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**Preparation of Benzoenyne-Allenenes, Enyne-Isocyanates and Enyne-
Carbodiimides and Their Applications in the Synthesis of Polycyclic
Aromatic Hydrocarbons and Heterocycles**

Hongbin Li

**A dissertation submitted to the
Eberly College of Arts and Science
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Organic Chemistry**

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**Keywords: Cycloaromatization, Biradical, Enyne-allene, Enyne-Isocyanate, Enyne-
Carbodiimide**

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ABSTRACT

Preparation of Benzoenyne-Allenes, Enyne-Isocyanates and Enyne-Carbodiimides and Their Applications in the Synthesis of Polycyclic Aromatic Hydrocarbons and Heterocycles

Hongbin Li

The thionyl chloride-induced cascade cyclization of enediynyl propargylic alcohols provides an efficient synthetic route 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 pathway especially attractive. Interestingly, in certain cases the intramolecular [2 + 2] cycloaddition reaction of the chlorinated benzoenyne–allene intermediates occurred preferentially to form 1*H*-cyclobut[*a*]indenes. Competition from the intramolecular [2 + 2] cycloaddition reaction could be avoided with the non-chlorinated benzoenyne–allenenes, providing direct access to novel polycyclic aromatic hydrocarbons. Several indeno-fused 4,5-diarylphenanrenes were synthesized by a consecutive C²–C⁶ cyclization of a symmetrical benzoenyne-allene. The formal Diels-Alder reaction involving a C²–C⁶ cyclization reaction followed by a radical–radical coupling reaction of the benzannulated enyne–allenenes is key to the efficient assembly of the phenanthrene system. The buttressing effects due to the indeno-fused rings and the two *tert*-butyl groups at the 1- and 8-positions are responsible for increasing the activation barrier for the helix inversion of the resulting 4,5-diarylphenanthrenes.

Thermolysis of enyne-isocyanates represents a new way of generating biradicals and/or zwitterions from unsaturated molecules having nitrogen and oxygen atom in the conjugated system. Due to the ring strain, cycloaromatization of cyclopentene-based enyne-isocyanates and enyne-carbodiimides underwent predominately C²–C⁷ cyclization pathway. The existence of intramolecular decay routes for the initially formed biradicals or zwitterions made these cyclization reactions essentially useful, leading to a variety of polycyclic heterocycles.

DEDICATED TO

my wife, Shu Chen, and my lovely son, Kevin

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PART I

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

1. Introduction

The enediyne antitumor antibiotics that were derived from bacterial sources emerged as a novel class of compounds with unprecedented molecular architecture, fascinating mode of action, and very important biological activities. This family of compounds includes the calicheamicins **1**,¹ esperamicins **2**,² dynemicin A **3**,³ C-1027 chromophore **4**,⁴ and kedarcidin **5**⁵ (Figure 1). A common structure feature is that they all contain a (Z)-3-ene-1,5-diyne moiety, although neocarzinostatin chromophore **6**⁶ does not contain an (Z)-enediyne part, it is included in this family of compounds because of its similar mode of action.

Figure 1. Structures of Enediyne Antitumor Antibiotics **1-6**

These DNA cleaving compounds burst onto the scene in the latter half of the 1980s when their structures became known and the biradical serving as key intermediate in the mode of action was revealed.⁷ The discovery of these novel and biologically active nature substances stimulated the research on the chemistry and medicine of enediyne and enyne-allene systems. Among these biradical-forming reactions, the Bergman cyclization of enediyne, the Myers-Saito cyclization of enyne-allene and the Moore cyclization of enyne-ketene have been investigated extensively.⁸

1.1. Mechanism of DNA-Cleavage by Enediyne Antitumor Antibiotics

The proposed mechanism suggests that initially the oligosaccharide fragment of the Calicheamicin γ_1^1 **1** binds to the DNA molecule, followed by the attack of a nucleophile on the central sulfur atom of the trisulfide group to form a thiolate intermediate **7**. This labile intermediate **7** then suffers rapid cycloaromatization to form the 1,4-benzoid biradical **8**, which proceeds to attack DNA by hydrogen atom abstraction, resulting in the formation of **9** (Scheme 1).^{1,2}

Scheme 1. Mechanism of DNA Cleavage by **1** and **6**

It is believed that the NCS chromophore **6** causes the DNA cleavage in a similar way. According to the hypothesis by Myers,⁹ initially a nucleophile attacks stereospecifically at C12, resulting in the ring skeleton rearrangement with the epoxide ring opening and the formation of cumulene **10**. The highly stained and labile intermediate **10** undergoes cycloaromatization to generate the biradical **11**, which then abstracts two hydrogen atoms from DNA to give **12**, causing DNA damage (Scheme 1).

1.2. The Bergman Cyclization of Enediyne System

Scheme 2. Cyclization of Enediyne Observed by Masamune

In 1971, Masamune¹⁰ described the conversion of two cyclic enediynes **13** into the corresponding benzoid products **14** without mentioning the biradical intermediate (Scheme 2).

Scheme 3. The Bergman Cyclization of Enediyne **15**

It was Bergman who first demonstrated the formation of the biradical intermediate in the cycloaromatization reaction of the parent (Z)-1,5-hexadiyn-3-ene.¹¹

He found that the enediyne **15a** underwent a rapid deuterium scrambling reaction at 200°C, producing a 1:1 mixture of **15a** and **15b** (Scheme 3). Moreover, the pyrolysis of unlabeled **15** with different solvent media yielded the radical capture products, indicating that the 1,4-benzoid biradical **16** was a true reaction intermediate.

Sondheimer¹² also found the cycloaromatization of the strained cyclic enediyne **17**, generated in situ by two intermolecular S_N2 reactions, led to the cyclized compound **19**, and postulated the formation of the 1,4-benzoid biradical intermediate **18** (Scheme 4).

Scheme 4. Observation by Sondheimer

Turro and Nicolaou¹³ reported a direct cycloaromatization of the benzannulated enediyne **20** to the naphthalene derivative **22** (Scheme 5). These results are consistent with photo-induced cycloaromatization to the biradical intermediate **21**, which is converted to **22** via hydrogen atoms abstraction.

Scheme 5. The Photo-Induced Bergman Cyclization

1.3. The Myers-Satio Cyclization of Enyne-Allenes and the Moore Cyclization of Enyne-Ketenes

The understanding of the activation mechanism of the enediyne antitumor antibiotics along with their remarkable DNA cleavage properties through a biradical hydrogen atom abstraction process has stimulated the design of a number of novel molecular assemblies to probe and mimic their chemical and biological activities. Myers and Satio almost simultaneously reported the cyclization of the enyne-allene system, in which they replaced an acetylenic moiety with an iso-electronic allenic moiety.

Myers demonstrated that the parent (Z)-1,2,4-heptatrien-6-yne (**23**) underwent a first-order thermal reaction to produce the $\alpha,3$ -didehydrotoluene **24**, and after two hydrogen atom abstractions, leading to toluene (**25**) (Scheme 6).¹⁴

Scheme 6. The Myers Cyclization of Enyne-Allene **23**

Scheme 7. The Hypothetical Cyclization of Enyne-Cumulene **26**

While the 1,4-didehydrobenzene **16** generated by the Bergman cyclization reaction and the 3,7-didehydroindene **11** generated by the cyclization of NCS chromophore **6** exist mainly as the σ, σ -radical pair, the $\alpha,3$ -didehydrotoluene **24**, generated by the Myers cyclization reaction exists as the σ, π -radical pair, and is capable of full benzylic resonance. As a result, the cyclization of **23** to **24** is calculated to be exothermic by ~ 15 kcal/mol. By contrast, the hypothetical cyclization of **26** to **27** is

estimated to be exothermic by only 1 kcal/mol (Scheme 7), and the Bergman cyclization of (Z)-3-hexen-1,5-diyne (**15**) to 1,4-didehydrobenzene (**16**) is inherently endothermic ($\Delta H = 14$ kcal/mol). Experimentally, the cyclization of enyne-allenes could be carried out under much milder reaction conditions, compared to the Bergman cyclization reaction.

Satio and coworkers also reported independently that the cyclization reaction of enyne-allenes **28** with a substituent at the C3 position generated biradical intermediate, which mimic to some extent the action of neocarzinostatin and cause clean scission of double stranded DNA at 37 °C in the absence of any additives (Scheme 8).¹⁵

Scheme 8. The Cyclization of Enyne-Allenes **27**

Before the magnificent work of Myers and Satio research groups, Moore had already demonstrated that enyne-ketenes, a hetero-analogue of enyne-allenes, could undergo a facile biradical-forming cyclization reaction.¹⁶ In his elegant studies, a masked

Scheme 9. The Moore Cyclization of Enyne-Ketene **32**

enyne-ketene precursor, 4-alkynylcyclobutenone, was applied. For example, thermolysis of 4-alkynylcyclobutenone **31** in acetonitrile at 82 °C afforded the quinone **34** (Scheme 9).¹⁷ In the reaction sequence, initially an electrocyclic ring opening of **31** produced the enyne-ketene **32**, which then underwent cyclization to give the biradical **33**. The

biradical **33** could undergo an intermolecular hydrogen-atom transfer to afford the quinone **34**.

1.4. The Schmittel Cyclization (C^2-C^6) versus the Myers-Satio Cyclization (C^2-C^7)

In 1989, the Moore's group found that besides the normal Moore cyclization mode of enyne-ketenes, there is a competing reaction pathway for the biradical-forming ring closure.¹⁸ For example, thermolysis of the enyne-ketene **37a** in refluxing *p*-xylene produced the 1,4-benzoquinone **39a** as the sole product, while under the same reaction conditions, two products **39b** and **41b** were observed for the thermal cyclization of the enyne-ketene **37b** (Scheme 10). Because the phenyl group could stabilize the adjacent vinyl radical, they assumed that the phenyl group at the acetylenic terminus is responsible for directing the reaction pathway towards the formation the five-membered ring product.

Scheme 10. A Competing Pathway to the Moore Cyclization

In 1995, Schmittel discovered a remarkable switch from the well-known Myers-Satio cyclization (also termed as the C^2-C^7 cyclization) to the C^2-C^6 cyclization (Scheme

11).¹⁹ In his elegant studies, the aromatic substituents are placed to the acetylenic terminus. The enyne-allene **42a** without a substituent at the acetylenic terminus was heated with an excess of 1,4-CHD as hydrogen-atom donor in toluene, and the reaction was found to proceed through the normal C²-C⁷ pathway. Whereas thermolysis of the enyne-allenes **42b**, **42c** and **42d** with an aryl substituent at the acetylenic terminus afforded the benzofulvene derivatives. They assumed a stepwise biradical mechanism, in which the C²-C⁶ cyclization took place to generate the benzofulvene biradical intermediates **45**. The biradical intermediate **45b** decayed to afford the formal ene reaction product **46** through a 1,5-hydrogen shift. In the case of the biradicals **45c** and **45d**, an intramolecular radical-radical coupling occurred to give the formal Diels-Alder adducts **47c** and **47d**, tautomerization of **47c** then gave the aromatized adduct **48**.

Scheme 11. A Switch from the Myers-Satio Cyclization to the C²-C⁶ Cyclization

However, Schmitt and coworkers were unable to trap the postulated biradicals by an intermolecular reaction (O₂, PhSH, (Me₃Si)₃SiH, 1,4-CHD, 2,2,6,6-tetramethylpiperidine *N*-oxide), presumably due to exceedingly fast intramolecular

radical-radical coupling (rate considerations have implied an approximate life time of the biradical species of less than 10^{-8} s). They could exclude a proton-catalyzed cyclization mode because they did not find any significant effect due to the acid addition; and also ruled out a polar reaction mechanism (zwitterions intermediate) because of the lack of the solvent effect. The almost identical activation barrier for the different reactions like the formal ene reaction and the formal Diels-Alder cycloaddition supported the proposed stepwise biradical mechanism instead of the concerted reaction pathway. For a concerted Diels-Alder reaction mechanism, the activation barrier of the transformation from **42d** to **47d** would be expected to be much higher than that of the transformation from **42c** to **47c** because of the steric effect of the bulky mesityl group. Instead these two reactions were found to have very similar activation barriers. Moreover, the postulated formation of the biradical intermediate is supported by the observation that thermolysis of the enyne-allenes **42** induced DNA cleavage as demonstrated by the formation of the open circular DNA.^{19c,19g}

Scheme 12. The C²-C⁶ Type Cyclization Observed by Gillmann

The Gillmann group²⁰ and the Rodriguez group²¹ also reported a switch from the Myers-Satio cyclization to the C²-C⁶ cyclization mode (Schemes 12 and 13). Interestingly, in both cases, when the bulky TMS group was placed at the acetylenic

terminus, the C²-C⁶ type cyclization took place to produce the benzofulvene derivatives. Although no mechanistic investigations were described for either contribution, it seems reasonable to assume a stepwise biradical process for the formal [2+2] cycloadditions as well.

Scheme 13. The Observation by Rodriguez

In conclusion, thermal cyclization of benzoenynes provides an easy access to the naphthalene biradicals or the benzofulvene biradicals. The nature of the substituent at the acetylenic terminus is responsible for directing the reaction toward either the Myers-Satio cyclization reaction to generate the naphthalene biradicals or the C²-C⁶ cyclization reaction to furnish the benzofulvene biradicals. With an aryl substituent or a sterically demanding group, such as the trimethylsilyl group and *tert*-butyl group, at the acetylenic terminus, the C²-C⁶ cyclization reaction becomes the preferred pathway. The effect of the aryl substituent is attributed to its ability to stabilize the alkenyl radical center. The sterically demanding group inhibits the Myers-Satio cyclization reaction because of the emergence of severe nonbonding steric interaction.

2. Research Objective

Over the past two decades, the enediyne and enyne-allene chemistry has received considerable attention due to the discovery of several classes of very potent antitumor

antibiotics having the enediyne structure. Since then many methods have been developed to prepare the enyne-allene systems. Our research group recently reported a thionyl chloride-promoted formation of chlorinated benzoenyne-allene and its C²-C⁶ cyclization to produce a C₄₄H₂₆ hydrocarbon having a carbon framework represented on the surface of C₆₀.²² We were interested in investigating the scope and limitation of the thionyl chloride-induced cascade transformation.

3. Literature Survey on Synthetic Methodologies for Preparation of Benzoenyne-Allenenes

Incorporation of the central carbon-carbon double bond of the acyclic enyne-allene to a benzene ring has little effect on the rate of the Myers-Satio cyclization reaction.²³ For example, the half lives (*t*_{1/2}) of cycloaromatization of the enyne-allene **61** and the benzoenyne-allene **63** at 37 °C are 8 h and 23 h, respectively (Scheme 14).

Scheme14. Nicolaou's Work on the Cyclization of Enyne-Allenenes

There are several advantages of using the benzannulated enyne-allenes for the cycloaromatization reaction. First, the carbon-carbon double bond is locked in the Z-configuration, which is necessary for the cyclization process. Second, the benzannulated enyne-allenes are more stable and thus easier to handle for subsequent manipulation.

Third, there are a wide variety of 1,2-disubstituted benzenes, providing many choices for the preparation of the benzannulated enyne-allenes.

Gillmann used the Pd-catalyzed cross-coupling reaction between arylzinc halides/ arylboronic acids and haloallenes to produce the benzoenyne-allenes in moderate yield.²⁰ A specific example is shown in Scheme 15. Coupling of the haloallene **67** (X = Br, I) with the arylzinc chloride **66a**, prepared by lithium halogen exchange followed by transmetalation with zinc chloride, proceeded at room temperature to give the benzoenyne-allene **68** in 40% yield.

Scheme 15. a. *n*-BuLi, -90°C; then ZnCl₂, -90°C to -20°C; b. *n*-BuLi, -90°C; then B(OMe)₃, -90°C to 0°C; c. coupling of **66a**: Pd(PPh₃)₄ (5 mol%), AsPh₃ (40 mol%), THF, rt (40%); d. coupling of **66b**: AsPh₃ (40 mol%), Pd(dba)₂·CHCl₃ (5 mol%), 1 M aq. Ag₂O (4 equiv.), THF, 0°C to rt, 2h (42%)

Finn developed a convergent method for the assembly of allene compounds from two aldehyde units and a doubly oxophilic carbon atom synthon.²⁴ However, the benzoenyne-allenes were produced in poor to moderate yield by employing the doubly oxophilic ylide reagent, prepared in situ from TiCl₂(O-*i*-Pr)₂, (Me₂N)₃P=CH₂, and NaN(SiMe₃)₂ (Scheme 16).

Scheme 16. Finn's Approach to Benzoenyne-Allenenes

Cunico²⁵ reported a specific example for the preparation of the benzoenyne-allene **73** by a facile elimination and TMS group migration within the propargylic framework of **72** (Scheme 17).

Scheme 17. Cunico's Approach to Benzoenyne-Allene

With the precedents of allene formation by [2,3] sigmatropic rearrangement of the propargylic phosphinites and sulfinates, the Nicolaou's group treated the propargylic alcohol **74** with chlorodiphenylphosphine in methylene chloride at -78°C in the presence of triethylamine to produce the allenyl phosphonate **76** in excellent yield (Scheme 18).²⁶ Satio and coworkers also reported a similar system for preparation of enyne-allenes at the same time.¹⁵ This synthetic method was later adopted by the Grissom's group²⁷ and the Schmittel's group²⁸ for the preparation of benzoenyne-allenes.

Scheme 18. Nicolaou's General Approach to Enyne-Allenes

Grissom reported a similar synthetic route to benzoenyne-allenes via a [3,3] sigmatropic rearrangement of propargyl vinyl ethers.²⁹ In the event, the diyne **77** was treated with a catalytic amount of AgBF_4 at room temperature to afford the benzoenyne-allene **78** in 98% yield by a Lewis acid-catalyzed [3,3] sigmatropic rearrangement (Scheme 19).³⁰

Scheme 19. Grissom's Approach to Benzoenyne-Allenenes

Scheme 20. Base-Catalyzed Isomerization of Enediyne Sulfone to Enyne-Allene Sulfone

Grissom and coworkers also demonstrated that isomerization of the enediyne sulfone **79** catalyzed with a base led to the corresponding labile benzoenyne-allene sulfone **80**, which underwent cyclization at ambient temperature to give **81** (Scheme 20).³¹

4. Results and discussions

4.1. Synthesis of 11*H*-Benzo[*b*]fluoren-11-ols and Related Compounds

The reaction sequence outlined in Scheme 21 depicted the use of benzophenone (**82a**) for condensation with the lithium acetylide **83** to furnish the propargylic alcohol **84a** in 93% yield. Upon treatment with thionyl chloride in the presence of pyridine, the alcohol **84a** was converted to the chlorosulfite **85a**, which then underwent an S_N1' reaction to generate in situ the chloroallene **86a**. The subsequent C^2 - C^6 cyclization furnished the benzofulvene biradical **87a**, which in turn underwent an intramolecular radical-radical coupling to give the formal Diels-Alder adduct **88a** and, after tautomerization, the chloride **89a**. The chloride **89a** was prone to hydrolysis and, on

exposure to water/silica gel, was converted to the corresponding 11*H*-benzo[*b*]fluoren-11-ol **90a** in 85% overall yield from **84a**.

Scheme 21. C²-C⁶ Cyclization of Chloronated Benzoenyne-Allene

The ¹³C NMR spectrum of **90a** exhibited 27 signals for the aromatic carbons with the signal at δ 129.1 having twice the intensity of those from other aromatic methine (CH) carbons. This observation indicates that the two phenyl substituents are oriented perpendicular to the rest of the aromatic system, and the rates of their rotation are slower than the NMR time scale. As a result, the aromatic hydrogen indicated with an arrow is shielded by one of the phenyl groups, shifting its ¹H NMR signal upfield to δ 6.39 (doublet). In every case of this study, the adducts derived from the formal Diels–Alder reaction of benzoenyne–allenes exhibited such an upfield shift signal.

Several other benzophenone derivatives were also used for the synthesis of 11*H*-benzo[*b*]fluoren-11-ols (Table 1). With **84c** and **84d**, the intramolecular radical–radical

coupling slightly favored the attack of the benzene ring having a bromo or a methoxyl substituent. In the case of **84e**, the attack of the benzene ring having the fluoro substituent resulted in the loss of one fluorine substituent, leading to the benzo[fluorenone **90e'**.

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

Dr. Hai-Ren Zhang³² of our research group observed that the use of 9-fluorenone **91** as a diaryl ketone produced **94** in 74% yield (Scheme 22). Interestingly, a small amount of the 1*H*-cyclobut[*a*]indene **95** (12%), produced from the intramolecular [2 + 2] cycloaddition reaction between the allenic and the acetylenic moieties in **93**, was also isolated. The structure of **95** was unequivocally established by X-ray analysis. While an intramolecular [2 + 2] cycloaddition reaction of a benzoenyne–allene system was reported earlier,^{20,21} no such precedent was observed for the benzoenyne–allenes having a phenyl substituent at the allenic terminus, which invariably resulted in the formation of the adducts derived only from the formal Diels–Alder reaction.

Scheme 22. An Unexpected Formal [2 + 2] Cycloaddition

4.2. [4 + 2] Cycloaddition versus [2 + 2] Cycloaddition.

Dr. Zhang³² also observed that treatment of **97**, derived from dibenzosuberone **96** and **83**, with thionyl chloride produced the [2 + 2] cycloaddition adduct **98** exclusively (Scheme 23). The structure of **98** was unequivocally established by X-ray analysis.

Scheme 23. [2 + 2] Cycloaddition versus [4 + 2] Cycloaddition

On the other hand, with **100**, derived from dibenzosuberone **99** and **83**, the formal [4 + 2] cycloaddition reaction of the chlorinated benzoenyne–allene was again the preferred pathway, leading to the formation of the alcohol **101** (Scheme 23).³² The reason for such a dramatic change of the reaction pathway is not clear at this time. Molecular model studies suggest the emergence of a steric strain due to the nonbonding interactions between the chloro substituent and one of the benzene rings of dibenzosuberone along the pathway toward the formal [4 + 2] cycloaddition reaction, leading to the Diels–Alder adduct **102**. Replacing the central ethylenic linkage in **97** with the dimethylene linkage in **100** appears to reduce the nonbonded interactions.

The importance of the steric interactions in determining the reaction pathway was supported by the following two cases of the mono-protected phenanthrenequinone. With a sterically more demanding 5,5-dimethyl-1,3-dioxane protective group in **104**, only the formal [2 + 2] cycloaddition adduct **105** was obtained (Scheme 24). On the other hand, with a sterically less demanding ethylene ketal protective group in **107**, an essentially 1:1 mixture of the formal [2 + 2] and the formal [4 + 2] cycloaddition adducts **108** and **109** was produced.

With **111**, derived from 2,2-dimethylpropiophenone (**110**), the [2 + 2] cycloaddition adduct **113** was produced predominantly (Scheme 25). However,

Scheme 24. Steric Effect on the Formation of Formal [2 + 2] and [4 + 2] Adducts

connecting one of the methyl groups in **111** to the benzene ring to form **116** and **117** appears to reduce the steric interactions between the *gem*-dimethyl group and the chloro substituent along the pathway of the [4 + 2] cycloaddition reactions. As a result, **118** and **119** were formed predominantly with the effect particularly dramatic in the case of **116** having a five-membered ring.

Scheme 25. [2 + 2] vs. [4 + 2] Cycloaddition

4.3. A New Pathway to Benzoenyne–Allenes.

We have also developed a new synthetic pathway to benzoenyne–allenenes without a chloro substituent. Treatment of **111** with trifluoroacetic acid in the presence of triethylsilane³³ produced **126** in excellent yield (Scheme 26). Prototropic isomerization,

Scheme 26. Cycloaromatization of the Benzoenyne-Allene **123**

promoted by potassium *tert*-butoxide in refluxing toluene,³⁴ produced the benzoenyne–allene **123** in situ, which in turn underwent a formal [4 + 2] cycloaddition reaction to furnish **125** and, after tautomerization, the hydrocarbon **126**. At a lower reaction temperature (refluxing THF at 66 °C), the formation of **123** as the major isomer in equilibrium with **122** (**123**:**122** = 6:1) was detected. The benzoenyne-allene **123** gave a ^1H NMR signal at δ 6.93 ppm as a singlet for the allenic hydrogen and a ^{13}C NMR signal at δ 203.8 ppm for the center allenic carbon.

It is worth noting that only the [4 + 2] cycloaddition adduct **126** was produced from **123**, in sharp contrast with the formation of predominantly the [2 + 2] cycloaddition adduct **113** from the chlorinated system. The fact that replacing the chloro substituent with the sterically less demanding allenic hydrogen in **123** dramatically altered the course of the reaction is consistent with the proposition regarding the importance of the steric

interactions in directing the reaction toward the [2 + 2] cycloaddition pathway. Similarly, the exclusive formation of the [4 + 2] cycloaddition adducts **129**, **130**, and **132** was also observed (Scheme 27).

Scheme 27. The Exclusive Formation of [4 + 2] Adducts

5. Conclusions

The thionyl chloride-induced cascade cyclization of enediynyl propargylic alcohols provides an efficient synthetic route to 11*H*-benzo[*b*]fluoren-11-ols and related compounds.³⁵ The simplicity of the synthetic sequence and the mildness of the reaction condition make this pathway especially attractive. Interestingly, in certain cases the intramolecular [2 + 2] cycloaddition reaction of the chlorinated benzoenyne–allene intermediates occurred preferentially to form 1*H*-cyclobut[*a*]indenes. Competition from the intramolecular [2 + 2] cycloaddition reaction could be avoided with the non-chlorinated benzoenyne–allenes, providing direct access to novel polycyclic aromatic hydrocarbons.³⁶

PART II

Novel Synthesis of 4,5-Diarylphenanthrenes via C²–C⁶ Cyclization of Benzannulated Enyne–Allenenes

1. Introduction

Because of steric hindrance, the aromatic system of the 4,5-disubstituted phenanthrenes is twisted and the two substituents are bent out of the plane of the aromatic rings. Such structural distortion was first demonstrated with the partial resolution of the enantiomers of 4,5,8-trimethyl-1-phenanthrylacetic acid (**133a**) in 1947.³⁷

Figure 2. 4,5-Disubstituted Phenanthrenes

More recently, the activation barrier for racemization ($\Delta G_{\text{rac}}^{\ddagger}$) of **133a** was determined to be 18.7 kcal/mol at $-11\text{ }^{\circ}\text{C}$.³⁸ The X-ray crystal structure of 4,5-dimethylphenanthrene (**133b**) was also reported, allowing direct measurement of a pronounced 27.9° twist between the mean planes of the outer rings and providing information regarding the distortion of the molecular geometry.³⁹ The enantiomers of **133b** were separated by chromatography on chiral stationary phases, and the $\Delta G_{\text{rac}}^{\ddagger}$ was determined to be 16.1 kcal/mol at $25\text{ }^{\circ}\text{C}$.^{39a}

Other 4,5-disubstituted phenanthrene derivatives, including 4,5-diphenylphenanthrene (**133c**)⁴⁰ and closely related 4,5-diaryltriphenylenes (**134**)^{40,41} and 13,14-bis(2-pyridyl)pentaphenes,⁴² have also been reported. The presence of the diastereotopic hydrogens in the methylene group of **134a** and **134b** allowed the determination of $\Delta G_{\text{rac}}^{\ddagger}$ through the analysis of the temperature-dependent NMR spectra.

A $\Delta G_{\text{rac}}^\ddagger$ of ca. 15.3 kcal/mol was determined for **134a**, whereas a significantly higher barrier of at least 21 kcal/mol was estimated for **134b**.⁴¹ The steric hindrance also restricts the rotation of the aryl substituents in **134**. Analysis of the temperature-dependent NMR spectra gave the rotational barriers ($\Delta G_{\text{rac}}^\ddagger$) of ca. 14.3, 15, and 15 kcal/mol for **134a**, **134b**, and **134c**, respectively.⁴¹

- 134a:** Ar = Ph,
Ar' = 3-(bromomethyl)-5-methylphenyl
- 134b:** Ar = 3,5-dimethylphenyl,
Ar' = 3-(bromomethyl)-5-methylphenyl
- 134c:** Ar = Ar' = 3,5-dimethylphenyl

Figure 3. 4,5-Diaryltriphenylenes

2. Literature Survey for the Preparation of the 4,5-Disubstituted Phenanthrenes and Related Compounds

Several synthetic methods for 4,5-dimethylphenanthrenes and related compounds have been reported, including ozonolysis of pyrene,⁴³ intramolecular cyclization of 2,2'-bis(halomethyl)-6,6'-dimethylbiphenyls,⁴⁴ photochemically-induced dehydrocyclization of stilbenes,^{38,45} and desulfurization of a phenanthrene derivative containing two fused thiophene rings.⁴⁶

Scheme 28. The Intramolecular Photocycloaddition for Preparation of 4,5-Diarylphenanthrenes

Photocyclization of 1-(8-phenyl-2-naphthyl)-4-phenyl-1-buten-3-yne (**135**) was reported to produce 4,5-diphenylphenanthrene (**133c**) in 65% yield (Scheme 28).⁴⁰

Similarly, 4,5-diaryltriphenylenes (**134**) were obtained by photocyclization of suitably substituted 1,4-diaryl-1-buten-3-ynes.^{40,41}

3. Research Objective

We recently reported the use of the C^2-C^6 cyclization reaction of the benzannulated enyne-allenes for the synthesis of polycyclic aromatic hydrocarbons. A similar reaction involving a benzannulated enyne-carbodiimide system led to the formation of an indolo-fused 4,7-phenanthroline derivative having a helical twist due to steric interactions as observed in **133b**.⁴⁷ We envisioned that a consecutive C^2-C^6 cyclization of a symmetrical benzoenyne-allene could possibly provide a useful synthetic strategy to the synthesis of 4,5-diarylphenanthrenes. The possible problem is the second cyclization reaction could produce the formal [2+2] adduct because of the highly congested structure, along with the unlikely product of the linear molecule.

4. Results and Discussion

4.1. Synthesis of 4,5-Diarylphenanthrene Derivatives

The synthetic sequence outlined in Scheme 29 involves the condensation of the diketone **137**⁴⁸ with two equiv of lithium acetylide of **138** to afford the propargylic alcohols **139** as an essentially 1:1 mixture of diastereomers in excellent yields. Treatment of **139** with trifluoroacetic acid in the presence of triethylsilane³³ allowed an efficient conversion to the tetraacetylenic hydrocarbons **140** also as an essentially 1:1 mixture of diastereomers. On exposure to potassium *tert*-butoxide under refluxing toluene at 110 °C for up to 10 hours, the hydrocarbons **140** were transformed to the 4,5-diarylphenanthrenes **141**.

Scheme 29. Synthesis of 4,5-Diarylphenanthrenes **141**

Apparently, the transformation from **140** to **141** involved initial prototropic isomerizations³⁴ to form the benzannulated enyne–allenes **143**. The formation of **143a** (Ar = Ph) was detected under a milder reaction condition. After three hours of heating under refluxing THF at 65 °C, a major portion (ca. 80%) of the ¹H NMR signals belonging to the propargylic hydrogens in **140a** was converted to a singlet at δ 6.91, attributable to the allenic hydrogens in **143a**. A subsequent C²–C⁶ cyclization reaction generated the biradicals **144**, which in turn underwent an intramolecular radical–radical coupling to give **145**. Although the transformation from **143** to **145** could also be regarded as a Diels–Alder reaction, mechanistic and DNA-cleaving studies of analogous systems suggest a two-step biradical pathway.¹⁹ A second formal Diels–Alder reaction of

145 then produced **147** and, after two subsequent tautomerizations, the 4,5-diarylphenanthrenes **141** (Scheme 30).

Scheme 30. The Proposed Mechanism Accounts for the Formation of **141**

4.2. The Structure Analysis of Compound **141a**

The structure of **141a** was unequivocally established by the X-ray structure analysis. The ORTEP drawings of **141a** from three different perspectives are given in Figure 4 to illustrate the severity of the structural distortion. As expected, the two phenyl substituents are bent away from each other with overlaps of the carbon–carbon bonds occurring only at the C33–C34 edge and the C39–C44 edge. In addition, the two phenyl groups are oriented essentially parallel to each other (within 1.3°), but are at a 53.1° angle from the central aromatic system. The perpendicular distance between the planes of the two nearly parallel phenyl groups is ca. $2.9 \text{ \AA}$, much shorter than the usual π -system van der Waals contact distance of ca. $3.4 \text{ \AA}$ between parallel aromatic hydrocarbons in crystals⁴⁹ or even the graphite layer distance of $3.35 \text{ \AA}$. A pronounced 46.1° twist between the mean planes of the outer rings (planes 1-2-3-4-4a-10a and 4b-5-6-7-8-8a) of the phenanthrene system of **141a** is much larger than that of **133b** at 27.9° , further indicating a profound structural distortion due to nonbonding steric interactions.

Figure 4. ORTEP drawing of the crystal structure of **141a** from three different perspectives: (a) viewing along the axis perpendicular to the phenanthrene ring, (b) viewing along the crystallographic C_2 axis with hydrogen atoms omitted for clarity, and (c) viewing along the C4a-C4b axis with hydrogen atoms omitted for clarity.

The structures of **141** were also elucidated with high resolution mass spectroscopy and ^1H and ^{13}C NMR spectroscopy. The molecular ions with the correct exact mass were detected. The ^1H NMR spectra showed the right numbers of signals and patterns of multiplicity consistent with the structures of **141**. The chemical shift assignments for **141a** are shown in Figure 5.

Figure 5. ^1H -NMR Spectrum of the Compound **141a**

It is interesting to note that the helical twist in **141a** was manifested with a set of signals from the diastereotopic methylene hydrogens on the five-membered rings. An AB pattern at δ 4.39 and 4.15 with a large geminal coupling constant of 21.0 Hz was observed. Such an AB pattern was also observed for **141b** and **141c**. The upfield shift aromatic signal at δ 6.20, attributable to the two aromatic hydrogens closest to the phenyl substituents, indicates that the phenyl substituents are oriented, to a large degree, perpendicular to the central aromatic system as observed in the X-ray structure. Such an orientation will place the neighboring aromatic hydrogens in the shielding region of the

induced aromatic ring current as in other similar structures.²² The signal for the *ortho* hydrogens of the phenyl substituents was shifted upfield to δ 6.52, consistent with the reported chemical shift of δ 6.43 for those of 4,5-diphenylphenanthrene (**133c**).^{40a} In the ¹³C NMR spectrum of **141a**, three signals in the aliphatic region for the *tert*-butyl groups and the methylene carbons were observed. In addition, sixteen signals in the aromatic region were clearly discernable along with a broad hump at around δ 132.5. The presence of such a hump was also observed in the cases of **141b** and **141c**, indicating that the coalescence temperatures for some of the ¹³C signals are at or around the ambient temperature, presumably due to somewhat restricted rotation of the aryl substituents.

The formation of **141** in nearly 50% yields may indicate that the rate of transformation from **145** to **147** is at least competitive with that of the tautomerization of **145** to **148** (Scheme 31). A rapid initial tautomerization could lead to the formation of the linearly fused hydrocarbons **150** as the major products from **149** because of reduced nonbonded steric interactions in the step for the intramolecular radical–radical coupling. Without tautomerization, the biradicals **146** would not be able to cyclize to form **150**. It is also interesting to note that photocyclization of **3** produced 4,5-diphenylphenanthrene (**133c**) instead of the sterically less congested 1,5-diphenylanthracene (Scheme 28).⁴⁰ The higher reactivity of the α - than the β -position of naphthalene in homolytic addition may be responsible for the high regioselectivity in producing **133c**. A similar preference could also account for the formation of **141** from **149** in the event of a rapid tautomerization from **145** to **148**. The ¹H NMR spectra of the crude reaction mixtures before separation and purification by column chromatography indicated that the hydrocarbons **150** were either not formed or were produced only in minute quantities.

The four methylene hydrogens in **150** are magnetically equivalent and could be expected to exhibit a singlet ^1H NMR signal at around δ 4.5.

Scheme 31. The Competitive Pathway to Linear Molecule **150**

It is worth noting that in the cases of **141b** and **141c**, minor amounts of **142b** (9%) and **142c** (12%) were also isolated. Although **142a** was not isolated, the ^1H NMR spectrum of the crude reaction mixture before column chromatography indicated the presence of substantial amount of **142a** (**141a**:**142a** = 1.8:1). The amount of **142a** diminished after prolonged heating of the reaction mixture. Apparently, direct coupling of the radical centers depicted in **146** led to the formation of the [2 + 2] cycloaddition adducts having the 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 reported previously.^{20,21} Unlike **141**, the ^1H and ^{13}C NMR spectra of **142** clearly showed a lack of symmetry in their structures. For example, in the case of **142b** the ^1H NMR signals for the two *tert*-butyl groups were observed at δ 1.87 and 1.12. The methylene hydrogens became essentially a singlet at δ 4.47. A new signal as a singlet at δ 6.19 attributable to the alkenyl hydrogen on the five-membered ring also appeared. The isolated aromatic hydrogen on the naphthalene ring gave a signal at δ 7.91 as a doublet due to a long-range coupling ($J = 2.2$ Hz). The signals for the other two aromatic hydrogens *meta* or *para* to the isolated aromatic hydrogen on the naphthalene

ring occurred at δ 7.67 (dd, $J = 9.3$ and 2.2 Hz) and δ 8.51 (d, $J = 9.3$ Hz), respectively. A ^{13}C NMR signal at δ 75.7 for the sp^3 carbon in the four-membered ring was also observed.

The well resolved AB pattern of the ^1H NMR signals for the methylene hydrogens in **141** provided an opportunity to determine the activation barriers for racemization by dynamic NMR studies. However, the AB signals of **141a** in 1,1,2,2-tetrachloroethane- d_2 remained well separated and exhibited no line broadening even at 125°C , indicating that the rate of the helix inversion is relatively slow on the NMR time scale. The $\Delta G_{\text{rac}}^\ddagger$ of **141a** is estimated to be at least 19.4 kcal/mol on the basis of the AB signals at δ 4.42 and 4.19 ($\delta_{\text{A}} - \delta_{\text{B}} = 60.7$ Hz) with a coupling constant of 20.8 Hz at 125°C .

It was reported that due to buttressing effect of the two methyl groups at the 3- and 6-positions, the $\Delta G_{\text{rac}}^\ddagger$ of **133d** at 25°C is 23.1 kcal/mol, which is 7 kcal/mol higher than that of **133b**.^{39a} Introducing two more methyl groups at the 1- and 8-positions further increases the $\Delta G_{\text{rac}}^\ddagger$ of **133e** at 49°C to 25.1 kcal/mol.^{38,50} Therefore, it could be expected that **141a** having two fused indeno rings at the 2,3- and 6,7-positions and two sterically demanding *tert*-butyl groups at the 1- and 8-positions would have a relatively high value for $\Delta G_{\text{rac}}^\ddagger$.

4.3. Synthesis of the Diacetylenes 138.

The diacetylene **138a** was prepared from 1-bromo-2-iodobenzene (**151**) via two consecutive palladium-catalyzed cross-coupling reactions with phenylacetylene and (trimethylsilyl)acetylene followed by desilylation as described previously (Scheme 32).²² The diacetylenes **138b** and **138c** were likewise synthesized. However, direct coupling of the bromide **154b** or **154c** with (trimethylsilyl)acetylene was sluggish, requiring three

days of heating at 60 °C and giving a low yield in the case of **156b**. This problem was circumvented by treatment of the bromides **154** with *n*-butyllithium at -78 °C followed by iodine to convert them to the iodides **155**. The subsequent coupling reaction went to completion within one hour at room temperature and gave good overall yields for the two-step procedure.

Scheme 32. The Preparation of Diacetylenes **138**

5. Conclusions

The reaction sequence outlined in Scheme 29 represents a new synthetic route to the indeno-fused 4,5-diarylphenanthrenes. The formal Diels-Alder reaction involving a C²–C⁶ cyclization reaction followed by a radical–radical coupling reaction of the benzannulated enyne–allenes is key to the efficient assembly of the phenanthrene system. The buttressing effects due to the indeno-fused rings and the two *tert*-butyl groups at the 1- and 8-positions are responsible for increasing the activation barrier for the helix inversion of the resulting 4,5-diarylphenanthrenes.

PART III

Synthesis of 2-Pyridone, 2-Alkoxypyridine and Related Polycyclic Heterocycles via the Cycloaromatization of Enyne-Isocyanates

1. Introduction

With their unprecedented molecular architecture, fascinating mode of action, and phenomenal biological activities, the enediyne antitumor antibiotics have excited the pulse and imagination of many researchers and thus established a vibrant field of investigations. Many synthetic chemists explored the various precursors that can undergo cycloaromatization to produce biradical intermediates and mimic the naturally occurring enediyne antibiotics. Most systems are capable of DNA-cleavage. The utilization of these novel cyclization reactions for the construction of complex molecules has also attracted a lot of attention.

Scheme 33. Unsaturation Systems that Can Cyclize to Form Aromatic Biradicals

Scheme 33 lists some basic systems that can undergo biradical-forming cyclization.^{11,14-18,26,51,52} In the parent system, the (Z)-enediyne, each of the unsaturated groups might be replaced with an iso-electronic group. Moore first successfully

incorporated a hetero-atom, oxygen, into the highly unsaturated conjugated system with the choice of enyne-ketenes. The Moore cyclization of enyne-ketenes is similar to that of enyne-allenes, producing a biradical intermediate containing an aryl and a phenoxy radical center. One of the useful applications of the Moore cyclization is that it provides a versatile and convenient synthetic route to highly substituted aromatic compounds.

Interestingly, Kerwin reported that *C,N*-dialkynyl imines **160** underwent a facile thermal rearrangement to β -alkynylacrylonitrile **162** in excellent yield. It was assumed that the 2,5-didehydropyridine **161** is the reaction intermediate (Scheme 35).⁵⁵ However, They were unable to capture the biradical species either by 1,4-cyclohexadiene (1,4-CHD) intermolecularly, or by the carbon-carbon double bond intramolecularly. Later on, a very small amount of the biradical-trapping product, 2-methyl-4,5-diphenylpyridine, was observed when the reaction was conducted in the presence of an intermediate amount of acid (e.g. 2.5 equiv of HBF₄ · Et₂O).⁵⁶

Scheme 35. Kerwin' Observation of Isomerization of *C,N*-Dialkynyl Imines

Although the failure of incorporation of a nitrile group into the conjugated systems to generate biradicals seems very disappointing, the great success of the Moore cyclization of enyne-ketenes provided hope and possibility of using the hetero-analogues of enyne-allenes to generate biradicals. Almost at the same time, our research group and the Schmittel's group in Germany independently reported incorporation of nitrogen atom(s) into the conjugated systems with the use of enyne-ketenimines and enyne-carbodiimides to generate biradicals.

Scheme 36. Cycloaromatization of Benzoenyne-Ketenimines **164**

Our research group first reported that cycloaromatization of the enyne-ketenimines, readily available by the aza-Wittig reaction between the iminophosphorane

163 and diphenylketene, underwent either C²-C⁶ cyclization or C²-C⁷ cyclization depending on the substituent at the acetylenic terminus.⁵⁷ After hydrogen-atom abstraction or the intramolecular radical-radical coupling, the quinolines **166** or the 5*H*-benzo[*b*]carbazoles **169** were produced in good to excellent yield (Scheme 36). A similar cyclization of enyne-ketenimines was reported by Ghosez and Differding without mentioning the biradical intermediates.⁵⁸

Scheme 37. Cycloaromatization of Benzoenyne-Carbodiimides **170**

As a continuous effort to explore the cycloaromatization reactions of enyne-heterocumulenes, our research group reported the biradical-forming cyclization of enyne-carbodiimides **170** and their subsequent transformations to 2-(phenylamino)quinoline (**171**) and the 6*H*-indolo[2,3-*b*]quinolines **172** (Scheme 37).⁵⁹ In the event, the precursors for cyclizations, enyne-carbodiimides **170**, were prepared by the aza-Wittig reaction between the iminophosphorane **163** and phenyl isocyanate in a manner similar to the preparation of the enyne-ketenimines **164**. Thermolysis of **170a** in refluxing γ -terpinene afforded the C²-C⁷ cyclization product **171a** in 49% yield, along with 16% of the C²-C⁶ cyclization product **172a**. Interestingly, Molina and coworkers have already carried out this reaction a few years earlier.⁶⁰ Thermolysis of other benzoenyne-carbodiimides **170b-f** having a substituent at the acetylenic terminus under the same reaction condition afforded exclusively the C²-C⁶ cyclization products **172b-f** in excellent yield.

The Schmittel's research group also carried out the cycloaromatization reactions of benzoenyne-ketenimines and benzoenyne-carbodiimides.⁶¹ The precursors for cycloaromatization were prepared by dehydration of amides to give the corresponding enyne-ketenimines and by the extrusion of hydrogen sulfide from thiourea to give the corresponding enyne-carbodiimides. The chemical reactivities of the cyclization reactions of enyne-ketenimines and enyne-carbodiimides reported by Schmittel et al. were consistent with what was observed in our research group.

The introduction of nitrogen atom into the conjugated enyne-allene systems provides a new avenue for the design of novel DNA-cleavage agents. Moreover, the existence of intramolecular decay routes for the initially formed biradicals made these cyclization reactions of enyne-hetero-allenes essentially useful. The applications of such cyclization reactions have led to the development of versatile and convergent synthetic routes to many important biologically active alkaloids,^{57,59,61,62} such as benzocarbazoles, indoloquinolines, and indolonaphthyridines.

2. Research Objective

With ample precedents of aryl substituent or bulky groups at the acetylenic terminus directing the reaction course of cyclization of enyne-allenes towards the C²-C⁶ mode, our previous result involving **173** was quite surprising.⁶³ Thermolysis of the cyclopentene-based enyne-allenes **173** only produced the C²-C⁷ cyclization products **175** (Scheme 38).

Scheme 38. The C²-C⁷ Cyclization of Cyclopentene-Based Enyne-Allenes **173**

Nakatani also observed the C²-C⁷ reaction mode in the biradical-forming cyclization of the cyclopentene-based enyne-ketenes with an aryl substituent at the acetylenic terminus.⁶⁴ Recently, Schmittl systematically investigated the ring size effects on regioselectivity.⁶⁵ They assessed that because of the ring strain, the cyclopentene-based enyne-allenes underwent predominately the C²-C⁷ cyclization reactions, while with the larger cycloalkenyne-allenes the C²-C⁶ cyclization products were produced.

As a part of our continuing efforts on the investigation of the enyne-allene chemistry, we envisioned that enyne-isocyanates having a nitrogen and an oxygen atom in the conjugated system could serve as precursors for the biradical-forming cyclizations and could be transformed into novel heterocyclic compounds. With the cyclopentene-base enyne-isocyanates, the C²-C⁷ cyclization reaction pathway was the preferred one. In addition to controlling the regioselectivity of the thermal cyclization, incorporation of the alkene moiety into a five-membered ring also has other advantages. The requisite enyne-isocyanates are easy to prepare, and the alkene geometry is locked in the Z-configuration, which is necessary for cyclization.

3. Literature Survey on 2-Pyrinone and its Derivatives

The 2(1*H*)-pyridone moiety is a prominent structure feature in a variety of natural products as well as in other species of medicinal interest.⁶⁶

NMR spectroscopy analysis indicates that 2-pyridone and many of their derivatives appear to exist predominately in the pyridone form under all conditions.⁶⁷ An electron-withdrawing group alpha to the nitrogen shifts the equilibrium in favor of the pyridinol tautomer. Unlike the corresponding pyridone, 2-aminopyridine prefers the

amino form (Scheme 39). In 2-aminopyridine, stabilization of **178** and **179** by charge separated forms (**178a** and **179a**) are similar and moderate, and the aromatic nature of **178b** is responsible for the predominance of **178**. However, in the case of 2-pyridone, stabilization of **176** by the charge separated form **176a** where oxygen bears a positive charge is much less preferred than stabilization of **177** by **177a** where oxygen is negatively charged, thus **177** predominates.

Scheme 39. The Tautomers of 2-Pyridone and 2-Aminopyridine

Beak reported that in the case of *N*-alkyl-2-pyridone and 2-alkoxypyridine, the equilibrium favors *N*-alkyl-2-pyridone over 2-alkoxy-pyridine: 2-methoxypyridine $\rightarrow$ *N*-methyl-2-pyridone ($\Delta G^\circ > -9.3$ kcal/mol).⁶⁸ This experimental observation was consistent with the fact that 2-pyridone is much more stable than its tautomer 2-pyridinol.

4. Results and Discussions

4.1. Preparation and Thermal Cyclization of Cyclopentene-Based Enyne-Isocyanates

Scheme 40 outlined the preparation of the enyne-isocyanates **185**. Starting with the enol triflate **181**, which could be easily prepared from ethyl 2-oxocyclopentanecarboxylate **180** in nearly quantitative yield,⁶⁹ the palladium-catalyzed cross coupling reaction with terminal acetylenes **182** afforded the esters **183** in excellent yield.⁷⁰ Saponification of the esters **183** gave the corresponding carboxylic acids **184**.

Then the carboxylic acids **184** were treated with diphenylphosphoryl azide (DPPA)⁷¹ in the presence of triethylamine to furnish the desired enyne-isocyanates **185**. The results for all the reaction steps towards the isocyanates **185** are summarized in Table 2.

Scheme 40. Preparation of the Enyne-Isocyanates **185**

	R	coupling product 183	Acid 184	Isocyanate 185
a,		90	96	91
b,		98	92	86
c,		92	92	84
d,		91	85	87
e,		91	89	91
f,		97	86	89
g,		91	89	87
h,		91	80	68

Table 2. Yield (%) of the Reactions toward the Isocyanates **185**

Compared to the cycloaromatization of the enyne-ketenimine and enyne-carbodiimide system, the cycloaromatization of enyne-isocyanates requires much higher reaction temperature. The cyclization reactions of enyne-isocyanates **185** occur at 180 °C under refluxing 1,2-dichlorobenzene.

Scheme 41. Cyclization of the Enyne-Isocyanates **185a** and **185b**

Thermal cyclization of the enyne-isocyanate **185a** proceeded through the C²-C⁷ reaction pathway to generate the biradical intermediate **186**, followed by the 1,5 hydrogen shift to give the new biradical intermediate **187** (Scheme 41). The intramolecular radical-radical coupling of **187** furnished the cyclized product **188** in 40% yield. Similarly, cyclization of the enyne-isocyanate **185b** furnished the 2-pyridone **192** in nearly quantitative yield (Scheme 41). Apparently, the aryl radical of the initially formed biradical **189** is trapped intramolecularly by the carbon-carbon double bond of the phenyl group in a 6-endo fashion to give **190**, which then underwent intermolecular hydrogen transfer to afford **192** either directly or indirectly through tautomerization of **191**. The much higher yield compared to the previous case may be attributed to the perfect geometry of the transition state in the intramolecular radical trapping process. The structure of the pyridone **192** was unequivocally established by the X-ray structure

analysis. It is worth noting that the isolated product is the 2-pyridone form, not the 2-pyridinol form. In all the cases of this study, the isolated products are the 2-pyridone derivatives.

4.2. Zwitterion Mechanism versus Biradical Mechanism

The cycloaromatization reactions of enyne-cumulene and enyne-heterocumulene discussed so far are consistent with the reaction mechanism involving biradical species. However, Moore pointed out that sometimes the reaction intermediates generated by the cycloaromatization of enyne-ketenes could best be described as zwitterions instead of biradicals.^{16,72}

Scheme 42. The Moore Cyclization of an Enyne-Ketene Involving Zwitterion Mechanism

Moore and coworkers designed a beautiful experiment to delineate the dual chemical properties of biradicals and zwitterions (Scheme 42). In their elegant studies, the enyne-ketene **194** generated in situ by thermolysis of 3-azido-1,2-benzoquinone **193** underwent ring closure to give the zwitterion intermediate **195**. In benzene **195** was trapped to give the terphenyl **196** in 84% yield. In the presence of dihydropyran (DHP), **197** was produced, and when thermolysis was conducted in THF/TMSCl, **198** was obtained in 72% yield.

Although the radical intermediate could account for the formation of **196** and **197**, only a carbocation is a reasonable precursor for **198**. Moreover, an interesting hydroxylation reaction was observed when **195** was decomposed in ethyl acetate containing an excess of TMSCl (10 equiv). This resulted in the formation of a mixture of **200** and **201**, which were isolated in the yields of 39% and 27%, respectively. These products are viewed as arising from the intermediate **199**, which upon silylation would release chloride ion, and this could facilitate deethylation to give a trimethylsilyl derivative of **201**. Subsequent hydrolysis during workup would lead to the observed products. It was noted that without TMSCl, a very complex mixture of products is formed and no pure compound could be isolated. Again, the reasonable reaction mechanism would involve the zwitterion species.

We observed that thermal cyclization of the isocyanate **185c** produced two cyclized products **205** and **206** in the yields of 52% and 10%, respectively (Scheme 43). Here, the zwitterion mechanism could count for the reaction course. Thus, the cycloaromatization reaction of **185c** generated the zwitterion intermediate **203**. The carbocation of the zwitterion intermediate **203** was captured by the methoxyl group to

give **204**. Intermolecular methyl group transfer afforded the cyclized product **205**. If the oxygen anion picked up a proton from elsewhere and a nucleophile attacked the oxonium ion, the 2-pyridone **206** was produced. Similarly, the cyclization reaction of **185d** afforded **207** and **208** in the yield of 38% and 28%, respectively. It is worth noting that the intermolecular methyl transfer would occur on the oxygen anion or on the nitrogen anion to give the 2-methoxypyridine derivative **208** or the *N*-methyl-2-pyridone derivative **207**.

Scheme 43. Thermal Cyclization of the Enyne-Isocyanates **185c** and **185d**

When **185f** was subjected to heating in refluxing 1,2-dichlorobenzene, the pyridone **212** (24%) along with the 2-methoxypyridine **213** (18%), *N*-methylpyridone **214** (10%), and the dimer **215** (1%) were isolated (Scheme 44). Based on the previous results, it is not surprising to observe the formation of **212**, **213**, and **214**. Scheme 45 outlined a pathway to account for the formation of **215**. An initial C²-C⁷ cyclization of

Scheme 44. Cyclization of the Isocyanate **185f**

185f generated the zwitterion intermediate **209**, then the carbocationic center of **209** was captured by the methoxyl group to give **210** (Scheme 44). Attack of the methylene carbon instead of the methyl carbon by the oxygen anion of a second molecule, followed by intermolecular methyl transfer produced the dimer **215**. The structures of all four

Scheme 45. Proposed Mechanism for the Formation of the Dimer **215**

products are consistent with their characteristic data. The correct molecular ion ($m/e = 410$) was detected by GC-MS analysis for the dimer **215**. The carbon-13 NMR shows 24 different signals, consistent with the structure of the unsymmetrical dimer **215**.

The following example shows the dual chemical roles of zwitterion and biradical existing in one reaction sequence. The cyclization reaction of **185e** in refluxing 1,2-dichlorobenzene at 180 °C afforded **223** and **219** in the yields of 58% and 18%, respectively (Scheme 46). Apparently, the initial C²-C⁷ cyclization of **185e** generated the

Scheme 46. Cyclization of the Isocyanate **185e**

intermediate that possesses both the biradical and the zwitterion character. A 1,5 hydrogen shift of the biradical intermediate **217** gave a new biradical **218**, which in turn underwent intramolecular radical-radical coupling to furnish the polycyclic compound **219**. The carbocationic center of the zwitterion intermediate **216** could also be captured by the methoxyl group to give **220**, which then underwent ring opening to produce the *ortho*-quinodimethane derivative **221**. The *ortho*-quinodimethane **221** could be regarded as a biradical species **222**. After a rotation of the single carbon-carbon bond between the two six-membered rings, an intramolecular radical-radical coupling would give rise to **223**. Interestingly, when the reaction was carried out at a lower temperature (150 °C), only **223** arising from the zwitterion intermediate **216** was observed in 59% yield.

4.3. Cycloaromatization of Benzoenyne-Isocyanates

The success in the cyclization of cyclopentene-based enyne-isocyanates encouraged us to explore the reactivity of benzannulated enyne-isocyanates. The benzoenyne-isocyanates **227** were prepared from 2-iodoaniline (**224**) according to the reported procedure (Scheme 47).⁵⁹ The Pd-catalyzed cross-coupling reaction between 2-iodoaniline (**224**) and the terminal acetylenes **225** afforded **226**, which upon treatment with triphosgene in the presence of triethylamine gave the isocyanates **227** in good yield.

Scheme 47. Preparation of the Benzoenyne-Isocyanates **227**

When **227a** was subjected to thermolysis in refluxing 1,2-dichlorobenzene in the presence of γ -terpinene for 15 days, an essentially 1:1 mixture of **228** and **229** was isolated in the yields of 21% and 20%, respectively (Scheme 48). Apparently, The biradical intermediate **230** generated from the $\text{C}^2\text{-C}^6$ type cyclization of **227a** abstracted two hydrogen-atoms from γ -terpinene to form **228** directly or indirectly through **231**.

Scheme 48. Cyclization of **227a** and the Plausible Mechanism

The formation of **229** is quite surprising. The structure of **229** was unequivocally established by the X-ray crystal analysis. The difference of molecule formulas of the product **229** and the starting isocyanate **227a** is two more oxygen atoms in **229**, suggesting that a molecule of oxygen was involved in the reaction course. The competing pathway of the C²-C⁷ cyclization could generate the biradical **232**, which possibly could be captured by a molecule of oxygen to give **233**. The intramolecular radical-radical coupling of **233** gave the hyperperoxide **234**. A ring opening of **234** could afford **235**, which then underwent an electrocyclic reaction to give **229**.

Interestingly, when the reaction was carried out in the presence of chlorodimethylphenylsilane for 21 days, only the C²-C⁷ type cyclization product **238** was isolated in 53% yield. Apparently, the C²-C⁷ cyclization of **227a** generated the zwitterion **236**, the oxygen-anion was captured by the silyl group and the carbocationic center of the zwitterion **236** was captured by the methoxyl group. Chlorodimethylphenylsilane could also facilitate the demethylation process with the chloride ion serving as a nucleophile. Subsequent hydrolysis during work-up would lead to the observed product. It is worth noting that when the reaction was carried out in refluxing 1,2-dichlorobenzene for 21 days without chlorodimethylphenylsilane and γ -terpinene, only 11% of **238** was obtained along with a small amount of *N*-methylated **238** (9%).

Scheme 49. Cyclization of **227a** in the Presence of Chlorodimethylphenylsilane

Thermal cyclization of **227b** afforded **239** in 27% yield in a manner similar to that of **185b** (Scheme 49). Similarly, cycloaromatization of **227c** afforded the 2-pyridone **240** (31%) and the 2-methoxypyridine **241** (9%). The much lower reaction rate and poor yield may be attributed to the fact that the aromaticity gained during cyclization of **227** is not as much as that of cyclization of **185**.

Scheme 49. Cyclization of the Benzoenyne-Isocyanates **227b** and **227c**

5. Conclusions

Thermolysis of enyne-isocyanates represents a new way of generating biradicals and/or zwitterions from unsaturated molecules having nitrogen and oxygen atom in the conjugated system. Due to the ring strain, cycloaromatization of cyclopentene-based enyne-isocyanates underwent predominately C²-C⁷ cyclization pathway. The existence of intramolecular decay routes for the initially formed biradicals or zwitterions made these cyclization reactions essentially useful, leading to a variety of polycyclic heterocycles.

PART IV

Cycloaromatization of Cyclopentene-Based Enyne-Carbodiimide

1. Research Objective

Incorporation of hetero-atom (N, O) into the enyne-allene system renewed the research interest in the biradical-forming cycloaromatization reactions, not only because these hetero enyne-allenes provided alternative ways for producing the DNA-cleavage agents; but also because the cyclization reactions of hetero enyne-allenes provided convergent synthetic routes to many heterocycles by employing the intramolecular radical decay strategy.

Our research group recently reported an efficient synthetic route to the 6*H*-indolo[2,3-*b*]quinolines and a variety of indolonaphthyridines as the 5-aza analogues of ellipticines and isoellipticines via thermolysis of benzoenyne-carbodiimides.^{59,62} In the event, the precursors for the thermal cyclization reactions were prepared by the aza-Wittig reaction between isocyanate and iminophosphorane. The cycloaromatization reaction underwent predominately the C²-C⁶ cyclization pathway, except that thermolysis of carbodiimide the **170a** without substituent at the acetylenic terminus produced both the C²-C⁷ cyclization and the C²-C⁶ cyclization products **171a** and **172a**, respectively. The Schmittle's group also observed similar reaction results.⁶¹

Because we have the cyclopentene-based enyne-isocyanates in hand, it is a logical extension for us to convert them into the corresponding carbodiimides and carry out the thermal cyclization reactions. We envisioned that carbodiimides could be obtained by dehydration of the urea derivatives with dibromotriphenylphosphorane in the presence of triethylamine. It was anticipated that due to the ring strain, the cycloaromatization of

cyclopentene-based enyne-carbodiimides would proceed through predominately the C²-C⁷ cyclization pathway to give a variety of novel heterocyclic compounds. Such a switch from the C²-C⁶ cyclization reaction to the C²-C⁷ cyclization of the cyclopentene-based enyne-allenes was observed previously by our research group⁶³ and the Schmittel's group.⁶⁵

2. Results and Discussions

Initial attempts for the preparation of the carbodiimide **243a** by the aza-Wittig reaction between the isocyanate **185a** and phenyl iminophosphorane (**242**) were not very successful (Scheme 50). The desired carbodiimide **243a** was only obtained in approximately 20% yield, along with the two symmetrical carbodiimides **244** and **245**. A plausible mechanism to account for the formation of **244** and **245** is outlined in Scheme 50. It is possible that the initial formed carbodiimide **243a** would react with **185a** to give

Scheme 50. Initial Attempt to Synthesis Carbodiimide by Aza-Wittig Reaction

246 in a [2 + 2] fashion.⁷³ Ring opening of **246** by a retro [2 + 2] reaction then gave **244** and the exchanged isocyanate **247**. The aza-Wittig reaction between the resulting isocyanate **247** and **242** would give **245**. Another possibility is that **243a** would react with **242** to give **245** and the exchanged iminophosphorane **248** and, **244** was produced by aza-Wittig reaction between **248** and **185a**. A similar result was observed by Tsuge et al.⁷⁴

The aza-Wittig reaction between the isocyanate **185a** and the benzylic iminophosphorane **249** at $-78\text{ }^{\circ}\text{C}$ produced the expected carbodiimide **243a'** in excellent yield (Scheme 51). Interestingly, at a higher reaction temperature, the yield of **243a'** decreased, and the exchanged symmetrical carbodiimides appeared. However,

Scheme 51. Preparation and Cyclization of the Carbodiimide **243a'**

thermal cyclization of the carbodiimide **243a'** under refluxing 1,2-dichlorobenzene afforded the cyclized product **250** only in 36% yield. Apparently, an initial $\text{C}^2\text{-C}^7$ cyclization of **243a'** generated the biradical **251**, which then underwent the 1,5 hydrogen shift to give the biradical **252**. Simple intramolecular radical-radical coupling would give rise to the cyclized product **250**. However, the benzyl radical of the biradical intermediate **252** could abstract a hydrogen atom from methylene next to the nitrogen

radical to give the imine **253**, which is labile and could undergo polymerization reaction. The broad peaks on the ^1H NMR spectrum and the black color of the crude product are good indication of the formation of polymers.

Since the aza-Wittig reaction gave unsatisfactory results, we tried to use other synthetic routes to prepare the requisite carbodiimides. It appeared that dehydration of the urea derivatives was a possible synthetic pathway. Preparation of carbodiimides by dehydration of the corresponding urea derivatives was well documented.⁷⁵ Many dehydrating reagents were available for this transformation, among them are P_2O_5 ,⁷⁶ metal carbonyls, such as $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_4\text{CNPh}$, and $\text{Mo}(\text{CO})_6$,⁷⁷ *p*-toluenesulfonyl chloride,⁷⁸ Burgess reagent,⁷⁹ triphenylphosphine/carbon tetrachloride,⁸⁰ dimethylphosgeniminium chloride,⁸¹ and dibromotriphenylphosphorane.⁸²

Scheme 52. Preparation of the Carbodiimides **243**

Unfortunately, our preparation of the carbodiimides **243** by dehydration of the urea derivatives **254** employing the dehydrating reagents, such as *p*-toluenesulfonyl chloride, triphenylphosphine/carbon tetrachloride, and dimethylphosgeniminium chloride all failed. Finally, employing Palomo's method^{82a} gave satisfactory results (Scheme 52). In the event, a solution of the urea derivatives **254**, easily prepared by the condensation reaction between the isocyanates **185** and aniline, was added dropwise into a solution of dibromotriphenylphosphorane (2 equiv) and triethylamine (4 equiv) in methylene chloride over a period of 45 min. The carbodiimides **243** were quite stable and could be purified by column chromatography. It is worth noting that the reverse addition of the

reagents or a rapid addition of the urea solution afforded very poor yield or even no product at all. The yields of all the reaction steps towards the carbodiimides **243** were summarized in Table 3.

	R	254 , Yield	243 , Yield
a		85%	85%
b		72%	72%
c		69%	82%
d		76%	50%
g		72%	65%

Table 3. Reaction Yields towards the Carbodimimdes **243**

Thermal cyclization of the carbodiimide **243a** under refluxing chlorobenzene produced the cyclic compound **257** in 56% yield (Scheme 53). This compound is unstable and underwent autoxidation to form amide **258** on standing under air. Apparently, the reaction mechanism is very similar to that of cyclization of the enyne-isocyanate **185a**. An initial C²-C⁷ cyclization of **243a** generated the biradical **255**, which

Scheme 53. Cyclization of the Carbodiimide **243a**

then underwent the 1,5 hydrogen shift to give the biradical **256**. An intermolecular radical-radical coupling furnished the cyclized product **257**.

Cycloaromatization of the carbodiimide **243b** afforded the 2-(phenylamino)pyridine **261** in 73% yield in a manner similar to the cyclization reaction of the isocyanate **185b** (Scheme 54).

Scheme 54. Cyclization of the Carbodiimide **243b**

Thermal cyclization of the carbodiimide **243g** in refluxing *p*-xylene seemed quite messy. Many products were produced. However, when the reaction was carried out in refluxing chlorobenzene, only three products, **262**, **263**, and **264**, were isolated in the yields of 35%, 28%, and 12%, respectively (Scheme 55). The GC-MS analysis of the

Scheme 55. Cyclization of **243g** in Refluxing Chlorobenzene

reaction carried out in *p*-xylene indicated that in addition to the expected products, there were six more major peaks [with molecule ion $m/z = 122, 210, 356$ (4 peaks)]. A search of the mass spectrum library suggested that *p*-methylbenzyl alcohol and 1,2-di(*p*-methylphenyl)ethane were produced. The formation of these two compounds indicated the formation of the *p*-methylbenzyl radical during the course of the reaction sequence (Scheme 56). Apparently, the C^2-C^7 cyclization reaction of the carbodiimide **243g**

generated the biradical **265**, which then underwent a 1,5 hydrogen shift to give the biradical **266**. The primary alkyl radical center of the biradical **266** could abstract a proton from the methyl group of *p*-xylene to give **267** and the *p*-methylbenzyl radical **268**. Upon the formation of the *p*-methylbenzyl radical **268**, several possibilities for the radical-radical coupling could occur. The coupling of **268** and the radical intermediate **267** could give rise to **271** with a molecule weight of 356. A second intramolecular 1,5

Scheme 56. Cyclization of **243g** in Refluxing *p*-Xylene

hydrogen shift of **266** could afford **263**. A simple intramolecular radical-radical coupling of **266** could give the polycyclic compound **262**, while the biradical **266** may also abstract two hydrogen atoms from elsewhere to furnish **264**. The structures of **262**, **263**, and **264** were consistent with their spectral data. The GC-MS analysis gave the correct molecular ion ($m/z = 249$ for **262** and **263**, $m/z = 251$ for **264**). The IR spectra of **263** and **264** show a strong absorption band at 3423 and 3456 cm^{-1} , respectively, indicating the presence of a secondary amine functional group. The ^1H NMR spectrum of **263** showed

typical signal for the allylic protons, while the signals for the *n*-propyl group were observed on the ^1H NMR spectrum of **264**.

Thermal cyclization of the carbodiimide **243c** afforded solely the 2-(phenylamino)pyridine **274** in 43% yield (Scheme 57). Here the zwitterion mechanism could account for the course of the reaction by considering the electron-donor character of the methoxyl group. Thus, the cyclization reaction of **243c** generated the zwitterion intermediate **272**. The carbocationic center of the zwitterion **272** was captured by the methoxyl group to give **273**. Due to the steric hindrance, the intermolecular methyl group transformation was hard to achieve. Instead, the nitrogen anion of **273** picked up a proton from elsewhere and a nucleophile took away the methyl group to give the 2-(phenylamino)pyridine **274**. The structure of **274** was unequivocally established by the X-ray structure analysis.

Scheme 57. Cyclization of the Carbodiimide **243c**

Thermolysis of the carbodiimide **243d** afforded both the $\text{C}^2\text{-C}^7$ cyclization product **275** (14%) and the $\text{C}^2\text{-C}^6$ cyclization products **276** and **277** in the yields of 48% and 6%, respectively (Scheme 58). The formation of majority $\text{C}^2\text{-C}^6$ cyclization products was quite surprising. The emergence of nonbonding steric interaction in the zwitterion intermediate **278** may be responsible for the unfavorable $\text{C}^2\text{-C}^7$ cyclization mode. The carbocationic center of the zwitterion intermediate **278**, generated from the $\text{C}^2\text{-C}^7$ cyclization pathway, was captured by the amine group to give **279**. Protonation of the

nitrogen anion along with the loss of one methyl group led to **275** as observed previously in the case of **243c**. The C²-C⁶ cyclization reaction of **243d** generated the biradical intermediate **280**, which in turn underwent intramolecular radical-radical coupling to give **281** and, after tautomerization, the polycyclic compound **276**. Losing a proton from **281** followed by methylation would lead to **277**.

Scheme 58. Cyclization of the Carbodiimide **243d**

The switch from the C²-C⁷ cyclization to the C²-C⁶ cyclization due to simple steric hindrance indicates that the difference of the activation energies for the two cyclization modes is very small. The theoretical calculations by Schmittl indicated that the activation energies for the cyclizations of the model compound **282** are +30.3 kcal/mol for the C²-C⁶ pathway and +30.9 kcal/mol for the C²-C⁷ pathway,^{61b} which is consistent with this experimental observation.

Interestingly, when the reaction was carried out in the presence of chlorodimethylphenylsilane, a 5:1 mixture of **275** and **276** was produced in the yields of

70% and 14%, respectively. Apparently, here the chlorodimethylphenylsilane could stabilize the zwitterion intermediate **278** by silylation of the nitrogen anion and, the resulting chloride could facilitate the demethylation, which made the C²-C⁷ cyclization preferred over the C²-C⁶ cyclization.

We also prepared the carbodiimide **285** in a manner similar to that of the carbodiimides **243** (Scheme 59). The condensation reaction between the isocyanate **185h** and the aniline **283** afforded the urea **284** in 72% yield, which was then converted to the carbodiimide **285** by the dehydration reaction with dibromotriphenylphosphorane in the presence of triethylamine. Thermal cyclization of **285** afforded two cyclized products

Scheme 59. Preparation and Cyclization of the Carbodiimide **285**

288 and **291** in the yields of 49% and 30%, respectively. Apparently, an initial C²-C⁷ cyclization of **285** generated the biradical **286**, which then underwent a 1,5 hydrogen shift to give biradical **287**. A simple intramolecular radical-radical coupling of **287** then produced **288**. However, the biradical intermediate **287** could undergo fragmentation by losing one molecule of formaldehyde to give the biradical **289**, which could also be regarded as the aza-*ortho*-quinodimethane derivative **290**. Finally, an intramolecular Diels-Alder reaction produced the cyclized product **291**.

3. Conclusions

The carbodiimides **243** and **285** were prepared in moderate to good yield by dehydration of the urea derivatives with excess amounts of dibromotriphenylphosphorane in the presence of triethylamine. The cyclization reactions of the carbodiimides **243** and **285** preferred the C²-C⁷ pathway. The intramolecular decay of the biradical or the zwitterion intermediates gave rise to a variety of novel heterocyclic compounds. Due to steric interactions, both the C²-C⁶ and the C²-C⁷ cyclization products in the case of **243d** were observed.

EXPERIMENTAL SECTION

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. Triethylamine and benzene were distilled over CaH₂ prior to use. *n*-Butyllithium (2.5 M) in hexanes, *tert*-butyllithium (1.7 M) in pentane, thionyl chloride, pyridine (anhydrous), benzophenones, dibenzosuberone (**96**), phenanthrenequinone, 2,2-dimethyl-1,3-propanediol, ethylene glycol, 2,2-dimethylpropiophenone (**110**), triethylsilane, and potassium *tert*-butoxide (1.0 M) in THF, CuBr·SMe₂, 4-bromobiphenyl, 5-iodo-*m*-xylene (1-iodo-3,5-dimethylbenzene), Pd(PPh₃)₂Cl₂, copper(I) iodide, *N,N*-diisopropylethylamine, sodium hydride, trifluoromethanesulfonic anhydride, diphenylphosphoryl azide (DPPA), dibromotriphenylphosphorane, aniline, sodium azide, triphenylphosphine, benzyl chloride, ethyl 2-oxocyclopentanecarboxylate, triphosgene, γ -terpinene, chlorodimethylphenylsilane, 2-iodotoluene, 2-iodoanisole, and 2-iodoaniline were purchased from Aldrich and were used as received. 1-Pentyne, methyl propargylic ether, 4-phenyl-1-butyne, and (trimethylsilyl)acetylene were purchased from GFS Chemicals, Inc. and used without further purification. Trifluoroacetic acid, terephthaloyl chloride, and 2-iodobenzyl alcohol were purchased from Acros. 1-Bromo-2-iodobenzene was purchased from Alfa. The 2,2-dimethylpropylene monoketal **103** of phenanthrenequinone was prepared in 96% yield according to the reported procedure.⁸³ Similarly, **106** was prepared from phenanthrenequinone and ethylene glycol in 55% yield. 4-Iodobiphenyl was prepared from 4-bromobiphenyl using the procedure described for **155**. 1-Bromo-2-ethynylbenzene (**153**)⁸⁴ was obtained by desilylation of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene⁸⁵ with sodium hydroxide as described for **138**.

2-Methylphenylethyne and 2-ethynylanisole were prepared from 2-iodotoluene and 2-iodoanisole respectively using the procedure described for **138**. 1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthylene (**114**)⁸⁶ and 2,2-dimethyl-1-indanone (**115**),⁸⁷ 5-methoxy-1-pentyne,⁸⁸ *N,N*-dimethyl-2-iodoaniline,⁸⁹ methyl 2-iodobenzyl ether,⁹⁰ 2-aminophenyl allyl ether (**283**),⁹¹ *N*-(triphenylphosphoranylidene)aniline (**242**),⁹² and *N*-(triphenylphosphoranylidene)benzylamine (**249**)⁹³ were prepared according to the reported procedure. Silica gel for flash column chromatography was purchased from ICN. Melting points were uncorrected. ¹H (270 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.00) as internal standards unless otherwise indicated. IR spectra were taken on Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were obtained on Hewlett Packard 5970B GC/MSD instrument at 70 eV.

1,1-Diphenyl-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (84a). The following procedure is representative for the preparation of the diacetylenic propargylic alcohols. To 0.395 g (1.95 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne^{22,85,94} in 18 mL of THF under a nitrogen atmosphere at 0 °C was added 0.78 mL of a 2.5 M solution of *n*-butyllithium (1.95 mmol) in hexanes. After 30 min of stirring, 0.322 g (1.77 mmol) of benzophenone (**82a**) in 40 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 hours, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/5% CH₂Cl₂ and 5% Et₂O in hexanes) to provide 0.633 g (1.65 mmol, 93% yield) of **84a** as a viscous liquid: *R_f* = 0.56

(hexanes:Et₂O = 2:1); IR 3545, 2217, 756, 692 cm⁻¹; ¹H NMR δ 7.79–7.75 (4 H, m), 7.60–7.53 (2 H, m), 7.43–7.23 (13 H, m), 3.00 (1 H, s); ¹³C NMR δ 144.9, 132.2, 132.0, 131.8, 128.41, 128.36, 128.25, 127.9, 127.6, 126.1, 125.9, 124.8, 122.9, 95.6, 93.5, 88.1, 85.9, 75.0; MS *m/z* 384 (M⁺), 367, 307, 279, 105; HRMS calcd for C₂₉H₂₀O 384.1514, found 384.1520.

5,10-Diphenyl-11*H*-benzo[*b*]fluoren-11-ol (90a). The following procedure is representative for the synthesis of 11*H*-benzo[*b*]fluoren-11-ols. To 0.575 g (1.50 mmol) of **84a** in 50 mL of anhydrous diethyl ether under a nitrogen atmosphere at 0 °C was added a mixture of 0.12 mL of thionyl chloride (1.65 mmol) and 0.27 mL of pyridine (3.30 mmol) in 30 mL of anhydrous diethyl ether. The reaction mixture was then allowed to warm to room temperature. After 4 hours, 50 mL of water was added, and the mixture was extracted with diethyl ether. The combined organic extracts were washed with a saturated sodium chloride solution (50 mL) and water (50 mL), dried over sodium sulfate, and concentrated to give the crude chloride **89a**. Purification by flash column chromatography (silica gel/5% CH₂Cl₂ and 5% Et₂O in hexanes) resulted in the conversion of the chloride to the alcohol **90a**, which was obtained (0.489 g, 1.27 mmol, 85% yield) as a light yellow solid: *R_f* = 0.30 (hexanes:Et₂O = 3:1); mp 142–144 °C; IR (KBr) 3448, 763, 701 cm⁻¹; ¹H δ 7.7–7.34 (15 H, m), 7.23 (1 H, t, *J* = 7.5 Hz), 7.06 (1 H, t, *J* = 7.5 Hz), 6.39 (1 H, d, *J* = 7.7 Hz), 5.83 (1 H, s), 1.84 (1 H, br s); ¹³C δ 145.6, 141.0, 139.9, 138.6, 137.7, 136.6, 135.1, 134.1, 133.5, 132.3, 130.8, 130.1, 130.0, 129.3, 129.2, 129.1, 128.9, 128.6, 128.0, 127.96, 127.9, 126.6, 126.1, 126.06, 125.7, 125.2, 123.6, 73.5; MS *m/z* 384 (M⁺), 367, 307; HRMS calcd for C₂₉H₂₀O 384.1514, found 384.1500. Anal. Calcd for C₂₉H₂₀O: C, 90.60; H, 5.24. Found: C, 90.17; H, 5.34.

1,1-Di(4-bromophenyl)-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (84b). The same procedure was repeated as described for **84a** except that 0.339 g (1.00 mmol) of **82b** was treated with **83** derived from 0.222 g of 1-(2-ethynylphenyl)-2-phenylethyne (1.08 mmol) and 0.43 mL of a 2.5 M solution of *n*-butyllithium (1.08 mmol) in hexanes to afford **84b** (0.479 g, 0.88 mmol, 88% yield) as a light yellow solid: IR 3420, 2218 cm⁻¹; ¹H δ 7.56–7.44 (6 H, m), 7.36–7.25 (11 H, m), 2.95 (1 H, s); ¹³C δ 143.6, 132.2, 132.1, 131.7, 131.5, 128.8, 128.4, 128.1, 127.8, 126.1, 124.3, 122.6, 122.0, 94.2, 93.6, 87.9, 86.5, 74.2.

1-(4-Bromophenyl)-1-phenyl-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (84c). The same procedure was repeated as described for **84a** except that 0.262 g (1.00 mmol) of **82c** was treated with **83** derived from 0.222 g (1.08 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.43 mL of a 2.5 M solution of *n*-butyllithium (1.08 mmol) in hexanes to afford **84c** (0.401 g, 0.86 mmol, 86% yield) as a viscous liquid: IR 3451, 2217 cm⁻¹; ¹H δ 7.76–7.68 (2 H, m), 7.64–7.51 (4 H, m), 7.40–7.23 (12 H, m), 2.99 (1 H, s); ¹³C δ 144.4, 144.0, 132.2, 132.0, 131.7, 131.3, 128.6, 128.4, 128.3, 128.0, 127.9, 126.0, 124.5, 122.8, 121.7, 94.8, 93.5, 88.0, 86.2, 74.6.

1-(4-Methoxyphenyl)-1-phenyl-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (84d). The same procedure was repeated as described for **84a** except that 0.255 g (1.20 mmol) of **82d** was treated with **83** derived from 0.267 g (1.32 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.52 mL of a 2.5 M solution of *n*-butyllithium (1.32 mmol) in hexanes to afford **84d** (0.367 g, 0.89 mmol, 74% yield) as a viscous liquid: IR 3446, 2219 cm⁻¹; ¹H δ 7.76–7.70 (2 H, m), 7.65 (2 H, d, *J* = 8.9 Hz), 7.59–7.51 (2 H, m), 7.42–7.22 (10 H, m), 6.73 (2 H, d, *J* = 8.9 Hz), 3.72 (3 H, s), 2.90 (1 H, s); ¹³C δ 159.0, 145.1, 137.2,

132.2, 132.0, 131.8, 128.4, 128.33, 128.27, 128.22, 128.0, 127.54, 127.49, 126.0, 125.9, 124.9, 122.9, 113.5, 95.8, 93.4, 88.1, 85.7, 74.7, 55.2.

7-Bromo-10-(4-bromophenyl)-5-phenyl-11H-benzo[*b*]fluoren-11-ol (90b). The same procedure was repeated as described for **90a** except that 0.463 g (0.85 mmol) of **84b** was treated with a mixture of 0.07 mL of thionyl chloride (0.96 mmol) and 0.16 mL of pyridine (1.92 mmol) to afford **90b** (0.296 g, 0.55 mmol, 65% yield) as a yellow solid: IR 3409, 762, 703 cm^{-1} ; ^1H δ 7.75–7.61 (6 H, m), 7.51 (1 H, d, $J = 7.5$ Hz), 7.44–7.34 (6 H, m), 7.24 (1 H, td, $J = 7.5$ and 1.0 Hz), 7.06 (1 H, t, $J = 7.2$ Hz), 6.33 (1 H, d, $J = 7.9$ Hz), 5.73 (1 H, s), 1.80 (1 H, br s); ^{13}C δ 145.7, 141.3, 139.3, 137.6, 136.3, 136.1, 135.6, 135.5, 132.9, 132.6, 132.3, 131.7, 130.8, 130.7, 129.9, 129.8, 129.42, 129.39, 129.2, 129.1, 128.7, 128.5, 128.3, 127.6, 125.2, 123.8, 122.3, 121.0, 73.3.

7-Bromo-5,10-diphenyl-11H-benzo[*b*]fluoren-11-ol (90c) and 10-(4-Bromophenyl)-5-phenyl-11H-benzo[*b*]fluoren-11-ol (90c'). The same procedure was repeated as described for **90a** except that 0.372 g (0.80 mmol) of **84c** was treated with a mixture of 0.07 mL of thionyl chloride (0.96 mmol) and 0.16 mL of pyridine (1.92 mmol) to afford **90c** (0.138 g, 0.30 mmol, 37% yield) and **90c'** (0.103 g, 0.22 mmol, 28% yield) as yellow solids. **90c:** IR 3429, 701 cm^{-1} ; ^1H δ 7.70–7.40 (14 H, m), 7.24 (1 H, td, $J = 7.5$ and 1 Hz), 7.06 (1 H, t, $J = 7.5$ Hz), 6.34 (1 H, d, $J = 7.7$ Hz), 5.80 (1 H, s), 1.87 (1 H, br s); ^{13}C δ 145.7, 141.4, 139.5, 137.7, 137.1, 136.6, 136.3, 135.5, 132.6, 130.9, 130.7, 130.0, 129.8, 129.4, 129.3, 129.05, 128.96, 128.94, 128.63, 128.56, 128.35, 128.25, 128.16, 127.9, 125.2, 123.8, 120.8, 73.4. **90c':** IR 3429, 702 cm^{-1} ; ^1H δ 7.73 (2 H, d, $J = 8.7$ Hz), 7.65–7.37 (12 H, m), 7.23 (1 H, td, $J = 7.3$ and 1 Hz), 7.06 (1 H, t, $J = 7.3$ Hz), 6.38 (1 H, d, $J = 7.9$ Hz), 5.76 (1 H, s), 1.77 (1 H, br s); ^{13}C δ 145.7, 140.9, 139.8, 138.4, 136.7,

135.6, 135.1, 134.2, 133.8, 132.7, 132.3, 132.2, 131.6, 130.9, 130.0, 129.9, 129.21, 129.18, 129.0, 128.1, 128.0, 126.7, 126.2, 125.9, 125.2, 123.7, 122.1, 73.4.

7-Methoxy-5,10-diphenyl-11*H*-benzo[*b*]fluoren-11-ol (90d) and 10-(4-Methoxyphenyl)-5-phenyl-11*H*-benzo[*b*]fluoren-11-ol (90d'). The same procedure was repeated as described for **90a** except that 0.348 g (0.84 mmol) of **84d** was treated with a mixture of 0.07 mL of thionyl chloride (0.96 mmol) and 0.16 mL of pyridine (1.92 mmol) to afford **90d** (0.157 g, 0.38 mmol, 45% yield) and **90d'** (0.087 g, 0.21 mmol, 25% yield) as yellow solids. **90d**: IR 3453, 702 cm^{-1} ; ^1H δ 7.66–7.43 (12 H, m), 7.22 (1 H, t, $J = 7.5$ Hz), 7.08–7.01 (2 H, m), 6.87 (1 H, d, $J = 2.6$ Hz), 6.37 (1 H, d, $J = 7.9$ Hz), 5.80 (1 H, s), 3.70 (3 H, s), 1.86 (1 H, br s); ^{13}C δ 157.8, 145.9, 140.0, 138.9, 138.7, 137.8, 136.5, 135.7, 135.5, 132.4, 130.7, 130.0, 129.9, 129.28, 129.26, 129.23, 129.1, 128.7, 128.5, 127.92, 127.90, 127.7, 125.2, 123.6, 117.4, 105.8, 73.4, 55.1. **90d'**: IR 3453, 765, 703 cm^{-1} ; ^1H δ 7.70–7.36 (12 H, m), 7.23 (1 H, t, $J = 7.5$ Hz), 7.15 (2 H, d, $J = 8.7$ Hz), 7.06 (1 H, t, $J = 7.5$ Hz), 6.38 (1 H, d, $J = 7.7$ Hz), 5.84 (1 H, s), 3.94 (3 H, s), 1.95 (1 H, br s); ^{13}C δ 159.3, 145.6, 141.3, 140.0, 138.6, 136.3, 135.1, 134.2, 133.4, 132.7, 131.9, 130.3, 130.1, 130.0, 129.6, 129.2, 129.1, 128.8, 128.0, 127.9, 126.6, 126.1, 126.0, 125.6, 125.2, 123.6, 114.8, 114.0, 73.5, 55.4.

1-(2,6-Difluorophenyl)-1-phenyl-3-[2-(phenylethynyl)phenyl]-2-propyn-1-ol (84e).

The same procedure was repeated as described for **84a** except that 0.234 g (1.07 mmol) of **82e** was treated with **83** derived from 0.240 g (1.19 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.47 mL of a 2.5 M solution of *n*-butyllithium (1.18 mmol) in hexanes to afford **84e** (0.422 g, 1.00 mmol, 94% yield) as a viscous liquid: IR 3555, 2218 cm^{-1} ; ^1H δ 7.84–7.79 (2 H, m), 7.58–7.53 (2 H, m), 7.45–7.39 (2 H, m), 7.37–7.15 (9 H, m),

6.82 (2 H, t, $J = 8.5$ Hz), 3.58 (1 H, br s); ^{13}C δ 160.1 (dd, $J = 251.5$ and 6.5 Hz), 143.4, 132.3, 131.9, 131.8, 129.5 (t, $J = 11.4$ Hz), 128.5, 128.3, 128.24, 128.19, 128.14, 127.9, 126.0, 125.9, 124.7, 123.0, 120.7 (t, $J = 12.2$ Hz), 112.6 (d, $J = 26.9$ Hz), 93.4, 93.3, 87.8, 85.6, 72.5; MS m/z 420 (M^+), 343, 315, 279, 141; HRMS calcd for $\text{C}_{29}\text{H}_{18}\text{F}_2\text{O}$ 420.1326, found 420.1335.

10-(2,6-Difluorophenyl)-5-phenyl-11H-benzo[*b*]fluoren-11-ol (90e) and 9-Fluoro-5,10-diphenyl-11H-benzo[*b*]fluoren-11-one (90e'). The same procedure was repeated as described for **90a** except that 0.420 g (1.00 mmol) of **84e** was treated with a mixture of 0.08 mL of thionyl chloride (1.10 mmol) and 0.18 mL of pyridine (2.20 mmol) to afford **90e** (0.220 g, 0.52 mmol, 52% yield) and **90e'** (0.150 g, 0.37 mmol, 37% yield) as yellow solids. **90e**: IR 3422, 764, 702 cm^{-1} ; ^1H δ 7.7–7.4 (11 H, m), 7.27–7.12 (3 H, m), 7.09 (1 H, t, $J = 7.5$ Hz), 6.42 (1 H, d, $J = 7.7$ Hz), 5.69 (1 H, s), 1.81 (1 H, br s); ^{13}C δ 161.3 (dd, $J = 247.4$ and 7.3 Hz), 160.1 (dd, $J = 247.3$ and 7.2 Hz), 146.1, 142.7, 139.6, 138.3, 135.1, 134.7, 134.2, 132.1, 130.2 (t, $J = 9.8$ Hz), 130.0, 129.8, 129.17, 129.14, 129.0, 128.1, 128.0, 126.9, 126.35, 126.26, 125.2, 125.0, 124.3, 123.6, 114.4 (t, $J = 22.0$ Hz), 111.8 (dd, $J = 22.5$ and 3.6 Hz), 111.4 (dd, $J = 22.5$ and 3.6 Hz), 74.1; MS m/z 420 (M^+), 403, 343, 307; HRMS calcd for $\text{C}_{29}\text{H}_{18}\text{F}_2\text{O}$ 420.1326, found 420.1311. **90e'**: IR 1713, 776, 699 cm^{-1} ; ^1H δ 7.7–7.24 (13 H, m), 7.22–7.16 (2 H, m), 7.02 (1 H, ddd, $J = 12.6$, 7.4 and 1.4 Hz), 6.26 (1 H, dd, $J = 6.2$ and 1.8 Hz); ^{13}C δ 191.8, 161.8 (d, $J = 259.4$ Hz), 143.5, 138.7, 138.6, 138.4, 138.3, 137.9, 137.5, 136.6, 136.11, 136.08, 134.4, 134.00, 133.97, 129.6, 129.5, 129.4, 129.1, 128.9, 128.5, 127.8, 127.7, 127.6, 127.3, 123.9 ($J = 6.2$ Hz), 123.4 ($J = 4.1$ Hz), 122.9 ($J = 8.3$ Hz), 112.9 ($J = 22.8$ Hz); MS m/z 400 (M^+), 383, 368, 350; HRMS calcd for $\text{C}_{29}\text{H}_{17}\text{FO}$ 400.1263, found 400.1248.

5-[[2-(Phenylethynyl)phenyl]ethynyl]-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (97). The same procedure was repeated as described for **84a** except that 0.206 g **96** (1.00 mmol) was treated with **83** derived from 0.202 g (1.00 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.40 mL of a 2.5 M solution of *n*-butyllithium (1.00 mmol) in hexanes to afford **97** (0.394 g, 0.97 mmol, 97% yield) as a white solid: mp 134–135 °C; IR 3543, 2219 cm⁻¹; ¹H δ 8.26 (2 H, d, *J* = 6.9 Hz), 7.55 (1 H, dd, *J* = 6.9 and 1.8 Hz), 7.51 (1 H, dd, *J* = 6.9 and 1.8 Hz), 7.40–7.24 (13 H, m), 7.18 (2 H, s), 3.23 (1 H, s); ¹³C δ 140.2, 132.6, 132.3, 131.9, 131.8, 131.4, 129.2, 128.3, 128.2, 127.9, 127.1, 125.8, 124.8, 124.2 (br), 122.9, 94.2, 93.4, 88.1, 84.6 (br), 73.4 (br); MS *m/z* 408 (M⁺), 389, 331, 202; HRMS calcd for C₃₁H₂₀O 408.1514, found 408.1513. The broad ¹³C NMR signals at δ 124.2, 84.6, and 73.4 suggest a relatively slow conformational inversion of the central seven-membered ring.

Propargylic Alcohol 104. The same procedure was repeated as described for **84a** except that 0.289 g **103** (0.98 mmol) was treated with **83** derived from 0.213 g (1.05 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.42 mL of a 2.5 M solution of *n*-butyllithium (1.05 mmol) in hexanes to afford **104** (0.354 g, 0.71 mmol, 73% yield) as a white solid: IR 3446, 2215 cm⁻¹; ¹H δ 8.25 (1 H, br s), 7.91 (1 H, d, *J* = 6.7 Hz), 7.82–7.74 (2 H, m), 7.60–7.16 (13 H, m), 4.4 (1 H, br), 3.7 (3 H, br), 3.27 (1 H, s), 1.15 (3 H, s), 1.03 (3 H, s); ¹³C δ 136.0 (br), 134.1, 134.0, 132.3, 131.8, 131.7, 129.2, 129.1, 128.4, 128.3, 128.1, 127.7, 127.1, 127.0, 126.0, 125.0, 124.8, 123.5, 123.0, 99.4, 93.4, 93.1, 88.0, 85.5 (br), 75.1, 72.6 (br), 71.5 (br), 31.8, 24.5, 24.1. The broad ¹H NMR signals at δ 8.25, 4.4, and 3.7 and the ¹³C NMR signals at δ 136.0, 85.5, 72.6, and 71.5 suggest a relatively slow interconversion of the conformational isomers.

Propargylic Alcohol 107. The same procedure was repeated as described for **84a** except that 0.481 g (1.91 mmol) of **106** was treated with **83** derived from 0.466 g (2.30 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.92 mL of a 2.5 M solution of *n*-butyllithium (2.30 mmol) in hexanes to afford **107** (0.764 g, 1.68 mmol, 88% yield) as a white solid: IR 3456, 2215 cm^{-1} ; ^1H δ 8.13 (1 H, dd, $J = 7.7$ and 1.2 Hz), 7.78 (2 H, t, $J = 7.7$ Hz), 7.61 (1 H, dd, $J = 7.4$ and 1.2 Hz), 7.55–7.22 (12 H, m), 7.17 (1 H, td, $J = 7.5$ and 1.2 Hz), 4.49 (1 H, q, $J = 6.6$ Hz), 4.39–4.32 (1 H, m), 4.30–4.22 (1 H, m), 4.10 (1 H, q, $J = 6.8$ Hz), 3.04 (1 H, s); ^{13}C δ 135.7, 134.9, 133.4, 132.3, 132.1, 131.90, 131.86, 129.6, 129.5, 128.5, 128.4, 128.32, 128.26, 128.0, 127.83, 127.77, 126.0, 125.2, 124.8, 124.2, 124.0, 123.0, 109.4, 93.5, 92.3, 87.9, 85.1, 74.6, 67.3, 66.6.

1*H*-Cyclobut[*a*]indene 105. The same procedure was repeated as described for **90a** except that 0.159 g of the alcohol **104** (0.320 mmol) was used to afford **105**⁹⁵ (0.131 g, 0.255 mmol, 80% yield) as an orange solid: mp 185–187 °C; IR 1206, 758, 689 cm^{-1} ; ^1H δ 8.1–7.9 (5 H, m), 7.80 (1 H, d, $J = 7.3$ Hz), 7.57 (1 H, td, $J = 7.6$ and 1.4 Hz), 7.5–7.13 (10 H, m), 3.60 (1 H, d, $J = 11.3$ Hz), 3.46 (1 H, d, $J = 11.3$ Hz), 3.37 (2 H, s), 0.99 (3 H, s), 0.70 (3 H, s); ^{13}C δ 148.9, 145.7, 139.6, 136.4, 134.9, 134.8, 133.3, 133.0, 129.82, 129.76, 129.4, 129.3, 128.8, 128.6, 128.0, 127.9, 127.7, 127.2, 126.8, 125.1, 124.7, 123.9, 123.6, 120.0, 111.3, 99.6, 71.7, 70.9, 68.1, 33.3, 24.9, 24.8; MS m/z 514 (M^+), 479, 428, 393, 365; HRMS calcd for $\text{C}_{35}\text{H}_{27}\text{ClO}_2$ 514.1700, found 514.1695. Anal. Calcd for $\text{C}_{35}\text{H}_{27}\text{ClO}_2$: C, 81.62; H, 5.28; Cl, 6.88. Found: C, 81.83; H, 5.53; Cl, 6.71. The broad ^1H NMR signal at δ 8.0 suggests a somewhat restricted rotation of the phenyl substituent and/or a relatively slow interconversion of the conformational isomers.

1H-Cyclobut[a]indene 108 and Alcohol 109. The same procedure was repeated as described for **90a** except that 0.123 g (0.27 mmol) of **107** was used to afford **108**⁹⁵ (0.044 g, 0.093 mmol, 34% yield) as an orange solid and **109** (0.043 g, 0.095 mmol, 35% yield) as a yellow solid. **108**: mp 246–247 °C; IR 1201, 734, 689 cm⁻¹; ¹H δ 7.94 (2 H, d, *J* = 7.7 Hz), 7.81–7.73 (3 H, m), 7.62 (1 H, dd, *J* = 7.7 and 1.3 Hz), 7.55 (1 H, td, *J* = 7.7 and 1.4 Hz), 7.43–7.17 (10 H, m), 4.14 (1 H, dt, *J* = 7.3 and 4.8 Hz), 3.95–3.88 (2 H, m), 3.83–3.75 (1 H, m); ¹³C δ 148.9, 147.4, 146.0, 139.4, 136.2, 134.3, 132.9, 132.7, 129.71, 129.66, 129.3, 128.8, 128.7, 128.24, 128.19, 128.0, 124.8, 124.63, 124.55, 124.0, 123.9, 120.1, 111.4, 108.0, 67.4, 66.7, 65.2; MS *m/z* 472 (M⁺), 437, 427, 393, 365; HRMS calcd for C₃₂H₂₁ClO₂ 472.1230, found 472.1235. **109**: IR 3492, 760 cm⁻¹; ¹H δ 8.22 (1 H, dd, *J* = 6.0 and 2.2 Hz), 8.13 (1 H, d, *J* = 7.7 Hz), 7.77 (1 H, dd, *J* = 7.6 and 1.5 Hz), 7.70 (1 H, d, *J* = 7.1 Hz), 7.63–7.38 (9 H, m), 7.28 (1 H, t, *J* = 7.3 Hz), 7.05 (1 H, t, *J* = 7.3 Hz), 6.30 (1 H, d, *J* = 7.7 Hz), 6.06 (1 H, d, *J* = 1.6 Hz), 4.97 (1 H, d, *J* = 2.0 Hz), 4.76–4.69 (2 H, m), 4.21–4.05 (2 H, m); ¹³C δ 145.1, 142.9, 139.3, 138.4, 137.3, 135.3, 134.8, 134.0, 133.1, 130.1, 129.7, 129.2, 129.15, 129.10, 128.7, 128.2, 128.0, 127.5, 127.3, 126.8, 126.4, 125.2, 124.7, 124.4, 123.6, 121.2, 107.1, 73.2, 67.3, 62.8.

4,4-Dimethyl-3-phenyl-1-[2-(2-phenylethynyl)phenyl]-1-pentyn-3-ol (111). The same procedure was repeated as described for **84a** except that **83** derived from 0.468 g of 1-(2-ethynylphenyl)-2-phenylethyne (2.31 mmol) and 0.341 g of 2,2-dimethylpropiophenone (**110**, 2.10 mmol) were used to afford **111** (0.722 g, 1.98 mmol, 94% yield) as a viscous liquid: IR (neat) 3562, 2215 cm⁻¹; ¹H δ 7.77–7.72 (2 H, m), 7.58–7.43 (4 H, m), 7.35–7.22 (8 H, m), 2.38 (1 H, s), 1.09 (9 H, s); ¹³C δ 142.0, 132.2, 132.1, 131.7, 128.4, 128.2,

128.0, 127.9, 127.8, 127.3, 127.0, 125.8, 125.1, 123.0, 96.3, 93.2, 88.3, 84.5, 79.5, 39.7, 25.6; MS m/z 364 (M^+), 349, 307.

10-(1,1-Dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluoren-11-ol (112) and 7-Chloro-1-(1,1-dimethylethyl)-1,2-diphenyl-1*H*-cyclobut[*a*]indene (113). The same procedure was repeated as described for **90a** except that 0.431 g (1.18 mmol) of **111** was used to afford **113**⁹⁵ (0.379 g, 0.99 mmol, 84% yield) as an orange solid and **112** (0.013 g, 0.036 mmol, 3% yield) as a yellow solid. **112**: IR 3372, 768, 702 cm^{-1} ; ^1H δ 8.59 (1 H, d, J = 8.9 Hz), 7.63–7.56 (4 H, m), 7.51 (1 H, dd, J = 8.3 and 1.6 Hz), 7.43 (1 H, td, J = 7.7 and 1.6 Hz), 7.39–7.29 (3 H, m), 7.22 (1 H, td, J = 7.5 and 1 Hz), 7.00 (1 H, td, J = 7.7 and 1 Hz), 6.33 (1 H, d, J = 10.1 Hz), 6.16 (1 H, d, J = 7.9 Hz), 1.95 (9 H, s), 1.83 (1 H, d, J = 10.1 Hz); ^{13}C δ 146.3, 144.7, 140.1, 139.2, 139.1, 135.9, 135.4, 133.2, 132.4, 130.2, 129.9, 129.3, 129.1, 128.7, 128.3, 127.83, 127.76, 127.3, 125.0, 124.5, 123.7, 74.2, 38.6, 33.4; MS m/z 364 (M^+), 331, 307; HRMS calcd for $\text{C}_{27}\text{H}_{24}\text{O}$ 364.1827, found 364.1816. **113**: mp 156–157 °C; IR 1203, 753, 691 cm^{-1} ; ^1H δ 8.01 (2 H, dd, J = 8.1 and 1.3 Hz), 7.66 (1 H, d, J = 7.5 Hz), 7.61–7.52 (4 H, m), 7.45 (2 H, t, J = 7.2 Hz), 7.37 (1 H, td, J = 7.5 and 1.1 Hz), 7.27 (2 H, t, J = 7.1 Hz), 7.20 (2 H, t, J = 7.3 Hz), 1.26 (9 H, s); ^{13}C δ 154.0, 148.5, 145.8, 143.2, 142.5, 135.0, 129.5, 129.2, 129.1, 128.9, 128.5, 128.4, 127.6, 126.4, 124.9, 123.4, 119.7, 112.5, 77.2, 37.1, 28.7; MS m/z 382 (M^+), 367, 347, 325, 289; HRMS calcd for $\text{C}_{27}\text{H}_{23}\text{Cl}$ 382.1488, found 382.1472. Anal. Calcd for $\text{C}_{27}\text{H}_{23}\text{Cl}$: C, 84.69; H, 6.05; Cl, 9.26. Found: C, 84.65; H, 6.20; Cl, 9.18.

2,3-Dihydro-2,2-dimethyl-1-[[2-(phenylethynyl)phenyl]ethynyl]-1*H*-inden-1-ol (116).

The same procedure was repeated as described for **84a** except that 0.447 g (2.79 mmol) of **114** was treated with **83** derived from 0.625 g (3.09 mmol) of 1-(2-ethynylphenyl)-2-

phenylethyne and 1.23 mL of a 2.5 M solution of *n*-butyllithium (3.08 mmol) in hexanes to afford **116** (0.906 g, 2.50 mmol, 90% yield) as a viscous liquid: IR 3442, 2216 cm^{-1} ; ^1H δ 7.67 (1 H, d, $J = 7.3$ Hz), 7.58–7.52 (2 H, m), 7.47–7.42 (2 H, m), 7.36–7.20 (7 H, m), 7.15 (1 H, t, $J = 7.0$ Hz), 3.03 (1 H, d, $J = 15.2$ Hz), 2.69 (1 H, d, $J = 15.2$ Hz), 2.25 (1 H, br s), 1.33 (3 H, s), 1.22 (3 H, s); ^{13}C δ 145.4, 142.4, 132.1, 131.9, 131.6, 128.6, 128.2, 128.1, 128.0, 127.8, 126.7, 125.7, 125.1, 125.0, 124.1, 122.9, 93.2, 92.7, 88.1, 85.4, 81.7, 48.8, 44.3, 26.2, 21.3.

1,2,3,4-Tetrahydro-2,2-dimethyl-1-[[2-(phenylethynyl)phenyl]ethynyl]-1-

naphthalenol (117). The same procedure was repeated as described for **84a** except that 0.348 g (2.00 mmol) of **115** was treated with **83** derived from 0.464 g (2.29 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne and 0.91 mL of a 2.5 M solution of *n*-butyllithium (2.28 mmol) in hexanes to afford **117** (0.720 g, 1.91 mmol, 96% yield) as a viscous liquid: IR 3561, 2216 cm^{-1} ; ^1H δ 8.01 (1 H, d, $J = 7.7$ Hz), 7.56–7.49 (2 H, m), 7.46–7.40 (2 H, m), 7.35–7.24 (5 H, m), 7.20 (1 H, t, $J = 7.3$ Hz), 7.12–7.05 (2 H, m), 2.9–2.82 (2 H, m), 2.32 (1 H, s), 2.12–1.99 (1 H, m), 1.77–1.67 (1 H, m), 1.24 (3 H, s), 1.17 (3 H, s); ^{13}C δ 138.6, 134.8, 132.1, 131.9, 131.6, 128.8, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 126.3, 125.6, 125.1, 122.9, 95.3, 93.1, 88.2, 84.9, 75.1, 37.5, 31.0, 25.6, 23.7; MS m/z 376 (M^+), 361, 320.

2,11-Dihydro-1,1-dimethyl-6-phenyl-1H-indeno[1,7-*ab*]fluoren-11-ol (118) and 1H-

Cyclobut[*a*]indene 120. The same procedure was repeated as described for **90a** except that 0.276 g of **116** (0.760 mmol) was used to afford **118** (0.213 g, 0.588 mmol, 77% yield) as a yellow solid and **120** (0.017 g, 0.045 mmol, 6% yield) as an orange solid. **118**: mp 140–142 $^{\circ}\text{C}$; IR 3389, 780, 763, 741, 703 cm^{-1} ; ^1H δ 7.63 (1 H, d, $J = 7.5$ Hz),

7.6–7.53 (3 H, m), 7.47–7.35 (3 H, m), 7.29–7.19 (3 H, m), 7.04 (1 H, t, $J = 7.6$ Hz), 6.46 (1 H, d, $J = 7.9$ Hz), 5.96 (1 H, d, $J = 10.3$ Hz), 3.35 (2 H, s), 1.88 (1 H, d, $J = 10.3$ Hz), 1.77 (3 H, s), 1.74 (3 H, s); ^{13}C δ 150.5, 146.5, 143.6, 140.1, 138.3, 137.3, 135.5, 132.3, 131.0, 130.1, 129.9, 129.0, 128.8, 128.2, 127.8, 127.7, 125.0, 123.6, 121.6, 119.7, 73.0, 48.9, 45.0, 31.6, 26.5; MS m/z 362 (M^+), 347, 345, 329; HRMS calcd for $\text{C}_{27}\text{H}_{22}\text{O}$ 362.1671, found 362.1657. Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{O}$: C, 89.47; H, 6.12. Found: C, 89.32; H, 6.12. **120**: IR 1200, 752, 738, 688 cm^{-1} ; ^1H δ 7.76 (1 H, d, $J = 7.5$ Hz), 7.48 (1 H, dm, $J = 7.5$ and 1 Hz), 7.43 (1 H, td, $J = 7.7$ and 1 Hz), 7.36–7.24 (8 H, m), 7.20–7.10 (2 H, m), 3.23 (1 H, d, $J = 15.8$ Hz), 3.02 (1 H, d, $J = 16.0$ Hz), 1.32 (3 H, s), 1.17 (3 H, s); ^{13}C δ 153.0, 149.3, 145.8, 144.9, 141.4, 140.7, 133.9, 129.6, 129.0, 128.9, 128.1, 127.9, 127.1, 125.4, 125.1, 124.6, 123.5, 119.9, 111.1, 75.5, 47.3, 45.6, 28.7, 24.5; MS m/z 380 (M^+), 365, 345, 330; HRMS calcd for $\text{C}_{27}\text{H}_{21}\text{Cl}$ 380.1332, found 380.1344.

Alcohol 119 and 1H-Cyclobut[a]indene 121. The same procedure was repeated as described for **90a** except that 0.187 g (0.496 mmol) of **117** was treated with a mixture of 0.071 g of thionyl chloride (0.60 mmol) and 0.10 mL of pyridine (1.2 mmol) to afford **119** (0.105 g, 0.28 mmol, 56% yield) as a yellow solid and **121** (0.063 g, 0.16 mmol, 32% yield) as an orange solid. **119**: IR 3406, 703 cm^{-1} ; ^1H δ 7.62–7.56 (4 H, m), 7.41–7.28 (5 H, m), 7.23 (1 H, td, $J = 7.4$ and 1.0 Hz), 7.02 (1 H, td, $J = 7.7$ and 1.0 Hz), 6.20 (1 H, d, $J = 7.9$ Hz), 6.16 (1 H, br s), 3.43 (1 H, td, $J = 15.1$ and 4.8 Hz), 3.10 (1 H, ddd, $J = 16.6$, 4.7, and 2.9 Hz), 2.13 (1 H, td, $J = 13.3$ and 4.5 Hz), 1.95 (3 H, s), 1.94–1.87 (2 H, m), 1.59 (3 H, s); ^{13}C δ 146.5, 142.6, 139.5, 139.3, 138.0, 136.4, 135.6, 134.8, 132.9, 130.1, 129.9, 129.6, 129.2, 129.1, 128.7, 127.8, 127.7, 125.3, 125.00, 124.97, 124.5, 123.6, 74.4, 40.3, 36.5, 29.0, 28.7, 27.9; MS m/z 376 (M^+), 343, 320; HRMS calcd for

C₂₈H₂₄O 376.1827, found 376.1823. **121**: IR 1426, 1200 cm⁻¹; ¹H δ 7.75 (1 H, d, *J* = 7.5 Hz), 7.49–7.42 (4 H, m), 7.40–7.31 (3 H, m), 7.30–7.22 (2 H, m), 7.22–7.17 (2 H, m), 7.08 (1 H, td, *J* = 7.3 and 1 Hz), 3.20–2.99 (2 H, m), 2.07–1.86 (2 H, m), 1.21 (3 H, s), 1.07 (3 H, s); ¹³C δ 153.3, 148.9, 145.6, 142.6, 137.8, 135.3, 134.3, 129.7, 129.4, 129.0, 128.9, 128.7, 128.3, 126.8, 126.4, 124.6, 123.4, 119.8, 110.7, 68.8, 35.6, 34.5, 27.4, 26.2, 25.6; MS *m/z* 394 (M⁺), 359, 338; HRMS calcd for C₂₈H₂₃Cl 394.1488, found 394.1471.

4,4-Dimethyl-3-phenyl-1-[2-(2-phenylethynyl)phenyl]-1-pentyne (122). The following procedure is representative for the preparation of the diacetylenic hydrocarbons from the diacetylenic propargylic alcohols. To a mixture of the alcohol **111** (0.250 g, 0.686 mmol) and triethylsilane (0.120 g, 1.03 mmol) in 6 mL of methylene chloride was added 0.21 mL of trifluoroacetic acid (0.313 g, 2.74 mmol). After 5 min of stirring at room temperature, 0.290 g of sodium carbonate (2.74 mmol) was added followed by 10 mL of water and 40 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes, *R_f* = 0.64) provided 0.230 g (0.660 mmol, 96% yield) of **122** as a yellow liquid: IR 2215, 755, 701, 690 cm⁻¹; ¹H δ 7.56–7.51 (1 H, m), 7.49–7.40 (5 H, m), 7.34–7.18 (8 H, m), 3.70 (1 H, s), 1.05 (9 H, s); ¹³C δ 139.2, 132.13, 132.07, 131.7, 129.8, 128.2, 127.9, 127.6, 127.3, 126.6, 126.3, 125.6, 123.3, 95.7, 92.8, 88.6, 82.4, 50.6, 35.5, 27.8; MS *m/z* 348 (M⁺), 333, 318, 291; HRMS calcd for C₂₇H₂₄ 348.1878, found 348.1870.

10-(1,1-Dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluorene (126). The following procedure is representative for the preparation of the polycyclic aromatic hydrocarbons from the diacetylenic hydrocarbons. To 0.224 g of **122** (0.643 mmol) in 10 mL of

anhydrous toluene under a nitrogen atmosphere were added 0.70 mL of a 1.0 M solution of potassium *tert*-butoxide in THF (0.70 mmol) and 0.5 mL of *tert*-butanol. The reaction mixture was heated under reflux for 6 hours. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 40 mL of diethyl ether were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.73) provided 0.202 g (0.580 mmol, 90% yield) of **126** as a yellow solid: mp 144–145 °C; IR 907, 764, 730, 702 cm^{-1} ; ^1H δ 8.62 (1 H, d, J = 8.7 Hz), 7.65–7.27 (9 H, m), 7.20 (1 H, td, J = 7.3 and 0.8 Hz), 6.96 (1 H, t, J = 7.4 Hz), 6.26 (1 H, d, J = 7.9 Hz), 4.51 (2 H, s), 1.92 (6 H, s); ^{13}C δ 144.2, 141.0, 140.3, 139.8, 138.1, 137.5, 134.5, 133.1, 131.3, 130.2, 129.2, 127.9, 127.6, 127.5, 126.8, 126.2, 124.1, 123.9, 123.6, 123.3, 40.2, 38.9, 34.3; MS m/z 348 (M^+), 333, 291; HRMS calcd for $\text{C}_{27}\text{H}_{24}$ 348.1878, found 348.1866. Anal. Calcd for $\text{C}_{27}\text{H}_{24}$: C, 93.06; H, 6.94. Found: C, 92.78; H, 6.93.

Diacetylene 127. The same procedure was repeated as described for **122** except that 0.169 g (0.47 mmol) of **116** was treated with 0.065 g of triethylsilane (0.56 mmol) and 0.212 g of trifluoroacetic acid (1.86 mmol) in 5 mL of methylene chloride to afford **127** (0.158 g, 0.46 mmol, 98% yield) as a viscous liquid: IR 2217, 756, 690 cm^{-1} ; ^1H δ 7.60–7.50 (3 H, m), 7.49–7.45 (2 H, m), 7.35–7.28 (5 H, m), 7.23–7.19 (2 H, m), 7.18–7.10 (1 H, m), 4.10 (1 H, s), 2.87 (1 H, d, J = 15.2 Hz), 2.76 (1 H, d, J = 15.2 Hz), 1.40 (3 H, s), 1.18 (3 H, s); ^{13}C δ 143.0, 142.1, 132.1, 132.0, 131.7, 128.2, 127.9, 127.4, 126.9, 126.5, 126.2, 125.7, 124.7, 124.6, 123.3, 92.9, 92.8, 88.5, 83.2, 49.1, 46.6, 45.7, 27.4, 24.2.

Diacetylene 128: The same procedure was repeated as described for **122** except that 0.150 g **117** (0.400 mmol) was treated with 0.070 g of triethylsilane (0.60 mmol) and 0.182 g of trifluoroacetic acid (1.60 mmol) in 5 mL of methylene chloride to afford **128** (0.141 g, 0.39 mmol, 98% yield) as a viscous liquid: IR 2216, 755, 690 cm^{-1} ; ^1H δ 7.72 (1 H, d, $J = 7.7$ Hz), 7.56–7.49 (2 H, m), 7.48–7.42 (2 H, m), 7.34–7.24 (5 H, m), 7.17–7.00 (3 H, m), 3.81 (1 H, s), 2.95–2.74 (2 H, m), 1.84 (1 H, ddd, $J = 13.2, 6.1$, and 4.8 Hz), 1.63 (1 H, ddd, $J = 13.3, 9.7$, and 6.7 Hz), 1.23 (3 H, s), 1.11 (3 H, s); ^{13}C δ 135.5, 134.9, 132.2, 132.0, 131.7, 129.6, 128.7, 128.2, 127.9, 127.4, 126.3, 126.0, 125.6, 123.3, 95.1, 92.8, 88.6, 82.9, 44.7, 35.1, 33.3, 29.1, 26.1, 22.6.

2,11-Dihydro-1,1-dimethyl-6-phenyl-1H-indeno[1,7-*ab*]fluorene (129). The same procedure was repeated as described for **126** except that 0.149 g (0.43 mmol) of **127** was treated with a mixture of 0.56 mL of a 1.0 M solution of potassium *tert*-butoxide (0.56 mmol) in THF and 0.5 mL of *tert*-butanol in 10 mL of anhydrous toluene to afford **129** (0.136 g, 0.39 mmol, 91% yield) as a yellow solid: mp 135–136 $^{\circ}\text{C}$; IR 1460, 773, 702 cm^{-1} ; ^1H δ 7.70–7.58 (4 H, m), 7.56–7.51 (2 H, m), 7.48–7.41 (1 H, m), 7.39–7.27 (3 H, m), 7.11 (1 H, t, $J = 7.6$ Hz), 6.73 (1 H, d, $J = 7.7$ Hz), 4.25 (2 H, s), 3.44 (2 H, s), 1.72 (6 H, s); ^{13}C δ 147.1, 144.2, 142.8, 141.5, 139.7, 138.8, 136.4, 133.0, 131.0, 130.6, 130.2, 128.9, 127.5, 127.3, 126.8, 126.4, 124.9, 123.7, 121.4, 119.1, 48.5, 44.3, 33.7, 28.0; MS m/z 346 (M^+), 331, 315; HRMS calcd for $\text{C}_{27}\text{H}_{22}$ 346.1722, found 346.1716.

Hydrocarbon 130. The same procedure was repeated as described for **126** except that 0.054 g (0.15 mmol) of **128** was treated with a mixture of 0.18 mL of a 1.0 M solution of potassium *tert*-butoxide (0.18 mmol) in THF and 0.5 mL of *tert*-butanol in 10 mL anhydrous toluene to afford **130** (0.046 g, 0.13 mmol, 86% yield) as a yellow solid: mp

180–181 °C; IR 1384, 775, 702 cm^{-1} ; ^1H δ 7.65–7.52 (4 H, m), 7.42–7.37 (3 H, m), 7.31–7.20 (3 H, m), 7.01 (1 H, t, J = 7.6 Hz), 6.36 (1 H, d, J = 7.9 Hz), 4.38 (2 H, s), 3.23 (2 H, t, J = 6.4 Hz), 2.08 (2 H, t, J = 6.5 Hz), 1.67 (6 H, s); ^{13}C δ 144.2, 140.8, 139.8, 138.9, 137.9, 136.7, 135.6, 133.5, 132.6, 130.2, 129.1, 128.9, 127.5, 126.8, 126.3, 124.8, 124.4, 124.2, 124.0, 123.6, 40.3, 38.6, 36.0, 28.8, 28.0; MS m/z 360 (M^+), 345, 304.

Diacetylene 131. The same procedure was repeated as described for **122** except that 0.409 g (1.00 mmol) of **97** was used to afford **131** (0.382 g, 0.973 mmol, 97% yield) as a light yellow solid: mp 45–47 °C; IR 2215, 796, 757, 690 cm^{-1} ; ^1H δ 8.12 (2 H, br), 7.63 (2 H, br m), 7.49 (2 H, d, J = 7.3 Hz), 7.40–7.18 (11 H, m), 7.16 (2 H, s), 4.81 (1 H, s); ^{13}C δ 137.5, 134.0, 132.2, 132.1, 131.9, 131.3, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 126.2, 125.9, 125.8, 125.6, 123.0, 93.3, 92.1, 88.5, 86.0 (br), 40.8 (br); MS m/z 392 (M^+), 391, 315. The broad ^1H NMR signals at δ 8.12 and 7.63 and the ^{13}C NMR signals at δ 86.0 and 40.8 suggest a relatively slow conformational inversion of the central seven-membered ring.

Hydrocarbon 132. The same procedure was repeated as described for **126** except that 0.099 g (0.25 mmol) of **131** was used to afford **132**⁹⁵ (0.080 g, 0.20 mmol, 81% yield) as a light yellow solid: mp 197–198 °C; IR 727, 703 cm^{-1} ; ^1H δ 7.67–7.55 (3 H, m), 7.50–7.27 (8 H, m), 7.25–7.17 (3 H, m), 7.00 (1 H, t, J = 7.7 Hz), 6.69 (1 H, d, J = 12.1 Hz), 6.62 (1 H, d, J = 11.9 Hz), 6.38 (1 H, d, J = 7.7 Hz), 4.63 (1 H, d, J = 22.6 Hz), 3.88 (1 H, d, J = 22.4 Hz); ^{13}C δ 144.0, 142.2, 140.8, 139.1, 139.0, 138.7, 137.9, 137.7, 136.0, 134.4, 134.1, 133.8, 133.6, 132.6, 130.5, 130.4, 129.9, 129.4, 129.3, 129.1, 128.7, 128.6, 127.9, 127.8, 127.1, 126.4, 125.1, 124.7, 124.3, 123.5, 38.4; MS m/z 392 (M^+), 315; HRMS calcd for $\text{C}_{31}\text{H}_{20}$ 392.1565, found 392.1571. Anal. Calcd for $\text{C}_{31}\text{H}_{20}$: C, 94.86; H,

5.14. Found: C, 94.56; H, 5.39. The observation of the two ^1H NMR signals at δ 4.63 and 3.88 attributable to the two hydrogens on the sp^3 carbon suggests a relatively slow interconversion of the two helical conformers of **132**. The relatively large geminal coupling constant of 22.5 Hz is consistent with the earlier report of $J = -22.3$ Hz for fluorene.⁹⁶

Diketone 137.⁴⁸ To a suspension of 4.52 g of $\text{CuBr}\cdot\text{SMe}_2$ (22.0 mmol) in 100 mL of THF was added 12.9 mL of a 1.7 M solution of *tert*-butyllithium (22.0 mmol) in pentane at $-50\text{ }^\circ\text{C}$. After 30 min of stirring, a solution of 2.03 g of terephthaloyl chloride (**136**, 10.0 mmol) in 40 mL of THF was introduced dropwise via cannula. After an additional four hours, the reaction mixture was allowed to warm to room temperature and then quenched with 50 mL a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 2.36 g of **137** (9.58 mmol, 96% yield) as a white solid: mp $83\text{--}84\text{ }^\circ\text{C}$ (lit.⁴⁸ mp $80.5\text{--}82\text{ }^\circ\text{C}$); IR 1672, 962 cm^{-1} ; ^1H δ 7.67 (4 H, s), 1.34 (18 H, s); ^{13}C δ 208.4, 140.2, 127.1, 44.0, 27.5; MS m/z 246 (M^+), 190, 189, 161.

Propargylic Alcohol 139a. The following procedure is representative for the preparation of the propargylic alcohols **139**. To 0.404 g (2.00 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne (**138a**) in 20 mL of THF under a nitrogen atmosphere at $0\text{ }^\circ\text{C}$ was added 0.80 mL of a 2.5 M solution of *n*-butyllithium (2.00 mmol) in hexanes. After 30 min of stirring, a solution of 0.223 g of **137** (0.90 mmol) in 40 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an

additional 2 hours, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/20% diethyl ether in hexanes) provided 0.540 g of **139a** (0.830 mmol, 92% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. **Diastereomer 1**: mp 177–178 °C; IR 3568, 3459, 2215 cm^{-1} ; ^1H δ 7.60 (4 H, s), 7.59–7.55 (2 H, m), 7.74–7.49 (2 H, m), 7.47–7.41 (4 H, m), 7.36–7.20 (10 H, m), 2.27 (2 H, s), 1.05 (18 H, s); ^{13}C δ 141.1, 132.2, 131.7, 128.4, 128.3, 128.1, 127.9, 126.5, 125.9, 125.2, 123.0, 96.3, 93.2, 88.3, 84.6, 79.4, 39.7, 25.6; MS m/z 673 (MNa^+), 633, 593, 576; HRMS calcd for $\text{C}_{48}\text{H}_{42}\text{O}_2\text{Na}$ (MNa^+) 673.3083, found 673.3114. **Diastereomer 2**: mp 189–190 °C; IR 3562, 3455, 2216 cm^{-1} ; ^1H δ 7.60 (4 H, s), 7.58–7.54 (2 H, m), 7.52–7.45 (6 H, m), 7.35–7.25 (10 H, m), 2.40 (2 H, s), 1.06 (18 H, s); ^{13}C δ 141.0, 132.2, 131.7, 128.4, 128.3, 128.0, 127.9, 126.5, 125.7, 125.1, 123.0, 96.2, 93.2, 88.3, 84.6, 79.4, 39.8, 25.6.

Propargylic Alcohol 139b. The same procedure was repeated as described for **139a** except that 0.123 g (0.50 mmol) of **137** was treated with the lithium acetylide derived from 0.343 g of **138b** (1.23 mmol) and 0.49 mL of a 2.5 M solution of *n*-butyllithium (1.23 mmol) in hexanes to afford 0.370 g of **139b** (0.461 mmol, 92% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. **Diastereomer 1**: mp 213–215 °C; IR 3568, 3456, 2215 cm^{-1} ; ^1H δ 7.73 (4 H, s), 7.58–7.48 (16 H, m), 7.42–7.32 (6 H, m), 7.31–7.22 (4 H, m), 2.37 (2 H, s), 1.08 (18 H, s); ^{13}C δ 141.1, 141.0, 140.1, 132.2, 132.1, 128.7, 128.1, 127.9, 127.5, 127.0, 126.9, 126.6, 125.8, 125.1, 121.8, 96.3, 93.2, 89.0, 84.7, 79.4, 39.7, 25.6; MS m/z

825 (MNa⁺), 785, 745, 728; HRMS calcd for C₆₀H₅₀O₂Na (MNa⁺) 825.3709, found 825.3729. **Diastereomer 2**: mp 258–259 °C; IR 3376, 2215 cm⁻¹; ¹H δ 7.62 (4 H, s), 7.58–7.50 (14 H, m), 7.49–7.38 (6 H, m), 7.36–7.23 (6 H, m), 2.37 (2 H, s), 1.04 (18 H, s); ¹³C δ 141.0, 140.2, 132.25, 132.17, 132.11, 128.8, 128.1, 127.9, 127.6, 126.97, 126.94, 126.5, 125.8, 125.1, 121.9, 96.2, 93.2, 88.9, 84.6, 79.4, 39.8, 25.6.

Propargylic Alcohol 139c. The same procedure was repeated as described for **139a** except that 0.443 g of **137** (1.80 mmol) was treated the lithium acetylide derived from 0.984 g of **138c** (4.27 mmol) and 1.71 mL of a 2.5 M solution of *n*-butyllithium (4.27 mmol) in hexanes to afford 1.243 g of **139c** (1.76 mmol, 98% yield, 1:1 mixture of diastereomers) as a white solid. Some fractions were found to contain only one of the two diastereomers. **Diastereomer 1**: IR 3549, 3464, 2209 cm⁻¹; ¹H δ 7.59 (4 H, s), 7.56–7.52 (2 H, m), 7.50–7.46 (2 H, m), 7.34–7.23 (4 H, m), 7.14 (4 H, s), 6.89 (2 H, s), 2.31 (2 H, s), 2.24 (12 H, s), 1.06 (18 H, s); ¹³C δ 141.0, 137.8, 132.1, 130.3, 129.4, 128.0, 127.7, 126.4, 126.0, 125.1, 122.6, 96.2, 93.7, 87.6, 84.6, 79.4, 39.7, 25.6, 21.1; MS *m/z* 729 (MNa⁺), 689, 649, 632; HRMS calcd for C₅₂H₅₀O₂Na (MNa⁺) 729.3709, found 729.3692. **Diastereomer 2**: mp 194–195 °C; IR 3567, 3469, 2209 cm⁻¹; ¹H δ 7.61 (4 H, s), 7.56–7.52 (2 H, m), 7.49–7.45 (2 H, m), 7.33–7.22 (4 H, m), 7.18 (4 H, s), 6.95 (2 H, s), 2.38 (2 H, s), 2.28 (12 H, s), 1.06 (18 H, s); ¹³C δ 141.0, 137.8, 132.17, 132.12, 130.4, 129.4, 128.0, 127.8, 126.5, 125.9, 125.1, 122.6, 96.1, 93.6, 87.6, 84.6, 79.4, 39.7, 25.6, 21.1.

Tetraacetylenic Hydrocarbon 140a. The following procedure is representative for the preparation of the tetraacetylenic hydrocarbons **140**. To a mixture of 0.310 g of **139a** (0.476 mmol) and 0.168 g of triethylsilane (1.42 mmol) in 10 mL of methylene chloride

was added 0.29 mL of trifluoroacetic acid (0.433 g, 3.80 mmol). After 5 min of stirring at room temperature, 0.202 g of sodium carbonate (1.90 mmol) was added followed by 10 mL of water and 50 mL of diethyl ether. The organic layer was separated, washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/5% diethyl ether in hexanes, $R_f = 0.49$) provided 0.274 g of **140a** (0.443 mmol, 93% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2216, 755 cm^{-1} ; ^1H (1:1 mixture) δ 7.57–7.40 (8 H, m), 7.32–7.22 (14 H, m), 3.64 and 3.62 (2 H, two singlets, 1:1 ratio), 1.00 (18 H, s); ^{13}C (1:1 mixture) δ 137.4, 137.3, 132.12, 132.05, 131.6, 128.9, 128.2, 127.8, 127.3, 126.33, 126.30, 125.58, 125.51, 123.25, 123.18, 95.76, 95.70, 92.82, 92.76, 88.66, 88.60, 82.44, 82.41, 50.2, 35.45, 35.41, 27.8; MS m/z 618 (M^+), 561, 505.

Tetraacetylenic Hydrocarbon 140b. The same procedure was repeated as described for **140a** except that 0.160 g of **139b** (0.20 mmol) was treated with 0.070 g of triethylsilane (0.60 mmol) and 0.12 mL of trifluoroacetic acid (1.6 mmol) in 40 mL of methylene chloride to afford 0.153 g of **140b** (0.198 mmol, 99% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2217, 761 cm^{-1} ; ^1H (1:1 mixture) δ 7.59–7.52 (12 H, m), 7.48–7.40 (6 H, m), 7.38–7.31 (8 H, m), 7.29–7.22 (4 H, m), 3.67 and 3.63 (2 H, two singlets, 1:1 ratio), 1.03 and 1.02 (18 H, two singlets, 1:1 ratio); ^{13}C (1:1 mixture) δ 140.8, 140.3, 140.2, 137.5, 137.4, 132.2, 132.13, 132.10, 129.0, 128.8, 128.7, 127.8, 127.53, 127.48, 127.3, 127.0, 126.9, 126.8, 126.3, 125.65, 125.59, 122.2, 122.1, 95.8, 92.7, 89.3, 82.6, 82.4, 50.3, 35.5, 27.8; MS m/z 770 (M^+), 713, 657; HRMS calcd for $\text{C}_{60}\text{H}_{50}$ (M^+) 770.3913, found 770.3899.

Tetraacetylenic Hydrocarbon 140c. The same procedure was repeated as described for **140a** except that 0.442 g of **139c** (0.626 mmol) was treated with 0.160 g of triethylsilane (1.38 mmol) and 0.39 mL of trifluoroacetic acid (5.0 mmol) in 10 mL of methylene chloride to afford 0.404 g of **140c** (0.599 mmol, 96% yield, 1:1 mixture of diastereomers) as a yellow solid: IR 2214, 848 cm^{-1} ; ^1H (1:1 mixture) δ 7.56–7.49 (2 H, m), 7.47–7.39 (2 H, m), 7.30–7.21 (8 H, m), 7.18–7.14 (4 H, m), 6.94 and 6.90 (2 H, two singlets, 1:1 ratio), 3.65 and 3.63 (2 H, two singlets, 1:1 ratio), 2.28 and 2.25 (12 H, two singlets, 1:1 ratio), 1.02 (18 H, s); ^{13}C (1:1 mixture) δ 137.7, 137.4, 137.3, 132.2, 132.1, 130.2, 129.4, 128.9, 127.7, 127.3, 126.31, 126.24, 125.75, 125.71, 122.9, 95.6, 93.2, 88.0, 82.5, 50.3, 35.5, 29.2, 27.8, 21.1; MS m/z 674 (M^+), 617, 561.

4,5-Diarylphenanthrene 141a. The following procedure is representative for the synthesis of the 4,5-diarylphenanthrenes **141**. To 0.191 g of **140a** (0.309 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere were added 0.65 mL of a 1.0 M solution of potassium *tert*-butoxide (0.65 mmol) in THF and 0.5 mL of 2-methyl-2-propanol. The reaction mixture was then heated under reflux for three hours. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 50 mL of methylene chloride were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/10% methylene chloride in hexanes, R_f = 0.73) provided 0.084 g of **141a**⁹⁵ (0.136 mmol, 44% yield) as a yellow solid: mp >340 °C; IR 1464, 705 cm^{-1} ; ^1H δ 7.83 (2 H, s), 7.39 (2 H, d, J = 7.3 Hz), 7.15 (2 H, t, J = 7.4 Hz), 7.05 (2 H, t, J = 7.3 Hz), 7.00 (4 H, t, J = 7.3 Hz), 6.74 (2 H, t, J = 7.5 Hz), 6.52 (4 H, d, J = 7.1 Hz), 6.20 (2 H, d, J = 8.1 Hz), 4.39 (2 H, d, J = 21.0 Hz), 4.15 (2 H, d, J = 21.0 Hz), 1.82 (18 H, s); ^{13}C δ 144.2, 141.2, 139.43,

139.36, 139.0, 137.1, 135.3, 132.5 (br), 131.9, 131.7, 128.1, 126.5, 126.0, 125.3, 123.6, 123.0, 122.0, 39.8, 37.8, 33.4; MS m/z 618 (M^+), 561; HRMS calcd for $C_{48}H_{42}$ (M^+) 618.3287, found 618.3296. Recrystallization of **141a** from CH_2Cl_2 /hexanes produced a crystal suitable for the X-ray structure analysis.

4,5-Diarylphenanthrene 141b and 1H-Cyclobut[a]indene 142b. The same procedure was repeated as described for **141a** except that 0.153 g of **140b** (0.198 mmol) was treated with a mixture of 0.48 mL of a 1.0 M solution of potassium *tert*-butoxide (0.48 mmol) in THF and 0.5 mL of 2-methyl-2-propanol in 10 mL of anhydrous toluene under reflux for 10 hours to afford 0.070 g of **141b** (0.091 mmol, 46% yield) as a yellow solid and 0.014 g of **142b** (0.018 mmol, 9% yield) as an orange solid. **141b**: mp 249–251 °C; IR 1486, 696 cm^{-1} ; 1H δ 7.92 (2 H, s), 7.70 (4 H, d, $J = 7.3$ Hz), 7.51–7.35 (12 H, m), 7.09 (2 H, t, $J = 7.0$ Hz), 6.78 (2 H, t, $J = 7.8$ Hz), 6.72 (4 H, d, $J = 8.5$ Hz), 6.42 (2 H, t, $J = 7.9$ Hz), 4.44 (2 H, d, $J = 21.0$ Hz), 4.20 (2 H, d, $J = 21.0$ Hz), 1.87 (18 H, s); ^{13}C δ 144.2, 141.1, 140.9, 139.7, 139.5, 139.0, 138.2, 137.2, 134.7, 132.2 (br), 131.9, 131.5, 128.7, 127.1, 126.9, 126.8, 126.1, 125.3, 123.7, 123.1, 122.0, 39.9, 37.8, 33.4; MS m/z 770 (M^+), 714, 659; HRMS calcd for $C_{60}H_{50}$ (M^+) 770.3913, found 770.3925. **142b**: mp 269–272 °C; IR 1487, 696 cm^{-1} ; 1H δ 8.51 (1 H, d, $J = 9.3$ Hz), 7.97 (1 H, dd, $J = 7.9$ and 2.0 Hz), 7.91 (1 H, d, $J = 2.2$ Hz), 7.83–7.76 (4 H, m), 7.72 (1 H, dd, $J = 7.9$ and 1.8 Hz), 7.67 (1 H, dd, $J = 9.3$ and 2.2 Hz), 7.66 (1 H, d, $J = 7.1$ Hz), 7.53–7.44 (7 H, m), 7.41–7.22 (8 H, m), 7.17 (1 H, td, $J = 7.5$ and 1 Hz), 7.07 (1 H, td, $J = 7.3$ and 1.4 Hz), 6.94 (1 H, t, $J = 7.3$ Hz), 6.19 (1 H, s), 4.47 (2 H, s), 1.87 (9 H, s), 1.12 (9 H, s). Spin decoupling indicates that the signal at δ 8.51 is coupled to the signal at δ 7.67, which is also coupled to the signal at δ 7.91.; ^{13}C δ 154.0, 152.3, 150.7, 148.0, 144.2, 141.2, 140.7, 140.5,

140.3, 139.9, 139.8, 139.1, 138.3, 138.2, 137.2, 134.0, 133.7, 132.7, 130.8, 130.6, 129.8, 129.6, 129.1, 128.9, 128.8, 127.8, 127.5, 127.4, 127.2, 127.0, 126.9, 126.8, 126.2, 125.8, 123.9, 123.6, 123.5, 121.5, 111.4, 75.7, 40.1, 38.8, 37.2, 34.3, 28.5; MS m/z 771 (MH^+), 770, 713; HRMS calcd for $C_{60}H_{51}$ (MH^+) 771.3991, found 771.3987.

4,5-Diarylphenanthrene 141c and 1H-Cyclobut[a]indene 142c. The same procedure was repeated as described for **141a** except that 0.270 g of **140c** (0.40 mmol) was treated with a mixture of 0.96 mL of a 1.0 M solution of potassium *tert*-butoxide (0.96 mmol) in THF and 0.5 mL of 2-methyl-2-propanol in 15 mL of anhydrous toluene under reflux for 10 hours to afford 0.108 g of **141c** (0.16 mmol, 40% yield) as a yellow solid and 0.033 g of **142c** (0.049 mmol, 12% yield) as an orange solid. **141c**: mp 265–270 °C; IR 1462, 707 cm^{-1} ; 1H δ 7.81 (2 H, s), 7.44 (2 H, d, $J = 7.3$ Hz), 7.10 (2 H, t, $J = 7.2$ Hz), 6.84 (2 H, d, $J = 7.9$ Hz), 6.81 (2 H, s), 6.49 (2 H, d, $J = 7.9$ Hz), 6.27 (4 H, s), 4.41 (2 H, d, $J = 21.0$ Hz), 4.20 (2 H, d, $J = 21.0$ Hz), 2.10 (12 H, s), 1.84 (18 H, s); ^{13}C δ 144.2, 141.4, 139.1, 139.0, 138.2, 136.6, 136.2, 135.5, 132.4, 131.7, 130.2 (br), 128.0, 125.9, 125.4, 123.6, 122.9, 121.8, 39.7, 37.7, 33.3, 21.3; MS m/z 674 (M^+), 617, 561; HRMS calcd for $C_{52}H_{50}$ (M^+) 674.3913, found 674.3935. **142c**: mp 212–215 °C; IR 1595, 1435 cm^{-1} ; 1H δ 8.40 (1 H, d, $J = 9.3$ Hz), 7.67 (1 H, d, $J = 2.2$ Hz), 7.64–7.57 (2 H, m), 7.54 (2 H, s), 7.46 (1 H, d, $J = 7.5$ Hz), 7.36–7.15 (4 H, m), 7.10–7.03 (2 H, m), 6.99 (1 H, t, $J = 7.5$ Hz), 6.92 (2 H, d, $J = 6.5$ Hz), 6.48 (1 H, d, $J = 7.7$ Hz), 5.88 (1 H, s), 4.46 (2 H, s), 2.43 (3 H, s), 2.41 (6 H, s), 2.31 (3 H, s), 1.85 (9 H, s), 1.14 (9 H, s); ^{13}C δ 154.8, 152.4, 151.3, 147.7, 144.1, 140.5, 140.2, 139.5, 138.6, 138.3, 138.1, 137.6, 137.0, 135.3, 134.1, 133.5, 131.0, 129.7, 129.2, 128.8, 128.6, 127.8, 127.7, 127.1, 126.7, 126.6, 126.1, 124.7,

123.8, 123.3, 121.4, 111.0, 75.3, 40.1, 38.7, 36.9, 34.3, 28.6, 21.6, 21.44, 21.36; MS m/z 675 (MH^+), 674, 617, 560; HRMS calcd for $C_{52}H_{50}$ (M^+) 674.3913, found 674.3922.

4-[(Trimethylsilyl)ethynyl]-1,1'-biphenyl.⁹⁷ To a mixture of 4-iodo-biphenyl (1.96 g, 7.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.147 g, 0.21 mmol), and copper(I) iodide (0.067 g, 0.35 mmol) in 30 mL of triethylamine was added 0.755 g of (trimethylsilyl)acetylene (7.70 mmol). After one hour of stirring at room temperature, 50 mL of a saturated aqueous ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, R_f = 0.38) afforded 1.70 g of 4-[(trimethylsilyl)ethynyl]-1,1'-biphenyl (6.79 mmol, 97% yield) as white crystals: mp 62–63 °C (lit.⁹⁷ mp 65–66 °C); IR 2162, 1252, 839 cm^{-1} ; 1H δ 7.69–7.60 (6 H, m), 7.52 (2 H, t, J = 7.4 Hz), 7.44 (1 H, t, J = 7.2 Hz), 0.44 (9 H, s); ^{13}C δ 141.1, 140.1, 132.3, 128.8, 127.6, 126.9, 126.8, 122.0, 105.1, 94.8, 0.0; MS m/z 250 (M^+), 239.

4-Ethynyl-1,1'-biphenyl (152b).⁹⁷ To a solution of 1.67 g of 4-[(trimethylsilyl)ethynyl]-1,1'-biphenyl (6.66 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution. After 10 min of stirring at room temperature, the reaction mixture was neutralized with a 1 M HCl solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated to afford, without further purification, 1.13 g of **152b** (6.34 mmol, 95% yield) as white crystals: mp 85–86 °C (lit.⁹⁷ mp 86–87 °C); IR 3273, 770 cm^{-1} ; 1H δ

7.64–7.57 (6 H, m), 7.46 (2 H, t, $J = 7.2$ Hz), 7.37 (1 H, t, $J = 7.1$ Hz), 3.14 (1 H, s); ^{13}C δ 141.6, 140.2, 132.5, 128.8, 127.7, 127.03, 126.98, 120.9, 83.5, 77.7; MS m/z 178 (M^+), 152.

154b. To a mixture of 1-bromo-2-iodobenzene (1.76 g, 6.22 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.131 g, 0.187 mmol), and copper(I) iodide (0.06 g, 0.32 mmol) in 30 mL of triethylamine was added via cannula a solution of 1.11 g of **152b** (6.22 mmol) in 10 mL of triethylamine. After one hour of stirring at room temperature, 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, $R_f = 0.27$) afforded 2.06 g of **154b** (6.18 mmol, 99% yield) as a yellow solid: mp 99–100 °C; IR 2218, 840, 763, 748 cm^{-1} ; ^1H δ 7.77–7.62 (8 H, m), 7.53 (2 H, t, $J = 7.2$ Hz), 7.44 (1 H, t, $J = 7.2$ Hz), 7.35 (1 H, t, $J = 7.2$ Hz), 7.23 (1 H, t, $J = 7.3$ Hz); ^{13}C δ 141.2, 140.1, 133.1, 132.4, 132.1, 129.3, 128.8, 127.6, 126.9, 125.6, 125.3, 121.7, 93.9, 88.7; MS m/z 334 and 332 (M^+), 252.

154c. To a mixture of 1-iodo-3,5-dimethylbenzene (2.32 g, 10.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.210 g, 0.30 mmol), and copper(I) iodide (0.095 g, 0.50 mmol) in 30 mL of triethylamine was added via cannula a solution of 1.81 g of 1-bromo-2-ethynylbenzene (**153**, 10.0 mmol) in 5 mL of triethylamine. After one hour of stirring at room temperature, 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and

water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, $R_f = 0.45$) afforded 2.71 g of **154c** (9.51 mmol, 95% yield) as a yellow liquid: IR 2213, 850, 752 cm^{-1} ; ^1H δ 7.61 (1 H, dd, $J = 7.9$ and 1.2 Hz), 7.55 (1 H, dd, $J = 7.7$ and 1.8 Hz), 7.28 (1 H, td, $J = 7.6$ and 1.2 Hz), 7.23 (2 H, s), 7.17 (1 H, td, $J = 7.6$ and 1.6 Hz), 7.00 (1 H, s), 2.32 (6 H, s); ^{13}C δ 137.9, 133.1, 132.4, 130.6, 129.3, 129.2, 127.0, 125.6, 122.5, 94.3, 87.3, 21.1; MS m/z 286 and 284 (M^+), 269, 202, 189.

156a.²² To a solution of 0.759 g of **154a** (2.95 mmol) in 30 mL of anhydrous diethyl ether at -78°C was added dropwise 1.4 mL of a 2.5 M solution of *n*-butyllithium (3.5 mmol) in hexanes. After one hour of stirring at -78°C , a solution of 0.898 g of iodine (3.54 mmol) in 40 mL of anhydrous diethyl ether was added dropwise via cannula. The reaction mixture was allowed to warm to 15°C before 20 mL of a 5% sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution was introduced. The organic layer was separated, washed with water, dried over sodium sulfate, and concentrated. The crude iodide **155a** was used in the next step without further purification. To a mixture of the crude iodide **155a**, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.063 g, 0.09 mmol), and copper(I) iodide (0.029 g, 0.15 mmol) in 30 mL of triethylamine was added dropwise via cannula a solution of 0.314 g of (trimethylsilyl)acetylene (3.2 mmol) in 5 mL of triethylamine. The reaction mixture was stirred at room temperature for one hour before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, $R_f =$

0.38) afforded 0.659 g of **156a** (2.40 mmol, 81% overall yield for two steps) having the spectral data identical to those reported previously.²²

156b. To a solution of 1.82 g of **154b** (5.46 mmol) in 150 mL of anhydrous diethyl ether at $-78\text{ }^{\circ}\text{C}$ was added dropwise 2.4 mL of a 2.5 M solution of *n*-butyllithium (6.00 mmol) in hexanes. After one hour of stirring at $-78\text{ }^{\circ}\text{C}$, a solution of 1.52 g of iodine (6.00 mmol) in 60 mL of anhydrous diethyl ether was added dropwise via cannula. The reaction mixture was then allowed to warm to $15\text{ }^{\circ}\text{C}$ 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, washed with water, dried over sodium sulfate, and concentrated to afford the crude iodide **155b**. The crude iodide **155b** was used in the next step without further purification. To a mixture of the crude iodide **155b**, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.115 g, 0.164 mmol), and copper(I) iodide (0.051 g, 0.27 mmol) in 30 mL of triethylamine was added via cannula a solution of 0.588 g of (trimethylsilyl)acetylene (6.00 mmol) in 5 mL of triethylamine. The reaction mixture was stirred at room temperature for one hour before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, $R_f = 0.19$) afforded 1.53 g of **156b** (4.36 mmol, 80% overall yield for two steps) as a yellow solid: mp $117\text{--}118\text{ }^{\circ}\text{C}$; IR 2216, 2158, 1249, 841 cm^{-1} ; ^1H δ 7.67–7.58 (6 H, m), 7.56–7.50 (2 H, m), 7.46 (2 H, t, $J = 7.4\text{ Hz}$), 7.37 (1 H, t, $J = 7.4\text{ Hz}$), 7.31–7.23 (2 H, m), 0.30 (9 H, s); ^{13}C δ 141.0, 140.2, 132.2, 132.1, 131.7, 128.8,

128.2, 127.8, 127.6, 126.95, 126.91, 126.0, 125.5, 122.1, 103.5, 98.6, 93.4, 88.9, 0.0; MS m/z 350 (M^+), 335, 319.

156c. To a solution of 2.42 g of **154c** (8.48 mmol) in 100 mL of anhydrous diethyl ether at $-78\text{ }^{\circ}\text{C}$ was added dropwise 4.1 mL of a 2.5 M solution of *n*-butyllithium (10.2 mmol) in hexanes. After one hour of stirring at $-78\text{ }^{\circ}\text{C}$, a solution of 2.59 g of iodine (10.2 mmol) in 100 mL of anhydrous diethyl ether was added dropwise via cannula. After the reaction mixture was allowed to warm to $15\text{ }^{\circ}\text{C}$, 50 mL of a 5% sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution was introduced. The organic layer was separated, washed with water, dried over sodium sulfate, and concentrated to afford the crude iodide **155c**. The crude iodide **155c** was used in the next step without further purification. To a mixture of the crude iodide **155c**, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.179 g, 0.255 mmol), and copper(I) iodide (0.080 g, 0.42 mmol) in 30 mL of triethylamine was added via cannula a solution of 0.916 g of (trimethylsilyl)acetylene (9.33 mmol) in 5 mL of triethylamine. The reaction mixture was stirred at room temperature for one hour before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes, $R_f = 0.33$) afforded 2.00 g of **156c** (6.61 mmol, 78% overall yield for two steps) as a yellow liquid: IR 2216, 2158, 1249, 843, 758 cm^{-1} ; ^1H δ 7.54–7.48 (2 H, m), 7.32–7.25 (2 H, m), 7.23 (2 H, s), 6.99 (1 H, s), 2.33 (6 H, s), 0.31 (9 H, s); ^{13}C δ 137.8, 132.2, 131.6, 130.3, 129.4, 128.2, 127.6, 126.3, 125.6, 122.9, 103.6, 98.4, 93.9, 87.5, 21.0, 0.0; MS m/z 302 (M^+), 287.

Diacetylene 138b. To a solution of 0.607 g of **156b** (1.73 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution. After 10 min of stirring at room temperature, the reaction mixture was neutralized with a 1 M HCl solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated to afford, without further purification, 0.478 g of **138b** (1.72 mmol, 99% yield) as a yellow solid: mp 59–60 °C; IR 3286, 2216, 760 cm^{-1} ; ^1H δ 7.71–7.56 (8 H, m), 7.49 (2 H, t, $J = 7.4$ Hz), 7.43–7.28 (3 H, m), 3.43 (1 H, s); ^{13}C δ 141.2, 140.3, 132.6, 132.2, 131.7, 128.8, 128.5, 127.9, 127.6, 127.0, 126.3, 124.6, 122.0, 93.5, 88.5, 82.2, 81.2; MS m/z 278 (M^+), 252.

Diacetylene 138c. To a solution of 1.36 g of **156c** (4.50 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution. After 10 min of stirring at room temperature, the reaction mixture was neutralized with a 1 M HCl solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated to afford, without further purification, 0.984 g of **138c** (4.27 mmol, 95% yield) as a yellow liquid: IR 3287, 2212, 758 cm^{-1} ; ^1H δ 7.57–7.52 (2 H, m), 7.34 (1 H, td, $J = 7.5$ and 1.7 Hz), 7.28 (1 H, td, $J = 7.5$ and 1.6 Hz), 7.22 (2 H, s), 7.00 (1 H, s), 3.39 (1 H, s), 2.34 (6 H, s); ^{13}C δ 137.8, 132.5, 131.7, 130.4, 129.8, 129.4, 128.5, 127.7, 126.5, 124.5, 122.7, 93.9, 87.1, 82.2, 81.1, 21.1; MS m/z 230 (M^+), 215.

Ethyl 2-(((Trifluoromethyl)sulfonyl)oxy)-1-cyclopentene-1-carboxylate (181). To a stirred suspension of 2.4 g of sodium hydride (60% dispersion in mineral oil, 60.0 mmol) in 120 mL anhydrous ether at 0 °C was added slowly a solution of ethyl 2-

oxocyclopentanecarboxylate (**180**, 7.809 g, 50.0 mmol) in 20 mL of dry ether. After 30 min of stirring at 0 °C, 10 mL of trifluoromethanesulfonic anhydride (60.0 mmol) was added and stirring was continued for 1 hour. Saturated aqueous ammonium chloride (50 mL) was added, the organic layer was separated, washed with water and brine, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/10% ether in hexanes, R_f = 0.42) afforded 13.540 g of the title compound **181** (46.98 mmol, 94% yield) as a colorless oil. IR (neat) 1723, 1669, 1213 cm^{-1} ; ^1H NMR δ 4.25 (2 H, q, J = 7.1 Hz), 2.78–2.66 (4 H, m), 2.00 (2 H, quintet, J = 7.7 Hz), 1.31 (3 H, t, J = 7.1 Hz); ^{13}C NMR δ 162.0, 153.4, 123.3, 118.2 (q, J = 320.1 Hz), 60.8, 32.4, 29.0, 18.5, 13.6; MS m/z 288 (M^+), 243, 179, 109, 85, 69.

Ethyl 2-(2-(2-Methylphenyl)ethynyl)-1-cyclopentene-1-carboxylate (183a). The following procedure is representative for the preparation of the ester **183**. To a mixture of enol triflate **181** (4.324 g, 15.0 mmol), *N,N*-diisopropylethylamine (2.6 mL, 15.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.316 g, 0.45 mmol), and copper(I) iodide (0.143 g, 0.75 mmol) in 30 mL of DMF, was added slowly a solution of 2-methylphenylacetylene (1.742 g 15.0 mmol) in 5 mL of DMF. After 2 hours of stirring at room temperature, 50 mL of a saturated aqueous ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% ether in hexanes, R_f = 0.33) afforded 3.459 g of **183a** (13.6 mmol, 90% yield) as a yellow liquid. IR (neat) 2197, 1700, 1610 cm^{-1} ; ^1H δ 7.47 (1 H, d, J = 7.5 Hz), 7.23–7.11 (3 H, m), 4.27 (2 H, q, J = 7.1 Hz), 2.76 (4 H, t, J = 7.7

Hz), 2.50 (3 H, s), 1.96 (2 H, quintet, $J = 7.7$ Hz), 1.32 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 164.5, 140.5, 137.4, 134.2, 132.1, 129.3, 128.7, 125.4, 122.7, 98.6, 89.4, 60.1, 39.4, 33.3, 22.1, 20.5, 14.3; MS m/z 254 (M^+), 225, 208, 197, 179, 165, 152.

2-(2-(2-Methylphenyl)ethynyl)-1-cyclopentene-1-carboxylic Acid (184a). The following procedure is representative for the hydrolysis of ester **183** to acid **184**. A solution of 4.274 g of ester **183a** (16.80 mmol) in 10 mL THF and 60 mL of 1 N aqueous sodium hydroxide was heated at 70 °C for 16 hours. The reaction mixture was cooled in an ice-bath and was acidified with dilute HCl. Filtration afforded 3.634 g of acid **184a** (16.06 mmol, 96% yield) as a white solid. mp 142–143 °C; IR (KBr) 2198, 1655, 1604, 1270, 759 cm^{-1} ; ^1H δ 12.15 (1 H, s br), 7.49 (1 H, d, $J = 7.2$ Hz), 7.28–7.12 (3 H, m), 2.81 (4 H, t, $J = 7.4$ Hz), 2.48 (3 H, s), 2.01 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 169.9, 141.0, 137.5, 136.8, 132.3, 129.5, 129.0, 125.5, 122.5, 100.5, 89.2, 39.6, 33.0, 22.2, 20.5; MS m/z 226 (M^+), 208, 197, 179, 165, 152, 115.

2-(2-(2-Methylphenyl)ethynyl)cyclopentenylisocyanate (185a). The following procedure is representative for the preparation of isocyanate **185** from acid **184**. To a solution of 1.253 g of acid **184a** (5.5 mmol) in 40 mL of anhydrous benzene was added a solution of 0.83 mL of triethylamine (6.0 mmol) and 1.514 g of DPPA (5.5 mmol) in 5 mL of benzene. After 6 hours of stirring at room temperature, the reaction mixture was then washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% ether in hexanes, $R_f = 0.72$) afforded 1.117 g of **185a** (5.00 mmol, 91% yield) as a pale yellow solid. mp 63–65 °C; IR 2254, 2159, 1642, 757 cm^{-1} ; ^1H δ 7.48 (1 H, d, $J = 7.3$ Hz), 7.27–7.11 (3 H, m), 2.62 (2 H, tt, $J = 7.3$ and 2.4 Hz), 2.52 (2 H, tt, $J = 7.3$ and 2.4 Hz),

2.48 (3 H, s), 2.00 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 139.9, 136.6, 131.7, 129.4, 128.3, 127.4, 125.5, 122.7, 115.1, 96.3, 87.3, 34.6, 33.9, 21.0, 20.6; MS m/z 223 (M^+), 194, 167, 115.

Ethyl 2-(4-Phenyl)butynyl-1-cyclopentene-1-carboxylate (183b). The same procedure was repeated as described for **183a** except that 2.882 g of enol triflate **181** (10.0 mmol) and 1.302 g of 4-phenylbutyne (10.0 mmol) were used to afford 2.637 g of ester **183b** (9.8 mmol, 98% yield) as a yellow liquid. IR (neat) 2218, 1698, 1611, 1225, 766 cm^{-1} ; ^1H δ 7.33–7.17 (5 H, m), 4.21 (2 H, q, $J = 7.1$ Hz), 2.91 (2 H, t, $J = 7.6$ Hz), 2.72 (2 H, t, $J = 7.8$ Hz), 2.68 (2 H, tt, $J = 7.7$ and 2.4 Hz), 2.59 (2 H, tt, $J = 7.7$ and 2.4 Hz), 1.88 (2 H, quintet, $J = 7.7$ Hz), 1.29 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 164.6, 140.4, 136.7, 135.2, 128.34, 128.26, 126.2, 100.9, 77.6, 60.0, 39.5, 34.9, 33.0, 22.2, 22.0, 14.2; MS m/z 268 (M^+), 267, 239, 222, 194, 91.

2-(4-Phenyl)butynyl-1-cyclopentene-1-carboxylic Acid (184b). The same procedure was repeated as described for **184a** except 2.637 g of ester **183b** (9.8 mmol) was used to afford 2.176 g of acid **184b** (9.06 mmol, 92% yield) as an off-white solid. mp 103–105 $^{\circ}\text{C}$; IR 2215, 1674, 1614, 747 cm^{-1} ; ^1H δ 9.60 (1 H, s br), 7.33–7.18 (5 H, m), 2.88 (2 H, t, $J = 7.3$ Hz), 2.75–2.59 (6 H, m), 1.92 (2 H, quintet, $J = 7.7$ Hz); ^{13}C δ 169.3, 140.3, 137.7, 136.2, 128.4, 128.3, 126.3, 103.1, 77.5, 39.9, 34.6, 32.8, 22.2, 22.0; MS m/z 240 (M^+), 135, 91, 77.

2-(4-Phenyl)butynyl-1-cyclopentenylisocyanate (185b). The same procedure was repeated as described for **185a** except that 0.961 g of acid **184b** (4.0 mmol) was used to afford 0.811 g of **185b** (3.42 mmol, 86% yield) as a yellow liquid. IR (neat) 2248, 2216, 2132, 1666, 1598, 737 cm^{-1} ; ^1H δ 7.35–7.20 (5 H, m), 2.93 (2 H, t, $J = 7.0$ Hz), 2.78 (2

H, t, $J = 7.4$ Hz), 2.70–2.60 (4 H, m), 1.89 (2 H, quintet, $J = 7.7$ Hz); ^{13}C δ 169.3, 140.3, 138.6, 137.2, 128.4, 128.3, 126.3, 104.3, 77.7, 40.3, 34.6, 32.9, 22.3, 21.9; MS m/z 237 (M^+), 208, 180, 146, 118, 91.

Ethyl 2-(2-(2-Methoxyphenyl)ethynyl)-1-cyclopentene-1-carboxylate (183c). The same procedure was repeated as described for **183a** except that 3.747 g of enol triflate **181** (13.0 mmol) and 1.743 g of 2-methoxyphenyl acetylene (13.2 mmol) were used to afford 3.240 g of ester **183c** (12.0 mmol, 92% yield) as a yellow solid. mp 53–54 °C; IR 2197, 1696, 1242, 752 cm^{-1} ; ^1H δ 7.42 (1 H, dd, $J = 7.6$ and 1.7 Hz), 7.25 (1 H, ddd, $J = 8.4$, 7.4 and 1.8 Hz), 6.87 (1 H, td, $J = 7.5$ and 1.0 Hz), 6.82 (1 H, d, $J = 7.9$ Hz), 4.22 (2 H, q, $J = 7.1$ Hz), 3.82 (3 H, s), 2.75–2.67 (4 H, m), 1.90 (2 H, quintet, $J = 7.6$ Hz), 1.28 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 164.4, 159.8, 137.4, 134.2, 133.6, 130.1, 120.2, 112.0, 110.4, 95.9, 89.5, 60.0, 55.5, 39.2, 33.1, 22.1, 14.1; MS m/z 270 (M^+), 241, 224, 207, 123.

2-(2-(2-Methoxyphenyl)ethynyl)-1-cyclopentene-1-carboxylic Acid (184c). The same procedure was repeated as described for **184a** except that 3.074 g of ester **183c** (11.37 mmol) was used to afford 2.543 g of acid **184c** (10.5 mmol, 92% yield) as a light yellow solid. mp 144–146 °C; IR 2197, 1670, 1606, 1273, 751 cm^{-1} ; ^1H δ 11.40 (1 H, s br), 7.44 (1 H, dd, $J = 7.5$ and 1.6 Hz), 7.34 (1 H, td, $J = 8.2$ and 1.7 Hz), 6.91 (1 H, t, $J = 7.5$ Hz), 6.86 (1 H, d, $J = 8.4$ Hz), 3.87 (3 H, s), 2.84–2.77 (4 H, m), 1.98 (2 H, quintet, $J = 7.7$ Hz); ^{13}C δ 167.1, 160.4, 138.3, 135.4, 133.2, 131.0, 120.5, 111.2, 110.5, 98.6, 89.1, 55.7, 39.1, 33.2, 22.1; MS m/z 242 (M^+), 214, 199, 183, 135, 77.

2-(2-(2-Methoxyphenyl)ethynyl)cyclopentenylisocyanate (185c). The same procedure was repeated as described for **185a** except that 0.485 g of acid **184c** (2.0 mmol) was used to afford 0.400 g of **185c** (1.67 mmol, 84% yield) as a yellow solid. mp 69–70 °C; IR

2249, 2133, 1665, 752 cm^{-1} ; ^1H δ 7.45 (1 H, dd, $J = 7.5$ and 1.8 Hz), 7.29 (1 H, td, $J = 8.3$ and 1.6 Hz), 6.91 (1 H, t, $J = 7.5$ Hz), 6.87 (1 H, d, $J = 8.3$ Hz), 3.89 (3 H, s), 2.62 (2 H, tt, $J = 7.3$ and 2.4 Hz), 2.49 (2 H, tt, $J = 7.3$ and 2.4 Hz), 1.97 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 159.7, 137.0, 133.2, 129.8, 127.4, 120.4, 115.3, 112.2, 110.5, 93.8, 87.5, 55.7, 34.6, 33.9, 21.1; MS m/z 239 (M^+), 210, 183, 157, 128, 113.

***N,N*-Dimethyl-2-(2-trimethylsilyl)ethynylaniline.** To a mixture of *N,N*-dimethyl-2-iodoaniline (2.877 g, 11.64 mmol), triethylamine (1.4 mL, 10.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.070 g, 0.10 mmol), and copper(I) iodide (0.057 g, 0.30 mmol) in 30 mL of DMF, was added slowly a solution of trimethylsilylacetylene (1.176 g, 12.0 mmol) in 5 mL of DMF. After 2 hours of stirring at room temperature, 50 mL of saturated aqueous ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% ether in hexanes, $R_f = 0.34$) afforded 2.401 g of the title compound (11.04 mmol, 95% yield) as a yellow liquid. IR (neat) 2150, 866, 842, 757 cm^{-1} ; ^1H δ 7.43 (1 H, dd, $J = 7.5$ and 1.8 Hz), 7.23 (1 H, ddd, $J = 8.3, 7.3$ and 1.6 Hz), 6.87 (1 H, d, $J = 7.5$ Hz), 6.83 (1 H, td, $J = 7.4$ and 1.1 Hz), 2.96 (6 H, s), 0.27 (9 H, s); ^{13}C δ 155.1, 134.8, 129.4, 120.1, 116.7, 114.6, 104.6, 99.5, 43.3, 0.0; MS m/z 217 (M^+), 144, 128, 100.

***N,N*-Dimethyl-2-ethynylaniline (182d).** To a solution of 1.943 g of *N,N*-dimethyl-2-trimethylsilylethynylaniline (8.94 mmol) in 50 mL of ethyl ether, was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide aqueous solution. After 10 min of stirring at room temperature, the reaction mixture was neutralized with a 1 N HCl

solution. The organic layer was separated, and the aqueous layer was back extracted with ethyl ether. The combined organic layer were washed with brine and water, dried over sodium sulfate, and concentrated to afford, without further purification, 1.272 g of *N,N*-dimethyl-2-ethynylaniline (**182d**, 8.76 mmol, 98% yield) as a yellow liquid. IR (neat) 3285, 2100, 758 cm^{-1} ; ^1H δ 7.47 (1 H, dd, $J = 7.6$ and 1.7 Hz), 7.27 (1 H, ddd, $J = 8.3$, 7.3 and 1.7 Hz), 6.93 (1 H, d, $J = 8.1$ Hz), 6.89 (1 H, td, $J = 7.4$ and 1.1 Hz), 3.43 (1 H, s), 2.94 (6 H, s); ^{13}C δ 155.5, 134.8, 129.6, 120.6, 117.0, 114.4, 82.9, 82.3, 43.6; MS m/z 145 (M^+), 144, 128, 115.

Ester 183d. The same procedure was repeated as described for **183a** except that 1.729 g of enol triflate **181** (6.0 mmol) and 0.915 g of *N,N*-dimethyl-2-ethynylaniline (**182d**, 6.3 mmol) were used to afford 1.551 g of ester **183d** (5.47 mmol, 91% yield) as a yellow liquid. IR (neat) 2188, 1695, 1609, 1247, 756 cm^{-1} ; ^1H δ 7.45 (1 H, dd, $J = 7.6$ and 1.5 Hz), 7.23 (1 H, ddd, $J = 8.6$, 7.2 and 1.7 Hz), 6.86 (1 H, d, $J = 8.3$ Hz), 6.83 (1 H, td, $J = 7.4$ and 1.0 Hz), 4.24 (2 H, q, $J = 7.1$ Hz), 2.96 (6 H, s), 2.80–2.70 (4 H, m), 1.94 (2 H, quintet, $J = 7.6$ Hz), 1.32 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 164.6, 154.7, 136.7, 134.8, 134.6, 129.8, 120.0, 116.6, 114.2, 99.4, 91.0, 60.2, 43.4, 39.2, 33.3, 22.2, 14.3; MS m/z 283 (M^+), 254, 237, 208, 181.

Carboxylic Acid 184d. The same procedure was repeated as described for **184a** except 1.472 g of ester **183d** (5.19 mmol) was used to afford 1.124 g of acid **184d** (4.4 mmol, 85% yield) as a bright yellow solid. mp 162–164 $^{\circ}\text{C}$; IR 2184, 1654, 1603, 750 cm^{-1} ; ^1H δ 10.91 (1 H, s, br), 7.45 (1 H, dd, $J = 7.7$ and 1.7 Hz), 7.25 (1 H, ddd, $J = 9.0$, 7.5 and 1.7 Hz), 6.89 (1 H, d, $J = 8.7$ Hz), 6.84 (1 H, td, $J = 7.4$ and 1.0 Hz), 2.93 (6 H, s), 2.83–2.76 (4 H, m), 1.98 (2 H, quintet, $J = 7.7$ Hz); ^{13}C δ 169.1, 155.0, 137.1, 136.4,

134.9, 130.1, 120.4, 116.9, 114.2, 101.1, 90.5, 43.6, 39.4, 33.1, 22.2; MS m/z 255 (M^+), 226, 184, 132, 117.

Isocyanate 185d. The same procedure was repeated as described for **185a** except 0.511 g of acid **184d** (2.0 mmol) was used to afford 0.441 g of **185d** (1.75 mmol, 87% yield) as a yellow viscous oil. IR 2182, 2132, 1666, 755 cm^{-1} ; ^1H δ 7.49 (1 H, dd, $J = 7.6$ and 1.7 Hz), 7.26 (1 H, ddd, $J = 8.3$, 7.4 and 1.8 Hz), 6.88 (1 H, d, $J = 8.5$ Hz), 6.86 (1 H, td, $J = 7.5$ and 1.1 Hz), 3.00 (6 H, s), 2.80 (2 H, tt, $J = 7.6$ and 2.3 Hz), 2.74 (2 H, tt, $J = 7.6$ and 2.2 Hz), 1.96 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 169.0, 154.9, 138.2, 136.9, 135.2, 130.3, 120.0, 116.6, 113.5, 102.8, 90.9, 43.4, 39.9, 33.0, 22.1; MS m/z 252 (M^+), 251, 207.

Methyl 2-(2-Trimethylsilylethynyl)benzyl Ether. The same procedure was repeated as described for *N,N*-Dimethyl-2-(2-trimethylsilyl)ethynylaniline except that 2.332 g of methyl 2-iodobenzyl ether (9.4 mmol) and 0.980 g of trimethylsilylacetylene (10.0 mmol) were used to afford 2.087 g of the title compound (9.19 mmol) as a pale yellow liquid. IR (neat) 2156, 1250, 868, 843, 759 cm^{-1} ; ^1H δ 7.48–7.42 (2 H, m), 7.33 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.22 (1 H, td, $J = 7.5$ and 1.5 Hz), 4.63 (2 H, s), 3.46 (3 H, s), 0.27 (9 H, s); ^{13}C δ 140.4, 132.2, 128.7, 127.3, 127.1, 121.7, 102.6, 98.9, 72.5, 58.6, 0.0; MS m/z 218 (M^+), 203, 173, 145, 73.

Methyl 2-Ethynylbenzyl Ether (182e). The same procedure was repeated as described for **182d** except 1.782 g of Methyl 2-(2-trimethylsilylethynyl)benzyl ether (8.16 mmol) was used to afford 1.094 g of **182e** (7.75 mmol, 95% yield) as a yellow liquid. IR (neat) 3293, 2104, 1090, 761 cm^{-1} ; ^1H δ 7.53–7.46 (2 H, m), 7.37 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.25 (1 H, td, $J = 7.5$ and 1.4 Hz), 4.66 (2 H, s), 3.45 (3 H, s), 3.32 (1 H, s); ^{13}C δ 140.6,

132.6, 128.9, 127.4, 127.2, 120.6, 81.6, 81.2, 72.4, 58.4; MS m/z 146 (M^+), 145, 131, 115, 103, 77.

Ethyl 2-(2-(2-Methoxymethylphenyl)ethynyl)-1-cyclopentene-1-carboxylate (183e).

The same procedure was repeated as described for **183a** except that 2.219 g of enol triflate **181** (7.7 mmol) and 1.094 g of methyl 2-ethynylbenzyl ether (**182e**, 7.75 mmol) were used to afford 1.985 g of ester **183e** (6.98 mmol, 91% yield) as a yellow liquid. IR (neat) 2197, 1698, 1612, 1248, 761 cm^{-1} ; ^1H δ 7.51–7.46 (2 H, m), 7.35 (1 H, td, J = 7.6 and 1.3 Hz), 7.25 (1 H, td, J = 7.5 and 1.4 Hz), 4.71 (2 H, s), 4.27 (2 H, q, J = 7.1 Hz), 3.45 (3 H, s), 2.76 (4 H, t, J = 7.6 Hz), 1.97 (2 H, quintet, J = 7.6 Hz), 1.32 (3 H, t, J = 7.1 Hz); ^{13}C δ 164.5, 140.4, 138.1, 134.0, 132.3, 129.0, 127.4, 127.2, 121.5, 97.1, 90.0, 72.4, 60.3, 58.4, 39.4, 33.4, 22.3, 14.4; MS m/z 284 (M^+), 269, 223, 195, 178, 165, 152.

2-(2-(2-Methoxymethylphenyl)ethynyl)-1-cyclopentene-1-carboxylic Acid (184e).

The same procedure was repeated as described for **184a** except 1.885 g of ester **183e** (6.63 mmol) was used to afford 1.503 g of acid **184e** (5.87 mmol, 89% yield) as a light yellow solid. mp 133–135 °C; IR (KBr) 2195, 1660, 1605, 1278, 1109, 763 cm^{-1} ; ^1H δ 10.76 (1 H, s, br), 7.50 (1 H, d, J = 7.2 Hz), 7.47 (1 H, d, J = 7.6 Hz), 7.36 (1 H, t, J = 7.4 Hz), 7.24 (1 H, t, J = 7.4 Hz), 4.69 (2 H, s), 3.44 (3 H, s), 2.83–2.76 (4 H, m), 2.00 (2 H, quintet, J = 7.7 Hz); ^{13}C δ 169.4, 140.8, 137.2, 137.0, 132.4, 129.3, 127.3, 127.2, 121.0, 98.9, 89.6, 72.3, 58.4, 39.6, 33.1, 22.2; MS m/z 256 (M^+), 241, 224, 207, 195, 148, 133, 91, 77.

Isocyanate 185e. The same procedure was repeated as described for **185a** except 0.513 g of acid **184e** (2.0 mmol) was used to afford 0.459 g of **185e** (1.81 mmol, 91% yield) as a white solid. mp 54–56 °C; IR 2192, 2135, 1667, 1603, 1190, 760 cm^{-1} ; ^1H δ 7.54–7.48

(2 H, m), 7.39 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.28 (1 H, td, $J = 7.5$ and 1.4 Hz), 4.73 (2 H, s), 3.47 (3 H, s), 2.84–2.71 (4 H, m), 1.98 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 169.0, 140.8, 138.2, 137.5, 132.6, 129.5, 127.5, 127.3, 121.0, 100.1, 89.6, 72.4, 58.4, 40.0, 33.1, 22.1; MS m/z 253 (M^+), 238, 210, 194, 165, 139, 115.

Ethyl 2-(5-Methoxy)pentynyl-1-cyclopentene-1-carboxylate (183f). The same procedure was repeated as described for **183a** except that 2.88 g of enol triflate **181** (10.0 mmol) and 1.18 g of 5-methoxy-1-pentyne (12.0 mmol) were used to afford 2.297 g of ester **183f** (9.72 mmol, 97% yield) as a yellow liquid. IR (neat) 2217, 1699, 1611, 1225, 1120, cm^{-1} ; ^1H δ 4.20 (2 H, q, $J = 7.1$ Hz), 3.48 (2 H, t, $J = 6.2$ Hz), 3.33 (3 H, s), 2.69–2.55 (4 H, m), 2.51 (2 H, t, $J = 7.0$ Hz), 1.93–1.77 (4 H, m), 1.28 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 164.7, 136.7, 135.2, 101.0, 77.3, 71.1, 60.1, 58.6, 39.6, 33.0, 28.5, 22.1, 16.7, 14.2; MS m/z 236 (M^+), 191, 178, 163, 150, 91, 77.

2-(5-Methoxy)pentynyl-1-cyclopentene-1-carboxylic Acid (184f). The same procedure was repeated as described for **184a** except that 2.297 g of ester **183f** (9.72 mmol) was used to afford 1.741 g of acid **184f** (8.36 mmol, 86% yield) as a light yellow solid. mp 47–48 °C; IR 2216, 1676, 1607, 1118 cm^{-1} ; ^1H δ 10.02 (1 H, s br), 3.49 (2 H, t, $J = 6.2$ Hz), 3.32 (3 H, s), 2.69–2.59 (4 H, m), 2.51 (2 H, t, $J = 6.9$ Hz), 1.94–1.76 (4 H, m); ^{13}C δ 169.1, 137.6, 136.3, 102.9, 77.1, 70.9, 58.5, 39.8, 32.8, 28.3, 21.9, 16.7; MS m/z 208 (M^+), 176, 163, 135, 108, 77.

2-(5-Methoxy)pentynyl-1-cyclopentenylisocyanate (185f). The same procedure was repeated as described for **185a** except that 1.04 g of acid **184f** (5.0 mmol) was used to afford 0.916 g of **185f** (4.46 mmol, 89% yield) as a yellow oil. IR (neat) 2248, 2131, 1668, 1597, 1205, 1119 cm^{-1} ; ^1H δ 3.47 (2 H, t, $J = 6.2$ Hz), 3.33 (3 H, s), 2.50–2.39 (6

H, m), 1.96–1.76 (4 H, m); ^{13}C δ 135.7, 127.6, 115.3, 98.1, 75.0, 71.1, 58.6, 34.3, 33.9, 28.5, 20.8, 16.4; MS m/z 205 (M^+), 173, 144, 130, 117, 91, 77.

Ethyl 2-(1-Pentynyl)-1-cyclopentene-1-carboxylate (183g). The same procedure was repeated as described for **183a** except that 2.882 g of enol triflate **181** (10.0 mmol) and 0.681 g of pentyne (10.0 mmol) were used to afford 1.874 g of ester **183g** (9.09 mmol, 91% yield) as a light yellow liquid. IR (neat) 2217, 1703, 1611, 1223 cm^{-1} ; ^1H δ 4.20 (2 H, q, $J = 7.1$ Hz), 2.69–2.57 (4 H, m), 2.40 (2 H, t, $J = 7.0$ Hz), 1.87 (2 H, quintet, $J = 7.6$ Hz), 1.59 (2 H, sextet, $J = 7.2$ Hz), 1.29 (3 H, t, $J = 7.1$ Hz), 1.01 (3 H, t, $J = 7.3$ Hz); ^{13}C δ 164.7, 136.5, 135.4, 101.8, 77.3, 60.0, 39.7, 33.1, 22.1, 22.03, 21.98, 14.3, 13.5; MS m/z 206 (M^+), 178, 161, 150.

2-(1-Pentynyl)-1-cyclopentene-1-carboxylic Acid (184g). The same procedure was repeated as described for **184a** except that 1.848 g of ester **183g** (8.96 mmol) was used to afford 1.417 g of acid **184g** (7.95 mmol, 89% yield) as an off-white solid. mp 85–86 $^{\circ}\text{C}$; IR 2208, 1680, 1661, 1605 cm^{-1} ; ^1H δ 11.90 (1 H, s br), 2.72–2.62 (4 H, m), 2.41 (2 H, t, $J = 6.9$ Hz), 1.91 (2 H, quintet, $J = 7.7$ Hz), 1.60 (2 H, sextet, $J = 7.2$ Hz), 1.02 (3 H, t, $J = 7.4$ Hz); ^{13}C δ 169.4, 137.9, 136.2, 104.1, 77.0, 39.9, 32.8, 22.02, 21.98, 21.9, 13.4; MS m/z 178 (M^+), 161, 150, 91, 77.

2-(1-Pentynyl)-1-cyclopentenylisocyanate (185g). The same procedure was repeated as described for **185a** except that 1.564 g of acid **184g** (8.78 mmol) was used to afford 1.341 g of **185g** (7.65 mmol, 87% yield) as a yellow liquid. IR (neat) 2236, 2149, 1648, 1626 cm^{-1} ; ^1H δ 2.49–2.38 (4 H, m), 2.37 (2 H, t, $J = 7.0$ Hz), 1.91 (2 H, quintet, $J = 7.5$ Hz), 1.58 (2 H, sextet, $J = 7.2$ Hz), 1.00 (3 H, t, $J = 7.3$ Hz); ^{13}C δ 135.5, 127.6, 115.4, 98.8, 74.8, 34.2, 33.9, 22.0, 21.6, 20.8, 13.4; MS m/z 175 (M^+), 146, 118, 91.

Ethyl 2-(3-Methoxy-1-propynyl)-1-cyclopentene-1-carboxylate (183h). The same procedure was repeated as described for **183a** except that 2.882 g of enol triflate **181** (10.0 mmol) and 0.701 g of methyl propargic ether (10.0 mmol) were used to afford 1.885 g of ester **183h** (9.05 mmol, 91% yield) as a yellow liquid. IR (neat) 1704, 1613, 1224 cm^{-1} ; ^1H δ 4.32 (2 H, s), 4.21 (2 H, q, $J = 7.1$ Hz), 3.42 (3 H, s), 2.72–2.61 (4 H, m), 1.91 (2 H, quintet, $J = 7.6$ Hz), 1.30 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 163.7, 137.9, 133.2, 95.3, 82.2, 59.9, 59.7, 57.0, 38.7, 32.7, 21.7, 13.7; MS m/z 208 (M^+), 178, 163, 150, 91, 85.

2-(3-Methoxy-1-propynyl)-1-cyclopentene-1-carboxylic Acid (184h). The same procedure was repeated as described for **184a** except that 1.837 g of ester **183h** (8.82 mmol) was used to afford 1.265 g of acid **184h** (7.02 mmol, 80% yield) as a white solid. mp 75–76 $^{\circ}\text{C}$; IR 1666, 1604, 1274 cm^{-1} ; ^1H δ 11.27 (1 H, s br), 4.33 (2 H, s), 3.42 (3 H, s), 2.74–2.65 (4 H, m), 1.94 (2 H, quintet, $J = 7.7$ Hz); ^{13}C δ 169.3, 137.7, 136.5, 97.5, 82.5, 60.4, 57.5, 39.5, 33.0, 22.1; MS m/z 180 (M^+), 150, 135, 77.

Isocyanate 185h. The same procedure was repeated as described for **185a** except that 0.766 g of acid **184h** (4.25 mmol) was used to afford 0.514 g of **185h** (2.90 mmol, 68% yield) as a yellow oil. IR (neat) 2254, 2133, 1672, 1599, 1204 cm^{-1} ; ^1H δ 4.27 (2 H, s), 3.39 (3 H, s), 2.52–2.42 (4 H, m), 1.93 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 137.6, 127.2, 113.9, 92.8, 80.4, 60.2, 57.4, 34.5, 33.6, 20.8; MS m/z 177 (M^+), 146, 118, 91.

188. The following procedure is representative for the cyclization of the enyne-isocyanate **185**. A solution of 0.178 g of **185a** (0.80 mmol) in 6 mL of 1,2-dichlorobenzene was heated under reflux for 2 days, then the solvent was removed under vacuum. Purification of the residue by flash chromatography (silica gel/50% ether in hexanes, $R_f = 0.26$)

afforded 0.072 g of **188**⁹⁵ (0.32 mmol, 40% yield) as a brown solid. Recrystallization from CH₂Cl₂/hexanes gave brown crystals. mp 103–104 °C; IR 1409, 1039, 782, 734 cm⁻¹; ¹H δ 7.82 (1 H, s), 7.61 (1 H, d, *J* = 7.7 Hz), 7.34 (1 H, td, *J* = 7.5 and 1.4 Hz), 7.26 (1 H, td, *J* = 7.4 and 1.3 Hz), 7.12 (1 H, d, *J* = 7.3 Hz), 5.27 (2 H, s), 2.92 (4 H, q, *J* = 7.6 Hz), 2.12 (2 H, quintet, *J* = 7.6 Hz); ¹³C δ 164.4, 160.4, 131.5, 130.5, 129.8, 128.4, 127.8, 127.7, 124.5, 121.7, 114.1, 68.9, 34.0, 30.0, 23.2; MS *m/z* 223 (M⁺), 222.

2-Pyridone 192. The same procedure was repeated as described for **188** except that 0.237 g of **185b** (1.0 mmol) was used to afford 0.232 g of **192**⁹⁵ (0.98 mmol, 98% yield) as light yellow crystals. mp 244–245 °C; IR (KBr) 3259, 1643, 1577, 764, 740 cm⁻¹; ¹H δ 13.51 (1 H, s br), 7.74–7.70 (1 H, m), 7.32–7.28 (3 H, m), 3.12 (2 H, t, *J* = 7.1 Hz), 2.99 (2 H, t, *J* = 7.5 Hz), 2.82 (4 H, s), 2.15 (2 H, quintet, *J* = 7.7 Hz); ¹³C δ 164.5, 147.6, 143.3, 139.9, 133.2, 129.0, 128.1, 126.9, 126.3, 123.2, 116.7, 32.5, 31.0, 28.8, 23.7, 21.2.

2-Methoxypyridine 205 and 2-Pyridone 206. The same procedure was repeated as described for **188** except that 0.104 g of **185c** (0.47 mmol) was refluxed in chlorobenzene for 36 hours to afford 0.054 g of **205** (0.24 mmol, 52% yield) as a white solid and 0.010 g of **206** (0.048 mmol, 10% yield) as a white solid. **205**: Recrystallization from CH₂Cl₂/hexanes gave brown crystals. mp 115–116 °C; IR 1594, 1067, 748 cm⁻¹; ¹H δ 8.02 (1 H, d, *J* = 6.7 Hz), 7.54 (1 H, d, *J* = 7.3 Hz), 7.43–7.33 (2 H, m), 4.17 (3 H, s), 3.11 (2 H, t, *J* = 7.3 Hz), 3.06 (2 H, t, *J* = 7.7 Hz), 2.24 (2 H, quintet, *J* = 7.5 Hz); ¹³C δ 161.7, 160.1, 159.6, 155.2, 126.0, 123.5, 122.6, 122.1, 113.4, 111.1, 105.5, 53.6, 34.7, 26.8, 23.1; MS *m/z* 239 (M⁺), 238, 210. **206**: mp 305 °C (decomp. with melting); IR 3421, 1656, 1623, 748 cm⁻¹; ¹H δ 10.74 (1 H, s br), 8.22–8.16 (1 H, m), 7.57–7.51 (1 H, m), 7.42–7.35 (2 H, m), 3.05 (4 H, t, *J* = 7.4 Hz), 2.30 (2 H, quintet, *J* = 7.4 Hz); ¹³C

(DMSO- d_6) δ 160.1, 159.7, 153.8, 150.2, 124.6, 124.1, 123.7, 120.1, 110.9, 106.9, 105.1, 30.9, 26.1, 22.0.

N-Methyl-2-pyridone 207 and 2-Methoxypyridine 208. A solution of 0.282 g of **185d** (1.12 mmol) in 5 mL of 1,2-dichlorobenzene was heated at 180°C for 5 hours, then the solvent was removed under vacuum. Purification of the residue by flash chromatography afforded 0.106 g of **207**⁹⁵ (0.42 mmol, 38% yield) as brown crystals and 0.079 g of **208**⁹⁵ (0.31 mmol, 28% yield) as yellow crystals. **207**: mp 238–240 °C; IR 1653, 1561, 747, 721 cm^{-1} ; ^1H δ 8.40 (1 H, dd, $J = 6.8$ and 1.9 Hz), 7.31 (1 H, td, $J = 7.0$ and 1.6 Hz), 7.28 (1 H, dd, $J = 6.7$ and 1.6 Hz), 7.21 (1 H, td, $J = 6.5$ and 1.6 Hz), 3.70 (3 H, s), 3.50 (3 H, s), 3.05 (2 H, t, $J = 7.4$ Hz), 2.81 (2 H, t, $J = 7.7$ Hz), 2.13 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 160.3, 147.5, 142.7, 138.9, 125.0, 123.3, 121.4, 121.0, 108.1, 105.3, 105.2, 32.0, 31.2, 30.4, 29.7, 22.0; MS m/z 252 (M^+), 251, 126. **208**: mp 205–206 °C; IR 1595, 1460, 752 cm^{-1} ; ^1H δ 8.21 (1 H, dd, $J = 6.8$ and 2.0 Hz), 7.42 (1 H, td, $J = 7.6$ and 1.2 Hz), 7.31–7.25 (2 H, m), 4.20 (3 H, s), 3.85 (3 H, s), 3.26 (2 H, t, $J = 7.3$ Hz), 3.04 (2 H, t, $J = 7.7$ Hz), 2.22 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 159.7, 158.6, 144.6, 139.8, 124.5, 122.1, 121.9, 120.2, 111.1, 108.1, 103.6, 53.2, 34.2, 30.5, 29.0, 23.0; MS m/z 252 (M^+), 251, 223.

212, 213, 214 and 215. The same procedure was repeated as described for **188** except that 0.916 g of **185f** (4.46 mmol) was used to afford 0.207 g of **212** (1.08 mmol, 24% yield) as a white solid along with 0.165 g of **213** (0.80 mmol, 18% yield) as a white solid and 0.087 g of **214** (0.42 mmol, 10% yield) as a yellow solid, as well as 0.016 g of dimer **215** (0.039 mmol, 0.9% yield) as a white solid. **212**: mp 255–257 °C; IR 3272, 1636, 1117 cm^{-1} ; ^1H δ 12.22 (1 H, s br), 4.18 (2 H, t, $J = 5.2$ Hz), 2.85 (2 H, t, $J = 7.5$ Hz), 2.66

(2 H, t, $J = 7.2$ Hz), 2.52 (2 H, t, $J = 6.3$ Hz), 2.06 (2 H, quintet, $J = 7.4$ Hz), 2.00–1.91 (2 H, m); ^{13}C δ 166.3, 161.5, 146.7, 111.6, 104.0, 66.8, 31.2, 27.0, 22.4, 21.5, 19.0. **213**: mp 50–51 °C; IR 1608, 1589, 1122 cm^{-1} ; ^1H δ 4.19 (2 H, t, $J = 5.1$ Hz), 3.92 (3 H, s), 2.86 (2 H, t, $J = 7.6$ Hz), 2.74 (2 H, t, $J = 7.3$ Hz), 2.55 (2 H, t, $J = 6.4$ Hz), 2.06 (2 H, quintet, $J = 7.5$ Hz), 2.01–1.92 (2 H, m); ^{13}C δ 162.4, 159.7, 159.1, 117.2, 101.3, 66.6, 53.5, 34.4, 26.8, 22.8, 21.6, 18.8; MS m/z 205 (M^+), 190, 176. **214**: IR 1650, 1574 cm^{-1} ; ^1H δ 4.14 (2 H, t, $J = 5.2$ Hz), 3.43 (3 H, s), 2.86 (2 H, t, $J = 7.6$ Hz), 2.71 (2 H, t, $J = 7.4$ Hz), 2.52 (2 H, t, $J = 6.4$ Hz), 2.08 (2 H, quintet, $J = 7.5$ Hz), 1.99–1.89 (2 H, m); ^{13}C δ 164.3, 159.6, 147.1, 111.1, 104.4, 66.6, 32.15, 32.07, 27.5, 21.7, 21.6, 19.6; MS m/z 205 (M^+), 204, 190, 176. **215**: mp 92–93 °C; IR 1587, 1119 cm^{-1} ; ^1H δ 4.28 (2 H, t, $J = 6.3$ Hz), 4.19 (2 H, t, $J = 5.1$ Hz), 3.86 (6 H, s), 3.01 (2 H, t, $J = 7.3$ Hz), 2.88–2.81 (4 H, m), 2.76–2.67 (4 H, m), 2.57 (2 H, t, $J = 6.4$ Hz), 2.13–2.02 (4 H, m), 1.99–1.86 (4 H, m); ^{13}C δ 163.2, 162.5, 162.4, 161.6, 159.7, 159.1, 118.1, 116.8, 111.3, 101.4, 66.6, 65.8, 58.9, 53.6, 34.4, 34.2, 29.6, 29.0, 26.9, 23.3, 22.8, 21.7, 19.9, 18.8; MS m/z 410 (M^+), 220, 204, 191, 176.

219 and 223. A solution of 0.306 g of **185e** (1.21 mmol) in 6 mL of 1,2-dichlorobenzene was heated at 150 °C for 20 hours, then the solvent was removed under vacuum. Purification of the residue by flash chromatography (silica gel/50% ether, 10% methylene chloride in hexanes, $R_f = 0.30$) afforded 0.182 g of **223**⁹⁵ (0.72 mmol, 59% yield) as white crystals. mp 125–126 °C; IR 1584, 1558, 1080, 795, 748 cm^{-1} ; ^1H δ 8.19 (1 H, d, $J = 7.9$ Hz), 7.34 (1 H, td, $J = 7.5$ and 1.2 Hz), 7.26 (1 H, t, $J = 7.9$ Hz), 7.16 (1 H, d, $J = 7.3$ Hz), 5.15 (2 H, s), 4.01 (3 H, s), 3.12 (2 H, t, $J = 7.3$ Hz), 2.92 (2 H, t, $J = 7.7$ Hz), 2.12 (2 H,

quintet, $J = 7.6$ Hz); ^{13}C δ 165.9, 163.1, 162.2, 131.2, 129.0, 128.1, 127.1, 126.3, 124.4, 120.8, 106.0, 69.1, 59.1, 34.3, 29.6, 23.0; MS m/z 253 (M^+), 252, 236.

A solution of 0.372 g of **185e** (1.47 mmol) in 6 mL of 1,2-dichlorobenzene was heated at 180 °C for 5 hours, then the solvent was removed under vacuum. Purification of the residue by flash chromatography (silica gel/50% ether, 10% methylene chloride in hexanes) afforded 0.215 g of **223** (0.85 mmol, 58%) as white crystals and 0.068 g of **219** (0.27 mmol, 18% yield) as a white solid. **219**: mp 84–86 °C; IR 1607, 1408, 1078, 782, 753, 733 cm^{-1} ; ^1H δ 7.97 (1 H, s), 7.78 (1 H, d, $J = 7.9$ Hz), 7.50–7.42 (1 H, m), 7.41–7.34 (2 H, m), 6.07 (1 H, s), 3.64 (3 H, s), 3.00 (2 H, td, $J = 7.6$ and 2.6 Hz), 2.96 (2 H, t, $J = 7.3$ Hz), 2.17 (2 H, quintet, $J = 7.6$ Hz); ^{13}C δ 164.6, 156.7, 131.9, 129.6, 129.4, 128.6, 127.9, 127.7, 126.4, 121.8, 113.1, 100.2, 56.0, 34.1, 30.1, 23.2; MS m/z 253 (M^+), 222.

2-(2-Methoxyphenylethynyl)aniline (226a). The following procedure is representative for the preparation of the amine **226**. To a mixture of 2-iodoaniline (**224**, 0.720 g, 3.3 mmol), triethylamine (0.55 mL, 4.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.069 g, 0.01 mmol), and copper(I) iodide (0.032 g, 0.17 mmol) in 30 mL of DMF, was added slowly a solution of 2-methoxyphenylacetylene (**182c**, 0.529 g, 4.0 mmol) in 5 mL of DMF. After 2 hours of stirring at room temperature, 50 mL of a saturated aqueous ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/50% ether in hexanes, $R_f = 0.30$) afforded 0.655 g of **226a** (2.94 mmol, 89%) as a yellow liquid. IR (neat) 3469,

3366, 1614, 718 cm^{-1} ; ^1H δ 7.50 (1 H, dd, $J = 7.5$ and 1.8 Hz), 7.38 (1 H, dd, $J = 7.7$ and 1.4 Hz), 7.31 (1 H, td, $J = 7.9$ and 1.6 Hz), 7.14 (1 H, td, $J = 7.7$ and 1.6 Hz), 6.99–6.90 (2 H, m), 6.75–6.69 (2 H, m), 4.45 (2 H, s br), 3.91 (3 H, s); ^{13}C δ 159.6, 148.1, 132.3, 131.3, 129.5, 129.4, 120.5, 117.5, 114.0, 112.6, 110.4, 108.1, 91.3, 90.6, 55.7.

Isocyanate 227a. The following procedure is representative for the preparation of benzoenyne-isocyanates **227** from amine **226**. To a solution of 0.104 g of triphosgene (0.35 mmol) in 15 mL of anhydrous benzene was added a mixture of 0.210 g of amine **226a** (0.94 mmol) and 0.28 mL of triethylamine (2.0 mmol) in 10 mL of benzene under a nitrogen atmosphere at room temperature. After 6 hours stirring, the white precipitate of triethylamine hydrochloride was removed by filtration, and filtrate was concentrated in vacuo. Purification of the residue by flash column chromatography (silica gel/20% ether in hexanes, $R_f = 0.40$) afforded 0.207 g of **227a** (0.83 mmol, 88%) as a pale yellow liquid. IR (neat) 2250, 1600, 753 cm^{-1} ; ^1H δ 7.62 (1 H, dd, $J = 7.6$ and 1.7 Hz), 7.58 (1 H, dd, $J = 7.6$ and 1.5 Hz), 7.34 (1 H, ddd, $J = 8.3$, 7.5 and 1.8 Hz), 7.26 (1 H, td, $J = 7.7$ and 1.7 Hz), 7.16 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.07 (1 H, dd, $J = 7.9$ and 1.0 Hz), 6.97 (1 H, td, $J = 7.5$ and 1.0 Hz), 6.91 (1 H, d, $J = 8.3$ Hz), 3.92 (3 H, s); ^{13}C δ 160.0, 134.6, 133.3, 132.4, 130.3, 129.0, 126.6, 125.3, 123.6, 121.1, 120.4, 111.6, 110.5, 93.7, 88.6, 55.6; MS m/z 249 (M^+), 220, 206.

2-(4-Phenyl-1-butynyl)aniline (226b). The same procedure was repeated as described for **226a** except that 1.095 g of 2-iodoaniline (**224**, 5.0 mmol) and 0.710 g of 4-phenyl-1-butyne (**182b**, 5.5 mmol) were used to afford 0.997 g of amine **226b** (4.5 mmol, 90%) as a light yellow liquid. IR (neat) 3470, 3376, 1613, 1493, 1454, 748, 700 cm^{-1} ; ^1H δ 7.37–7.21 (6 H, m), 7.08 (1 H, td, $J = 7.7$ and 1.6 Hz), 6.69–6.63 (2 H, m), 3.93 (2 H, s

br), 2.95 (2 H, t, $J = 7.0$ Hz), 2.81 (2 H, t, $J = 7.0$ Hz); ^{13}C δ 147.7, 140.5, 131.9, 128.9, 128.5, 128.4, 126.3, 117.6, 114.0, 108.5, 94.6, 77.9, 35.0, 21.6.

Isocyanate 227b. The same procedure was repeated as described for **227a** except that 0.208 g of amine **226b** (0.94 mmol) was used to afford 0.172 g of **227b** (0.70 mmol, 74%) as a pale yellow liquid. IR (neat) 2252, 1507, 755, 699 cm^{-1} ; ^1H δ 7.40–7.25 (6 H, m), 7.21 (1 H, dd, $J = 7.7$ and 1.6 Hz), 7.12 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.03 (1 H, dd, $J = 7.8$ and 1.1 Hz), 3.00 (2 H, t, $J = 7.5$ Hz), 2.81 (2 H, t, $J = 7.2$ Hz); ^{13}C δ 140.4, 135.2, 132.1, 128.7, 128.4, 127.4, 126.3, 125.2, 123.4, 123.3, 98.6, 76.9, 34.5, 21.8; MS m/z 247 (M^+), 218, 156, 91.

2-(5-Methoxy-1-pentynyl)aniline (226c). The same procedure was repeated as described for **226a** except that 0.438 g of 2-iodoaniline (**224**, 2.0 mmol) and 0.236 g of 5-methoxy-1-pentyne (**182f**, 2.4 mmol) were used to afford 0.314 g of amine **226c** (1.66 mmol, 83%) as a light yellow liquid. IR (neat) 3467, 3359, 1616, 1492, 1456, 1116, 749 cm^{-1} ; ^1H δ 7.23 (1 H, dd, $J = 7.7$ and 1.2 Hz), 7.07 (1 H, ddd, $J = 8.1$, 7.4 and 1.5 Hz), 6.68–6.62 (2 H, m), 4.11 (2 H, s br), 3.53 (2 H, t, $J = 6.1$ Hz), 3.35 (3 H, s), 2.56 (2 H, t, $J = 7.1$ Hz), 1.88 (2 H, quintet, $J = 6.6$ Hz); ^{13}C δ 147.7, 131.9, 128.8, 117.7, 114.1, 108.7, 94.8, 77.3, 71.3, 58.6, 28.9, 16.5.

Isocyanate 227c. The same procedure was repeated as described for **227a** except that 0.173 g of amine **226c** (0.92 mmol) was used to afford 0.148 g of **227c** (0.69 mmol, 75%) as a pale yellow liquid. IR (neat) 2245, 1600, 1506, 1120, 757 cm^{-1} ; ^1H δ 7.38 (1 H, dd, $J = 7.6$ and 1.7 Hz), 7.21 (1 H, td, $J = 7.7$ and 1.8 Hz), 7.10 (1 H, td, $J = 7.5$ and 1.4 Hz), 7.00 (1 H, dd, $J = 7.9$ and 1.2 Hz), 3.52 (2 H, t, $J = 6.1$ Hz), 3.36 (3 H, s), 2.58 (2 H, t, $J =$

7.1 Hz), 1.88 (2 H, quintet, $J = 6.3$ Hz); ^{13}C δ 135.1, 132.1, 128.6, 127.3, 125.3, 123.3, 121.4, 98.8, 76.5, 71.2, 58.6, 28.2, 16.4; MS m/z 215 (M^+), 200, 183, 154.

1,3-Dihydro-3-[(2-methoxyphenyl)methylene]-2(2*H*)-indolone (228) and Ketone 229.

A solution of **227a** (0.132 g, 0.53 mmol) and γ -terpinene (0.144 g, 1.06 mmol) in 10 mL of 1,2-dichlorobenzene was heated under reflux for 15 days. The solvent was removed under vacuum. Purification of the residue by column chromatography afforded 0.028 g of **228** (0.11 mmol, 21%) as a yellow solid and 0.030 g of **229**⁹⁵ (0.107 mmol, 20%) as light yellow crystals. **228**: mp 186–187 °C; IR 3248, 1694, 756 cm^{-1} ; ^1H δ 11.26 (1 H, s), 8.70 (1 H, d, $J = 8.4$ Hz), 8.10 (1 H, dd, $J = 8.0$ and 1.6 Hz), 7.60 (1 H, ddd, $J = 8.6$, 7.2 and 1.5 Hz), 7.43 (1 H, dd, $J = 7.5$ and 1.6 Hz), 7.32 (1 H, ddd, $J = 8.1$, 7.7 and 1.7 Hz), 7.15 (1 H, td, $J = 7.7$ and 1.0 Hz), 7.01 (1 H, td, $J = 7.5$ and 1.0 Hz), 6.94 (1 H, d, $J = 8.4$ Hz), 5.55 (1 H, s), 3.88 (3 H, s); ^{13}C (acetone- d_6) δ 172.7, 169.6, 158.0, 142.2, 142.1, 134.9, 132.2, 130.1, 129.9, 129.1, 123.3, 121.3, 120.9, 116.8, 111.9, 56.0. **229**: mp 136–137 °C; IR 1771, 1684, 1600, 758 cm^{-1} ; ^1H δ 8.29 (1 H, ddd, $J = 7.9$, 1.6 and 0.4 Hz), 7.88 (1 H, ddd, $J = 8.1$, 7.3 and 1.6 Hz), 7.82 (1 H, dd, $J = 7.7$ and 1.6 Hz), 7.76 (1 H, dd, $J = 8.1$ and 0.8 Hz), 7.67–7.57 (2 H, m), 7.12 (1 H, td, $J = 7.6$ and 0.86 Hz), 7.00 (1 H, d, $J = 8.5$ Hz), 3.72 (3 H, s); ^{13}C δ 184.9, 159.7, 158.3, 154.4, 145.6, 136.8, 135.7, 131.3, 129.8, 128.8, 128.1, 124.6, 121.2, 118.0, 112.0, 56.2.

6(5*H*)-Benzofuro[3,2-*c*]quinolinone (238) and 5-Methyl-6(5*H*)-benzofuro[3,2-*c*]quinolinone. A solution of **227a** (0.150, 0.6 mmol) and chlorodimethylphenylsilane (0.11 mL, 0.66 mmol) in 6 mL of 1,2-dichlorobenzene was heated under reflux for 21 days. The solvent was removed under vacuum. Purification of the residue by column chromatography afforded 0.076 g of **238** (0.32 mmol, 53%) as a light brown solid. mp

294–295 °C (lit.⁹⁸ 294–296 °C); IR 3169, 1685, 736 cm⁻¹; ¹H (DMSO-*d*₆) δ 12.01 (1 H, s), 8.10 (1 H, dd, *J* = 6.9 and 2.0 Hz), 8.05 (1 H, d, *J* = 7.9 Hz), 7.84 (1 H, dd, *J* = 7.1 and 1.4 Hz), 7.61 (1 H, ddd, *J* = 8.4, 7.1 and 1.3 Hz), 7.54–7.44 (3 H, m), 7.33 (1 H, td, *J* = 7.5 and 0.9 Hz); ¹³C (DMSO-*d*₆) δ 159.1, 157.9, 154.8, 138.4, 130.9, 126.3, 124.7, 123.8, 122.5, 121.3, 121.2, 116.2, 111.8, 110.7, 110.0.

A solution of **227a** (0.095 g, 0.38 mmol) in 4 mL of 1,2-dichlorobenzene was heated under reflux for 21 days. The solvent was removed under vacuum. Purification of the residue by column chromatography afforded 0.010 g of **238** (0.043 mmol, 11%) and 0.009 g of *N*-methylated **238** (0.036 mmol, 9%) as a white solid. *N*-methylated **238**: mp 201–202 °C (lit.⁹⁹ 202–204 °C); IR 1660, 742 cm⁻¹; ¹H δ 8.32–8.27 (1 H, m), 8.17 (1 H, dd, *J* = 7.7 and 1.4 Hz), 7.68–7.61 (2 H, m), 7.50 (1 H, d, *J* = 8.9 Hz), 7.47–7.41 (2 H, m), 7.37 (1 H, ddd, *J* = 7.9, 7.1 and 1.1 Hz), 3.85 (3 H, s); ¹³C δ 159.6, 157.3, 155.4, 139.3, 130.7, 126.1, 124.6, 124.4, 122.3, 122.2, 115.1, 112.8, 111.3, 110.3, 29.2.

7,8-Dihydrobenzo[*k*]phenanthridin-6(5*H*)-one (239). A solution of **227b** (0.186 g, 0.75 mmol) in 10 mL of 1,2-dichlorobenzene was heated under reflux for 14 days. The solvent was removed under vacuum. Purification of the residue by column chromatography afforded 0.050 g of **239**⁹⁵ (0.20 mmol, 27%) as brown crystals. mp 245–246 °C (lit.¹⁰⁰ 250–252 °C); IR 1646, 1393, 755 cm⁻¹; ¹H δ 12.04 (1 H, s br), 8.18 (1 H, d, *J* = 8.2 Hz), 7.90–7.85 (1 H, m), 7.52–7.51 (2 H, m), 7.44–7.33 (3 H, m), 7.29–7.20 (1 H, m), 2.94–2.81 (4 H, m); ¹³C δ 163.4, 142.6, 140.3, 138.0, 131.8, 129.4, 129.3, 129.0, 128.3, 128.2, 126.2, 126.0, 122.2, 117.9, 116.9, 28.4, 21.9.

2-Pyridone 240 and 2-Methoxyquinoline 241. A solution of **227c** (0.166 g, 0.77 mmol) in 10 mL of 1,2-dichlorobenzene was heated under reflux for 14 days. The solvent was

removed under vacuum. Purification of the residue by column chromatography afforded 0.048 g of **240** (0.24 mmol, 31%) as a light brown solid and 0.015 g of **241** (0.07 mmol, 9%) as a yellow oil. **240**: mp 243–244 °C; IR 1651, 1610, 1405, 1130, 754 cm⁻¹; ¹H δ 11.87 (1 H, s), 7.83 (1 H, dd, *J* = 7.9 and 1.0 Hz), 7.46 (1 H, ddd, *J* = 8.2, 7.0 and 1.3 Hz), 7.38 (1 H, dd, *J* = 8.2 and 1.0 Hz), 7.17 (1 H, ddd, *J* = 8.1, 6.9 and 1.3 Hz), 4.36 (2 H, t, *J* = 5.2 Hz), 2.70 (2 H, t, *J* = 6.4 Hz), 2.08 (2 H, quintet, *J* = 5.7 Hz); ¹³C δ 165.0, 158.5, 136.9, 130.0, 122.0, 121.8, 115.8, 115.4, 106.7, 67.1, 21.3, 19.0. **241**: IR 1627, 1605, 1123, 763 cm⁻¹; ¹H δ 7.96 (1 H, dd, *J* = 8.2 and 1.5 Hz), 7.75 (1 H, d, *J* = 8.3 Hz), 7.54 (1 H, ddd, *J* = 8.4, 6.9 and 1.5 Hz), 7.31 (1 H, ddd, *J* = 8.1, 7.0 and 1.1 Hz), 4.37 (2 H, t, *J* = 5.2 Hz), 4.07 (3 H, s), 2.70 (2 H, t, *J* = 6.4 Hz), 2.09 (2 H, quintet, *J* = 5.8 Hz); ¹³C δ 161.6, 157.7, 145.2, 128.9, 126.7, 123.0, 121.1, 118.8, 102.5, 66.9, 53.4, 21.4, 19.0; MS *m/z* 215 (M⁺), 200.

1-Benzyl-3-(2-(2-(2-methylphenyl)ethynyl)cyclopentenyl)carbodiimide (243a'). To a solution of 0.492 g of *N*-(triphenylphosphoranylidene)benzylamine (1.34 mmol) in 20 mL of methylene chloride at -78 °C was added slowly a solution of 0.276 g of **185a** (1.24 mmol) in 5 mL of methylene chloride. After the reaction mixture was warmed to room temperature, the solvent was removed under vacuum, and the residue was purified by flash chromatography (silica gel/5% ether in hexanes, *R_f* = 0.30) to afford 0.332 g of **243a'** (1.06 mmol, 86% yield) as a yellow liquid. IR (neat) 2124, 1626, 756; ¹H δ 7.41 (1 H, d, *J* = 7.5 Hz), 7.37–7.28 (5 H, m), 7.18 (2 H, d, *J* = 3.8 Hz), 7.14–7.07 (1 H, m), 4.50 (2 H, s), 2.58 (2 H, tt, *J* = 7.3 and 2.2 Hz), 2.44 (3 H, s), 2.42 (2 H, tt, *J* = 8.1 and 2.0 Hz), 1.94 (2 H, quintet, *J* = 7.5 Hz); ¹³C δ 143.8, 139.9, 137.6, 137.2, 131.6, 129.3, 128.6, 128.0, 127.7, 127.3, 125.4, 123.3, 111.3, 95.0, 88.6, 50.6, 34.6, 34.5, 21.1, 20.8.

250. A solution of 0.332 g of **243a'** (1.06 mmol) in 15 mL of 1,2-dichlorobenzene was heated at 180 °C for 10 hours, then the solvent was removed under vacuum. Purification of the residue by flash chromatography (silica gel/20% ether in hexanes, R_f = 0.62) afforded 0.119 g of **250** (0.381 mmol, 36% yield) as a yellow solid. mp 128–133 °C; IR 1602, 1429, 781, 746 cm^{-1} ; ^1H δ 7.78 (1 H, s), 7.67 (1 H, d, J = 7.7 Hz), 7.43 (2 H, d, J = 6.7 Hz), 7.37–7.26 (4 H, m), 7.19 (1 H, t, J = 7.2 Hz), 7.01 (1 H, d, J = 7.5 Hz), 4.95 (2 H, s), 4.37 (2 H, s), 2.92 (4 H, q, J = 7.7 Hz), 2.14 (2 H, quintet, J = 7.4 Hz); ^{13}C δ 163.4, 155.7, 138.5, 131.6, 131.4, 128.3, 128.2, 127.5, 126.9, 126.84, 126.78, 125.9, 125.8, 121.8, 113.8, 51.0, 50.7, 34.5, 30.1, 23.2; MS m/z 312 (M^+), 311, 221, 207, 91.

1-(2-(2-(2-Methylphenyl)ethynyl)cyclopentenyl)-3-phenylurea (254a). The following procedure is representative for the preparation of urea **254** from isocyanate **185**. A solution of 0.250 g of **185a** (1.12 mmol) and 0.115 g of aniline (1.23 mmol) in 5 mL of methylene chloride was stirred for 8 hours at room temperature, then 5 mL of hexanes was added. Filtration afforded 0.302 g of urea **254a** (0.954 mmol, 85% yield) as a white solid. mp 198–199 °C; IR (KBr) 3302, 2187, 1644, 1596, 752 cm^{-1} ; ^1H (DMSO- d_6) δ 9.34 (1 H, s), 8.35 (1 H, s), 7.57 (1 H, d, J = 6.9 Hz), 7.50 (2 H, d, J = 7.9 Hz), 7.38–7.27 (5 H, m), 7.05 (1 H, t, J = 7.2 Hz), 3.09 (2 H, t, J = 7.2 Hz), 2.53 (2 H, t, J = 6.7 Hz), 1.98 (2 H, quintet, J = 7.3 Hz); ^{13}C (DMSO- d_6) δ 151.3, 146.4, 139.4, 139.0, 131.3, 129.5, 128.8, 128.1, 125.8, 123.1, 122.0, 118.1, 96.6, 94.0, 89.1, 32.8, 32.4, 21.6, 20.5.

1-(2-(2-(2-Methylphenyl)ethynyl)cyclopentenyl)-3-phenylcarbodiimide (243a). The following procedure is representative for the preparation of carbodiimide **243** from urea **254**. To a solution of 0.241 g of dibromotriphenylphosphorane (0.57 mmol) and 0.115 g of triethylamine (1.14 mmol) in 10 mL of methylene chloride, was added a suspension of

0.090 g of urea **254a** (0.285 mmol) in 5 mL of methylene chloride over a period of 45 min. After 1 hour of stirring at room temperature, the solvent was removed, and the residue was taken up by ether. The ether layer was concentrated, and the residue was purified by flash column chromatography (silica gel/5% ether in hexanes, $R_f = 0.53$) to afford 0.072 g of **243a** (0.241 mmol, 85% yield) as a yellow liquid. IR (neat) 2130, 1628, 754 cm^{-1} ; ^1H δ 7.31–7.23 (3 H, m), 7.18–7.03 (6 H, m), 2.68–2.57 (4 H, m), 2.43 (3 H, s), 2.02 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 141.9, 139.9, 138.4, 134.9, 131.7, 129.3, 129.2, 128.1, 125.4, 125.3, 124.1, 123.0, 113.4, 95.8, 88.2, 34.8, 34.6, 21.2, 20.7.

1-Phenyl-3-(2-(4-phenyl)butynyl)cyclopentenylurea (254b). The same procedure was repeated as described for **254a** except that 0.414 g of **185b** (1.74 mmol) and 0.178 g of aniline (1.91 mmol) were used to afford 0.416 g of urea **254b** (1.26 mmol, 72% yield) as a yellow solid. mp 132–134 $^{\circ}\text{C}$; IR 3319, 2205, 1643, 1600, 750 cm^{-1} ; ^1H δ 7.38–7.31 (6 H, m), 7.27–7.22 (3 H, m), 7.15–7.07 (1 H, m), 6.56 (1 H, s), 6.28 (1 H, s), 2.99 (2 H, t, $J = 7.5$ Hz), 2.81 (2 H, t, $J = 6.9$ Hz), 2.66 (2 H, t, $J = 6.9$ Hz), 2.36 (2 H, tt, $J = 7.4$ and 2.1 Hz), 1.89 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 152.2, 144.8, 140.7, 138.1, 128.9, 128.5, 128.3, 126.1, 123.7, 120.6, 99.6, 96.0, 76.4, 35.2, 32.54, 32.47, 21.8, 21.7.

1-(2-(2-(2-Methoxyphenyl)ethynyl)cyclopentenyl)-3-phenylurea (254c). The same procedure was repeated as described for **254a** except that 0.328 g of **185c** (1.37 mmol) was used to afford 0.311 g of urea **254c** (0.94 mmol, 69% yield) as a light yellow solid. mp 184–185 $^{\circ}\text{C}$; IR 3356, 3265, 2186, 1656, 1633, 750 cm^{-1} ; ^1H δ 7.63 (1 H, s), 7.46 (1 H, s), 7.31–7.15 (6 H, m), 7.00 (1 H, t, $J = 7.2$ Hz), 6.82 (1 H, t, $J = 7.4$ Hz), 6.72 (1 H, d, $J = 8.3$ Hz), 3.80 (3 H, s), 3.08 (2 H, t, $J = 7.2$ Hz), 2.39 (2 H, t, $J = 7.0$ Hz), 1.89 (2 H,

quintet, $J = 7.3$ Hz); ^{13}C δ 159.0, 151.6, 147.4, 138.3, 132.8, 129.4, 129.0, 123.4, 120.7, 119.8, 112.3, 110.4, 98.1, 91.9, 89.3, 55.6, 32.7, 32.0, 22.1.

Urea 254d. The same procedure was repeated as described for **254a** except that 0.168 g of **185d** (0.666 mmol) was used to afford 0.176 g of urea **254d** (0.509 mmol, 76% yield) as a yellow solid. mp 164–165 °C; IR 3323, 2183, 1636, 1600, 753 cm^{-1} ; ^1H δ 7.85 (1 H, s), 7.40 (1 H, s), 7.37–7.33 (2 H, m), 7.31–7.19 (4 H, m), 7.04 (1 H, tt, $J = 7.2$ and 1.3 Hz), 6.95 (1 H, d, $J = 7.7$ Hz), 6.91 (1 H, td, $J = 7.2$ and 1.1 Hz), 3.09 (2 H, t, $J = 7.5$ Hz), 2.87 (6 H, s), 2.51 (2 H, t, $J = 7.3$ Hz), 1.96 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 153.5, 151.9, 146.5, 138.3, 133.6, 129.1, 128.7, 123.6, 121.8, 120.2, 117.4, 116.7, 98.9, 94.8, 90.8, 43.9, 32.7, 32.1, 22.0.

1-((2-Pentynyl)cyclopentenyl)- 3-phenylurea (254g). The same procedure was repeated as described for **254a** except that 0.302 g of **185g** (1.72 mmol) was used to afford 0.334 g of urea **254g** (1.24 mmol, 72% yield) as a white solid. mp 167–169 °C; IR 3318, 1644, 1600, 1243 cm^{-1} ; ^1H δ 7.56 (1 H, s), 7.44 (1 H, s), 7.32–7.23 (4 H, m), 7.09–7.03 (1 H, m), 3.01 (2 H, t, $J = 7.4$ Hz), 2.36 (2 H, t, $J = 7.4$ Hz), 2.25 (2 H, t, $J = 7.1$ Hz), 1.87 (2 H, quintet, $J = 7.5$ Hz), 1.46 (2 H, sextet, $J = 7.2$ Hz), 0.91 (3 H, t, $J = 7.3$ Hz); ^{13}C δ 152.6, 144.2, 137.9, 129.1, 124.2, 121.4, 100.3, 97.1, 75.5, 32.8, 32.6, 22.4, 21.8, 21.7, 13.5.

1-Phenyl-3-(2-(4-phenyl)butynyl)cyclopentenylcarbodiimide (243b). The same procedure was repeated as described for **243a** except that 0.370 g of urea **254b** (1.10 mmol) was used to afford 0.248 g of **243b** (0.79 mmol, 72% yield) as a yellow liquid. IR (neat) 2128, 2051, 1594, 756 cm^{-1} ; ^1H δ 7.36–7.28 (4 H, m), 7.25–7.15 (6 H, m), 2.79 (2 H, t, $J = 7.7$ Hz), 2.60–2.49 (6 H, m), 1.96 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 141.0, 140.6,

138.7, 135.9, 129.3, 128.4, 128.2, 126.1, 125.4, 124.1, 113.8, 97.7, 76.0, 35.0, 34.5, 34.3, 22.1, 21.0.

1-(2-(2-(2-Methoxyphenyl)ethynyl)cyclopentenyl)-3-phenylcarbodiimide (243c). The same procedure was repeated as described for **243a** except that 0.162 g of urea **254c** (0.49 mmol) was used to afford 0.127 g of **243c** (0.40 mmol, 82% yield) as a yellow oil. IR (neat) 2127, 2051, 1630, 752 cm^{-1} ; ^1H δ 7.34–7.20 (4 H, m), 7.17–7.07 (3 H, m), 6.82 (2 H, t, $J = 7.8$ Hz), 3.80 (3 H, s), 2.66 (2 H, tt, $J = 7.3$ and 2.3 Hz), 2.58 (2 H, tt, $J = 7.3$ and 2.2 Hz), 1.99 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 159.5, 142.0, 138.3, 134.8, 133.3, 129.5, 129.2, 125.2, 124.0, 120.1, 113.4, 112.3, 110.3, 93.1, 88.3, 55.6, 34.7, 34.5, 21.1.

Carbodiimide 243d. The same procedure was repeated as described for **243a** except that 0.176 g of urea **254d** (0.509 mmol) was used to afford 0.084 g of **243d** (0.257 mmol, 50% yield) as a yellow oil. IR (neat) 2132, 1628, 743, 696 cm^{-1} ; ^1H δ 7.30–7.23 (3 H, m), 7.21–7.09 (4 H, m), 6.86 (1 H, t, $J = 7.5$ Hz), 6.77 (1 H, td, $J = 7.4$ and 1.1 Hz), 2.94 (6 H, s), 2.69–2.56 (4 H, m), 2.01 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 154.5, 141.3, 138.5, 135.0, 134.2, 129.4, 129.0, 125.3, 124.1, 120.2, 116.7, 115.1, 113.8, 96.3, 89.8, 43.5, 34.9, 34.4, 21.2.

1-((2-Pentynyl)cyclopentenyl)-3-phenylcarbodiimide (243g). The same procedure was repeated as described for **243a** except that 0.212 g of urea **254g** (0.79 mmol) was used to afford 0.128 g of **243g** (0.51 mmol, 65% yield) as a brown oil. IR (neat) 2125, 2051, 1633, 1205, 755 cm^{-1} ; ^1H δ 7.32–7.25 (2 H, m), 7.18–7.10 (3 H, m), 2.50 (4 H, t, $J = 7.6$ Hz), 2.23 (2 H, t, $J = 7.0$ Hz), 1.92 (2 H, quintet, $J = 7.5$ Hz), 1.46 (2 H, sextet, $J = 7.3$ Hz), 0.92 (3 H, t, $J = 7.4$ Hz); ^{13}C δ 140.5, 138.7, 135.8, 129.2, 125.2, 124.0, 114.0, 98.5, 75.5, 34.6, 34.3, 22.0, 21.7, 20.9, 13.4.

257. A solution of 0.072 g of **243a** (0.241 mmol) in 5 mL of chlorobenzene was heated under reflux for 10 hours, then the solvent was removed under vacuum. Purification of the residue by flash column chromatography (silica gel/20% ether in hexanes, R_f = 0.30) afforded 0.040 g of **257** (0.0134 mmol, 56 % yield) as a yellow solid. IR 1593, 1417, 731 cm^{-1} ; ^1H δ 7.85 (1 H, s), 7.72 (1 H, d, J = 7.5 Hz), 7.39–7.33 (5 H, m), 7.25 (1 H, td, J = 7.3 and 1.1 Hz), 7.15 (1 H, d, J = 7.3 Hz), 7.12–7.06 (1 H, m), 4.91 (2 H, s), 2.91 (2 H, t, J = 7.5 Hz), 2.85 (2 H, t, J = 7.7 Hz), 2.09 (2 H, quintet, J = 7.5 Hz); ^{13}C δ 163.9, 153.9, 145.2, 132.1, 131.4, 128.9, 128.4, 127.7, 127.4, 127.2, 125.6, 123.0, 122.2, 116.2, 52.7, 34.4, 30.2, 23.3; MS m/z 298 (M^+), 297, 219.

2-(Phenylamino)pyridine 261. The same procedure was repeated as described for **257** except that 0.132 g of **243b** (0.422 mmol) was used to afford 0.097 g of **261** (0.309 mmol, 73% yield) as a yellow solid. mp 83–85 °C; IR 3370, 1578, 747 cm^{-1} ; ^1H δ 7.73 (1 H, dd, J = 6.2 and 2.3 Hz), 7.38–7.21 (5 H, m), 7.16–7.12 (2 H, m), 6.91 (1 H, tt, J = 7.2 and 1.2 Hz), 6.24 (1 H, s), 3.23 (2 H, t, J = 7.1 Hz), 3.00 (2 H, t, J = 7.5 Hz), 2.82–2.77 (2 H, m), 2.63–2.58 (2 H, m), 2.14 (2 H, quintet, J = 7.4 Hz); ^{13}C δ 162.9, 151.3, 142.7, 140.2, 139.0, 133.4, 128.8, 128.4, 127.8, 127.0, 126.4, 126.2, 120.7, 117.8, 117.5, 34.2, 32.6, 28.9, 24.0, 23.4. MS m/z 312 (M^+), 311.

262, 263, and 264. A solution of 0.165 g of **243g** (0.66 mmol) in 10 mL of chlorobenzene was heated under reflux for 12 hours, then the solvent was removed under vacuum. Purification of the residue by flash chromatography afforded 0.058 g of **262** (0.23 mmol, 35% yield), 0.047 g of **263** (0.19 mmol, 28% yield) and 0.020 g of **264** (0.079 mmol, 12% yield). **262**: mp 74–77 °C; IR 1595, 1569, 1422, 756 cm^{-1} ; ^1H δ 7.34–7.28 (4 H, m), 7.12 (1 H, s), 7.08–7.02 (1 H, m), 3.76 (2 H, t, J = 5.6 Hz),

2.82–2.73 (6 H, m), 2.06–1.95 (4 H, m); ^{13}C δ 161.1, 153.9, 147.0, 133.1, 128.5, 126.9, 124.4, 123.1, 115.9, 50.8, 34.2, 30.0, 27.7, 23.3, 22.4; MS m/z 250 (M^+), 249, 221. **263**: IR 3423, 1596, 1577, 1427, 748 cm^{-1} ; ^1H δ 7.48–7.43 (2 H, m), 7.30–7.23 (3 H, m), 6.92 (1 H, tt, $J = 7.3$ and 1.2 Hz), 6.35 (1 H, s), 5.96 (1 H, ddt, $J = 16.8$, 10.5 and 6.2 Hz), 5.24 (1 H, dq, $J = 10.3$ and 1.6 Hz), 5.22 (1 H, dq, $J = 16.9$ and 1.6 Hz), 3.32 (2 H, d, $J = 6.1$ Hz), 2.93 (2 H, t, $J = 7.6$ Hz), 2.84 (2 H, t, $J = 7.3$ Hz), 2.10 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 161.7, 152.6, 141.7, 135.7, 134.6, 128.8, 128.3, 120.9, 118.1, 117.22, 117.16, 36.5, 34.2, 30.1, 23.4; MS m/z 250 (M^+), 249, 235. **264**: IR 3456, 1596, 1578, 748 cm^{-1} ; ^1H δ 7.51–7.46 (2 H, m), 7.31–7.23 (3 H, m), 6.92 (1 H, tt, $J = 7.3$ and 1.1 Hz), 6.12 (1 H, s), 2.92 (2 H, t, $J = 7.6$ Hz), 2.84 (2 H, t, $J = 7.3$ Hz), 2.49 (2 H, t, $J = 7.6$ Hz), 2.09 (2 H, quintet, $J = 7.5$ Hz), 1.67 (2 H, sextet, $J = 7.4$ Hz), 1.00 (3 H, t, $J = 7.3$ Hz); ^{13}C δ 160.7, 151.9, 141.8, 133.9, 128.9, 128.4, 121.0, 120.4, 118.2, 34.0, 33.3, 30.2, 23.4, 21.9, 14.0; MS m/z 252 (M^+), 251, 237, 223, 195, 147.

274. The same procedure was repeated as described for **257** except that 0.127 g of **243c** (0.40 mmol) was used to afford 0.052 g of **274**⁹⁵ (0.172 mmol, 43% yield) as brown crystals. mp 174–175 °C; IR 3431, 1642, 1600, 745 cm^{-1} ; ^1H δ 7.59 (1 H, d, $J = 8.1$ Hz), 7.51–7.45 (3 H, m), 7.41 (1 H, td, $J = 7.8$ and 1.4 Hz), 7.35–7.27 (3 H, m), 7.02 (1 H, t, $J = 7.3$ Hz), 6.77 (1 H, s), 3.17 (2 H, t, $J = 7.4$ Hz), 3.10 (2 H, t, $J = 7.9$ Hz), 2.26 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 163.5, 159.8, 155.2, 149.9, 141.0, 129.1, 126.0, 123.3, 122.1, 121.9, 121.0, 118.7, 112.9, 111.4, 105.9, 34.9, 27.1, 23.2; MS m/z 300 (M^+), 299.

275, 276, and 277. The same procedure was repeated as described for **257** except that 0.073 g of **243d** (0.22 mmol) was used to afford 0.010 g of **275** (0.03 mmol, 14% yield)

as a brown solid, 0.035 g of **276**⁹⁵ (0.107 mmol, 48%) as brown crystals and 0.005 g of **277** (0.015 mmol, 7%) as a brown solid.

A solution of carbodiimide **243d** (0.112 g, 0.342 mmol) and chlorodimethylphenylsilane (0.070 g, 0.41 mmol) in 10 mL of chlorobenzene was heated at 132 °C under reflux for 3 hrs. After cooling, the solvent was removed under vacuum. The residue was purified by column chromatography to afford 0.075 g of **275** (0.24 mmol, 70%) and 0.016 g of **276** (0.049 mmol, 14%). **275**: mp 177–178 °C; IR 3460, 1601, 1574, 747 cm⁻¹; ¹H δ 7.78 (1 H, d, *J* = 7.7 Hz), 7.55 (2 H, d, *J* = 7.7 Hz), 7.48–7.39 (2 H, m), 7.34–7.23 (3 H, m), 6.97 (1 H, t, *J* = 7.3 Hz), 6.87 (1 H, s br), 4.01 (3 H, s), 3.41 (2 H, t, *J* = 7.3 Hz), 3.09 (2 H, t, *J* = 7.7 Hz), 2.26 (2 H, quintet, *J* = 7.5 Hz); ¹³C δ 159.5, 149.6, 144.6, 141.4, 140.3, 129.0, 124.6, 121.5, 121.2, 120.8, 120.3, 118.6, 110.7, 108.6, 104.5, 34.1, 30.8, 29.5, 23.1; MS *m/z* 313 (M⁺), 312. **276**: mp 260–261 °C (decomp. with melting); IR 3149, 758, 732 cm⁻¹; ¹H δ 11.75 (1 H, s br), 8.11 (1 H, d, *J* = 8.2 Hz), 7.82 (1 H, dd, *J* = 8.5 and 1.4 Hz), 7.62 (1 H, ddd, *J* = 8.5, 6.9 and 1.5 Hz), 7.43 (1 H, ddd, *J* = 8.4, 7.2 and 1.7 Hz), 7.33 (1 H, ddd, *J* = 8.3, 6.9 and 1.1 Hz), 7.22 (1 H, dd, *J* = 7.4 and 1.7 Hz), 7.14 (1 H, d, *J* = 8.2 Hz), 7.05 (1 H, td, *J* = 7.3 and 1.0 Hz), 3.14–3.07 (2 H, m), 2.49–2.37 (10 H, m); ¹³C δ 154.6, 152.4, 148.7, 143.2, 138.2, 132.9, 128.9, 128.4, 127.06, 127.02, 126.6, 126.4, 122.9, 122.6, 120.1, 119.1, 117.1, 43.2, 27.6, 26.8, 25.4; MS *m/z* 327 (M⁺), 312, 298. **277**: mp 130–131 °C; IR 1594, 1446, 758 cm⁻¹; ¹H δ 8.15 (1 H, d, *J* = 8.5 Hz), 7.77 (1 H, dd, *J* = 8.5 and 1.2 Hz), 7.58 (1 H, ddd, *J* = 8.4, 6.8 and 1.4 Hz), 7.40 (1 H, ddd, *J* = 8.4, 7.2 and 1.7 Hz), 7.29 (1 H, ddd, *J* = 8.5, 7.0 and 1.2 Hz), 7.18 (1 H, dd, *J* = 7.5 and 1.8 Hz), 7.12 (1 H, d, *J* = 7.5 Hz), 7.02 (1 H, td, *J* = 7.4 and 1.1 Hz), 3.90 (3 H, m), 2.98–2.91 (2 H, m), 2.44–2.33 (10 H, m); ¹³C δ 153.4, 152.4, 150.7, 144.0, 137.6, 132.9,

128.74, 128.68, 127.6, 126.7, 126.4, 122.8, 122.4, 120.1, 118.3, 117.0, 115.0, 43.1, 29.6, 27.0, 25.65, 25.61; MS m/z 341 (M^+), 326, 312.

Urea 284. The same procedure was repeated as described for **254a** except that 0.412 g of **185h** (2.32 mmol) and 0.347 g of 2-aminophenyl allyl ether (**283**, 2.32 mmol) were used to afford 0.545 g of urea **284** (1.67 mmol, 72% yield) as a light yellow solid. mp 123–125 °C; IR 3321, 2202, 1670, 1638, 1602, 1539, 1245, 748 cm^{-1} ; ^1H δ 8.00 (1 H, dd, $J = 7.4$ and 1.8 Hz), 7.14 (1 H, s br), 7.12 (1 H, s, br), 6.99 (1 H, td, $J = 7.2$ and 2.0 Hz), 6.94 (1 H, td, $J = 7.3$ and 1.9 Hz), 6.87 (1 H, dd, $J = 7.5$ and 2.0 Hz), 6.07 (1 H, ddt, $J = 17.2$, 10.5 and 5.3 Hz), 5.40 (1 H, dq, $J = 17.2$ and 1.4 Hz), 5.32 (1 H, dq, $J = 10.5$ and 1.4 Hz), 4.60 (2 H, dt, $J = 5.5$ and 1.4 Hz), 4.27 (2 H, s), 3.39 (3 H, s), 3.06 (2 H, t, $J = 7.5$ Hz), 2.42 (2 H, t, $J = 7.4$ Hz), 1.93 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 151.4, 147.6, 147.0, 132.9, 127.9, 123.2, 121.2, 120.3, 118.2, 111.6, 97.9, 91.5, 81.7, 69.5, 60.6, 57.5, 32.7, 32.4, 21.9.

Carbodiimide 285. The same procedure was repeated as described for **243a** except that 0.294 g of urea **284** (0.90 mmol) was used to afford 0.158 g of **285** (0.513 mmol, 57% yield) as a yellow oil. IR (neat) 2134, 1632, 1099, 750 cm^{-1} ; ^1H δ 7.13–7.04 (2 H, m), 6.90–6.85 (2 H, m), 6.05 (1 H, ddt, $J = 17.4$, 10.5 and 5.3 Hz), 5.43 (1 H, dq, $J = 17.3$ and 1.6 Hz), 5.32 (1 H, dq, $J = 10.5$ and 1.4 Hz), 4.59 (2 H, dt, $J = 5.5$ and 1.5 Hz), 4.21 (2 H, s), 3.34 (3 H, s), 2.59–2.48 (4 H, m), 1.93 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 153.2, 144.0, 137.2, 132.6, 127.0, 126.3, 125.0, 121.0, 118.0, 112.2, 110.7, 91.4, 81.7, 69.6, 60.5, 57.4, 34.5, 34.3, 21.1.

288 and 291. A solution of 0.086 g of **285** (0.278 mmol) in 10 mL of chlorobenzene was heated under reflux for 8 hours, then the solvent was removed under vacuum. The

residue was purified by column chromatography to afford 0.042 g of **288** (0.136 mmol, 49 % yield) as a light yellow oil and 0.023 g of **291** (0.083 mmol, 30% yield) as a pale yellow oil. **288**: IR 1608, 1573, 1424, 1269, 748 cm^{-1} ; ^1H δ 7.19 (1 H, dd, $J = 8.2$ and 1.5 Hz), 7.16–7.09 (1 H, m), 7.08 (1 H, s), 6.96–6.90 (2 H, m), 5.92 (1 H, ddt, $J = 17.2$, 10.5 and 5.3 Hz), 5.29 (1 H, dq, $J = 17.3$ and 1.6 Hz), 5.17 (1 H, dq, $J = 10.6$ and 1.4 Hz), 5.06 (2 H, s), 4.91 (2 H, s), 4.52 (2 H, dt, $J = 5.0$ and 1.6 Hz), 2.82 (2 H, t, $J = 7.3$ Hz), 2.80 (2 H, t, $J = 7.5$ Hz), 2.03 (2 H, quintet, $J = 7.5$ Hz); ^{13}C δ 162.7, 153.4, 152.3, 134.2, 133.3, 128.9, 128.2, 127.7, 126.0, 121.1, 116.8, 115.0, 113.9, 81.8, 69.1, 67.7, 34.2, 30.0, 23.2; MS m/z 308 (M^+), 293, 277, 160, 148. **291**: IR 1571, 1494, 1419, 745 cm^{-1} ; ^1H δ 7.96–7.94 (1 H, m), 7.16 (1 H, s), 6.87–6.82 (3 H, m), 4.44 (1 H, dd, $J = 10.2$ and 1.9 Hz), 3.95 (1 H, t, $J = 9.8$ Hz), 3.87–3.76 (1 H, m), 2.92 (2 H, t, $J = 7.2$ Hz), 2.82 (2 H, t, $J = 7.3$ Hz), 2.72 (2 H, tt, $J = 15.2$ and 3.9 Hz), 2.28–2.19 (1 H, m), 2.08 (2 H, quintet, $J = 7.5$ Hz), 1.46 (1 H, qd, $J = 12.3$ and 4.8 Hz); ^{13}C δ 161.2, 151.1, 145.9, 132.3, 128.2, 127.7, 122.2, 121.2, 120.0, 118.8, 116.9, 70.3, 53.3, 34.2, 30.1, 26.3, 25.1, 23.3; MS m/z 278 (M^+), 277.

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Figure 6. ORTEP drawing of the crystal structure of 1*H*-cyclobut[*a*]indene **105**

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PUBLICATIONS

1. "Biradicals from Benzoenyne-Allenenes. Application in the Synthesis of 11*H*-Benzo[*b*]fluoren-11-ols, 1*H*-Cyclobut[*a*]indenes, and Related Compounds" Hongbin Li, Hai-Ren Zhang, Jeffrey L. Petersen, Kung K. Wang. *J. Org. Chem.* **2001**, *66*, 6662-6669.
2. "Novel Synthesis of 4,5-Diarylphenanthrenes via C²-C⁶ Cyclization of Benannulated Enyne-Allenenes" Hongbin Li, Jeffrey L. Petersen, Kung K. Wang. *J. Org. Chem.* **2001**, *66*, 7804-7810.
3. "Synthesis of 11*H*-Benzo[*b*]fluoran-11-ols and Related Polyaromatic Compounds via Biradicals Generated from Benzoenyne-Allenenes" Kung K. Wang, Hai-Ren Zhang, Hongbin Li. 218th ACS meeting, New Orleans, August 1999.