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## Synthesis of 1,1'-binaphthyl derivatives via benzannulated enyne-allenes

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**Synthesis of 1,1'-Binaphthyl Derivatives  
via Benzannulated Enyne-Allenes**

**Joshua F. Bailey**

**Thesis submitted to the Eberly College of Arts and Sciences  
at West Virginia University in partial fulfillment of  
the requirements for the degree of**

**Master of Sciences  
In  
Chemistry**

**Kung K. Wang, Ph.D., Committee Chair  
Jeffrey L. Petersen, PhD.  
George O'Doherty, PhD.**

**C. Eugene Bennett Department of Chemistry**

**Morgantown, WV  
2004**

**Keywords: Enyne-Allene, 1,1'-Binaphthyl, Cascade Cyclization**

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## **Abstract**

### **Synthesis of 1,1'-Binaphthyl Derivatives**

#### **via Benzannulated Enyne-Allenenes**

**Joshua F. Bailey**

The generation of benzannulated enyne-allenes in situ via a prototropic isomerization promotes a cascade radical cyclization to the formation of 1,1'-binaphthyl derivatives. The simplicity of the synthetic method and the mildness of the reaction conditions make this cascade cyclization process an intriguing alternative route to the generation of 1,1'-binaphthyl derivatives. The transformation from a precursor benzannulated enyne-allene to a novel binaphthyl system proceeds through a C<sup>2</sup>-C<sup>6</sup> cyclization reaction followed by a radical-radical coupling reaction and tautomerization to provide the formal Diels-Alder adduct.

**Dedicated to**  
**My parents, My grandparents,**  
**and**  
**My dearest friend Megan Breeden**

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## 1. Introduction

In our world today the chirality of an organic molecule can be a key constituent in many areas of science.<sup>1</sup> The ranging disciplines such as that of materials, medicine, and catalysis are vastly important to industry and healthcare. Yet, achieving a pure chiral center or molecule still remains a most difficult challenge. To address the situations of developing chirality in everyday life, it is best to have an understanding of how this term and knowledge arose.

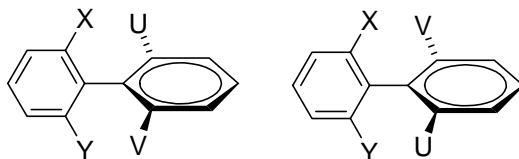
The history of chirality began in the early 1800s when Jean-Baptiste Biot reported the first chirality of a molecule.<sup>2</sup> Following Biot's statement of the first chiral molecule, the scientific term lay dormant for nearly 40 years until the early 1850s. In the early 1850s Louis Pasteur separated a mixture a tartaric acid salt mixtures by hand. Upon completion of his separation Pasteur discovered that the two separate compounds rotated plane polarized light differently.<sup>2</sup> This insightful discovery led to more research.

Of great importance was Kekulé's discovery that carbon has a valence of four.<sup>2</sup> By the time the 1870s arrived knowledge of the carbon atom and how it existed in nature were very interesting topics in the scientific community. It was recognized by van't Hoff and Le Bel that when four different groups are attached to a carbon atom, arrayed at the corners of a tetrahedron, the arrangements can exist in two different forms.<sup>2</sup> As the term chirality evolved, van't Hoff predicted that more than one type of chirality may exist. His prediction was true and valuable because not only did it predict a new term, axial chirality, it laid the foundations of what is known today as stereochemistry.<sup>3,4</sup>

The molecules that van't Hoff described existed with a chiral axis whose helical sense is maintained through hindered rotation about single bonds, the hindrance in general being due to steric congestion.<sup>5</sup> The classical examples of such molecules are the

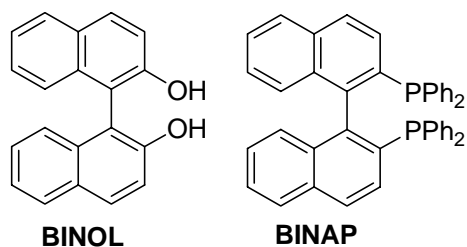
biphenyls (or biaryls in general) shown in Figure 1. If  $X \neq Y$  and  $U \neq W$  and, moreover, the steric interaction of X-U, X-V, and/ or Y-V, Y-U is large enough to make the planar conformation an energy maximum, two nonplanar, axially chiral enantiomers (Figure 1) exist. If interconversion through the planar conformation is slow enough they may, under suitable circumstances, be isolated (resolved). This type of enantiomerism was first discovered by Christie and Kenner (1922) in the case of 6,6'-dinitro-2,2'-diphenic acid (Figure 1,  $X = U = \text{CO}_2\text{H}$ ;  $Y = V = \text{NO}_2$ ), which they were able to resolve.<sup>5</sup>

**Figure 1.** Enantiometric chiral biphenyls



BINOL, one of the first molecules to exhibit axial chirality was first prepared as a racemate in 1873, and later on as an optically active compound.<sup>6</sup> In 1979 Noyori showed

**Figure 2.** Early synthetic biphenyls



BINOL to be a superb chiral ligand in the stoichiometric reduction of ketones with  $\text{LiAlH}_4$ , giving corresponding alcohols in  $\geq 99\%$  ee.<sup>7</sup> Afterward, Noyori demonstrated that BINAP can serve as a chiral version of  $\text{Ph}_3\text{P}$  in Ru- and Rh- catalyzed asymmetric hydrogenations and allylic hydrogen shifts.<sup>8,9</sup> Once these two axially chiral molecules were synthesized and shown to contain extremely interesting characteristics, the doors

became wide open for the synthesis of 2,2'-disubstituted 1,1'-binaphthyl systems as chiral ligands in transition metal-catalyzed asymmetric reactions.

Binaphthyl and binaphthyl derivatives are known as optically active materials. The chirality of these systems being derived from the restricted rotation of the two naphthalene rings.<sup>10</sup> This restricted rotation leads to the formation of di-symmetric planes within the molecule. The non-planar planes that arise lead to the arrangement of the four groups attached to the chirality axis to be in different planes, therefore, giving binaphthyl systems true axial chirality. Many studies have been performed on the racemization of 1,1'-binaphthyls. The calculations demonstrate that the racemization developed by the hindered rotation about the internuclear bonds is greater as substituents are added to the 2,2' positions.<sup>11</sup> The calculations can be located in Table 1.

**Table 1. Racemization of 1,1'-Binaphthyl and BINOL**

Compound	T (°C)	solvent	$t^{1/2}$ (min)	$\Delta G^\ddagger$ (kJ/mol)	ref
1,1'-Binaphthyl	44	benzene	68	100.7	12
1,1'-Binaphthyl	50	DMF	14.5	98.5	13
BINOL	195	naphthalene	270	155.5	14a,b

The racemization barriers of 1,1'-binaphthyl and BINOL have been computed using molecular mechanics<sup>15</sup> and semiempirical methods.<sup>16</sup> The barriers suggest as steric hindrance increases the rate of racemization decreases. The data provide evidence that restricted rotation does not allow for a planar molecule to exist in time, and that axial chirality is present in each molecule.

Currently several methods and synthetic processes exist for the formation of binaphthyl systems. A review of the literature revealed some of the plausible processes that can lead to the formation of these systems.

### 1.1 Literature Review of the Synthetic Developments for 1,1'-Binaphthyls

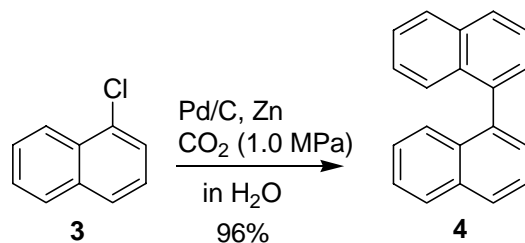
One method that has been used to synthesize biaryl units is the palladium-mediated cross-coupling reaction between aryl halides and aryl boronic acids (the Suzuki reaction).<sup>17</sup> In 2003, Leadbeater demonstrated that the Suzuki reaction can also be applied to naphthyl boronic acids to yield the corresponding 1,1'-binaphthyl system.<sup>18</sup> The reaction sequence is described in Scheme 1.

**Scheme 1.** Cross-coupling formation of a biaryl



This generation of the 1,1'-binaphthyl biaryl complex was performed in mild conditions and is one of many sequences to the synthetic analogue. Another approach for the generation of 1,1'-binaphthyl was employed by Yin. In 2003, he reported that CO<sub>2</sub> could be used as a selective agent in palladium-catalyzed reductive Ullmann coupling with zinc in water.<sup>19</sup> This reaction was shown to form biaryls in good yield. His approach to the 1,1'-binaphthyl synthon is described in Scheme 2.

**Scheme 2.** Medal mediated formation of a biaryl



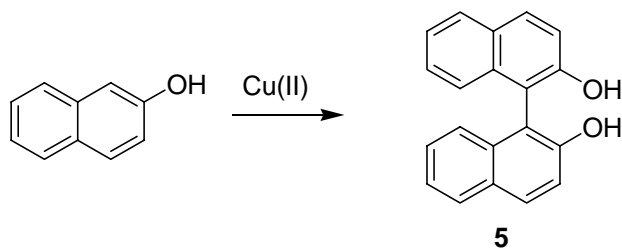
In conclusion, he observed that CO<sub>2</sub> strongly influenced the yield of aromatic halides that are less reactive.<sup>19</sup> Both of these syntheses are different in synthetic scheme, but they do reach the same target without known problems.

### 1.2 Synthetic Methods for the Development of BINOL and BINOL type 1,1'-Binaphthyls

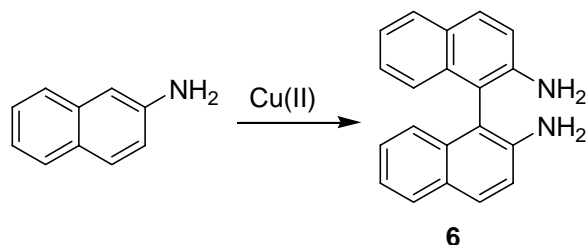
The unparallel success of BINOL and BINAP and related phosphines stimulated research worldwide. As a result, numerous BINAP, BINOL, and other binaphthyl analogues have been synthesized since the mid-1980s and tested as chiral ligands in a variety of transition metal catalyzed reactions.<sup>9,20</sup>

One of the synthetic methods of BINOL **5** is straightforward, it relies upon mild oxidizing agents, such as Cu(II),<sup>21,22,23</sup> Fe(III), Mn(III), to effect high-yielding, stoichiometric oxidative coupling of  $\beta$ -naphthol (Scheme 3).<sup>24</sup> Similar coupling of  $\beta$ -naphthylamine leads to BINAM **72**<sup>25,26</sup> (Scheme 4).

**Scheme 3.** A formation of BINOL

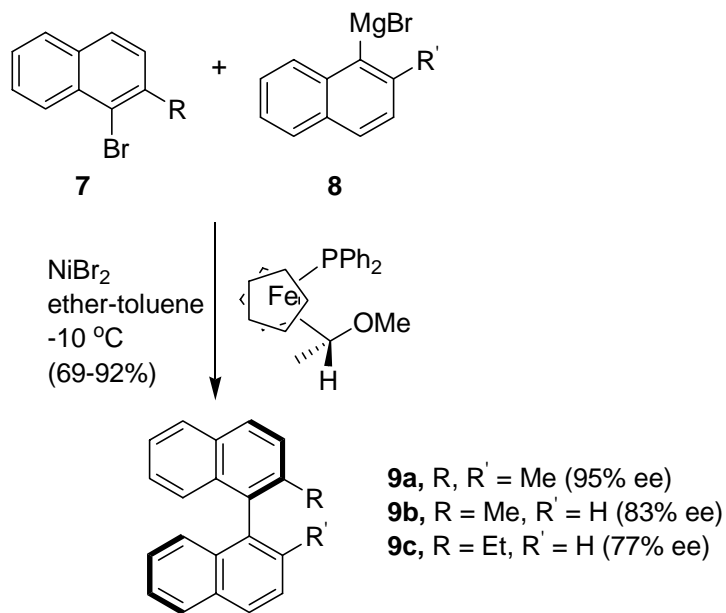


**Scheme 4.** A formation of BINAM



Once the central dogma and the many syntheses of homo-bidentate  $C_2$ -symmetrical ligands, such as binaphthyls **5** and **6** were complete, several groups began to investigate a different approach, the potential formation of hetero-bidentate binaphthyls (i.e., with non-identical coordinating groups, lacking the notorious  $C_2$  symmetry.)<sup>24</sup> Pioneering work to the development of these hetero-bidentate 1,1'-binaphthyls used a metal-mediated cross-coupling via a nickel catalyzed coupling of aryl halides with aryl Grignard reagents (Kumada coupling)<sup>27</sup> to give the corresponding cross-coupled products described in Scheme 5.

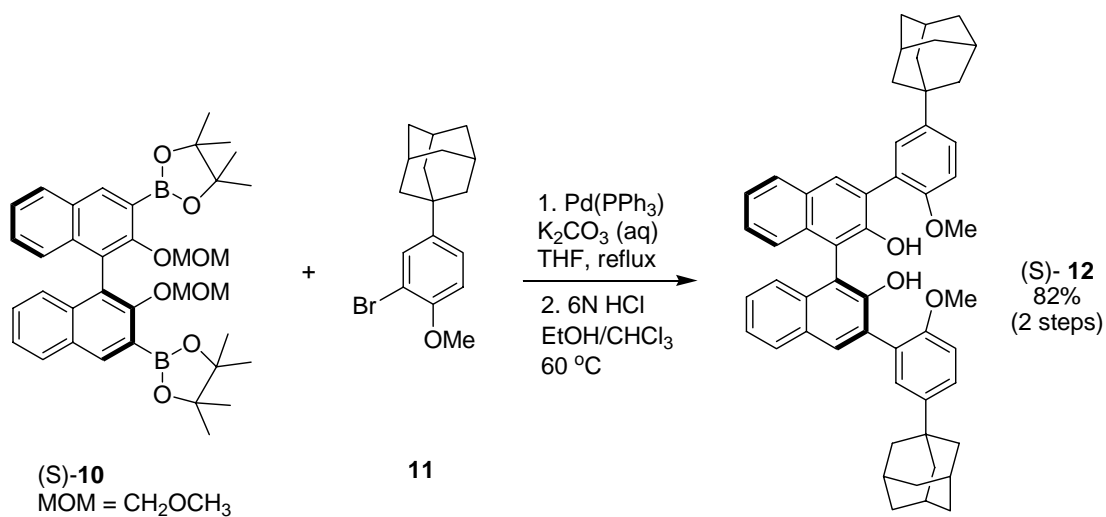
**Scheme 5.** A 1,1'-2,2'-binaphthyl formed by a Kumada coupling



### 1.3 Known Systems and Applications

Of the many transition metal-catalyzed reactions, those which use novel 1,1'-binaphthyl systems as an additional catalyst, have been gaining great respect for their ability to generate chiral propargyl and secondary alcohols. Two recent examples of the capabilities that binaphthyl compounds exhibit were demonstrated in 2002 and 2003. In 2002 Pu presented a new 1,1'-binaphthyl based catalyst for the enantioselective phenylacetylene addition to aromatic aldehydes.<sup>28</sup> The compound that he developed contained bulky 3,3' aryl substituents and was found to catalyze the reaction of a terminal alkynes with various aromatic aldehydes under mild conditions to generate chiral propargyl alcohols with 80-94% ee.<sup>28</sup> The compound was synthesized according to Scheme 6.

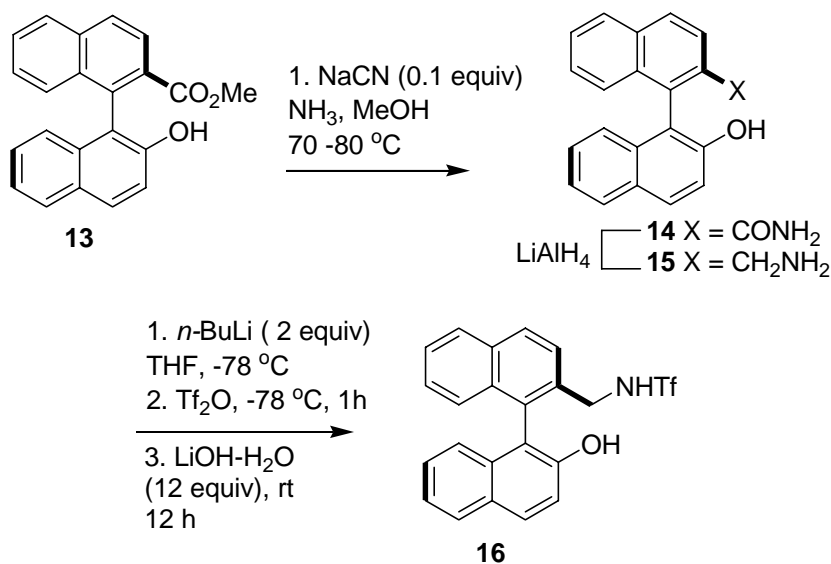
**Scheme 6.** The generation of a 1,1'-binaphthyl derivative used as a catalyst for the addition of terminal alkynes to aromatic aldehydes



The novel 1,1'-binaphthyl derivative, albeit a sterically hindered structure, is a good enantioselective catalyst for the reaction of phenylacetylene with various aromatic aldehydes under various mild conditions.<sup>28</sup> It is one example of the diverse structural characteristics that these systems can adopt. Another example was presented in 2002 by

Ha. This novel 1,1'-binaphthyl system also demonstrated that it possessed catalytic properties. His new *N*-triflated amino alcohol-titanium catalyst was designed for the asymmetric ethylation of aldehydes.<sup>29</sup> The synthetic process is described in Scheme 7.

**Scheme 7.** A new *N*-triflated amino alcohol catalyst



Compound **16** is a new binaphthyl-based *N*-triflated amino alcohol ligand and it was applied to the enantioselective addition of diethyl zinc to various aldehydes.<sup>29</sup> Both of the compounds presented serve as catalyst in synthetic processes used to generate chiral alcohols. The synthesis of these synthetic binaphthyl analogues not only demonstrates the diverse structural characteristics of two different systems, it also illustrates that chiral alcohols can result from the addition of various binaphthyls as a catalyst. This is one of the reasons that binaphthyl derivatives remain of great interest in the synthetic community.

The formation of binaphthyl systems continues to be of great interest because of their lack of symmetry and potential ligand capabilities. Due to the chirality developed in the molecule, possible future metal coordination to a corresponding cyclopentadienyl

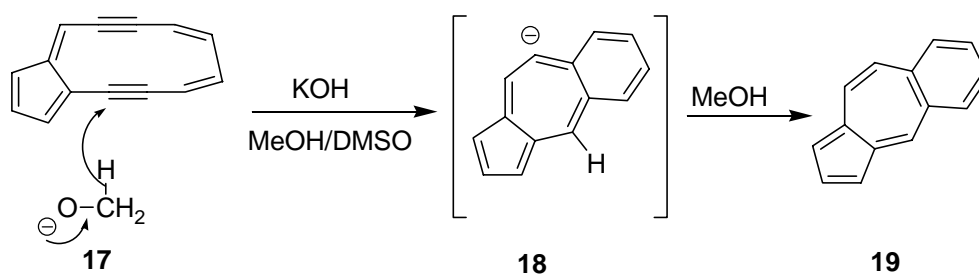


anion or transition metal could allow for the generation of a chiral ligand and catalyst. The generation of this chiral ligand could be of great benefit to the industrial community and the synthetic chemistry field for its use in asymmetric catalysis.

## 2. Cyclization Reaction of Enediynes via the Bergman Cyclization

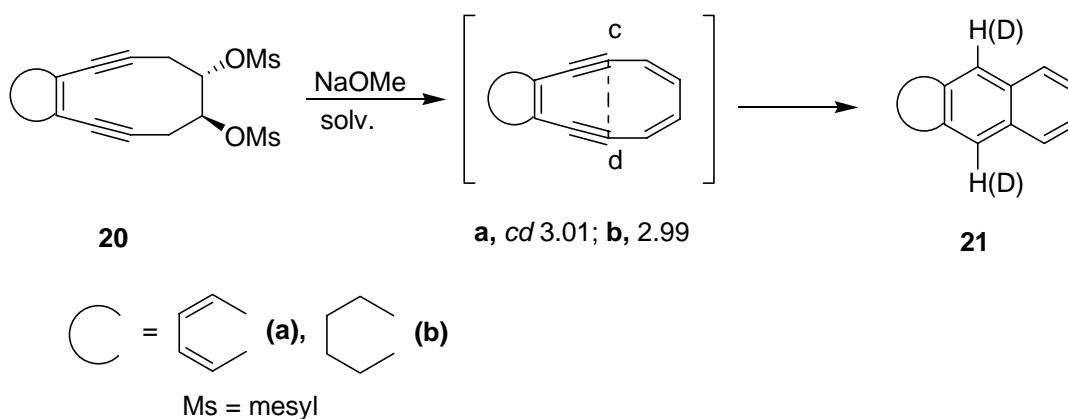
The chemistry of enediynes can date back to 1966. Sondheimer reported the reaction from **17** to **19** and a proposed cyclization mechanism via an ionic intermediate **18** (Scheme 8).<sup>30</sup>

**Scheme 8.** Formation of **19** via an ionic intermediate



In 1971, Masamune *et al.* reported the reaction of converting two cyclic enediynes **20** to benzoid systems **21**, but without proposing the reaction via a biradical intermediate (Scheme 9).<sup>31</sup>

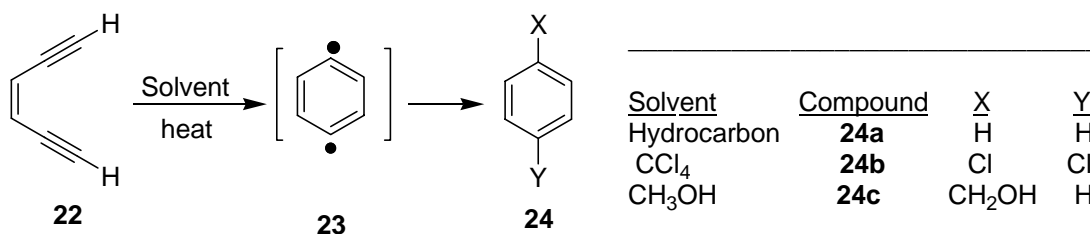
**Scheme 9.** Generation of a benzoid system



In 1972, Bergman published his detailed study on the cycloaromization of enediynes.<sup>32</sup> He first proposed 1,4-didehydrobenzene biradical as a key intermediate for the cyclization reaction of enediynes. As a good indirect evidence of the Bergman

cyclization via a biradical intermediate, when **22** was heated in solution, the observed products were benzene or derivatives **24** via a biradical intermediate **23**, depending on the solvent used (Scheme 10).<sup>33</sup>

**Scheme 10.** Bergman's generation of benzene

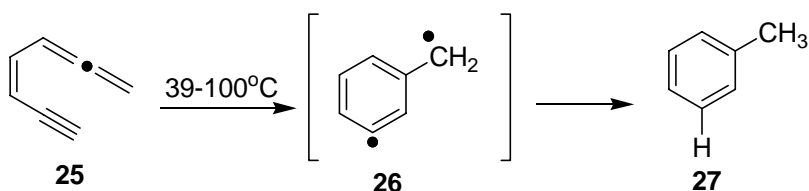


### 3. Cyclization Reactions of Enyne-Allenes

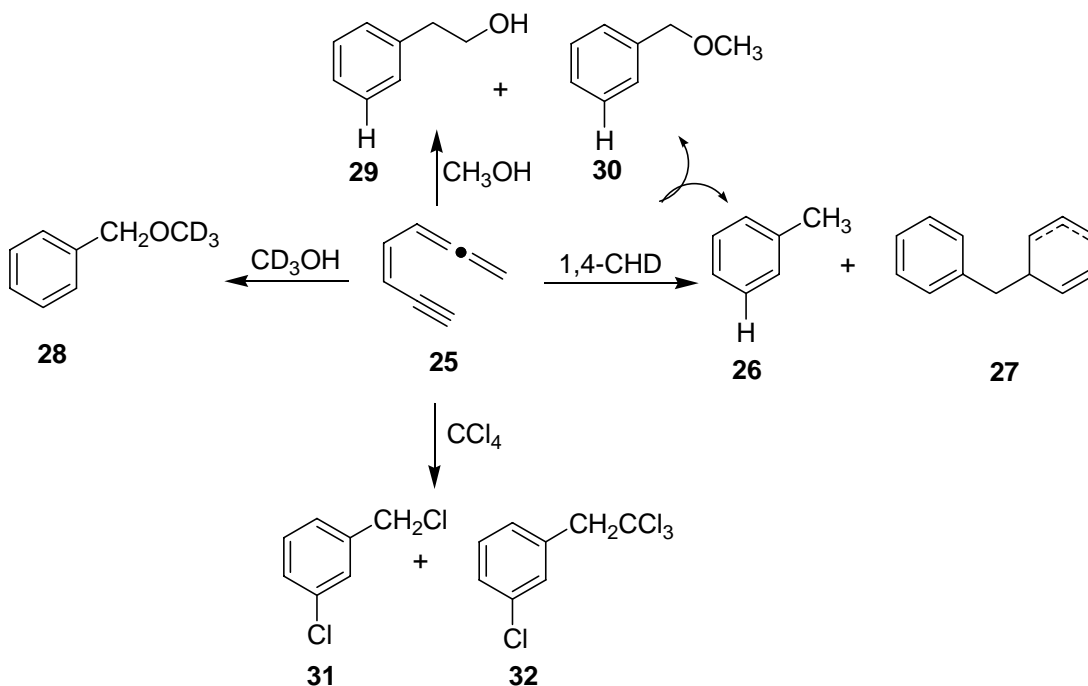
#### 3.1 Myers-Saito ( $C^2-C^7$ ) Cyclization

In the investigation of conjugated unsaturated structures that could cyclize via biradical intermediates at mild conditions, Myer's,<sup>34</sup> and Saito's<sup>35</sup> groups reported a new variant of the Bergman type cyclization with the parent system (*Z*)-1,2,4-heptatrien-6-yne **25** (Scheme 11) in 1989, respectively. This cycloaromatization was recognized as the Myers-Saito cyclization, also termed as the  $C^2-C^7$  cyclization, which proceeds through an  $\alpha,3$ -didehydrotoluene biradical **26** leading to toluene **27** upon hydrogen atom abstraction. As evidence of the cyclization via a biradical mechanism, thermolysis of acyclic enyne-allene **25** in various solvents was studied. The results are summarized in Figure 3.

**Scheme 11.** The Myers-Saito cyclization.



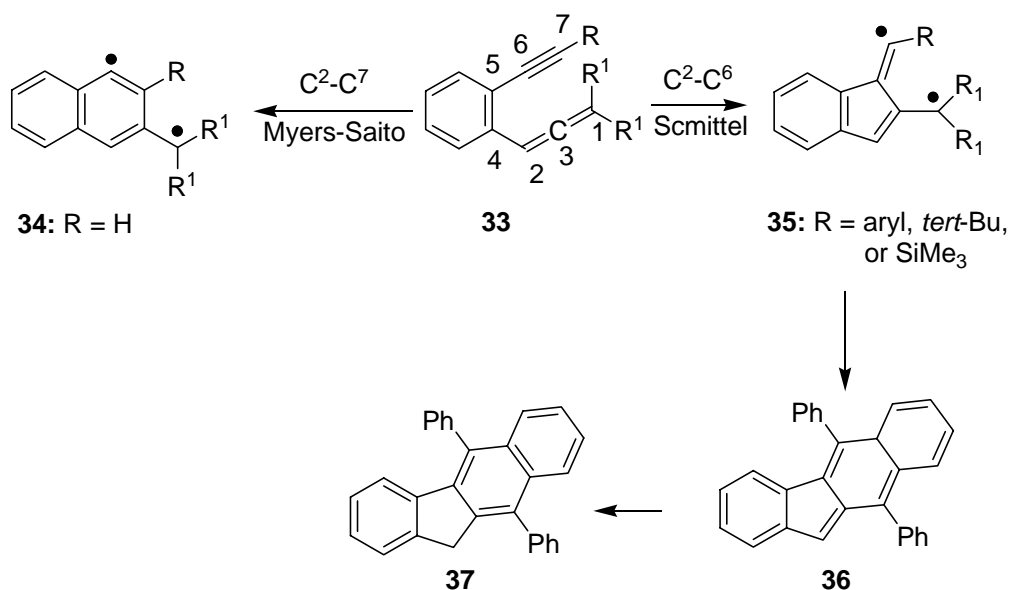
**Figure 3.** Products of thermolysis of (*Z*)-1,2,4-heptatrien-6-yne (**25**) in various solvents



### 3.2 Schmittel (C<sup>2</sup>-C<sup>6</sup>) Cyclization

As just shown biradicals generated from the cyclization of (Z)-1,2,4-heptatrien-6-ynes (enyne-allenes) and benzannulated analogs under mild thermal conditions provide many opportunities for subsequent synthetic applications.<sup>36</sup> Thermal cyclization of the enyne-allene **33** could proceed either via the C<sup>2</sup>-C<sup>7</sup> pathway (Myers-Saito cyclization) to form the  $\alpha,3$ -didehydrotoluene/naphthalene biradical **34**<sup>37</sup> or via the C<sup>2</sup>-C<sup>6</sup> pathway (Schmittel cyclization) to produce the fulvene/benzofluovene biradical **35** (Scheme 12).<sup>38</sup> The nature of the substituent at the acetylenic terminus is responsible for directing the reaction toward either the Myers-Saito cyclization reaction to generate the naphthalene biradicals **34** or the C<sup>2</sup>-C<sup>6</sup> cyclization reaction to furnish the benzofulvene biradicals **35**. With an aryl substituent or a sterically demanding group, such as the *tert*-butyl group and the trimethylsilyl group, at the acetylenic terminus, the C<sup>2</sup>-C<sup>6</sup> cyclization reaction becomes the preferred pathway. The effect of the aryl substituent is attributed to its ability to stabilize the alkenyl radical center in **35**.<sup>39a, b</sup> The sterically demanding group inhibits the Myers-Saito cyclization reaction because of the emergence of severe nonbonded steric interactions in the biradicals **34**.<sup>39c, d, f</sup> If R<sup>1</sup> is a phenyl group, the biradical **35** undergoes an intramolecular radical-radical coupling to form **36** and subsequently, after tautomerization, the benzofluorene **37**.<sup>39, 40</sup> Although this transformation from **33** to **37** could also be regarded as a Diels-Alder reaction, mechanistic<sup>39d</sup> and DNA-cleaving<sup>39e</sup> studies suggest a two-step biradical pathway.

**Scheme 12.** Two synthetic generations of a biradical species

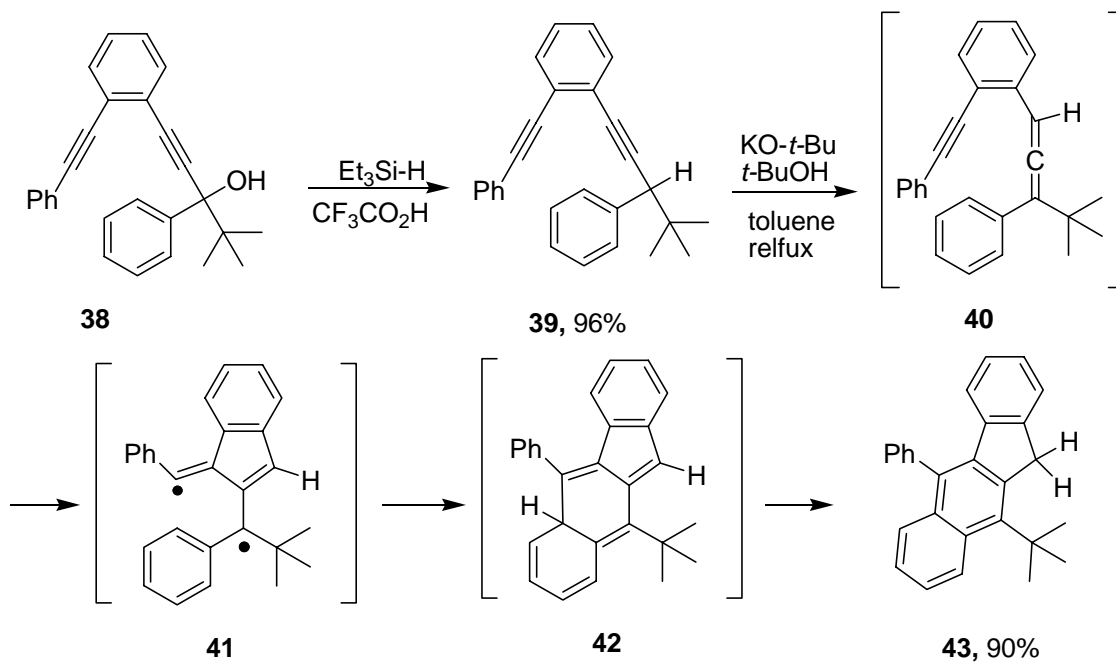


### 3.3 Construction of Polycyclic Ring Systems via Cycloaromatization of Enyne-Allenenes

The current research on the thermal biradical cyclization of enediynes and enyne-allenes is focused on the synthesis of model compounds with similar analogous antitumor antibiotic activity as natural enediynes. This cycloaromatization methodology has also shown high potential for the construction of polycyclic ring systems.

Dr. Hongbin Li developed a new synthetic pathway to the benzannulated enyne-allenes without a chloro-substituent, followed by similar cyclization and tautomerization leading to the corresponding polycyclic aromatic hydrocarbons directly (Scheme 13).<sup>41</sup> This strategy was adopted for the preparation of twisted 4,5-diarylphenanthrenes,<sup>42</sup> polycyclic hydrocarbons,<sup>41</sup> and helical hydrocarbons.<sup>43</sup>

**Scheme 13.** Li's development of a benzannulated enyne-allene

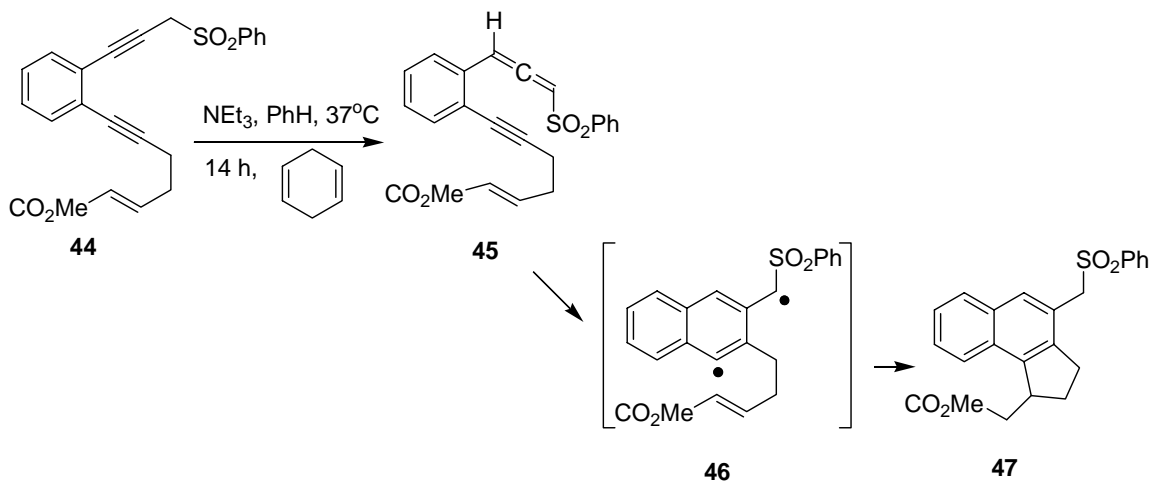


#### 4. Literature Survey on the Synthetic Methodologies for the Preparation of Benzannulated Enyne-Allenes

The cyclization reaction of enyne-allene systems is widely used in the field of synthetic chemistry for the formation of polycyclic structures. Today several synthetic methods exist for the preparation of enyne-allenes with diverse structural features.

Enyne-allenes can be synthesized via base-catalyzed isomerization of enediyne sulfones.<sup>44</sup> A synthetic sequence for the formation is outlined in Scheme 14.<sup>45</sup> The enediyne sulfone **44** was treated with triethylamine in benzene and 1,4-cyclohexadiene at 37 °C. Upon generation of the enyne-allene the cyclization product **47** was isolated in 76% yield.

**Scheme 14.** The formation of an enyne-allene via an enediyne sulfone.

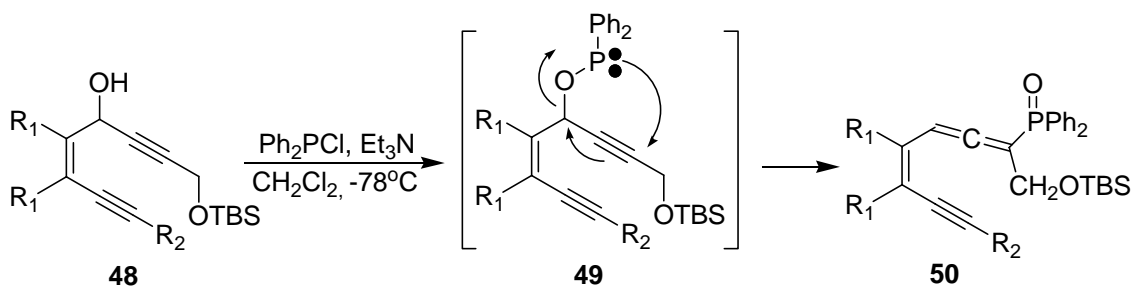


Enyne-allenes can be obtained by using a [2,3] sigmatropic rearrangement of propargylic phosphate or phosphinite to form allenyl phosphonate or phosphine oxide; this scheme was first reported by Sevin *et al.* in 1967.<sup>45</sup> This synthetic method was also adopted by Saito,<sup>35</sup> Nicolaou,<sup>46</sup> and Schmittl<sup>47</sup> for the preparation of enyne-allenes. For example, Nicolaou was one of the first to reported that propargylic alcohol **48** on



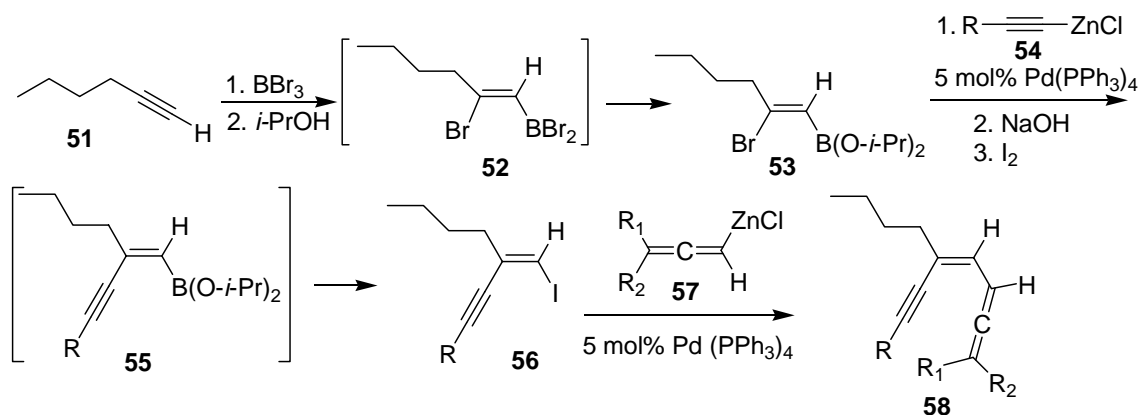
treatment with chlorodiphenylphosphine in methylene chloride at  $-78\text{ }^{\circ}\text{C}$  in the presence of triethylamine produced allenyl phosphine oxide **50** in good yield (Scheme 15).

**Scheme 15.** Enyne-allene formation via a [2,3] sigmatropic rearrangement



Our group developed several convenient procedures for the synthesis of enyne-allenes.<sup>48</sup> One method involves bromoboration of 1-alkynes with  $\text{BBr}_3$  producing alkenyl boronic esters, followed by subsequent  $\text{Pd}(0)$ -catalyzed cross-coupling with acetylenic zinc chlorides (Scheme 16).<sup>48a</sup>

**Scheme 16.** Wang's development of an enyne-allene



## 5. Research Objective

Our group recently reported a new synthetic route for the formation of polycyclic aromatic hydrocarbons via a C<sup>2</sup>-C<sup>6</sup> (Schmittel) cyclization reaction of benzannulated enyne-allenes. This procedure was successfully adopted for the synthesis of 4,5-diarylphenanthrenes having a helical twist due to steric interactions.<sup>42</sup> Using Dr. Hongbin Li's synthetic pathway as a guide to generate polycyclic aromatic hydrocarbons,<sup>41</sup> our goal is to develop a synthetic method following this same chemistry for the formation of 1,1'-binaphthyl derivatives. We envision that by using different combinations of benzoenediynes with various aryl ketones for condensation, it is possible that a variety of 1,1'-binaphthyl systems containing a fluorene moiety could also be likewise synthesized. The fluorene will not only serve as a part of the synthetic compound but will also allow for an ease in characterization by <sup>1</sup>H-NMR.

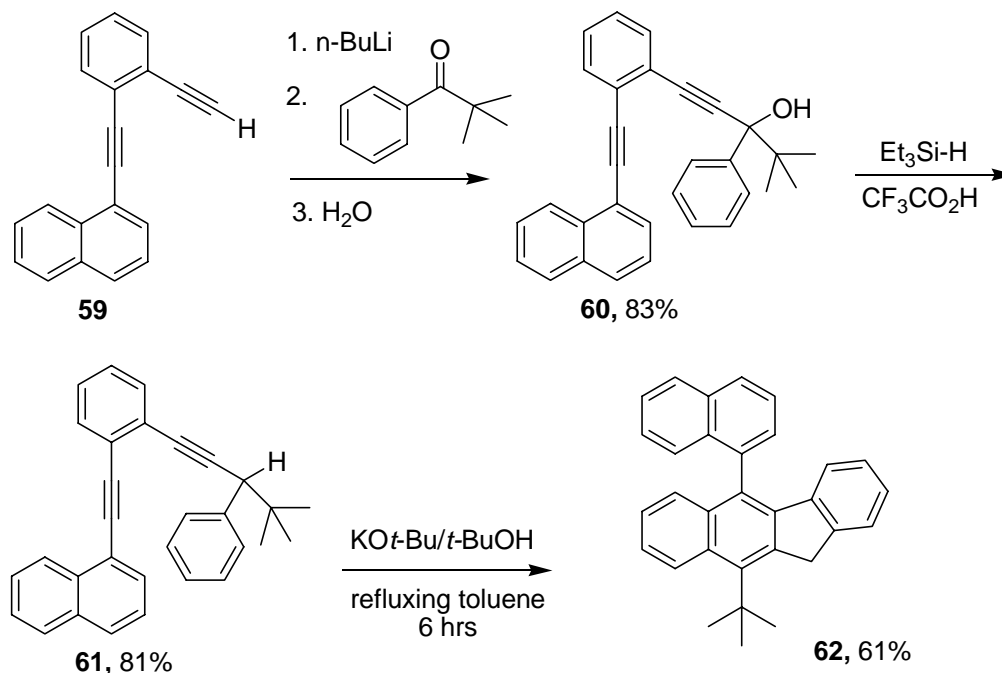
## 6. Results and Discussion

### 6.1 Synthesis of a 1,1'-Binaphthyl Derivative

In this research project, **62**, a derivative of 1,1'-binaphthyl was prepared according to the synthetic pathway of Li. The derivative system generated, via a base induced prototropic rearrangement followed by a Schmittel cyclization produces **62** in moderate yield. With additional synthetic substituents the derivative could possibly serve as a ligand for asymmetric catalysis in future events. Connecting an electron donating moiety to the 2' position of the 1,1'-binaphthyl derivative may allow for the coordination of transition metals to the cyclopentadienyl ring that is formed in the synthesis of **62**.

A synthetic outline for the formation of the 1,1'-binaphthyl derivative **62** is given in Scheme 17.

**Scheme 17.** A new 1,1'-Binaphthyl derivative via a benzannulated enyne-allene.

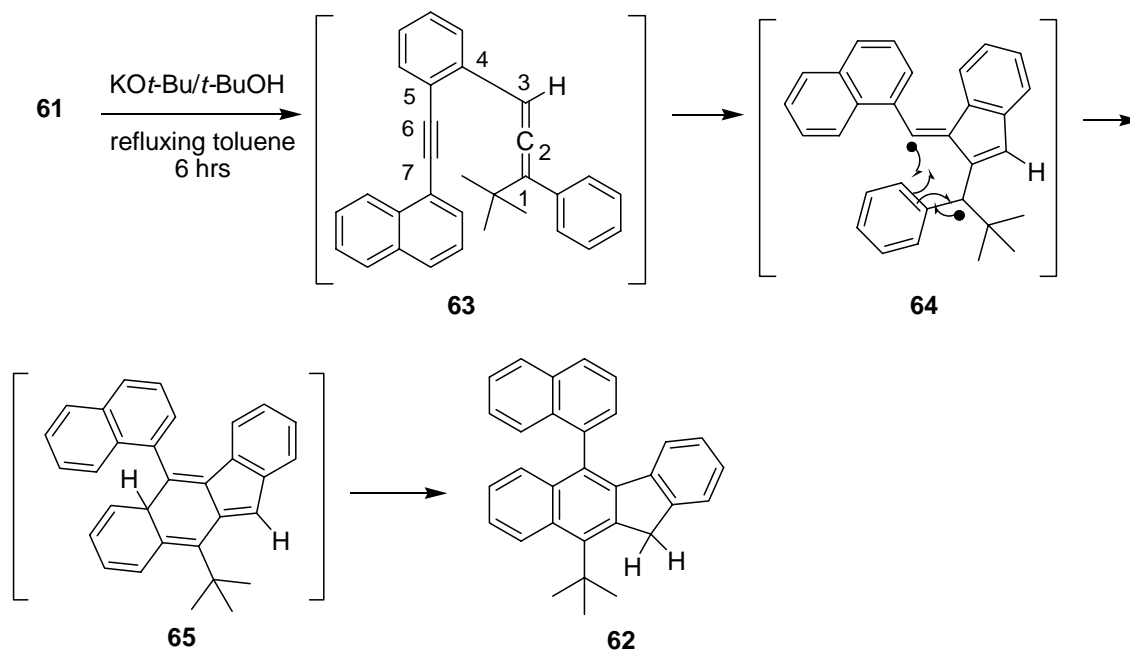


The synthetic sequence for **62**, depicted in Scheme 17, begins with the lithiation of the diacetylene **59**. The diacetylene is lithiated using *n*-butyllithium followed by a condensation with 2,2-dimethylpropiophenone to afford the propargylic alcohol **60** as a mixture of 1:1 diastereomers in good yield.<sup>42</sup> Treatment of **60** with triethylsilane in the presence of trifluoroacetic acid provides the diacetylenic hydrocarbon **61** in good yield as 1:1 diastereomeric isomers. Exposure of **61** to potassium *tert*-butoxide under refluxing toluene for 6 h provides the 1,1'-binaphthyl hydrocarbon **62** via a benzannulated enyne-allene in moderate yield following purification by column chromatography.

The transformation from **61** to **62** involves an initial prototropic rearrangement to form the benzannulated enyne-allene **63** (Scheme 18). A subsequent C<sup>2</sup>-C<sup>6</sup> cyclization generates the biradical **64**, it in turn undergoes an intramolecular radical-radical coupling to give **65**. Perhaps the transformation from **63** to **65** could be seen as a Diels-Alder reaction, however, mechanistic and DNA-cleavage studies of analogous systems supports

a two-step biradical pathway.<sup>40e,h</sup> The tautomerization of **63** transforms it to the more stable 1,1'-binaphthyl derivative **62**.

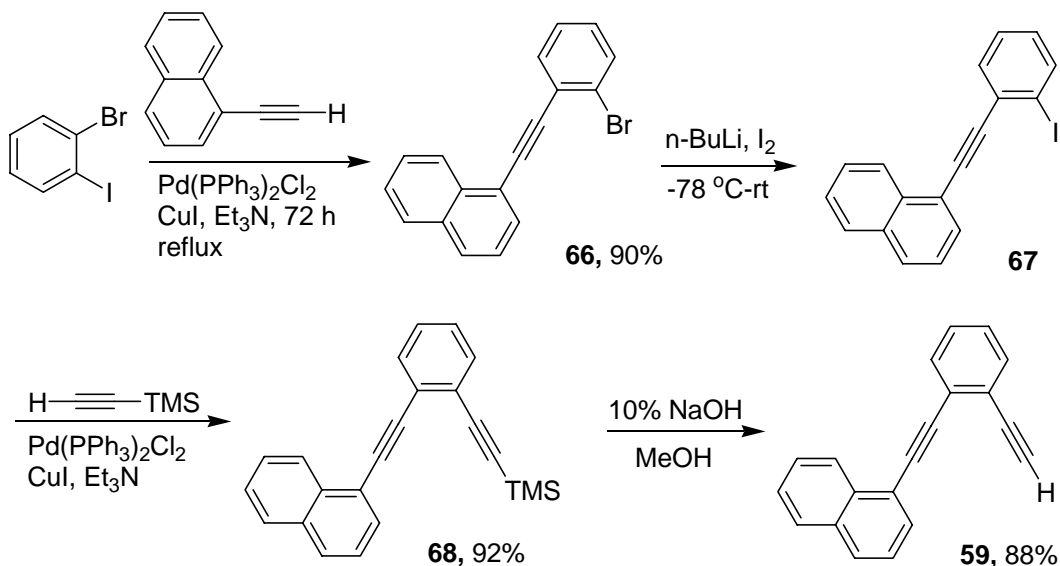
**Scheme 18.** A new 1,1'-binaphthyl derivative via a benzannulated enyne-allene.



## 6.2 Synthesis of Diacetylene **59**

The diacetylene **59** used in the preparation of compound **62**, the 1,1'-binaphthyl derivative, in Scheme 18, was prepared from 1-bromo-2-iodobenzene via back to back Sonogashira coupling reactions with first 1-ethynynaphthalene followed by (trimethylsilyl)acetylene. Once the trimethylsilane protected diacetylene was formed, it was subjected to desilylation with a NaOH/MeOH mixture as described in Scheme 19.<sup>42</sup> The second coupling reaction with TMS-acetylene was significantly improved in yield and reaction time by converting the reaction conditions from the bromide **66** to iodide **67**.

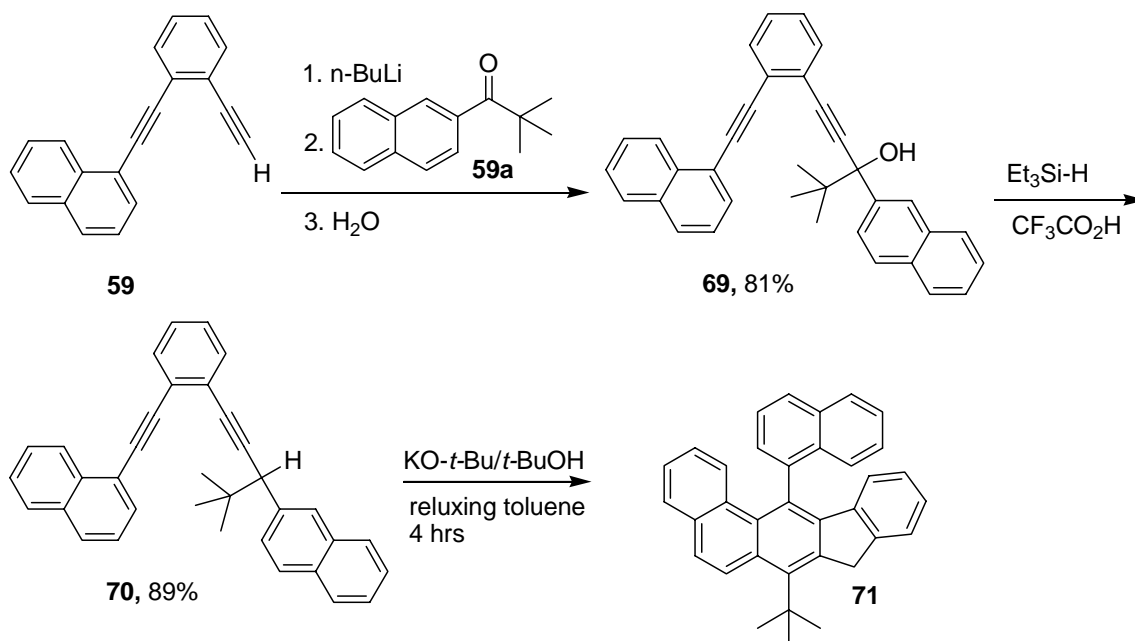
### Scheme 19. Synthesis of diacetylene **59**



### 6.3 An Additional Example of a 1,1'-Binaphthyl System

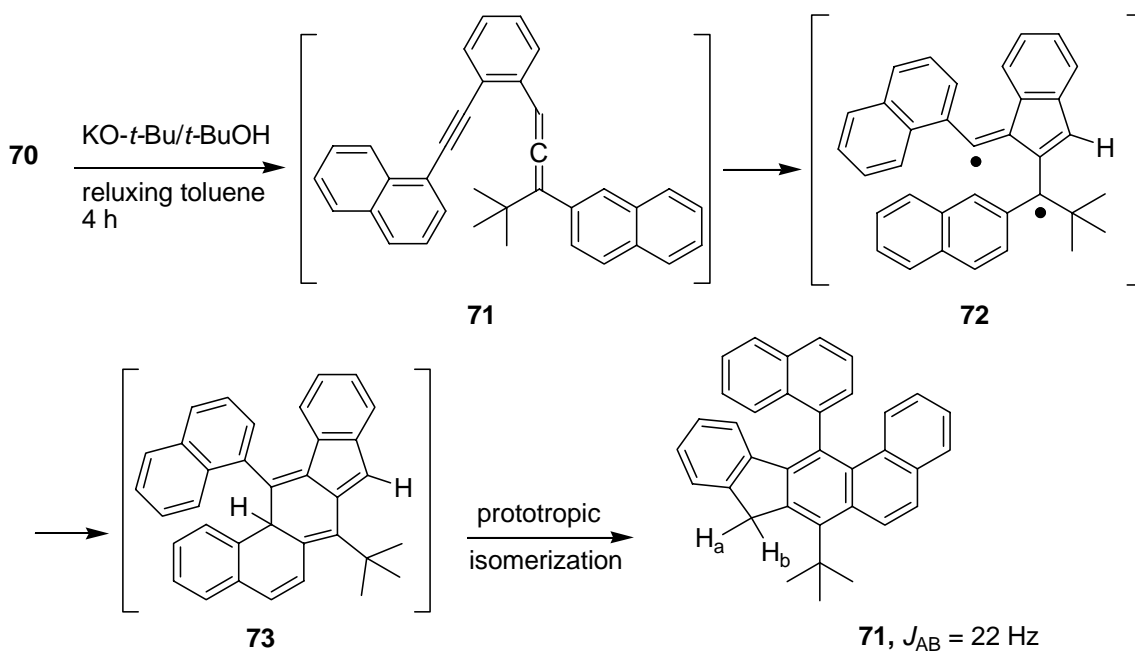
Beginning with compound **59**, described in Scheme 19 and previously used in the formation of **62** in Scheme 18, is once again introduced to *n*-butyllithium to become lithiated for the proceeding condensation. The lithiated diacetylene is allowed to react at  $0\text{ }^\circ\text{C}$  with the naphthyl *tert*-butyl ketone to form the corresponding propargylic alcohol **69** (Scheme 20) as a diastereomeric mixture. Continuing the synthetic sequence with the treatment of **69** with triethylsilane in the presence of trifluoroacetic acid provides **70** the tertiary hydrocarbon **70** as a diastereomeric mixture as well. Introduction of **70** to potassium *tert*-butoxide under refluxing toluene for 4 h provides **71** 1,1'-binaphthyl system in a 43% yield after purification. The hydrocarbon **71** exhibits a second order *AB* pattern representing the two diastereotopic hydrogens of the five-membered ring contained within the compound, suggesting a relatively slow rate of racemization on the  $^1\text{H}$  NMR time scale. The synthetic sequence describing the formation of compound **71** is outlined in the following Scheme 20.

**Scheme 20.** An additional 1,1'-binaphthyl derivative



The transformation from **70** to **71** proceeds via a base induced prototropic isomerization as described in Scheme 18. The isomerization to the benzannulated enyne-allene **71** (Scheme 21) then undergoes a Schmittel (C<sup>2</sup>-C<sup>6</sup>) cyclization to once again generate the biradical species **72**. The species **72** leads to the intramolecular radical-radical coupling to yield **73**. A subsequent tautomerization then leads to the target compound **71** (Scheme 21).

**Scheme 21.** An additional new 1,1'-binaphthyl derivative.

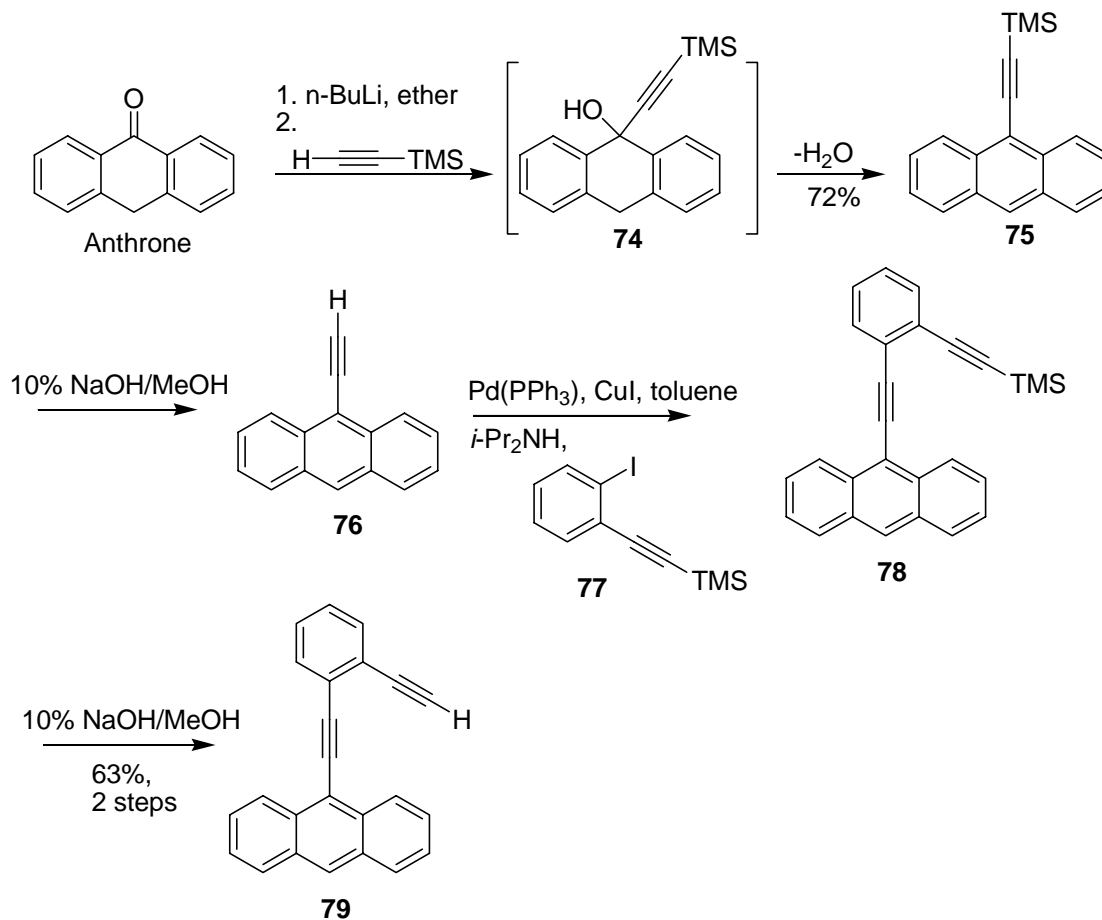


#### 6.4 An Attempt to Synthesize a Congested 1,1'-Binaphthyl Derivative

Scheme 23 outlines an attempt to synthesize a novel congested 1,1'-binaphthyl derivative **82** via a cascade radical cyclization from a new molecule containing a benzannulated enyne-allene. Applying the same chemistry as shown in Schemes 17 and 20 we envisioned that an anthracene derivative of a 1,1'-binaphthyl unit could be derived. The prospects of the development of **82** (Scheme 23) began from the commercially available anthrone without further purification. (Trimethylsilyl)acetylene was treated with *n*-butyllithium in the presence of diethyl ether to produce the anionic protected acetylenic species. This species was introduced to anthrone via a syringe according to the reported procedure.<sup>49</sup> The hydrated synthon **74** (Scheme 22) was immediately subjected to flash chromatography on silica gel with hexane as elutant. This final step eventually led to the formation the dehydrated 9-[(trimethylsilyl)ethynyl]anthracene **73** in good yield. Desilylation of the trimethylsilane protecting group with NaOH/MeOH provided **76**. A palladium catalyzed coupling of **76** with **77** gave the corresponding dialkyne **78** in

moderate yield. The crude synthon of **78** was then desilylated as previously described to afford **79**.

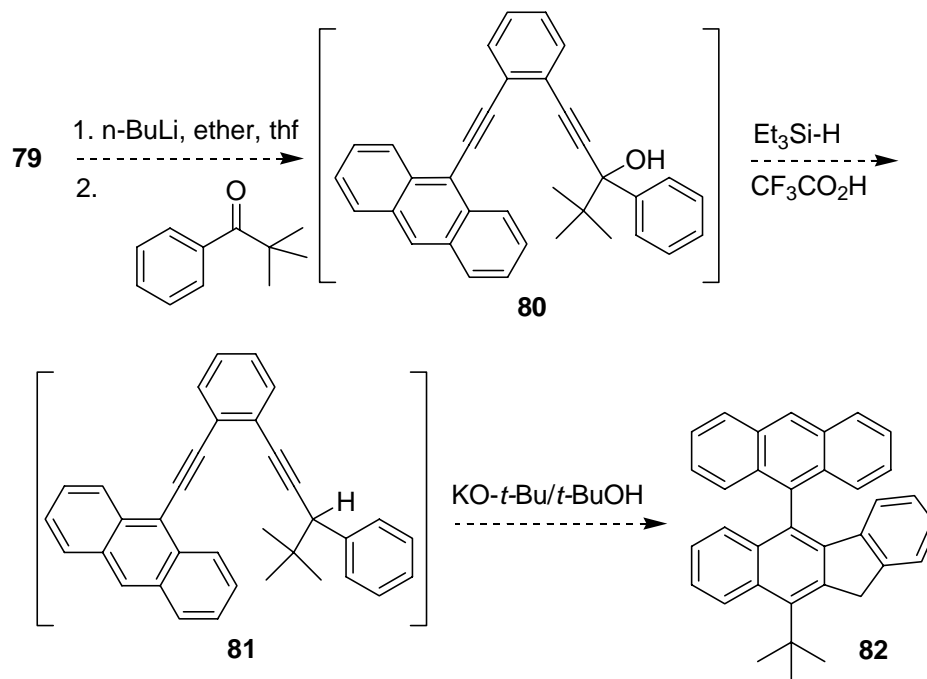
**Scheme 22.** Synthesis of dialkyne **79**



Many attempts at the condensation of **79** with 2,2-dimethylpropiophenone failed even in various solvents such as diethyl ether/tetrahydrofuran and tetrahydrofuran. The crude <sup>1</sup>H-NMR revealed only the appearance of starting material at the completion of various reactions. These failed processes could be attributed to severe congestive steric interactions of the systems, and/or the electronic effects of this reversible reaction. Our vision of producing **82** from **80** is described in Scheme 23 and is as follows.



**Scheme 23.** An attempt to synthesis a congested 1,1'-binaphthyl derivative.



## 7. Conclusions

The synthetic formation of two new novel binaphthyl derivatives has been achieved. These systems were prepared using a  $\text{C}^2\text{-C}^6$  (Schmittel) cyclization reaction followed by a radical-radical coupling reaction of the benzannulated enyne-allenes **62** and **71**. The formation of these 1,1'-binaphthyl derivatives could be of great benefit and interest to the industrial community for asymmetric catalysis. The growing demand for enantiomerically pure compounds is always increasing and by added transition metals and/or electron donating groups to the 2' position of our compounds one could envision the formation of ligand chelation and new synthetic analogues.

## 8. Experimental Section

All reactions were conducted in oven dried (125 °C) glassware under a nitrogen atmosphere except in the cases of **59** and **77**. Diethyl ether (Et<sub>2</sub>O) and Tetrahydrofuran (THF) were distilled from benzophenone ketyl and prior to use. Methylene chloride, benzene, and toluene were distilled over calcium hydride (CaH<sub>2</sub>) before use. Silica gel used for flash chromatography was purchased from chemical suppliers. Melting points were uncorrected. IR spectrum were performed on a Perkin-Elmer 1600 FT-IR spectrometer. <sup>1</sup>H (270 MHz, 600MHz) and <sup>13</sup>C (67.9 MHz) NMR spectra were recorded in CDCl<sub>3</sub> using CHCl<sub>3</sub> (<sup>1</sup>H δ 7.26) and CDCl<sub>3</sub> (<sup>13</sup>C δ 77.00) as internal standards.

*n*-Butyllithium (2.5 M) in hexanes, lithium diisopropylamide (LDA) (2.0 M) in heptane/tetrahydrofuran/ethylbenzene, potassium *tert*-butoxide (1.0 M) in 2-methyl-2-propanol, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Copper(I) iodide, triethylamine, phenylacetylene, 1-bromo-2-iodobenzene, trifluoroacetic acid, 2,2-dimethylpropiophenone, CuBr-SMe<sub>2</sub>, 1-ethynylnaphthalene, anthrone, and iodine were purchased from chemical suppliers and were used as received without further purification.

Compound **59a** was synthesized by Yanzhong Zhang recently from *tert*-butyl 2-naphthyl ketone which was prepared from 2-naphthoyl chloride according to the reported procedure.<sup>43</sup> Compound **68** was recently synthesized by Yonghong Yang and was freshly prepared according to procedure.<sup>36</sup>

**Propargylic Alcohol 60.** To a solution of 141.2 mg of **59** (0.558 mmol) in 10 mL of dry diethyl ether under a nitrogen atmosphere at 0 °C was added 0.22 mL of a 2.5 M solution of butyl lithium (0.551 mmol) in hexanes. After 30 minutes of stirring, 71.8 mg (0.443 mmol) of 2,2-dimethylpropiophenone in 4 mL of dry diethyl ether was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an

additional 3 hours, 15 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over magnesium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes: diethyl ether = 5:1) to provide 192 mg (0.463 mmol, 83% yield) of **60** as a viscous oil. IR 3567, 2211, 759, 703  $\text{cm}^{-1}$ ;  $^1\text{H}$   $\delta$  8.45 (1H, d,  $J = 7.2$  Hz), 7.87-7.83 (2H, m), 7.73-7.64 (4H, m), 7.59-7.48 (3H, m), 7.41-7.34 (3H, m), 7.18-7.10 (3H, m), 2.42 (1H, br s), 1.05 (9H, s);  $^{13}\text{C}$   $\delta$  141.9, 133.2, 133.1, 132.3, 132.2, 130.5, 128.9, 128.2, 128.1, 128.1, 127.7, 127.2, 127.0, 126.8, 126.4, 126.3, 125.8, 125.2, 120.6, 96.4, 93.0, 91.3, 84.6, 79.5, 39.7, 25.5.

**Tertiary Hydrocarbon-Compound 61.** To a mixture of **60** (124.6 mg, 0.309 mmol) and triethylsilane (189.2 mg, 1.63 mmol) in 10 mL of methylene chloride was added 0.35 mL of trifluoroacetic acid (10.0 equiv.). After stirring at room temperature for 5 minutes, the solution mixture was cooled to 0  $^{\circ}\text{C}$  using ice, and then 297 mg of sodium carbonate (1.79 mmol) was added followed by 10 mL of distilled water and 40 mL of diethyl ether. The organic fractions were then washed with sodium chloride, extracted, dried over magnesium sulfate, and concentrated. Purification by flash chromatography (silica gel/5% diethyl ether in hexanes) provided 98 mg (0.226 mmol, 81% yield) of **61** as a yellow oil: IR 2966, 2227, 1814, 1481, 758;  $^1\text{H}$   $\delta$  8.49-8.45 (1H, m), 7.87-7.82 (2H, m), 7.66-7.61 (2H, m), 7.55-7.47 (2H, m), 7.43-7.37 (3H, m), 7.32-7.29 (2H, m), 7.14-7.11 (3H, m), 3.69 (1H, s), 0.993 (9H, s);  $^{13}\text{C}$   $\delta$  138.9, 133.2, 133.1, 132.3, 132.1, 130.4, 129.7, 128.7, 128.1, 128.0, 127.5, 127.4, 126.7, 126.6, 126.4, 126.3, 125.6, 125.2, 120.9, 95.8, 93.4, 90.9, 82.6, 50.6, 50.5, 35.5, 27.7. The singlet at 3.69 integrating for 1 H is representing the tertiary hydrogen of the hydrocarbon moiety.

**Compound 62.** To a solution of 42.3 mg of **61** (0.106 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere was added 0.12 mL of a 1.0 M solution of potassium *t*-butoxide in THF (0.12 mmol) and 0.12 mL of *t*-butyl alcohol via syringe. The reaction mixture was then heated under reflux for 6 hours. After the reaction mixture was allowed to cool to room temperature, 20 mL of distilled water and 20 mL of diethyl ether were introduced; the organic layer was separated, dried over magnesium sulfate, and then concentrated. Purification by flash chromatography (silica gel/ 2% diethyl ether in hexanes) followed by concentration of the organic layer yielded a 26.3 mg of **62** (0.66 mmol, 61% yield) as a brownish oil: IR 2958, 2245, 1700, 1590, 1191, 1015, 908  $\text{cm}^{-1}$ ;  $^1\text{H}$   $\delta$  8.67 (1H, d,  $J= 8.90$ ), 8.10-7.99 (2H, dd,  $J= 8.16$ ), 7.71-7.65 (1H, t), 7.49-7.09 (11H, m), 6.78-6.73 (1H, t), 5.90 (1H, d,  $J= 7.67$ ), 4.57 (2H, broader s), 1.97 (9H, s);  $^{13}\text{C}$   $\delta$  144.2, 141.2, 139.9, 139.1, 137.6, 137.4, 134.9, 133.8, 132.8, 131.4, 130.8, 128.2, 128.0, 127.9, 127.9, 127.7, 126.7, 126.3, 126.2, 124.2, 123.8, 123.5, 123.4, 40.2, 38.9, 34.4, 30.3. The singlet in the  $^1\text{H}$  NMR at  $\delta$  4.57 representing 2 H corresponds to the two diastereotopic hydrogens of the fluorene system.

**Propargylic Alcohol 69.** To a solution of 458 mg of **59** (1.82 mmol) in 10 mL of dry diethyl ether under a nitrogen atmosphere at 0 °C was added 0.6 mL of a 2.5 M solution of butyl lithium (1.62 mmol) in hexanes. After 30 minutes of stirring, 304 mg (1.427 mmol) of *tert*-butyl-2-naphthyl ketone **59a** in 4 mL of dry diethyl ether was introduced via cannula drop wise, glassware subsequently rinsed with an additional 4 mL of diethyl ether, and then the reaction mixture was allowed to warm to room temperature. After an additional 6 hours of stirring, 30 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over magnesium sulfate and concentrated. The residue was purified by flash column

chromatography (silica gel/hexanes: diethyl ether = 5:1) to provide 689 mg (1.48 mmol, 81% yield) of **69** as a yellow solid (mp = 56- 59 °C). IR  $\text{cm}^{-1}$  3549, 2974, 2359, 1928, 1482, 1215, 990, 862;  $^1\text{H}$   $\delta$  8.43 (1H, d,  $J= 5.4$ ), 8.13 (1H, s), 7.86-7.78 (2H, m), 7.75-7.68 (3H, m), 7.62- 7.59 (1H, m), 7.56- 7.49 (2H, m), 7.47- 7.32 (6H, m), 7.24- 7.18 (1H, t,  $J= 8.1$ ), 1.09 (9H, s);  $^{13}\text{C}$   $\delta$  136.7, 133.2, 133.1, 133.0, 132.3, 132.2, 130.5, 128.9, 128.7, 128.3, 128.1, 128.0, 127.8, 127.5, 127.4, 127.3, 127.0, 126.8, 126.6, 126.3, 126.2, 125.7, 125.4, 125.1, 120.8, 95.8, 93.3, 91.0, 82.8, 50.8, 35.8, 27.9, 25.6.

**Tertiary Hydrocarbon 70.** To a mixture of **69** (18.6 mg, 0.040 mmol) and triethylsilane (20.9 mg, 0.180 mmol) in 6 mL of methylene chloride was added 0.15 mL of trifluoroacetic acid ( 10.0 equiv.) drop wise via a syringe at 0 °C with stirring for 10 minutes. After stirring for 10 minutes, the solution mixture was maintained at 0 °C using ice, and then 17 mg of sodium carbonate (0.162 mmol) was added followed by 5 mL of distilled water and 20 mL of diethyl ether. The organic fractions were then washed with 3.0 mL of saturated sodium chloride, extracted, dried over magnesium sulfate, and concentrated. Purification by flash chromatography (silica gel/ in hexanes) provided 16 mg (0.036 mmol, 89% yield) of **70** as a yellow solid (mp = 130-132 °C). IR 2965, 2359, 1480, 1215;  $^1\text{H}$   $\delta$  8.45 (1H, d,  $J=$ ), 7.84-7.78 (2H, m), 7.75-7.63 (3H, m), 7.58-7.54 (3H, t), 7.51- 7.42 (2H, m), 7.41- 7.30 (2H, m), 7.23- 7.17 (1H, m), 3.88 (1H, s), 1.06 (9H, s);  $^{13}\text{C}$   $\delta$  136.7, 133.2, 133.0, 132.9, 132.3, 132.2, 130.5, 128.7, 128.3, 128.1, 128.0, 127.8, 127.5, 127.4, 127.0, 126.6, 126.4, 126.3, 126.3, 125.7, 125.4, 125.1, 120.8, 95.8, 93.3, 91.0, 82.8, 50.7, 35.9, 27.9. The singlet at the  $\delta$  3.88 represents the tertiary hydrogen of the hydrocarbon moiety.

**Compound 71:** To a solution of 41.3 mg of **70** (0.092 mmol) in 3 mL of anhydrous toluene under a nitrogen atmosphere following vacuum pumping was added 0.092 mL of

a 1.0 M solution of potassium *t*-butoxide in THF (0.092 mmol) and 0.092 mL of *t*-butyl alcohol via syringe. The reaction mixture was then heated under reflux for 4 hours. After the reaction mixture was allowed to cool to room temperature, immediately added 20 mL of distilled water and 20 mL of diethyl ether were introduced; the organic layer was separated, washed until neutral with water, extracted, dried over magnesium sulfate, and then concentrated. Purification by flash chromatography (silica gel/ 10% diethyl ether in hexanes) followed by concentration of the organic layer yielded a 17.8 mg of **71** (0.040 mmol, 43% yield) as a yellow- brownish oil. IR 2923, 1462, 723 ;  $^1\text{H}$   $\delta$  8.47 (1H, d,  $J= 9.6$  Hz), 8.11- 7.99 (3H, m), 7.73 (1H, d,  $J= 8.15$  Hz), 7.64- 7.53 (4H, m), 7.48- 7.36 (6H, m), 7.22- 7.14 (1H, m), 7.08- 7.03 (1H, t,  $J= 7.40$ ), 6.74- 6.64 (2H, m), 5.46 (1H, d,  $J= 8.15$ ), 4.52- 4.38 (2H, dd,  $J= 22.3$  Hz), 1.93, (9H, s);  $^{13}\text{C}$   $\delta$  144.2, 142.2, 141.1, 140.8, 140.6, 138.9, 134.1, 132.9, 132.2, 131.7, 131.2, 128.4, 128.3, 128.1, 127.6, 127.1, 126.9, 126.6, 126.3, 126.2, 126.0, 125.8, 125.4, 123.8, 123.7, 40.4, 38.7, 34.2, 30.3, 28.6.

**1-2(2-Bromophenyl)-2-(1-naphthyl)ethyne 66.** To a flask containing 0.45 g (0.64 mmol) of dichlorobis(triphenylphosphine)palladium and 0.21 g (1.1 mmol) of CuI were added via cannula a solution of 3.76 g (13.3 mmol) 1-bromo-2-iodobenzene in 50 mL of triethylamine followed by a solution of 2.00 g (13.2 mmol) of 1-ethynyl-naphthalene in 30 mL of triethylamine. The resulting mixture was heated under reflux and stirred vigorously. After 3 days, the reaction mixture was allowed to cool to room temperature and concentrated. 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. After filtration, the filtrate was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica

gel/hexanes) afforded 3.66 g (11.9mmol, 90%) of **7** as a white solid: mp 58-60 °C; IR 2213,799, 772, 752 cm<sup>-1</sup>; <sup>1</sup>H δ 8.60 (1 H, dd, *J* = 8.5, 1.1 Hz), 7.87 (2 H, d, *J* = 8.2 Hz), 7.82 (1 H, dd, *J* = 7.2, 1.0 Hz), 7.70-7.45 (5 H, m), 7.35 (1 H, td, *J* = 8.9, 1.3 Hz), 7.22 (1 H, td, *J* = 7.8, 1.7 Hz); <sup>13</sup>C δ 133.4, 133.3, 133.2, 132.5, 130.7, 129.4, 129.2, 128.2, 127.1, 126.9, 126.5, 126.4, 125.6, 125.5, 125.2, 120.6, 92.7, 92.2; MS *m/z* 308 (M<sup>+</sup>), 226,220, 153.

**1-1(-Naphthyl)-2-[2-(trimethylsilylethynyl)phenyl]ethyne 68.** To a solution of 2.40 g (7.82 mmol) of **7** in 100 mL of anhydrous diethyl ether at -78 °C was added dropwise 4.70 mL of a 2.5 M solution of n-butyllithium (11.75 mmol) in hexanes. After one hour of stirring at -78 °C, a solution of 3.02 g (11.89 mmol) of iodine in 100 mL of anhydrous diethyl ether was added via a cannula. The reaction mixture was allowed to warm to 15 °C before 30 mL of a 5% sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution was introduced. The organic layer was then separated. The aqueous layer was subsequently back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The crude **67** was used in the next step without purification. To a flask containing 0.30 g (0.43 mmol) of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 0.12 g (0.63 mmol) of CuI were added via cannula a solution of 2.74 g (7.74 mmol) **6** in 70 mL of triethylamine followed by a solution of 2.22 g (22.6 mmol) of (trimethylsilyl)acetylene in 40 mL of triethylamine. The resulting mixture was stirred vigorously at room temperature for 20 h before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were added. After filtration, the filtrate was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 2.33 g (7.19 mmol, 92% overall yield for the two steps) of **68** as

colorless crystals: mp 78-80 °C; IR 2214, 2158, 861, 842, 799, 774, 758 cm<sup>-1</sup>; <sup>1</sup>H δ 8.61 (1 H, dd, *J* = 8.2, 0.7 Hz), 7.91-7.83 (3 H, m), 7.69-7.47 (5 H, m), 7.39-7.28 (2 H, m), 0.29 (9 H, s); <sup>13</sup>C δ 133.2, 132.6, 132.0, 130.7, 128.9, 128.3, 128.2, 127.9, 126.8, 126.5, 126.4, 126.0, 125.4, 125.2, 120.9, 103.7, 98.7, 92.9, 91.6, 0.02; MS *m/z* 324 (M<sup>+</sup>), 309, 293, 279, 263.

**1-(2-Ethynylphenyl)-2-(1-naphthyl)ethyne 59.** To 1.48 g (4.57 mmol) of **68** in 50 mL of diethyl ether were added 30 mL of a 10% sodium hydroxide solution and 50 mL of methanol. After 30 minutes at room temperature, the organic solvent was removed in vacuo. Water (50 mL) and diethyl ether (100 mL) were then added. The organic layer was separated. The aqueous layer was subsequently back extracted with diethyl ether. The combined organic extracts were washed with 2 M hydrochloric acid and water, dried over magnesium sulfate, and concentrated. Purification of the organic residue by flash column chromatography (silica gel/hexanes) afforded 1.13 g (4.48 mmol, 98%) of **59** as a light brown solid: mp 60-62 °C; IR 3285, 2212, 2106, 799, 773, 757 cm<sup>-1</sup>; <sup>1</sup>H δ 8.70 (1 H, d, *J* = 7.9 Hz), 7.90-7.83 (3 H, m), 7.70-7.46 (5 H, m), 7.43-7.30 (2 H, m), 3.48 (1 H, s); <sup>13</sup>C δ 133.3, 133.1, 132.7, 131.9, 130.6, 129.0, 128.6, 128.2, 128.0, 126.7, 126.6, 126.5, 126.4, 125.2, 124.5, 120.8, 92.6, 91.7, 82.7, 81.3; MS *m/z* 252 (M<sup>+</sup>), 224, 125.

**Dialkyne Anthracene 79.** To a flask cooled under nitrogen was added 27.7 mg (0.14 mmol) of the prepared 9-ethynylantracene **76** and subsequently dissolved in 5 mL of toluene and 1 mL isopropyl amine. To a separate flask was added 4.3 mg CuI (0.23 mmol), 22.0 mg of palladium triphenylphosphine, and 0.16 g (0.54 mmol) of **77**. To the flask containing the mixture of **75** was added dropwise the solution of **76** via a cannula. The whole was then warmed to 80 °C and allowed to stir for 12 h. The organic layer was separated, and the aqueous layer extracted with ether. The combined organic solution



was washed with a saturated solution of ammonium chloride, dried over magnesium sulfate, and concentrated to yield **78** as viscous oil. The crude product was carried on to the next step. To the crude product **78** in 10 mL of tetrahydrofuran was added 10 mL of 10% sodium hydroxide and 10 mL methanol. The whole was allowed to stir at room temperature for 4 h. After 4 h the organic solvents were removed in vacuo. Water (15 mL) and diethyl ether (20 mL) were added. The organic layer was then separated and washed with 2M hydrochloric acid and water, separated, dried over magnesium sulfate, and concentrated to yield **79**. **79** was subjected to flash column chromatography (silica gel/hexanes) to afford 32.1 mg (0.9 mmol, 63% yield) of **79** as an orange solid: mp 128-130 °C; IR 2924, 1670, 1461, 727 cm<sup>-1</sup>; <sup>1</sup>H 8.84 (2 H, d, *J* = 9.13 Hz), 8.46 (1 H, s), 8.03 (2 H, d, *J* = 8.64 Hz), 7.80 (1 H, d, *J* = 9.09 Hz), 7.63-7.27 (8 H, m), 3.52 (1 H, s); <sup>13</sup>C 132.8, 132.8, 132.0, 131.2, 128.7, 128.6, 128.0, 127.1, 126.8, 126.6, 125.7, 124.3, 117.1, 99.1, 90.5, 83.0, 81.5, 29.7, 1.0.

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