °C; IR 1449, 803, 732, 697 cm^{-1} ; ^1H δ 8.06 (2 H, s), 7.73 (2 H, d, $J = 8.7$ Hz), 7.65–7.54 (8 H, m), 7.47 (2 H, s), 7.40 (4 H, td, $J = 7.3, 1.2$ Hz), 7.33–7.26 (2 H, m), 7.17 (2 H, tt, $J = 7.9, 1.3$ Hz), 7.12 (4 H, d, $J = 8.4$ Hz), 6.68–6.59 (4 H, m), 6.54 (4 H, d, $J = 8.2$ Hz); ^{13}C δ 140.7, 140.5, 138.8, 138.6, 134.0, 132.7, 132.5, 132.4, 130.9, 129.0, 128.7, 128.1, 127.9, 127.5, 127.3, 127.2, 127.1, 126.7, 126.5, 125.9, 125.6, 123.9, 122.9; MS m/z 682 (M^+), 528, 448, 425. HRMS: calcd for $\text{C}_{54}\text{H}_{34}$, 682.2661; found, 682.2687.

Hydrocarbon 387. The same procedure was repeated as described for **379** except that 0.038 g (0.046 mmol) of **385a** and 0.300 g (2.11 mmol) of phosphorus pentoxide, followed by 40 mL of *p*-xylene under reflux for 12 h to afford 0.013 g of **387** (0.019 mmol, 41%) as a yellow solid: mp 186–189 °C; IR 908, 756, 732, 697 cm⁻¹; ¹H (270 MHz) NMR δ 8.035 (2 H, d, *J* = 8.4 Hz), 8.026 (2 H, d, *J* = 7.9 Hz), 7.89 (2 H, d, *J* = 8.4 Hz), 7.61 (2 H, d, *J* = 8.4 Hz), 7.54 (2 H, td, *J* = 7.9, 1.0 Hz), 7.35 (2 H, td, *J* = 8.4, 1.5 Hz), 7.22–7.10 (6 H, m), 7.04–6.96 (8 H, m), 6.89 (2 H, s), 6.86 (2 H, d, *J* = 8.7 Hz), 4.44 (4 H, s); ¹H (600 MHz) NMR δ (partial signals) 4.46 (2 H, d, *J* = 21.6 Hz), 4.43 (2 H, d, *J* = 22.2 Hz); ¹³C NMR δ 146.6, 145.3, 142.2, 140.9, 137.1, 134.9, 133.5, 132.5, 130.4, 129.0, 128.8, 128.4, 128.2, 127.1, 126.9, 126.8, 126.7, 126.4, 125.9, 125.1, 124.7, 124.1, 123.1, 54.0, 33.8; MS *m/z* 682 (M⁺), 529, 425. HRMS: calcd for C₅₄H₃₄, 682.2661; found, 682.2663.

Diol 385b. The same procedure was repeated as described for **376** except that 0.065 g (0.091 mmol) of **384** in 45 mL of THF was treated with 0.50 mL of a 2.0 M solution of LDA (1.0 mmol) in heptane/tetrahydrofuran/ethylbenzene, followed by 0.10 g (3.3 mmol) of paraformaldehyde to afford 0.054 g of **385b** (0.069 mmol, 76%, a mixture of several isomers) as an orange solid: mp 243–246 °C; IR 3413 (br), 908, 803, 779, 732 cm⁻¹; ¹H δ: 8.22–7.90 (2 H, m), 7.84–7.66 (2 H, m), 7.63–5.80 (18 H, m), 5.71–4.82 (2 H, d, *J* = 8.2 Hz), 4.82–4.40 (3 H, m), 3.90–2.97 (3 H, m), 1.94–1.86 (18 H, m); ¹³C δ (isomers) 146.6, 146.52, 146.49, 146.3, 146.2, 145.8, 145.7, 141.2, 140.80, 140.77, 140.68, 140.6, 140.53, 140.49, 140.4, 140.3, 140.0, 139.8, 139.3, 139.2, 139.1, 139.03, 138.96, 138.8, 138.6, 138.3, 138.2, 138.1, 138.0, 137.7, 137.6, 136.6, 136.1, 135.8, 135.4, 135.1, 134.8, 134.7, 134.5, 134.4, 134.1, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.4, 133.31, 133.25, 133.00, 132.97, 132.7, 132.5, 132.4, 132.2, 131.8, 131.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.93, 127.88, 127.81, 127.74, 127.68, 127.63, 127.4,

127.3, 127.1, 126.9, 126.6, 126.5, 126.3, 126.2, 126.1, 126.00, 125.95, 125.85, 125.79, 125.73, 125.64, 125.59, 125.5, 125.4, 125.12, 125.07, 124.98, 124.95, 124.8, 124.74, 124.67, 124.61, 124.60, 124.53, 124.42, 124.36, 124.3, 124.0, 123.9, 123.8, 123.4, 123.2, 123.13, 123.06, 122.9, 122.74, 122.65, 122.2, 122.1, 121.8, 69.6, 69.54, 69.50, 69.1, 67.1, 66.9, 66.8, 66.7, 66.5, 52.4, 52.31, 52.25, 52.18, 52.13, 51.9, 51.7, 50.7, 50.55, 50.51, 38.35, 38.29, 37.9, 37.82, 38.78, 37.7, 37.6, 34.6, 34.4, 34.3, 34.23, 34.18; MS m/z 778 (M^+), 764, 747, 691, 655. HRMS: calcd for $C_{58}H_{50}O_2$, 778.3805; found, 778.3833.

Hydrocarbon 386b. The same procedure was repeated as described for **377** except that 0.0061 g (0.0078 mmol) of diol and 0.100 g (0.704 mmol) of phosphorus pentoxide, followed by 15 mL of benzene at 90 °C for 15 min to afford 0.0047 g of **386b** (0.0075 mmol, 96%, a mixture of three isomers, isomer ratio = 7:2:1) as a yellow solid: mp 189–192 °C; IR 882, 799, 776, 746, 723 cm^{-1} ; 1H δ : isomer 1: 8.19 (1 H, s), 8.10 (1 H, s), 7.80–7.75 (1 H, m), 7.65–7.36 (11 H, m), 7.15–6.65 (10 H, m), 6.39–6.16 (1 H, m), 6.08–5.87 (2 H, m), 5.83–5.74 (1 H, m), 5.56–5.47 (2 H, m); isomer 2 (partial): 8.17 (2 H, s); isomer 3 (partial): 8.08 (2 H, s); ^{13}C δ (3 isomers) 137.6, 133.9, 133.62, 133.55, 133.4, 132.8, 132.7, 132.5, 132.2, 132.0, 131.5, 130.9, 130.8, 130.4, 129.8, 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 127.2, 126.9, 126.75, 126.69, 126.61, 126.56, 126.4, 126.0, 125.9, 125.24, 125.17, 125.02, 124.95, 124.85, 124.4, 124.29, 124.28, 122.9, 122.8, 121.1, 121.0; MS m/z 630 (M^+), 503, 350, 315. HRMS: calcd for $C_{50}H_{30}$, 630.2348; found, 630.2351.

Propargylic Diol 390. The following procedure is representative for the preparation of the propargylic alcohol. To a solution of 0.794 g (3.15 mmol) of 1-(2-ethynylphenyl)-2-(1-naphthyl)ethyne **388** in 50 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 1.20 mL of a 2.5 M solution of *n*-butyllithium (3.00 mmol) in hexanes. The reaction mixture

was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 0.331 g (1.35 mmol) **389** in 40 mL of diethyl ether was introduced via cannula. After an additional 2 h, 30 mL of water was introduced, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) provided 1.00 g of **390** (1.33 mmol, 99%, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. Diastereomer 1: mp 87–90 °C; IR 3566, 3447, 2214, 982, 841, 799, 773, 757 cm^{-1} ; ^1H δ 8.44 (2 H, dd, $J = 6.2, 3.5$ Hz), 7.77–7.66 (8 H, m), 7.61–7.56 (2 H, m), 7.47–7.34 (14 H, m), 2.13 (2 H, br), 0.98 (18 H, s); ^{13}C δ 140.8, 133.1, 133.0, 132.35, 132.26, 130.5, 129.0, 128.2, 128.13, 128.08, 126.8, 126.4, 126.3, 126.2, 125.8, 125.3, 125.2, 120.6, 96.5, 93.0, 91.4, 84.6, 79.3, 39.7, 25.5; MS m/z 773 (MNa^+), 733, 716, 693, 676. HRMS: calcd for $\text{C}_{56}\text{H}_{46}\text{O}_2\text{Na}$, 773.3390; found, 773.3419. Diastereomer 2: mp 191–193 °C; IR 3566, 3447, 2214, 982, 841, 799, 773, 757 cm^{-1} ; ^1H δ 8.47–8.42 (2 H, m), 7.83–7.77 (4 H, m), 7.72–7.65 (4 H, m), 7.54–7.42 (10 H, m), 7.40–7.28 (6 H, m), 2.33 (2 H, br), 0.96 (18 H, s); ^{13}C δ 140.8, 133.2, 133.1, 132.3, 132.2, 130.5, 128.9, 128.2, 128.1, 128.0, 126.8, 126.34, 126.27, 125.8, 125.2, 120.6, 96.4, 93.0, 91.3, 84.6, 79.3, 39.7, 25.5; MS m/z 773 (MNa^+), 733, 716, 693, 676. HRMS: calcd for $\text{C}_{56}\text{H}_{46}\text{O}_2\text{Na}$, 773.3390; found, 773.3419.

Tetraacetylenic Hydrocarbon 391. The following procedure is representative for the preparation of the di/tetraacetylenic hydrocarbons. To a mixture of 0.893 g (1.19 mmol) of **390** and 0.829 g (7.15 mmol) of triethylsilane in 50 mL of methylene chloride under a nitrogen atmosphere at 0 °C was added 1.00 mL trifluoroacetic acid (1.54 g, 13.5 mmol). After 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature. After an additional 10

min, 0.77 g (7.26 mmol) sodium carbonate was added followed by 10 mL of water and 50 mL of diethyl ether. The organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/5% diethyl ether in hexanes) provided 0.817 g of **391** (1.14 mmol, 96%, 1:1 mixture of diastereomers) as a light yellow solid: mp 155–158 °C; IR 2247, 2227, 907, 840, 800, 774, 758, 732 cm^{-1} ; ^1H δ 8.59–8.52 (2 H, m), 7.90–7.68 (8 H, m), 7.62–7.28 (12 H, m), 7.21–7.18 (4 H, m), 3.67–3.64 (2 H, s), 0.99 (18 H, s); ^{13}C δ 137.24, 137.16, 133.2, 133.1, 132.3, 132.2, 132.1, 130.5, 130.4, 128.83, 128.76, 128.1, 128.0, 127.4, 126.7, 126.46, 126.43, 126.3, 125.7, 125.6, 125.2, 120.9, 120.8, 96.01, 95.96, 93.44, 93.41, 91.0, 90.9, 82.6, 50.2, 35.5, 27.7; MS m/z 718 (M^+), 661, 605, 397. HRMS: calcd for $\text{C}_{56}\text{H}_{46}$, 718.3600; found, 718.3585.

4,5-Di(1-naphthyl)phenanthrene 384. The following procedure is representative for the cyclization reactions. To 0.552 g (0.769 mmol) of **391** in 50 mL of anhydrous toluene under a nitrogen atmosphere was added 1.7 mL of a 1.0 M solution of potassium *tert*-butoxide (1.7 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 4 h. After the reaction mixture cooled to room temperature, 10 mL of water was introduced, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over sodium sulfate, and concentrated. Crystallization of the residue from a mixture of hexanes and diethyl ether (4:1) afforded 0.163 g of **392** (0.227 mmol, 30%) as a yellow solid. The remaining part was purified by flash column chromatography to provide 0.285 g of **384** (0.397 mmol, 52%, a mixture of diastereomers of syn, anti 1, and anti 2, isomer ratio = 4.1:1.7:1) as a yellow solid. **392**: mp 287–290 °C; IR 903, 796, 778, 760, 724 cm^{-1} ; ^1H δ 8.46–8.45 (2 H, s), 8.14 (2 H, d, J = 8.2 Hz), 8.06 (2 H, d, J = 8.4 Hz),

7.77–7.70 (2 H, m), 7.59–7.39 (8 H, m), 7.24–7.17 (2 H, m), 7.11 (2 H, t, $J = 7.4$ Hz), 6.79 (2 H, t, $J = 7.7$ Hz), 6.22 (2 H, dd, $J = 7.8, 2.1$ Hz), 4.47 (4 H, s), 1.274–1.269 (18 H, s); ^{13}C δ 144.2, 140.2, 140.0, 138.43, 138.42, 138.00, 137.95, 136.63, 136.56, 134.0, 133.0, 132.1, 130.6, 128.1, 127.94, 127.86, 127.44, 127.42, 126.9, 126.5, 126.3, 126.2, 126.1, 123.9, 123.7, 39.8, 38.2, 33.5; MS m/z 718 (M^+), 662, 646, 605. HRMS: calcd for $\text{C}_{56}\text{H}_{46}$, 718.3600; found, 718.3592. **384** (syn isomer): mp 255–258 °C; IR 799, 776, 750, 738, 729 cm^{-1} ; ^1H δ 7.96 (1 H, d, $J = 9.4$ Hz), 7.92 (1 H, d, $J = 9.2$ Hz), 7.76 (1 H, d, $J = 7.4$ Hz), 7.73 (1 H, d, $J = 7.2$ Hz), 7.57 (1 H, d, $J = 7.9$ Hz), 7.33 (1 H, d, $J = 7.4$ Hz), 7.28–7.13 (4 H, m), 7.09 (1 H, d, $J = 7.9$ Hz), 6.93 (1 H, t, $J = 7.3$ Hz), 6.87–6.76 (3 H, m), 6.63–6.58 (2 H, m), 6.49–6.43 (2 H, m), 6.24 (1 H, t, $J = 7.8$ Hz), 5.97 (1 H, t, $J = 7.5$ Hz), 5.89 (1 H, dd, $J = 7.7, 1.6$ Hz), 5.01 (1 H, d, $J = 7.7$ Hz), 4.98 (1 H, d, $J = 7.9$ Hz), 4.41 (1 H, d, $J = 21.0$ Hz), 4.23 (1 H, d, $J = 20.5$ Hz), 4.19 (1 H, d, $J = 21.0$ Hz), 4.02 (1 H, d, $J = 20.8$ Hz), 1.88 (9 H, s), 1.83 (9 H, s); ^{13}C δ 144.0, 143.6, 141.2, 140.5, 139.8, 139.4, 138.9, 138.6, 138.4, 135.3, 134.5, 133.71, 133.67, 133.2, 132.9, 132.5, 132.4, 131.8, 131.7, 131.3, 130.0, 128.3, 127.9, 127.6, 127.5, 127.2, 126.1, 125.9, 125.80, 125.75, 125.6, 125.4, 125.03, 124.97, 124.6, 124.51, 124.48, 123.5, 122.98, 122.93, 122.3, 121.7, 39.9, 39.6, 38.0, 37.7, 33.5, 33.1; MS m/z 718 (M^+), 661, 605, 519. HRMS: calcd for $\text{C}_{56}\text{H}_{46}$, 718.3600; found, 718.3573. Recrystallization of the syn isomer of **384** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis (Figure 7). Anti isomer 1 (Partial signal): ^1H δ 7.94 (2 H, d, $J = 8.2$ Hz), 5.50 (2 H, d, $J = 7.9$ Hz), 4.15 (1 H, d, $J = 19.2$ Hz), 4.05 (1 H, d, $J = 21.0$ Hz), 1.85 (18 H, s); ^{13}C δ 143.9, 37.84, 33.3. Anti isomer 2 (Partial signal): ^1H δ 6.18 (2 H, t, $J = 7.7$ Hz), 4.58 (2 H, d, $J = 8.2$ Hz), 4.44 (1 H, d, $J = 21.0$ Hz), 1.92 (9 H, s), 1.90 (9 H, s); ^{13}C δ 143.6, 37.76, 33.1. The formation of **393** was detected in the crude reaction products with ^1H NMR signals (partial) at δ 8.48 (1 H, s), 8.46 (1 H, s), 1.05 (9 H, s), 1.02 (9 H, s).

1-(2-Bromophenyl)-2-(1-naphthyl)ethyne 402. To a flask containing 0.45 g (0.64 mmol) of dichlorobis(triphenylphosphine)palladium and 0.21 g (1.1 mmol) of CuI were added via cannula a solution of 3.76 g (13.3 mmol) 1-bromo-2-iodobenzene in 50 mL of triethylamine followed by a solution of 2.00 g (13.2 mmol) of 1-ethynynaphthalene in 30 mL of triethylamine. The resulting mixture was heated under reflux and stirred vigorously. After 3 days, the reaction mixture was allowed to cool to room temperature and concentrated. 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. After filtration, the filtrate was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 3.66 g (11.9 mmol, 90%) of **402** as a white solid: mp 58–60 °C; IR 2213, 799, 772, 752 cm^{-1} ; ^1H δ 8.60 (1 H, dd, $J = 8.5, 1.1$ Hz), 7.87 (2 H, d, $J = 8.2$ Hz), 7.82 (1 H, dd, $J = 7.2, 1.0$ Hz), 7.70–7.45 (5 H, m), 7.35 (1 H, td, $J = 8.9, 1.3$ Hz), 7.22 (1 H, td, $J = 7.8, 1.7$ Hz); ^{13}C δ 133.4, 133.3, 133.2, 132.5, 130.7, 129.4, 129.2, 128.2, 127.1, 126.9, 126.5, 126.4, 125.6, 125.5, 125.2, 120.6, 92.7, 92.2; MS m/z 308 (M^+), 226, 220, 153.

1-(1-Naphthyl)-2-[2-(trimethylsilylethynyl)phenyl]ethyne 404. To a solution of 2.40 g (7.82 mmol) of **402** in 100 mL of anhydrous diethyl ether at -78 °C was added dropwise 4.70 mL of a 2.5 M solution of *n*-butyllithium (11.75 mmol) in hexanes. After one hour of stirring at -78 °C, a solution of 3.02 g (11.89 mmol) of iodine in 100 mL of anhydrous diethyl ether was added via cannula. The reaction mixture was allowed to warm to 15 °C before 30 mL of a 5% sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution was introduced. The organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The crude **403** was used in the next step

without further purification. To a flask containing 0.30 g (0.43 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and 0.12 g (0.63 mmol) of CuI were added via cannula a solution of 2.74 g (7.74 mmol) **403** in 70 mL of triethylamine followed by a solution of 2.22 g (22.6 mmol) of (trimethylsilyl)acetylene in 40 mL of triethylamine. The resulting mixture was stirred vigorously at room temperature for 20 h before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. After filtration, the filtrate was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 2.33 g (7.19 mmol, 92% overall yield for two steps) of **404** as colorless crystals: mp 78–80 °C; IR 2214, 2158, 861, 842, 799, 774, 758 cm^{-1} ; ^1H δ 8.61 (1 H, dd, $J = 8.2, 0.7$ Hz), 7.91–7.83 (3 H, m), 7.69–7.47 (5 H, m), 7.39–7.28 (2 H, m), 0.29 (9 H, s); ^{13}C δ 133.2, 132.6, 132.0, 130.7, 128.9, 128.3, 128.2, 127.9, 126.8, 126.5, 126.4, 126.0, 125.4, 125.2, 120.9, 103.7, 98.7, 92.9, 91.6, 0.02; MS m/z 324 (M^+), 309, 293, 279, 263.

1-(2-Ethynylphenyl)-2-(1-naphthyl)ethyne 388. To 1.48 g (4.57 mmol) of **404** in 50 mL of diethyl ether were added 30 mL of a 10% sodium hydroxide solution and 50 mL of methanol. After 30 min at room temperature, the organic solvent was removed in vacuo. Water (50 mL) and diethyl ether (100 mL) were then added. The organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with 2 M hydrochloric acid and water, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 1.13 g (4.48 mmol, 98%) of **388** as a light brown solids: mp 60–62 °C; IR 3285, 2212, 2106, 799, 773, 757 cm^{-1} ; ^1H δ 8.70 (1 H, d, $J = 7.9$ Hz), 7.90–7.83 (3 H, m), 7.70–7.46 (5 H, m), 7.43–7.30 (2 H, m), 3.48 (1

H, s); ^{13}C δ 133.3, 133.1, 132.7, 131.9, 130.6, 129.0, 128.6, 128.2, 128.0, 126.7, 126.6, 126.5, 126.4, 125.2, 124.5, 120.8, 92.6, 91.7, 82.7, 81.3; MS m/z 252 (M^+), 224, 125.

Fluorenylmethanol 406. The same procedure was repeated as described for **376** except that 0.146 g (0.397 mmol) of **405** in 10 mL of THF was treated with 0.40 mL of a 2.0 M solution of LDA (0.80 mmol) in heptane/tetrahydrofuran/-ethylbenzene, followed by 0.021 g (0.70 mmol) of paraformaldehyde to afford 0.136 g of **406** (0.342 mmol, 86%) as a white solid: mp 182–185 °C; IR 3427 (br), 763, 745, 731, 702 cm^{-1} ; ^1H δ 7.70–7.50 (12 H, m), 7.45–7.35 (3 H, m), 7.25 (1 H, td, $J = 7.4, 1.0$ Hz), 7.06 (1 H, t, $J = 7.8$ Hz), 6.47 (1 H, d, $J = 7.9$ Hz), 4.38 (1 H, dd, $J = 5.4, 3.7$ Hz), 3.89 (1 H, dd, $J = 11.1, 3.6$ Hz), 3.35 (1 H, dd, $J = 10.9, 5.9$ Hz), 1.20 (1 H, br s); ^{13}C δ 145.9, 141.3, 139.0, 138.9, 138.6, 137.0, 135.7, 133.4, 133.3, 131.8, 130.7, 130.10, 130.08, 129.4, 129.23, 129.21, 129.1, 128.4, 127.8, 127.6, 127.42, 127.36, 126.4, 125.9, 125.51, 125.47, 124.4, 123.9, 63.5, 49.7.

Compound 407 and 408. To a flask containing 0.033 g (0.083 mmol) of **406** was added 0.201 g (1.42 mmol) of phosphorus pentoxide, followed by 10 mL of *p*-xylene via cannula. The reaction mixture was heated under reflux for 3 h. After the reaction mixture cooled to room temperature, 10 mL of saturated sodium bicarbonate solution was introduced and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water (3×30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/5% methylene chloride in hexanes) provided 0.017 g of **407** (0.045 mmol, 54%) as a yellow solid and 0.010 g of **408** (0.033 mmol, 40%) as a yellow solid. Compound **407**: mp 216–218 °C; IR 773, 750, 703 cm^{-1} ; ^1H δ 8.77 (1 H, d, $J = 8.2$ Hz), 8.43 (1 H, d, $J = 7.7$ Hz), 7.76–7.35 (11 H, m), 7.16 (1 H, td, $J = 7.2, 1.9$ Hz), 6.99–6.85 (3 H, m), 4.03 (1 H, dd, $J = 14.8, 5.4$ Hz), 3.47 (1 H, dd, $J = 13.9, 5.4$ Hz), 2.65 (1 H, t, $J = 14.3$ Hz);

^{13}C δ 147.3, 145.6, 143.3, 140.1, 139.4, 134.6, 134.5, 133.0, 131.8, 130.0, 129.4, 129.05, 129.00, 128.8, 128.7, 128.33, 128.27, 127.5, 127.4, 127.3, 126.2, 125.9, 125.0, 124.2, 123.5, 123.1, 45.4, 33.5; Compound **408**: ^1H δ 8.93 (1 H, d, J = 8.2 Hz), 8.50 (1 H, d, J = 7.9 Hz), 8.29 (1 H, s), 8.14 (1 H, d, J = 7.4 Hz), 8.00 (1 H, d, J = 7.9 Hz), 7.78–7.38 (10 H, m). The sample is too dilute to run ^{13}C NMR.

Repeated Experimental Procedures to synthesize hydrocarbon **369**

Propargylic Alcohol. The same procedure was repeated as described for synthesis of propargylic alcohol except that 0.668 g (3.31 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne was treated with 1.30 mL of a 2.5 M solution of *n*-butyllithium (3.25 mmol) in hexanes and 0.649 g (3.06 mmol) *t*-butyl 2-naphthyl ketone to afford 1.25 g of propargylic alcohol (3.02 mmol, 99%) as a light brown liquid: IR 3556, 3447, 2215, 823, 797, 756, 690 cm^{-1} ; ^1H δ 8.25 (1 H, d, J = 1.2 Hz), 7.96 (1 H, dd, J = 8.7, 1.7 Hz), 7.86–7.79 (2 H, m), 7.71 (1 H, d, J = 8.9 Hz), 7.65–7.55 (2 H, m), 7.54–7.40 (4 H, m), 7.38–7.27 (3 H, m), 7.22–7.17 (2 H, m), 2.65 (1 H, br), 1.20 (9 H, s); ^{13}C δ 139.7, 132.6, 132.4, 132.21, 132.15, 131.6, 128.38, 128.34, 128.2, 127.9, 127.3, 126.5, 126.4, 126.2, 125.9, 125.8, 125.0, 122.9, 96.2, 93.3, 88.2, 84.7, 79.6, 40.0, 25.6.

Diacetylenic Hydrocarbon. The same procedure was repeated as described for synthesis of di/tetraacetylenic hydrocarbons except that a mixture of 1.03 g (2.49 mmol) of propargylic alcohol and 0.866 g (7.47 mmol) of triethylsilane in 40 mL of methylene chloride was treated with 1.00 mL trifluoroacetic acid (1.54 g, 13.5 mmol), followed by 1.06 g (10.0 mmol) sodium carbonate to afford 0.971 g of diacetylenic hydrocarbon (2.44 mmol, 98%) as white crystals: mp 103–105 $^{\circ}\text{C}$; IR 2214, 820, 756, 691 cm^{-1} ; ^1H δ 7.86 (1 H, s), 7.81–7.61 (4 H, m), 7.58–7.40 (4 H, m), 7.36–7.23 (5 H, m), 7.17–7.11 (2 H, m), 3.90 (1 H, s), 1.12 (9 H, s); ^{13}C δ 136.9, 133.0,

132.4, 132.13, 132.07, 131.6, 128.4, 128.19, 128.17, 128.1, 127.88, 127.85, 127.5, 127.4, 127.0, 126.3, 125.8, 125.6, 125.5, 123.2, 95.6, 92.8, 88.5, 82.6, 50.8, 35.8, 27.9.

Hydrocarbon 369. The same procedure was repeated as described for the cyclization reactions except that a mixture of 0.629 g (1.58 mmol) of diacetylenic hydrocarbon in 50 mL of anhydrous toluene was treated with 1.74 mL of a 1.0 M solution of potassium *tert*-butoxide (1.74 mmol) in 2-methyl-2-propanol to provide 0.504 g of **369** (1.27 mmol, 80%) as a light yellow solid: mp 191–193 °C; IR 908, 825, 753, 734, 702 cm⁻¹; ¹H δ 8.42 (1 H, d, *J* = 9.4 Hz), 7.79 (1 H, d, *J* = 7.7 Hz), 7.70–7.59 (5 H, s), 7.52–7.35 (4 H, m), 7.19 (1 H, t, *J* = 7.3 Hz), 7.03–6.91 (2 H, m), 6.00 (1 H, d, *J* = 7.9 Hz), 4.46 (2 H, s), 1.90 (9 H, s); ¹³C δ 144.1, 143.2, 141.7, 141.0, 139.9, 138.8, 134.0, 132.5, 131.4, 131.3, 130.4, 130.1, 129.9, 129.1, 127.7, 127.1, 126.5, 126.1, 126.0, 125.4, 123.9, 123.8, 123.5, 40.3, 38.5, 34.0.

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Figure 5b. ORTEP drawing of the crystal structure of 1,1'-dipropyl-9,9'-bifluorenylidene **165**.

Figure 8. ORTEP drawing of the crystal structure of polycyclic compound **167**.

Figure 9. ORTEP drawing of the crystal structure of polycyclic compound **168**.

Figure 10. ORTEP drawing of the crystal structure of polycyclic compound **182**.

Figure 11. ORTEP drawing of the crystal structure of polycyclic compound **185**.

Figure 12. ORTEP drawing of the crystal structure of polycyclic carboxylic acid **283**.

Figure 13. ORTEP drawing of the crystal structure of polycyclic ketone **287**.

Figure 14. ORTEP drawing of the crystal structure of polycyclic ketone **291**.

Figure 15. ORTEP drawing of the crystal structure of polycyclic compound **306**.

Figure 16. ORTEP drawing of the crystal structure of polycyclic compound **310**.

Figure 17. ORTEP drawing of the crystal structure of polycyclic compound **380**.

PUBLICATIONS

1. “Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes. Unusual Cleavage of a Benzene Ring Leading to Twisted 1,1'- Dialkyl-9,9'-bifluorenylidenes and Spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes]” Yang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, 68, 5832–5837.
2. “Polycyclic Aromatic Compounds via Radical Cyclizations of Benzannulated Enyne–Allenenes Derived from Ireland–Claisen Rearrangement” Yang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, 68, 8545–8549.
3. “Unusual Cascade Reactions of Biradicals Generated from Benzoenyne–Allenenes” Yang, Y.; Petersen, J. L.; Wang, K. K., presented at The Third Annual Meeting In Miniature Organized by the WVU Chapter of the ACS Students Affiliates, March 18, 2000.
4. “Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes. Unusual Cleavage of a Benzene Ring Leading to Twisted 1,1'- Dialkyl-9,9'-bifluorenylidenes and Spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes]” Yang, Y.; Petersen, J. L.; Wang, K. K., presented at The 225th American Chemical Society National Meeting, New Orleans, LA, March 23–27, 2003.
5. “Unusual Cascade Radical Cyclizations of Molecules Having Two Units of Benzannulated Enyne–Allene Leading to Novel Polycyclic Compounds” Yang, Y.; Petersen, J. L.; Wang, K. K., presented at Meeting-In-Miniature Hosted by the WVU Chapter of the ACS Students Affiliates, April 5, 2003.