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Xiaoqing Han
West Virginia University

Synthesis of Derivatives of 4*H*-Cyclopenta[*def*]phenanthren-4-one and Development of Synthetic Strategies for the Polycyclic Aromatic Hydrocarbons with Carbon Frameworks Represented on the Surface of C_{60}

Xiaoqing Han

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Kung K. Wang, Ph.D., Chair
Paul W. Jagodzinski, Ph.D.
Björn C. Söderberg, Ph.D.

Department of Chemistry

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Abstract

Synthesis of Derivatives of 4H-Cyclopenta[def]phenanthren-4-one and Development of Synthetic Strategies for the Polycyclic Aromatic Hydrocarbons with Carbon Frameworks Represented on the Surface of C60

Xiaoqing Han

A derivative of 4*H*-cyclopenta[*def*]phenanthren-4-one, **51**, was synthesized from the protected ninhydrin **54** and 2 equivalents of 1-(2-ethynylphenyl)-2-phenylethyne. Condensation of the diketone **54** with the lithium acetylide **55** furnished the *trans* propargylic alcohol **56a** and the *cis* propargylic alcohol **56b**. Treatment of **56a** with thionyl chloride promoted a sequence of reactions presumably with an initial formation of the chlorinated benzoenyne-allene **58**. Two cycles of a C2-C6 biradical cyclization reaction followed by a radical-radical coupling then afforded the formal [4+2] Diels-Alder cycloaddition adduct **60**, which in turn underwent tautomerization to give **61**. Reduction with tri-*n*-butyltin hydride then gave the ketal **62** in 46% overall yield from **56a**. Hydrolysis of the ketal **62** gave the ketone **51** in 97% yield.

Another derivative of 4*H*-cyclopenta[*def*]phenanthren-4-one, **87**, was also synthesized from **54** and 2 equivalents of 1-(2-ethynylphenyl)-2-(4-*tert*-octylphenyl)ethyne (**78**) by using the same procedure. The dichloride **90** was also synthesized by using the ketone **87** as the precursor. Efforts are being made to synthesize polycyclic aromatic hydrocarbons with carbon frameworks represented on the surface of C_{60} via the dichloride **90**.

The chloride **85** was converted to the corresponding diketone **93**. The presence of two carbonyl groups allowed a second condensation with the lithium acetylide **79** to afford the propargylic alcohols **94** and **95**. Treatment of **94** with thionyl chloride using the same procedure as described for **56a** and **80** afforded the two isomeric 1*H*-

cyclobut[*a*]indenes **97a** and **97b** via the [2+2] cycloaddition reaction of the chlorinated benzoenyne-allene.

Dedicated to my parents

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Part I

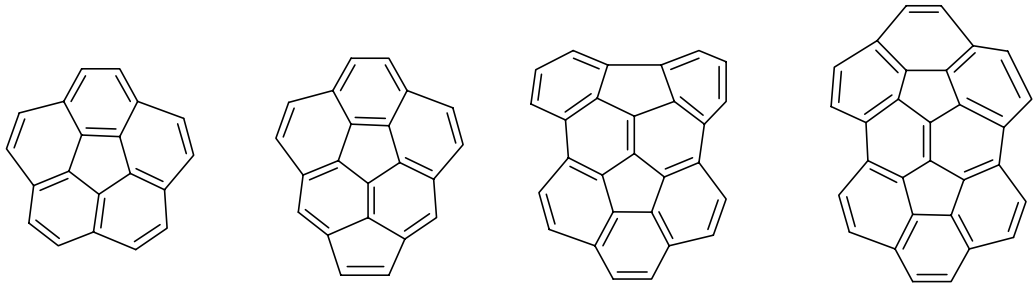
Synthesis of Derivatives of 4*H*-Cyclopenta[*def*]phenanthren-4-one and Development of Synthetic Strategies for the Polycyclic Aromatic Hydrocarbons with Carbon Frameworks Represented on the Surface of C_{60}

1. Introduction

Buckminsterfullerene, C_{60} (buckyball), discovered in 1985,[1] was named "Molecule of the Year" by *Science* in 1991.[2] Since then, there has been an explosion of research activities to explore its chemical reactivities and physical properties and to develop new synthetic methods for C_{60} and larger carbon clusters. It is amazing that buckyball and the related fullerene family have attracted this kind of attention from physicists, materials scientists, and inorganic as well as organic chemists.[3] Although now buckminsterfullerene and other higher fullerenes are readily available in quantity and at affordable prices from soot produced by the vaporization of graphite, access to this molecule through classical synthetic protocol constitutes a formidable intellectual and experimental challenge. For example, controlled modification, formation of higher energy isomers, and doping the cages with guest atoms may all be possible through total synthesis.

One of the most popular synthetic strategies to reach this goal is to first prepare curved hydrocarbon fragments (buckybowls) having the carbon frameworks represented on the surface of buckyball.[3,4] The synthesis of corannulene ($C_{20}H_{10}$) (**1**), the minimal structural subunit with a curvature of a fullerene, was first reported by Barth and Lawton in 1966, more than two decades prior to the discovery of C_{60}.[5] Several other examples of

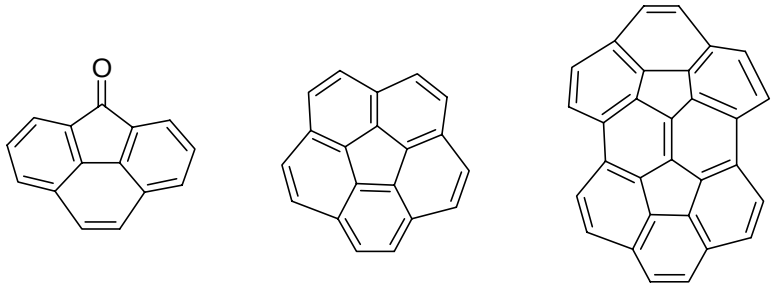
these bowl-shaped hydrocarbons, such as cyclopentacorannulene ($C_{22}H_{10}$) (**2**),[4a,6] fluorenocorannulene ($C_{28}H_{12}$) (**3**),[7] semibuckminsterfullerene ($C_{30}H_{12}$) (**4**),[6c,8] have been synthesized and characterized (Figure 1).



$C_{22}H_{10}$, **1** $C_{22}H_{10}$, **2** $C_{28}H_{12}$, **3** $C_{30}H_{12}$, **4**

Figure 1

While the flash vacuum pyrolysis (FVP) method has been successful in providing more direct access to corannulene and several other buckybowls in recent years, the yields of those highly strained buckybowls are low, usually below 5 %, and sometimes even below 1%. Moreover, this process normally requires heating the precursors to 1,000 °C or higher.[3,4] Under such condition, buckybowls with more delicate structures and higher energies may not survive. More recently, synthetic efforts by using non-pyrolytic pathways to prepare buckybowls are beginning to appear in the literature.[6b,6c,8d,9] To synthesize buckybowls which have five-membered rings surrounded by six-membered



$C_{15}H_8O$, **5** $C_{22}H_{10}$, **1** $C_{30}H_{12}$, **4**

Figure 2

rings, it is not hard to imagine that 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) and its derivatives can be used as potential precursors by comparing their structures with corannulene and other buckybowls (Figure 2).[3,4,10]

2. Research Objective

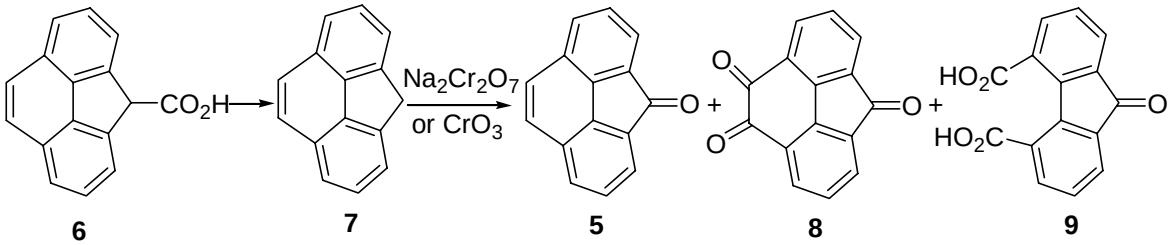
Our group recently reported a simple and efficient route to highly unsaturated polycyclic aromatic compounds via a new synthetic pathway to generate the chlorosubstituted benzoenyne-allenes in situ for the subsequent cascade radical cyclizations. This pathway was adopted for the preparation of a $C_{44}H_{26}$ hydrocarbon having a carbon framework represented on the surface of C_{60}.[9a] We envisioned that by using different combinations of benzoenediynes and aryl ketones for condensation, it is possible that a variety of other polycyclic aromatic hydrocarbons could also be likewise synthesized.

3. Literature Survey for the Synthesis of 4*H*-Cyclopenta[*def*]phenanthren-4-one and Its Derivatives

4*H*-Cyclopenta[*def*]phenanthren-4-one (**5**) and its derivatives attracted our interest because of their potential to be used as precursors for the synthesis of polycyclic aromatic hydrocarbons with carbon frameworks represented on the surface of C_{60}.

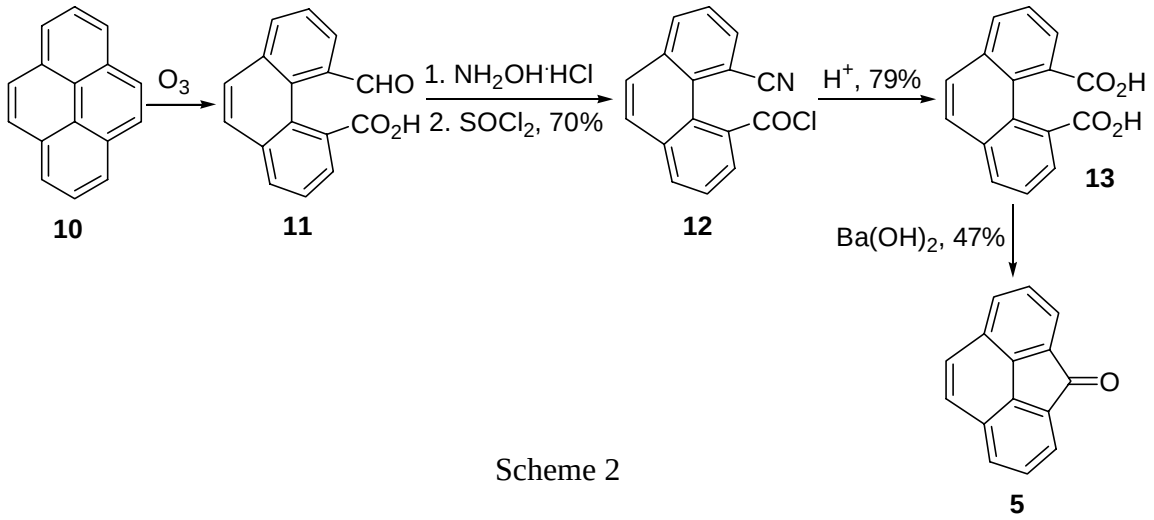
Kruber was the first to report the synthesis of 4*H*-cyclopenta[*def*]phenanthren-4-one in 1934.[11] The 350-360 °C fraction of the anthracene oil from coal tar was heated with Na at 135 °C for 3.5 hours followed by heating at the same temperature with a vigorous stream of CO_2 for 5 hours to give the acid **6**. Decarboxylation by heating above the melting point of the acid **6** then gave 4*H*-cyclopenta[*def*]phenanthrene (**7**). With $Na_2Cr_2O_7$ or CrO_3, the hydrocarbon **7** yielded various oxidation products which, even

with cautious work, were in part formed simultaneously and were difficult to separate (Scheme 1).



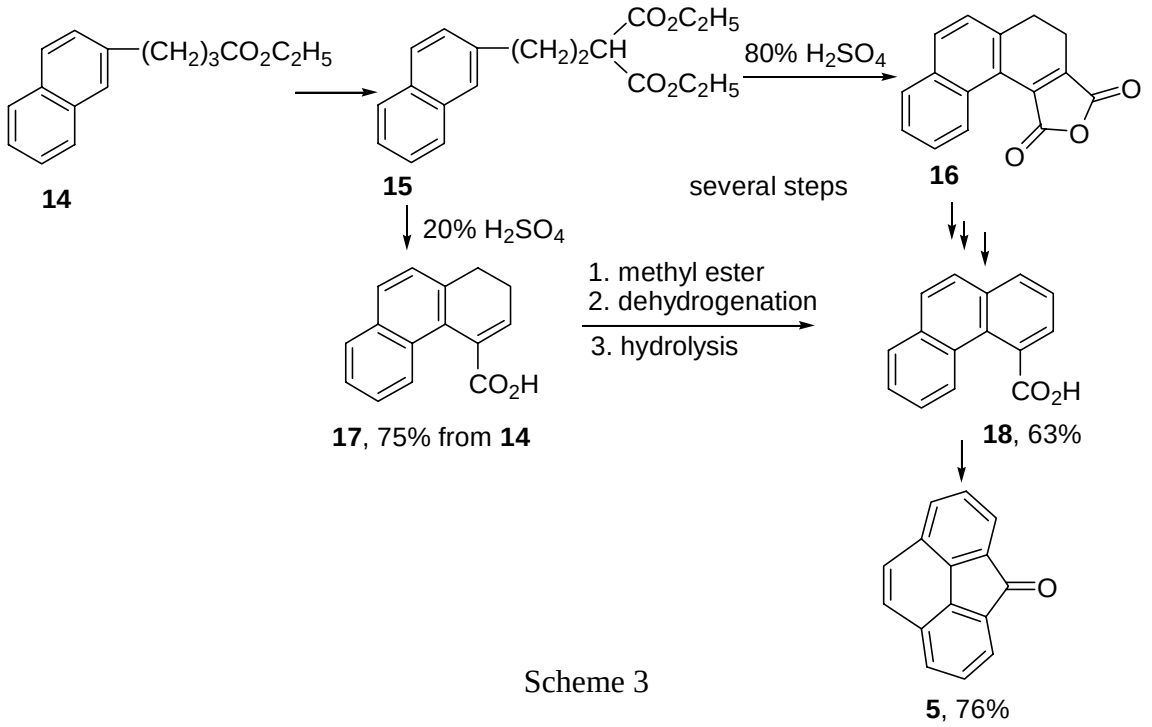
Scheme 1

In 1953, the synthesis of 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) was also reported by Medenwald.[12] It was obtained from heating phenanthrene-4,5-dicarboxylic acid (**13**) with $Ba(OH)_2$ in about 26% yield from compound **11** (Scheme 2).



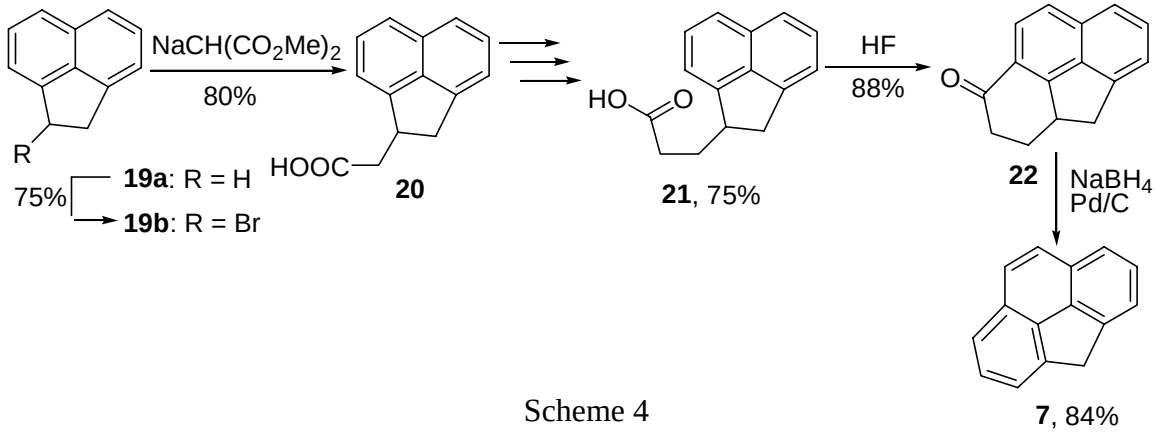
Scheme 2

Four years after Medenwald's work, Newman *et al.* reported another synthetic method for 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) in about 36% yield based on the cyclization of phenanthrene-4-carboxylic acid (**18**) in polyphosphoric acid (Scheme 3).[13a] In this paper they reported an efficient preparation of phenanthrene-4-carboxylic acid (**18**) through compound **17**. Compound **18** has also been obtained in several steps from **15** through compound **16** in small over-all yield.[13b,c]



Scheme 3

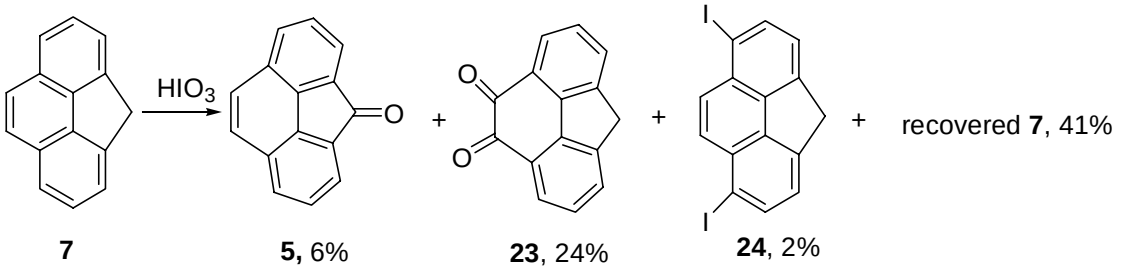
There were also several other synthetic approaches utilizing the parent hydrocarbon, 4*H*-cyclopenta[*def*]phenanthrene (**7**), as the starting compound. The newest method for the synthesis of this parent hydrocarbon is an improved modification of a method devised by Bachmann.[14] Bromination of acenaphthene (**19a**) with NBS catalyzed by benzoyl peroxide afforded 1-bromoacenaphthene (**19b**), followed by treatment with the sodium salt of malonic ester and thermal decarboxylation of the adduct to afford 1-(acenaphthenyl)acetic acid (**20)**. This acid was converted to 1-(acenaphthenyl)propionic



Scheme 4

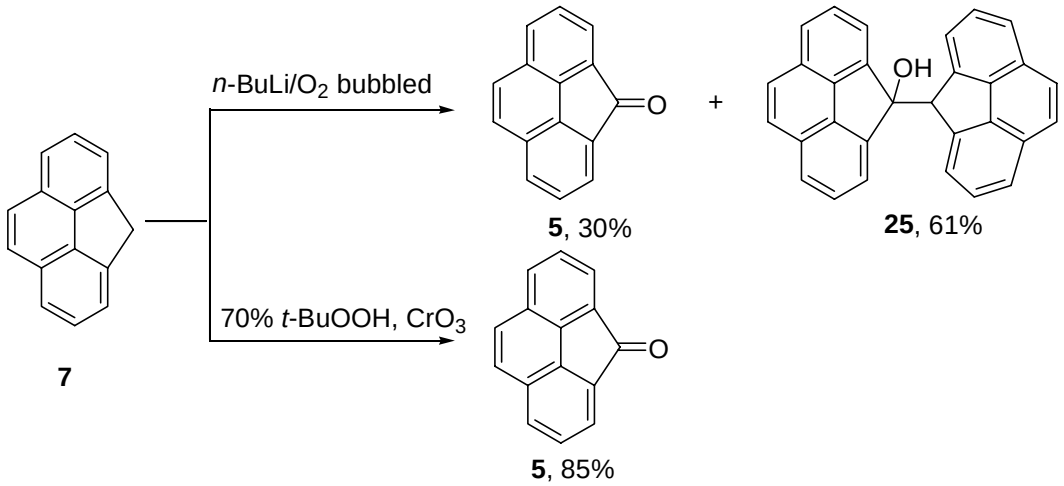
acid (**21)** and cyclized in liquid HF to provide the ketone **22**, which was transformed smoothly to 4*H*-cyclopenta[*def*]phenanthrene (**7)** by reduction with $NaBH_4$ and heating over 10% palladium/charcoal (Scheme 4). This route is most suitable for large-scale synthesis, despite the relatively large number of steps, because each of the steps is easy to carry out and provides a good yield.

Yoshida reported the synthesis of 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) by oxidizing the corresponding parent hydrocarbon **7** with iodic acid to give a mixture of oxidation products (Scheme 5).[15]



Scheme 5

Havey *et al*. also reported a synthesis of 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) by oxidizing the parent hydrocarbon **7**.[16] One of his synthetic routes involved treatment of a solution of the parent hydrocarbon **7** in anhydrous THF at -78 °C with a 2.5 M



Scheme 6

solution of *n*-BuLi in cyclohexane followed by bubbling dry O_2 through the solution to give the ketone **5** in 30% yield. The major product of this reaction was dimeric alcohol **25**. The other route involved oxidation of the parent hydrocarbon **7** with 70% aqueous *t*-BuOOH and CrO_3 in methylene chloride by the method of Muzart[17] to give the expected ketone 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) in 85% yield (Scheme 6). In the same paper,[16] they also reported the synthesis of several other polycyclic aromatic compounds which have a 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) unit using similar methods to oxidize the corresponding hydrocarbons (Figure 3).

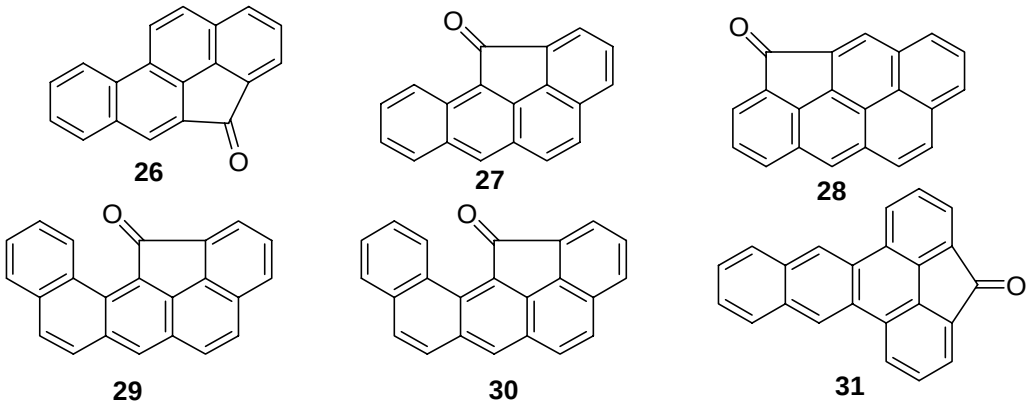
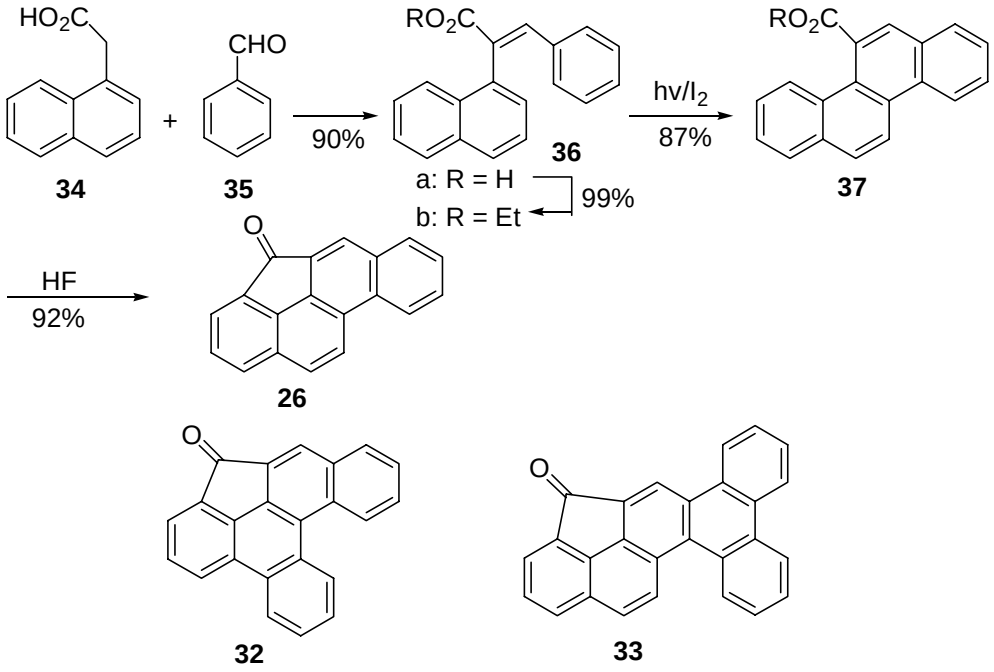


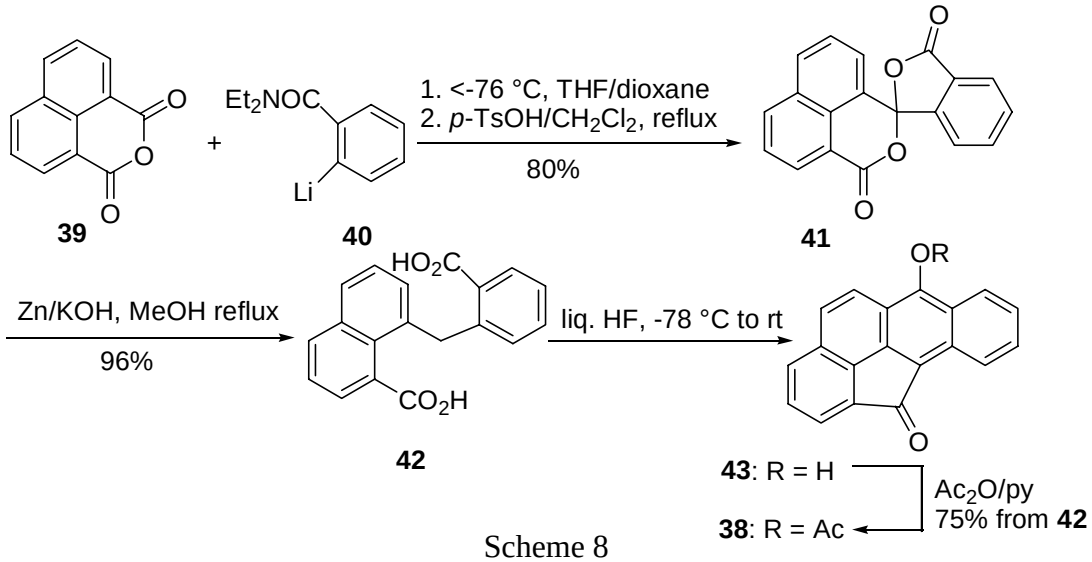
Figure 3

Five years later, Harvey *et al.* reported an improved synthetic approach to the ketone **26** in 71% overall yield from readily available precursors **34** and **35** and the application of this method for the synthesis of the previously unknown polycyclic compounds **32** and **33** in 1997.[18] Condensation of benzaldehyde (**35**) with 2-(1-naphthyl)acetic acid (**34**) furnished 2-(1-naphthyl)-3-phenylpropenoic acid (**36a**). After esterfication and photocyclization, cyclization of **37** to form the ketone **26** was promoted with HF. Compounds **32** and **33** were synthesized by a same procedure (Scheme 7).



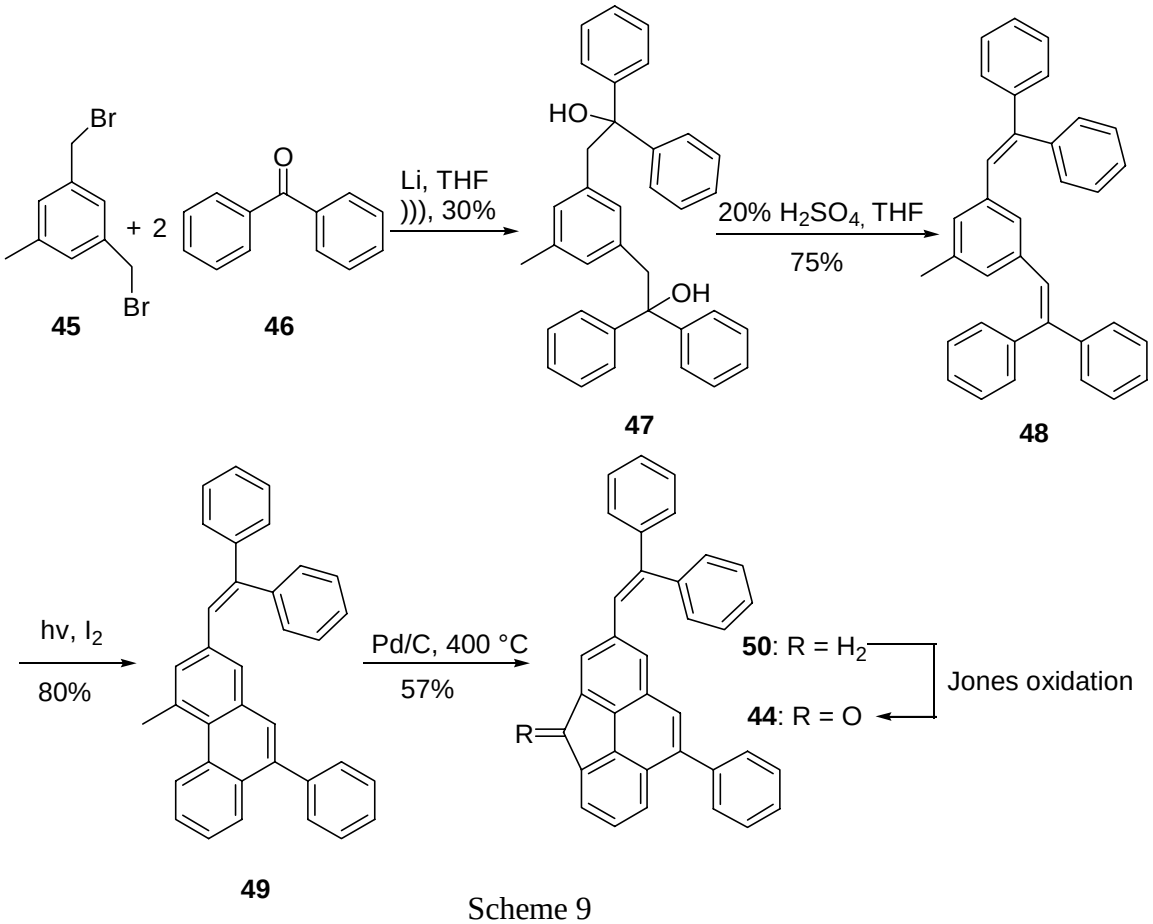
Scheme 7

In 1993, Gimisis *et al.* reported a convenient synthesis of another polycyclic aromatic compound **38** containing a 4*H*-cyclopenta[*def*]phenanthren-4-one (**5**) unit.[19] The reaction started from 1,8-naphthalic anhydride (**39**) and the ortho-lithiated derivative of *N*,*N*-diethylbenzamide (**40**), featuring a double Friedel-Crafts cyclization reaction of the diacid intermediate **42** to provide the relatively unstable keto phenol **43** which was converted to the corresponding acetate **38** (Scheme 8).



Scheme 8

Mehta *et al.* reported the synthesis of compound **44** in 1995.[20] The reaction between 1,3-bis(bromomethyl)-5-methylbenzene (**45**) and two molecules of benzophenone (**46**) furnished the C_{35}-diol **47** which underwent smooth dehydration to form **48**. On irradiation in the presence of I_2 as a catalyst, **48** furnished **49** in 80% yield. Cyclodehydrogenation of **49** gave the corresponding parent hydrocarbon **50**, which was oxidized to give the ketone **44** (Scheme 9).



Scheme 9

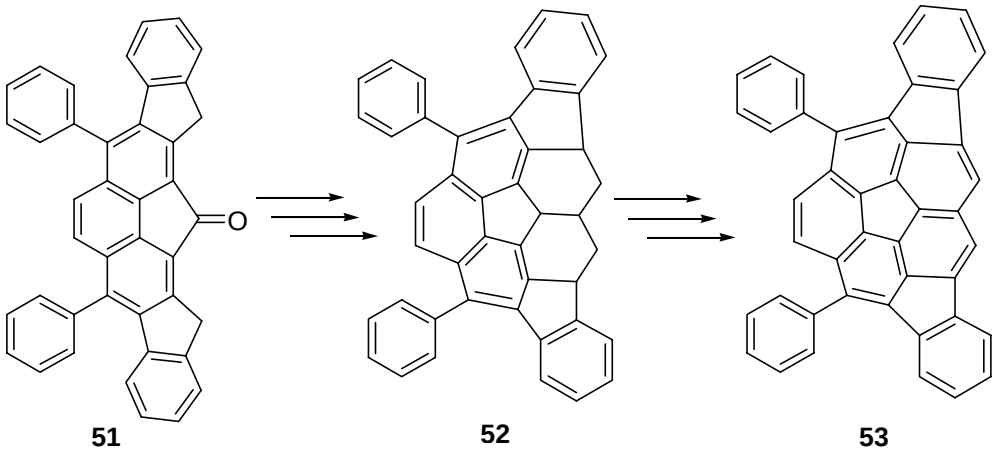
4. Results and Discussion

4.1. Synthesis of a Derivative of 4*H*-Cyclopenta[*def*]phenanthren-4-one

Our group recently reported a simple and efficient route to highly unsaturated polycyclic aromatic compounds. This pathway was successfully adopted for the

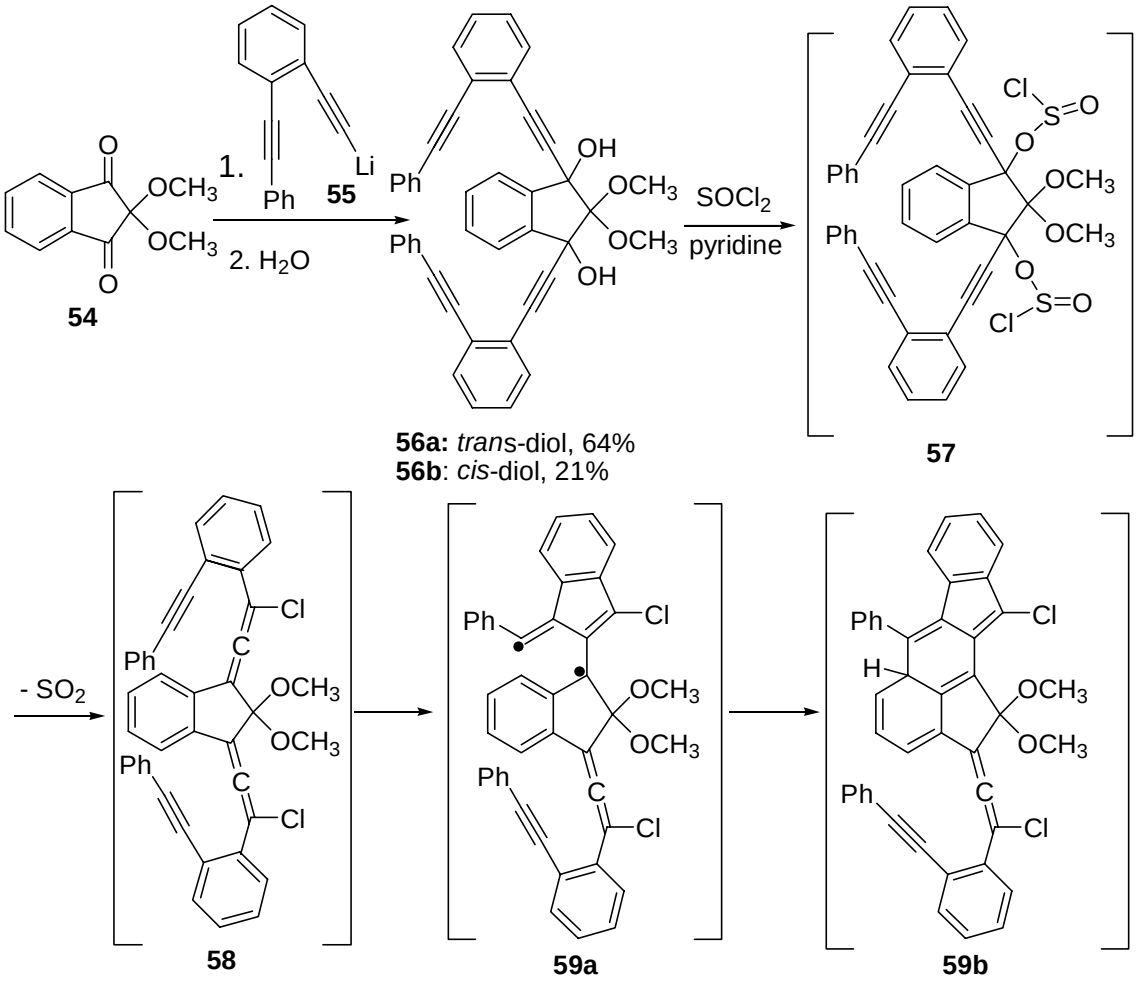
preparation for a $C_{44}H_{26}$ hydrocarbon having a carbon framework represented on the surface of C_{60}.[9a]

In this research project, **51**, a derivative of 4*H*-cyclopenta[*def*]phenanthren-4-one was also prepared using this pathway. This ketone could also serve as a potential precursor of buckybowls containing a corannulene unit. Further connecting a three-carbon unit and dehydrogenation would lead to the $C_{44}H_{22}$ fragment **53** (Scheme 10).



Scheme 10

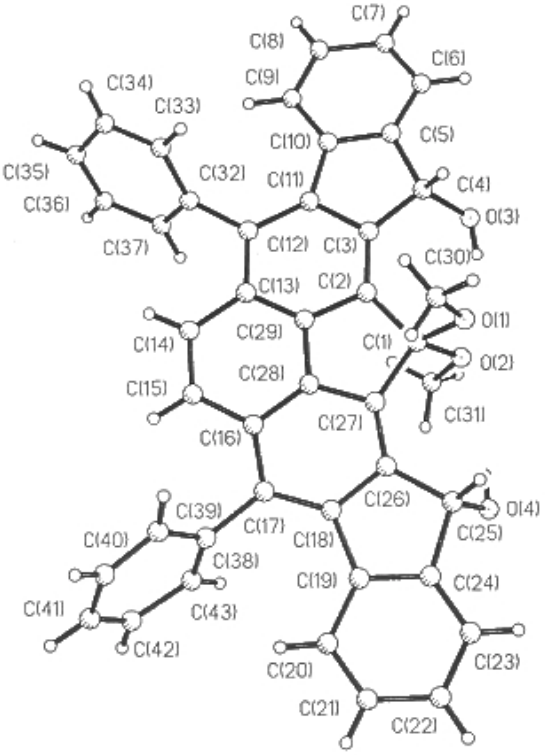
An outline of our synthetic route to the ketone **51** is given in Scheme 11a and 11b. 2,2-Dimethoxy-indan-1,3-dione (**54**) was prepared from ninhydrin according to the reported procedure in 90% yield.[21] Condensation of the diketone **54** with the lithium acetylide **55**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne with *n*-butyllithium,[22] followed by hydrolytic workup then furnished the *trans* propargylic alcohol **56a** in 64% yield and the *cis* propargylic alcohol **56b** in 21% yield. Treatment of **56a** with thionyl chloride promoted a sequence of reactions with an initial formation of the chlorosulfite **57** followed by two S_Ni' reactions[23] to produce in situ the chlorinated benzoenyne-allene **58**. A subsequent C2-C6 biradical cyclization reaction through the biradical **59a** followed by a radical-radical coupling reaction afforded the formal Diels-

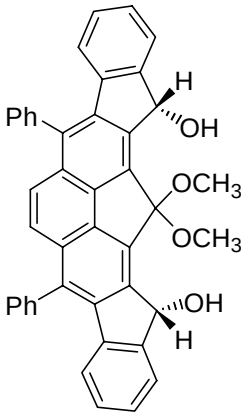


Scheme 11a

Alder adduct **59b,** and after a second round of cyclization and radical-radical coupling reaction to give **60**, which in turn underwent tautomerization to give **61**. The dichloride **61** was prone to hydrolysis. Attempts to recrystallize it from $CHCl_3$/hexanes open to air gave nice crystals of the corresponding *cis* alcohol **63**. The structure of **63** was established by an X-ray structure analysis (Figure 4).

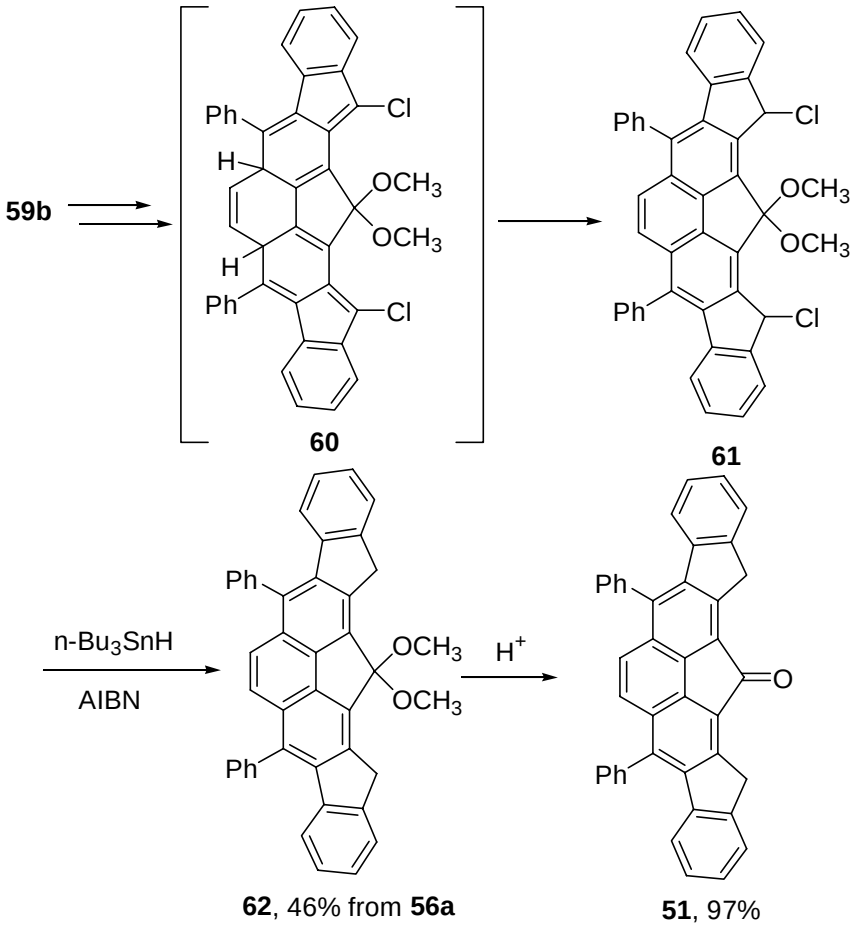
Because the dichloride **61** was prone to hydrolysis, it was operationally convenient to reduce the crude **61** without further purification with tri-*n*-butyltin hydride to furnish **62** in 46% overall yield from **56a**. Hydrolysis of the ketal group in **62** gave the ketone **51** in 97% yield which has a carbonyl group to allow further synthetic elaboration.





63

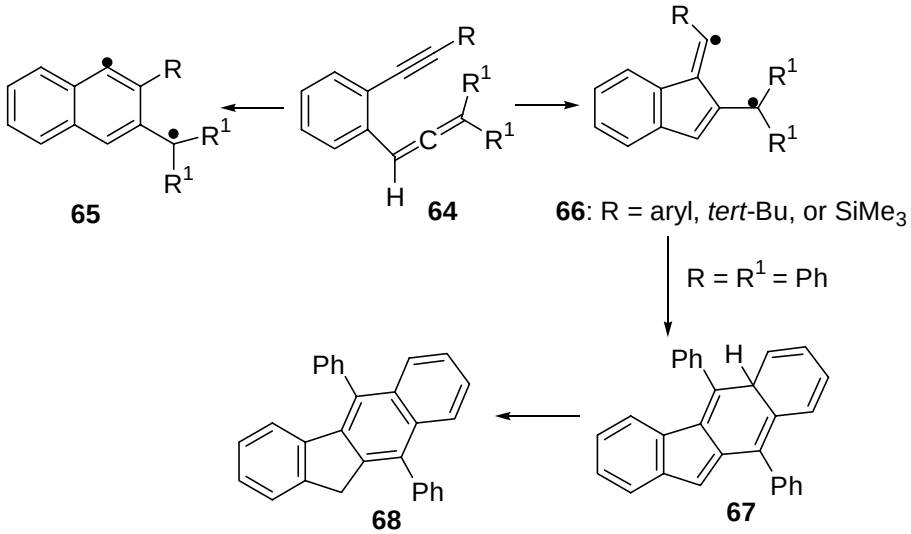
Figure 4. ORTEP drawing of the crystal structure of **63**



Scheme 11b

The ^{1}H NMR spectrum of **51** was recorded. However, due to its low solubility in common solvents, the ^{13}C NMR spectrum was not obtained.

The preference for **58** having a phenyl substituent at the acetylenic terminus to undergo the C2-C6 cyclization reaction, instead of the Myers cyclization reaction, is well precedented.[22b,24] Thermal cyclization of the benzoenyne-allenes **64** provides easy access to the naphthalene biradicals **65** and benzofulvene biradicals **66** (Scheme 12). The nature of the substituent at the acetylenic terminus is responsible for directing the reaction to generate the naphthalene biradicals **65** or the C2-C6 cyclization reaction to furnish the benzofulvene biradicals **66**.[9a] With an aryl substituent or a sterically demanding 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 in **66**. The sterically demanding group inhibits the Myers cyclization reaction because of the emergence of severe nonbonded steric interaction in the biradicals **65**. If R^1 is a phenyl group, the biradical **66** undergoes an intramolecular radical-radical coupling to form **67** and subsequently, after tautomerization, the benzofluorene **68**.



Scheme 12

The perpendicular orientation of the phenyl substituents in **62** and **51** is most likely responsible for shielding the neighboring aromatic hydrogen located on the top of the phenyl substituents, causing their ^{1}H NMR signals to shift upfield to δ 6.72 (doublet, **62**) and δ 6.65 (doublet, **51**) (Figure 5). The perpendicular orientation of the phenyl substituents was also observed in **63** by an X-ray structural analysis and in analogous cases.[9a,b]

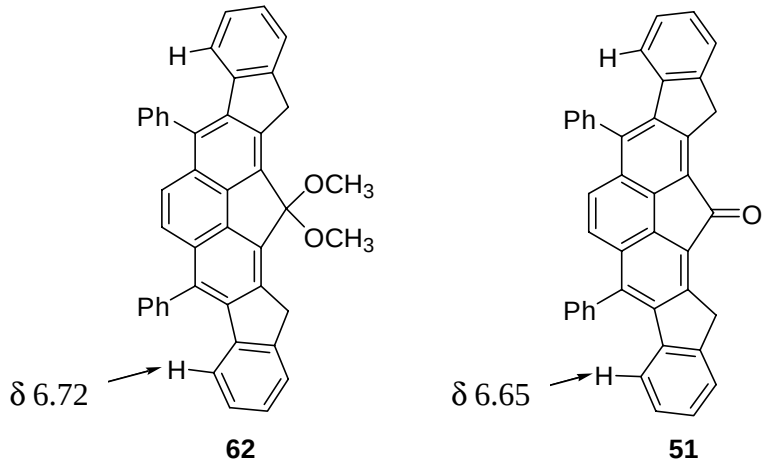
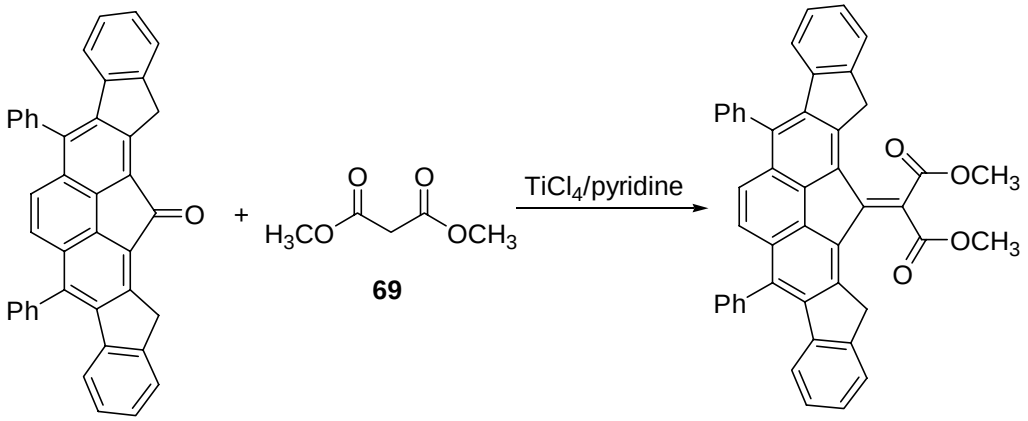


Figure 5

4.2. Development of New Synthetic Strategies for Polycyclic Aromatic Hydrocarbons

With the ketone **51** now synthesized, a missing 3-carbon fragment will be needed to convert **51** to the hydrocarbon **52** for further dehydrogenation to lead to the $C_{44}H_{22}$ fragment **53** having a corannulene unit as the core structure (Scheme 10).

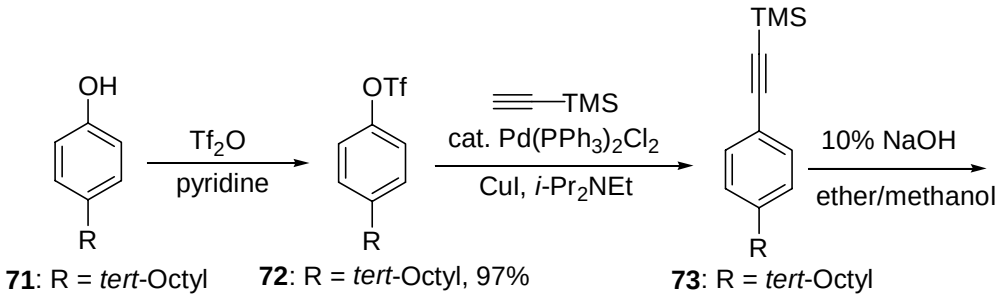
The ketone **51** was treated with dimethyl malonate (**69**) in the presence of $TiCl_4$ and pyridine according to the reported procedure[25] to produce the diester **70** in 38% yield (Scheme 13). But the very low solubility of ketone **51** prevented easy recovery of the unreacted ketone **51** and was responsible for the relatively low yield of the reaction.



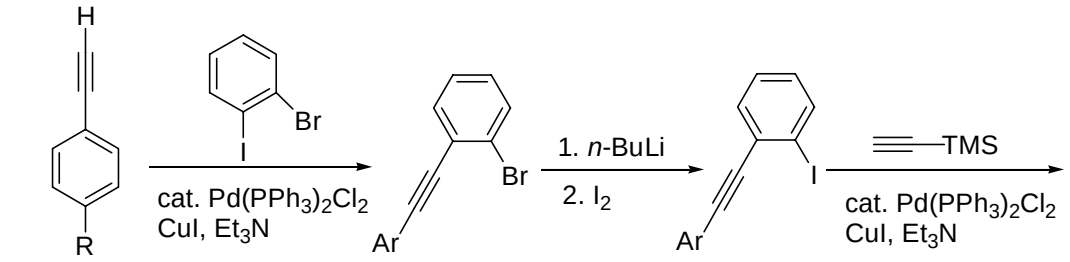
51 **70**, 38%

Scheme 13

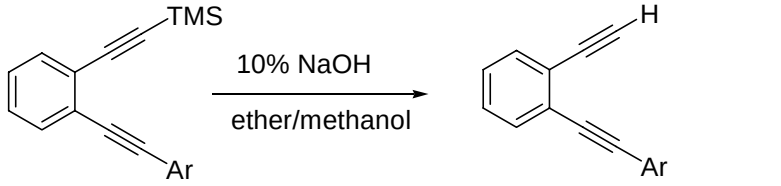
To circumvent this problem, it was envisioned that aliphatic substituents could be attached to the phenyl groups on **51** to improve its solubility. An outline of our synthetic route to modify the structure of the ketone **51** is given in Schemes 14 and 15. Treatment



71: R = *tert*-Octyl **72**: R = *tert*-Octyl, 97% **73**: R = *tert*-Octyl



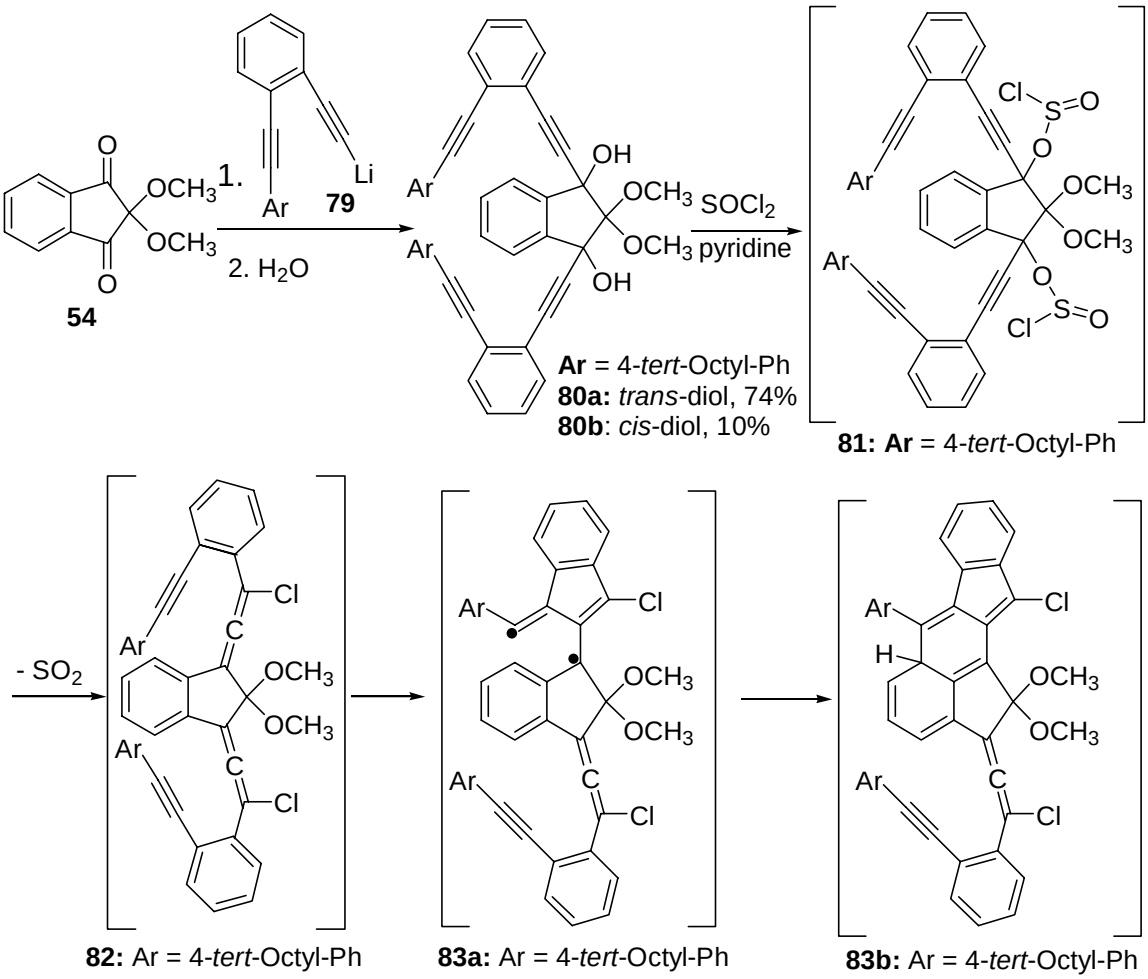
74: R = *tert*-Octyl, 92% **75**: Ar = 4-*tert*-Octyl-Ph, 97% **76**. Ar = 4-*tert*-Octyl-Ph



77: Ar = 4-*tert*-Octyl-Ph, 77% **78**: Ar = 4-*tert*-Octyl-Ph, 93%

Scheme 14

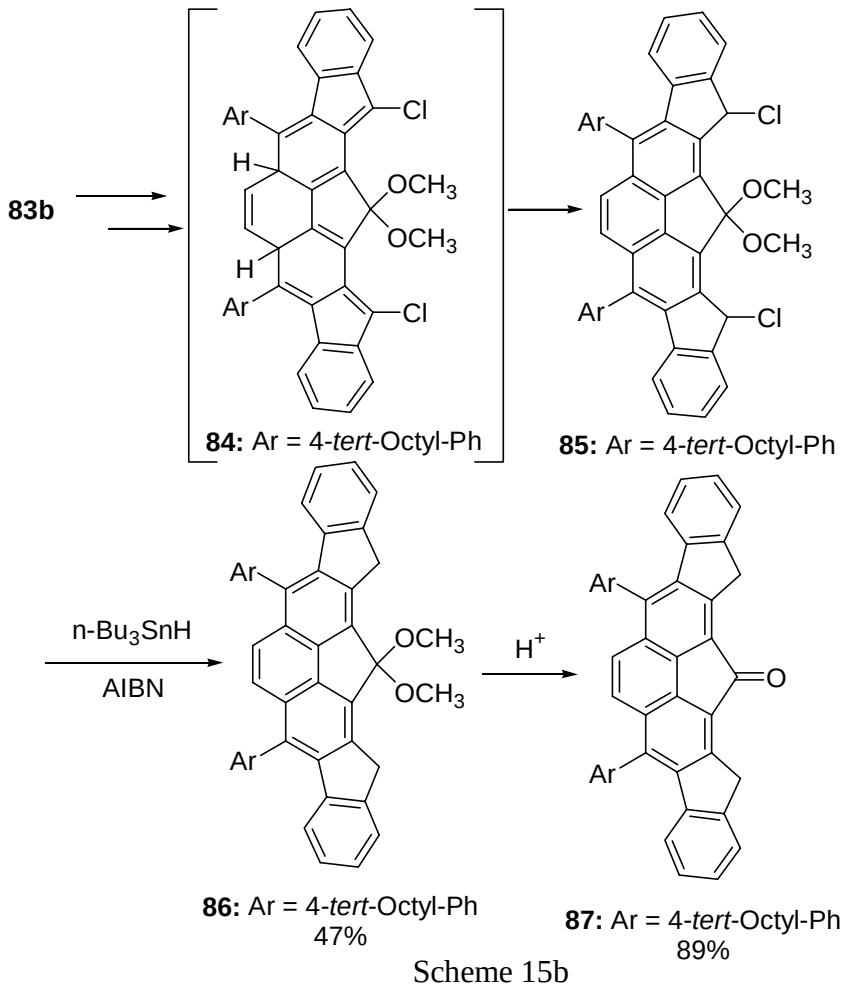
of the commercially available 4-(*tert*-octyl)phenol (**71**) with trifluoromethanesulfonic anhydride produced the corresponding triflate **72** in 97% yield. A Pd-catalyzed cross-coupling reaction with (trimethylsilyl)acetylene then furnished **73**. Initial attempt to isolate **73** from the unreacted triflate **72** by flash column chromatography was unsuccessful. However, hydrolysis of the crude product of **73** without further purification allowed isolation of **74** in 92% yield for two steps. After the hydrolysis, the unreacted triflate **72** reverted back to **71** and could be easily removed. A Pd-catalyzed cross-coupling reaction again with 1-bromo-2-iodobenzene furnished **75** in 98% yield. However, direct alkynylation of **75** was not very efficient and afforded only low yield.



Scheme 15a

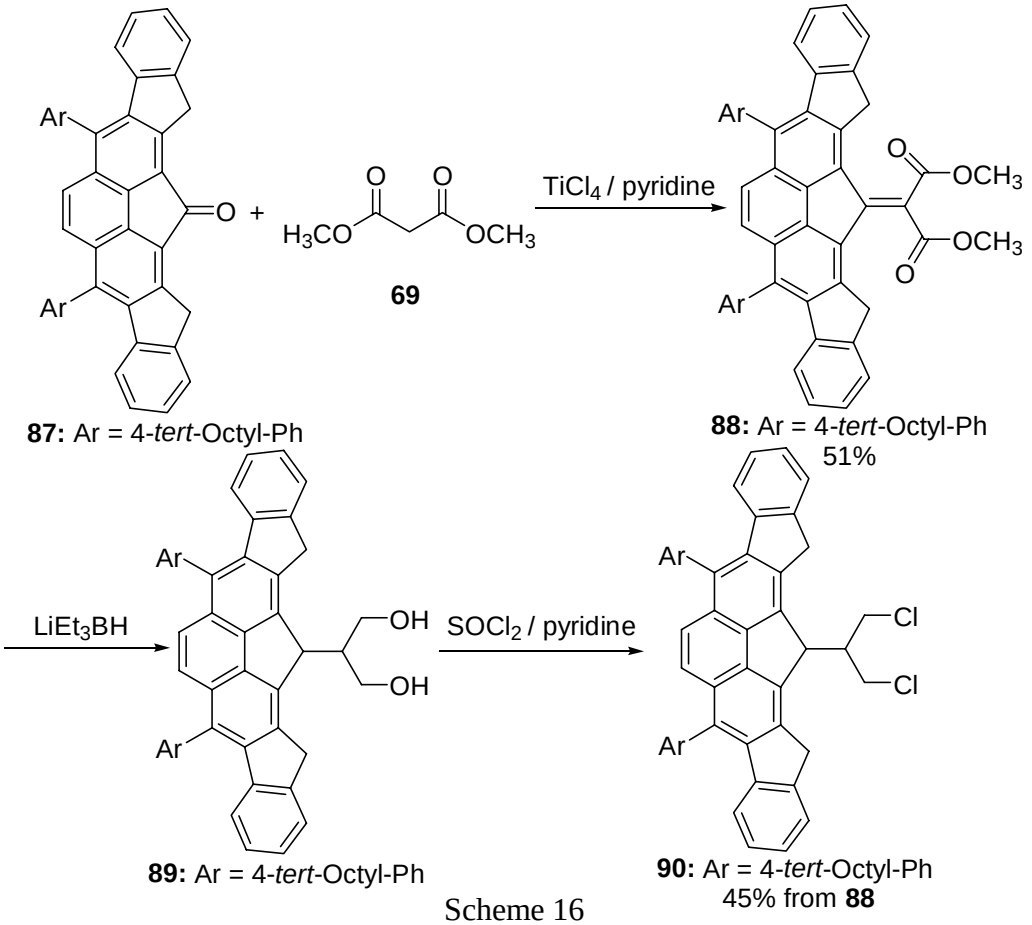
Conversion of **75** to the more reactive iodide **76** was achieved by treatment of **75** with *n*-BuLi following by I_2. Subsequent coupling with (trimethylsilyl)acetylene then provided the diacetylene **77** in 77% yield from **75**. Hydrolysis of the diacetylene **77** afforded **78** in 93% yield. The synthetic sequence outlined in Scheme 14 was mostly developed by Ms. Yonghong Yang in our research group.

The following reactions were carried out by using the same procedure as outlined in Scheme 11. Condensation of the diketone **54** with the lithium acetylide **79**, obtained by lithiation of 1-(2-ethynylphenyl)-2-(4-*tert*-octylphenyl)ethyne (**78**) with *n*-butyllithium,[22] followed by hydrolytic workup furnished two isomers, the *trans* propargylic alcohol **80a** in 74% yield and the *cis* propargylic alcohol **80b** in 10% yield. Treatment of the *trans*



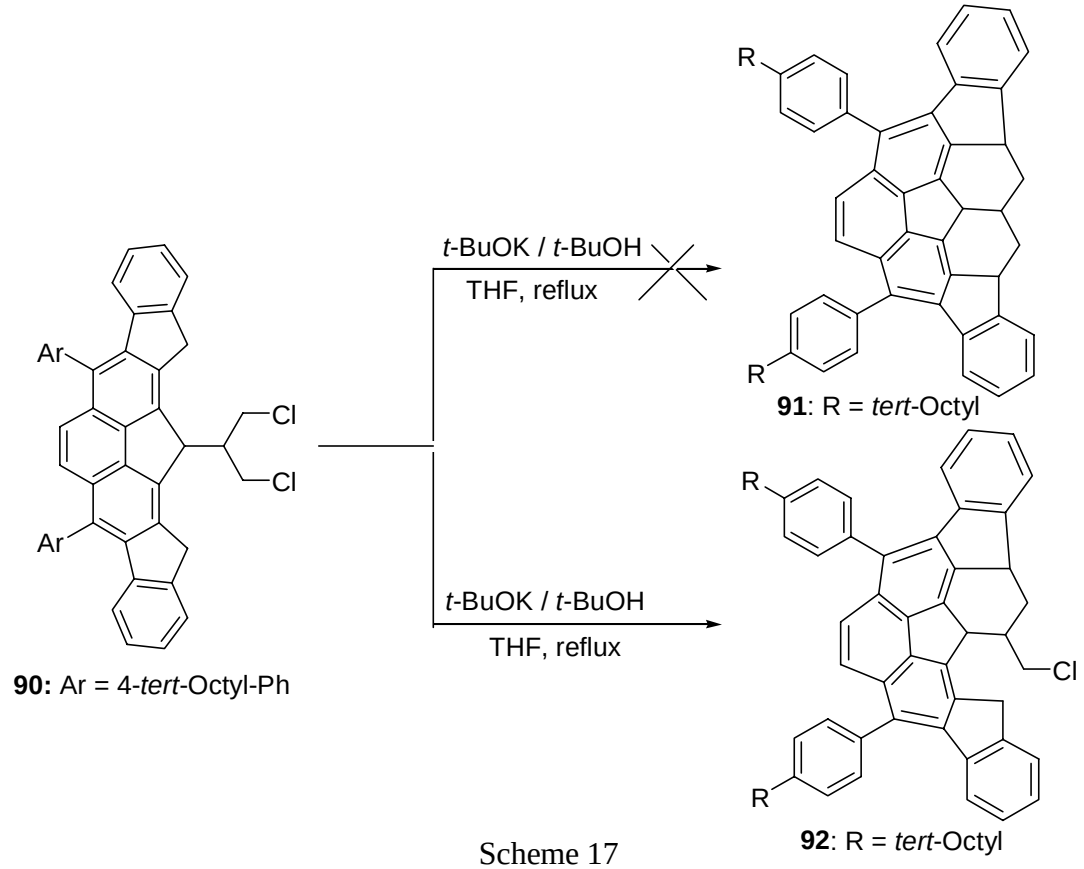
Scheme 15b

propargylic alcohol **80a** with thionyl chloride promoted a sequence of reactions with an initial formation of the chlorosulfite **81** followed by two S_Ni' reactions[23] to produce in situ the chlorinated benzoenyne-allene **82**. A subsequent C2-C6 biradical cyclization reaction through the biradical **83a** followed by a radical-radical coupling then afforded, after a second round of cyclization and radical-radical coupling, the formal Diels-Alder adduct **84**, which in turn underwent tautomerization to give **85**. The dichloride **85** was prone to hydrolysis. It was operationally convenient to reduce the crude product of **85** without further purification with tri-*n*-butyltin hydride to furnish **86** in 47% from **80a**. A similar result was obtained when **80b** was treated with thionyl chloride. Hydrolysis of the ketal group in **86** gave the ketone **87** in 89% yield. The ketone **87** has much better solubility in organic solvents compared with compound **51** (Scheme 15a and 15b).



Scheme 16

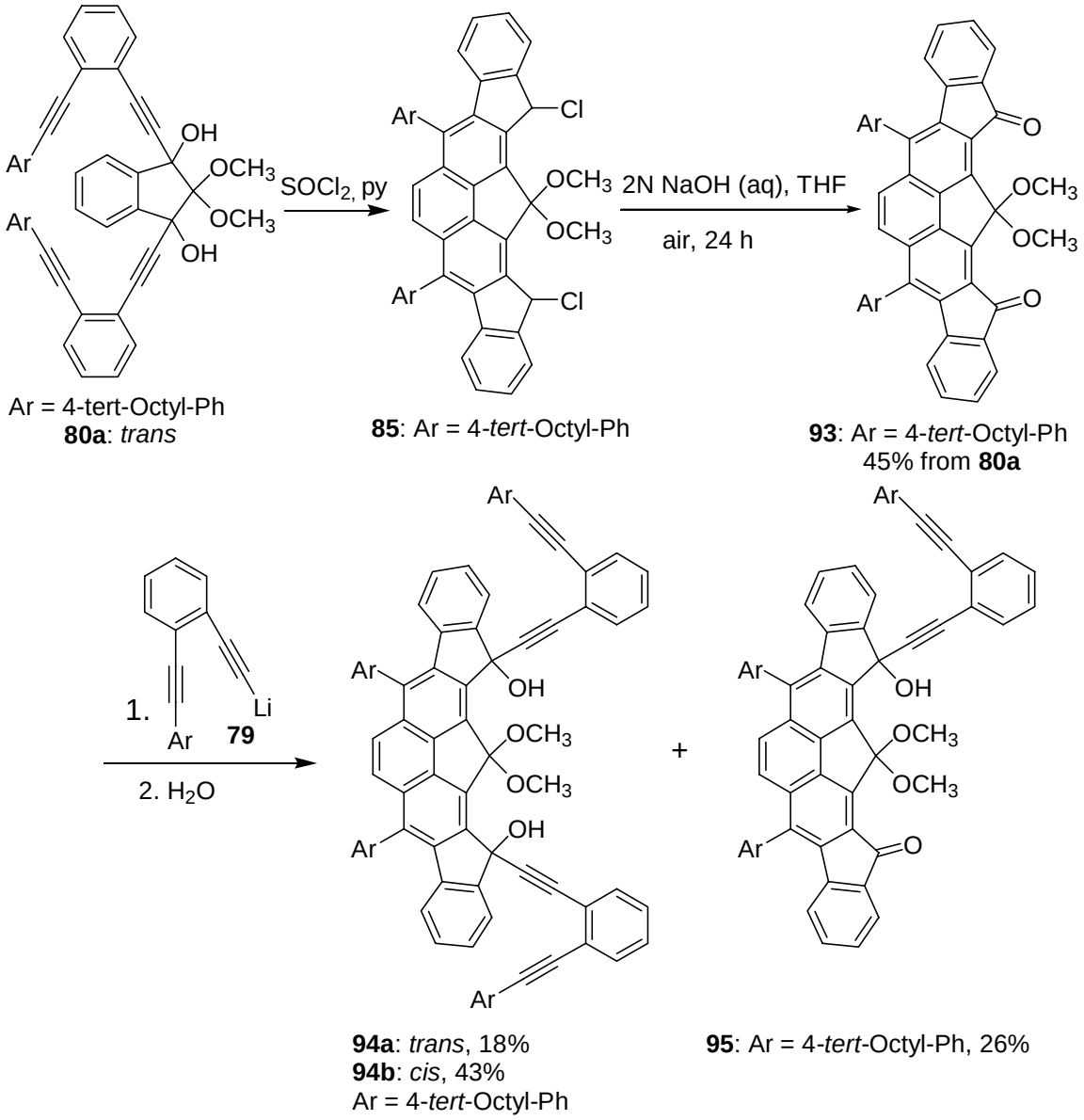
With the solubility problem resolved, the ketone **87** was treated with dimethyl malonate (**69**) in the presence of $TiCl_4$ and pyridine according to the reported procedure[25] to produce the diester **88** in 51% yield. Treatment of the diester **88** with super-hydride, followed by chlorination with thionyl chloride gave the dichloride **90** in 45% yield for two steps (Scheme 16). At this stage, we thought that treatment of the dichloride **90** with potassium *tert*-butoxide could deprotonate a hydrogen from each of the methylene groups of the five-membered rings. Two intramolecular S_N2 reactions could form the rings on both sides, leading to the hydrocarbon **91** (Scheme 17). Preliminary results appeared to suggest that the first intramolecular ring closure proceeded smoothly to give **92**. A molecular model of **92** indicated that the second closure would produce much higher ring strain and therefore would be more difficult to achieve. A solvent with a higher boiling point may be needed to overcome the developing ring strain.



Scheme 17

4.3. Synthesis of the Two Isomeric 1*H*-Cyclobut[*a*]indenes and Switching from the Formal [4+2] Cycloaddition to the [2+2] Cycloaddition of Benzoenyne-Allenes

With the presence of fluorene moieties in compound **85**, we envisaged that it could be converted to the corresponding diketone **93**, then the new carbonyl groups could allow a repeat of the cascade sequence. As described in the Ph. D. thesis of Dr. Hai-Ren Zhang,[9b] the crude chloride **85** was treated with a 2N sodium hydroxide solution in



Ar = 4-tert-Octyl-Ph
80a: *trans*

85: Ar = 4-*tert*-Octyl-Ph

93: Ar = 4-*tert*-Octyl-Ph
45% from **80a**

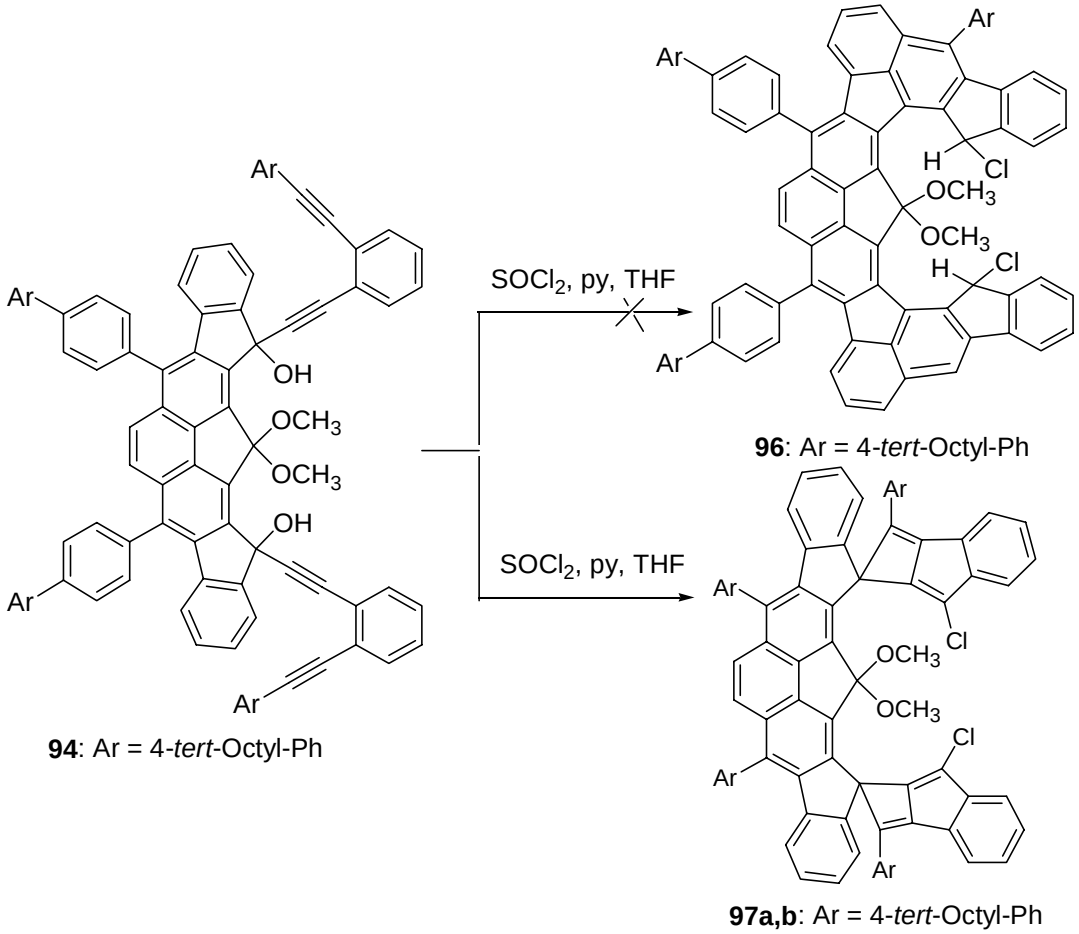
94a: *trans*, 18%
94b: *cis*, 43%
Ar = 4-*tert*-Octyl-Ph

95: Ar = 4-*tert*-Octyl-Ph, 26%

Scheme 18

aqueous THF under air to give the diketone **93** in 45% from **80a**. With the diketone **93** now available, a second condensation with the lithium acetylide **79** was carried out to give the *trans* propargylic alcohol **94a** in 18% yield, the *cis* propargylic alcohol **94b** in 43% yield, and the mono-propargylic alcohol **95** in 26% yield (Scheme 18).

After treatment of the propargylic alcohol **94** under the same condition for the cascade radical reaction of **80**, the desired formal [4+2] product **96** was not observed. Instead the products were two isomers of the formal [2+2] cycloaddition products, **97a** and **97b** (Scheme 19). The 1*H*-cyclobut[*a*]indene moieties in **97a** and **97b** are perpendicular to the central aromatic system and are most likely responsible for the shielding of the two middle methoxy groups located between the 1*H*-cyclobut[*a*]indene

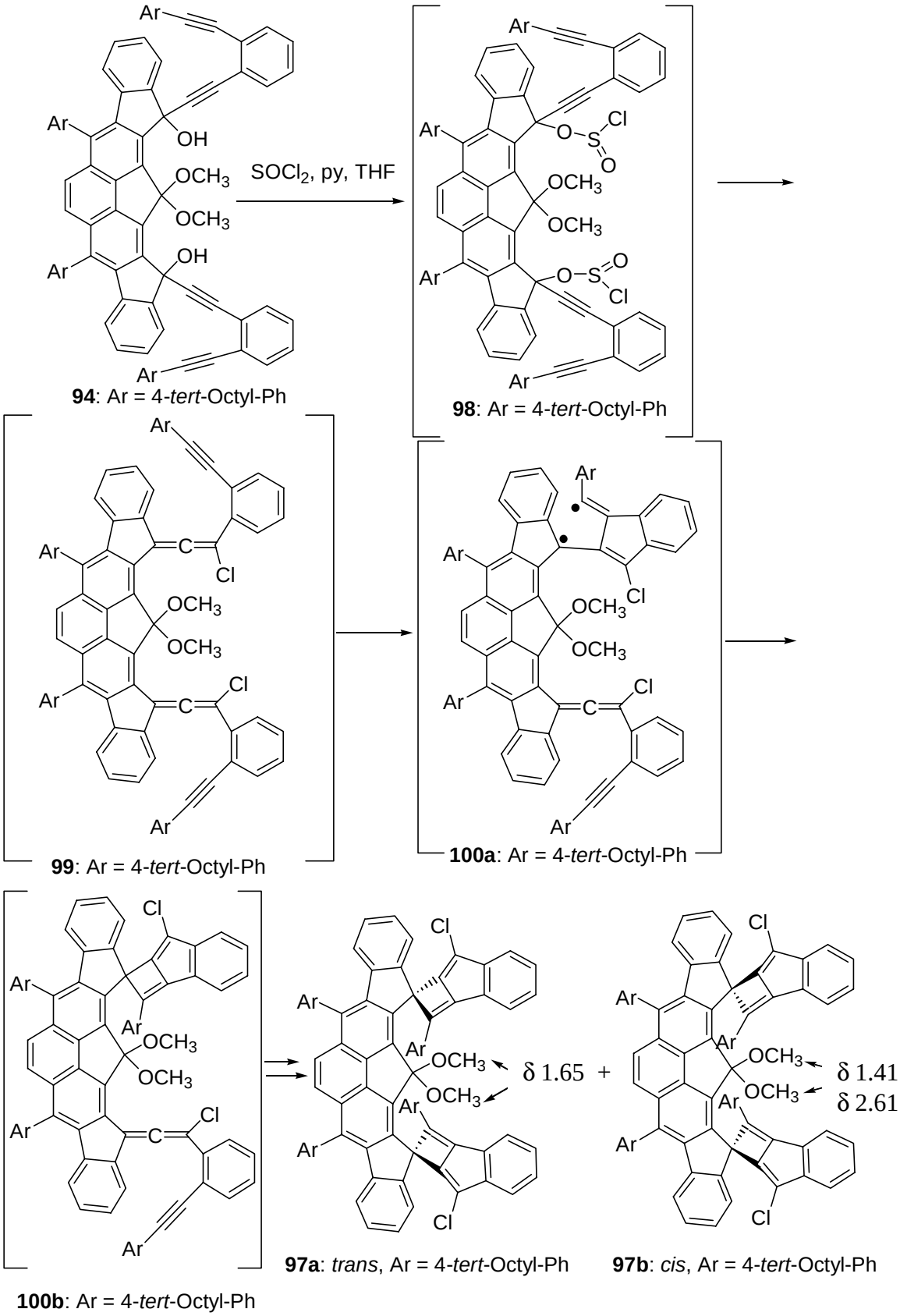


94: Ar = 4-*tert*-Octyl-Ph

96: Ar = 4-*tert*-Octyl-Ph

97a,b: Ar = 4-*tert*-Octyl-Ph

Scheme 19


Ar
OH
OCH3
OCH3
OH
Ar
Ar
SOCl2, py, THF
94: Ar = 4-tert-Octyl-Ph
O
S
Cl
O
Cl
98: Ar = 4-tert-Octyl-Ph
C
Cl
99: Ar = 4-tert-Octyl-Ph
100a: Ar = 4-tert-Octyl-Ph
100b: Ar = 4-tert-Octyl-Ph
δ 1.65 +
δ 1.41
δ 2.61
97a: trans, Ar = 4-tert-Octyl-Ph
97b: cis, Ar = 4-tert-Octyl-Ph

Scheme 20

rings causing their ^{1}H NMR signals to shift upfield to δ 1.65 for the *trans* isomer **97a** and δ 1.41 and 2.61 for the *cis* isomer **97b** (Scheme 20).

This type of formal [2+2] cycloaddition adduct has been reported before by Gillmann's group[26] and our group[9b]. Presumably, in the final step of the reaction, the phenylvinyl radical coupled with the allyl radical instead of attacking the outer phenyl ring of the central aromatic system (Scheme 20). The reason for such a dramatic change of the reaction parthway is not clear at this point. A molecular model suggests the emergence of a steric strain due to the nonbonded interaction between the chloro substituent and the methoxy group along the pathway toward the formal [4+2] cycloaddition reaction. It is also interesting to note that the *trans* propargylic alcohol **94a** gave a mixture of the *cis* dichloride **97a** in 13% yield and the *trans* dichloride **97b** in 42% yield. On the other hand, the *cis* propargylic alcohol **94b** gave a mixture of the *cis* dichloride **97a** in 28% yield and the *trans* dichloride **97b** in 32% yield.

5. Conclusions

Two derivatives of 4*H*-cyclopenta[*def*]phenanthren-4-one (**51** and **87**), which could serve as potential precursors for larger polycyclic aromatic hydrocarbons, were synthesized. The process involved the use of a simple and efficient route to generate the chlorinated benzoenyne-allenes in situ for subsequent cascade radical cyclizations. Attempts are being made to further extend this synthetic strategy for the constitution of curved polycyclic aromatic hydrocarbons. Two interesting polycyclic aromatic compounds (**97a** and **97b**) were likewise synthesized by using the similar pathway.

Part II

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere except in the cases of **51**, **78**, **87** and **93**. Tetrehydrofuran (THF) and diethyl ether (Et_2O) were distilled from benzophenone ketyl and benzene was distilled from CaH_2 prior to use. Ninhydrin, *N*,*N*-dimethylformamide (DMF), iodomethane, CuI, dichlorobis(triphenylphosphine)palladium, *n*-butyllithium (2.5 M) in hexanes, pyridine (anhydrous), thionyl chloride, triethylamine, AIBN, titanium (IV) chloride, lithium triethylborohydride (super hydride), trifluoromethanesulfonic anhydride, *N*,*N*–diisopropylethylamine, and potassium *tert*-butoxide (1.0 M) were purchased from Aldrich and were used as received. Tri-*n*-butyltin hydride was purchased from Acros and was used as received. Phenylacetylene and (trimethylsilyl)acetylene were purchased from GFS Chemicals, Inc. and were used without further purification. 1-Bromo-2-iodobenzene and Ag_2O were purchased from Alfa and Lancaster, respectively. The ketal **54** was prepared from ninhydrin according to the reported procedure in 90% yield.[19] Silica gel for flash column chromatography was purchased from ICN. Melting points were uncorrected. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^1H δ 7.26) and $CDCl_3$ (^{13}C δ 77.00) as internal standards.

Propargylic Alcohols 56a and 56b. To a solution 0.766 g of 1-(2-ethynylphenyl)-2-phenylethyne (3.79 mmol) in 15 mL of THF was added 1.45 mL of a 2.5 M solution of *n*-butyllithium (3.62 mmol) in hexanes at 0 °C. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a

solution of 0.355 g of **54** (1.72 mmol) in 10 mL of THF was added via cannula, and the mixture was stirred at room temperature for 12 h. Water (15 mL) was introduced and the reaction mixture was concentrated to remove organic solvent. Diethyl ether (25 mL) was added, and the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a light yellow solid. The solid was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to afford 0.673 g (1.10 mol, 64% yield) of the *trans* propargylic alcohol **56a** and 0.218 g (0.357 mol, 21% yield) of the *cis* propargylic alcohol **56b** as white solids. **56a**: R_f 0.28 (hexanes/CH_2Cl_2 = 1:1); IR 3517, 756 cm^{-1}; ^1H NMR δ 7.70–7.67 (2 H, m), 7.54–7.48 (4 H, m), 7.44–7.40 (4 H, m), 7.33–7.22 (12 H, m), 3.86 (2 H, s), 3.83 (6 H, s); ^{13}C NMR δ 142.24, 132.22, 131.91, 131.76, 129.82, 128.36, 128.32, 128.22, 127.84, 125.97, 124.78, 124.30, 122.97, 109.68, 93.32, 91.80, 87.96, 86.39, 53.18; **56b**: R_f 0.03 (hexanes/CH_2Cl_2 = 1:1); IR 3498, 2216, 756 cm^{-1}; ^1H NMR δ 7.82–7.76 (2 H, m), 7.56–7.46 (8 H, m), 7.35–7.23 (10 H, m), 7.21–7.16 (2 H, m), 3.87 (3 H, s), 3.67 (3 H, s), 3.63 (2 H, s); ^{13}C NMR δ 142.69, 132.18, 131.91, 131.76, 130.13, 128.37, 128.25, 127.85, 126.10, 124.92, 124.85, 122.99, 109.18, 93.40, 90.91, 87.98, 86.86, 78.11, 52.94, 52.27.

Ketal 62. To 0.643 g of the *trans* propargylic alcohol **56a** (1.05 mmol) in 15 mL of THF at 0 °C was added via cannula a solution of 0.421 g of thionyl chloride (3.54 mmol) and 0.570 g of anhydrous pyridine (7.21 mmol) in 10 mL of THF. The reaction mixture was then allowed to warm to rt. After 8 h, the reaction mixture was concentrated, and 20 mL of water and 30 mL of methylene chloride were added. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a light brown solid (crude product of chloride **61**). To a flask was added 0.016 g (0.11 mmol) of

AIBN, a solution of the crude product of **61** in 30 mL of benzene, and 0.85 mL of *n*-butyltin hydride (0.92 g, 3.2 mmol). The resulting mixture was heated to 80 °C for 18 h before it was allowed to cool rt. The mixture was treated with 20 mL of 10% KF solution, stirred for 2 h, and filtered. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a brown solid. The solid was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to afford 0.278 g (0.481 mmol, 46% yield from the *trans* propargylic alcohol **56a**) of **62** as a yellow solid: compound turns dark at 255 °C and becomes black without melting at 271 °C; R_f 0.13 (hexanes/CH_2Cl_2 = 1:1); IR 767, 747, 701 cm^{-1}; ^1H NMR δ 7.63–7.47 (12 H, m), 7.35 (2 H, s), 7.27 (2 H, t, *J* = 7.4 Hz), 7.07 (2 H, t, *J* = 7.5 Hz), 6.72 (2 H, d, *J* = 7.9 Hz), 4.33 (4 H, s), 3.32 (6 H, s); ^{13}C NMR δ 144.05, 141.51, 139.86, 138.06, 138.02, 135.11, 134.46, 133.86, 129.76, 129.01, 127.90, 126.88, 126.58, 126.53, 125.10, 123.60, 123.42, 114.68, 52.70, 34.63.

Ketone 51. To a solution of 0.134 g of **62** (0.232 mmol) in 20 mL of acetone was added 10 mL of a 10% HCl solution. After 2 h, the mixture was concentrated to remove acetone and centrifuged. The liquid phase was decanted, and after two cycles of washing the remaining solid with water followed by centrifugation, 0.119 g (0.224 mmol, 97%) of **51** was obtained as a yellow solid: compound turns dark at 342 °C and becomes black without melting at 357 °C; IR (KBr) 1705, 776, 762, 738, 700 cm^{-1}; ^1H NMR δ 7.64–7.57 (8 H, m), 7.47–7.44 (4 H, m), 7.28–7.23 (4 H, m), 7.05 (2 H, t, *J* = 7.6 Hz), 6.65 (2 H, d, *J* = 7.9 Hz), 4.37 (4 H, s).

Diester 70. To 5 mL of THF in a flask at 0 °C was added 0.22 mL of $TiCl_4$ (1.9 mmol). Then, a solution of 0.100 g of **51** (0.188 mmol) in 80 mL of THF and a solution

of 0.074 g of dimethyl malonate (**69**) (0.56 mmol) in 10 mL of THF were sequentially added. After 30 min, 0.668 g of pyridine (8.46 mmol) in 5 mL of THF was added slowly and the reaction mixture was stirred at room temperature for 40 h. Water (20 mL) was introduced, and the reaction mixture was concentrated to remove THF. Methylene chloride (40 mL) was added, and the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a red solid. The solid was purified by flash column chromatography (silica gel/33% CH_2Cl_2 in hexanes) to afford 0.046 g (0.071 mmol, 38%) of **70** as a red solid: IR (KBr) 1717, 737, 701 cm^{-1}; ^1H NMR δ 7.60–7.43 (12 H, m), 7.29 (2 H, s), 7.23 (2 H, t, *J* = 7.4 Hz), 7.01 (2 H, t, *J* = 7.6 Hz), 6.55 (2 H, d, *J* = 7.9 Hz), 4.18 (6 H, s), 4.02 (4 H, s); ^{13}C NMR δ 167.05, 148.75, 143.28, 140.93, 140.77, 137.82, 136.41, 136.02, 131.78, 129.59, 129.08, 128.06, 127.07, 126.88, 126.47, 126.19, 124.30, 123.33, 53.61, 37.45.

Triflate 72. To a solution of 5.036 g of **71** (24.45 mmol) and 13.8 mL of pyridine (13.5 g, 169 mmol) at 0 °C was added dropwise 8.3 mL (13.8 g, 48.9 mmol) of trifluoromethanesulfonic anhydride. The reaction mixture was then allowed to warm to room temperature. After 18 h, the reaction mixture was then poured into a flask containing 50 mL of water and 50 mL of diethyl ether. The organic layer was separated, washed with water, a 5% HCl solution, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/20% diethyl ether in hexanes) to afford 8.090 g (23.93 mmol, 98% yield) of **72** as a colorless liquid. R_f 0.85 (hexanes/diethyl ether = 4:1); IR (neat) 1503, 1426, 1210, 1144, 892, 836 cm^{-1}; ^1H NMR δ 7.32 (4 H, dd, *J* = 71.3 and 9.0 Hz), 1.77 (2 H, s), 1.39 (6 H, s), 0.73 (9 H, s); ^{13}C NMR

δ 150.82, 147.38, 127.92, 120.40, 118.80 (q, *J* = 320.6 Hz), 56.98, 38.60, 32.32, 31.68, 31.39; MS m/z 338 (M^+), 267, 175.

(4-*tert*-Octyl-phenyl)acetylene (74). To a flask containing 0.76 g of dichlorobis(triphenylphosphine)palladium (1.09 mmol) and 0.21 g of CuI (1.09 mmol) was added via cannula a mixture of 4.001 g of the triflate **72** (11.83 mmol) and 7.21 mL of *N*,*N*-diisopropylethylamine (41.4 mmol) in 30 mL of DMF followed by a solution of 2.32 g of (trimethylsilyl)acetylene (23.7 mmol) in 10 mL of DMF. The resulting mixture was heated at 45 °C. After 48 h, the mixture was allowed to cool to rt and concentrated. Water (40 mL) and hexanes (50 mL) were added. After filtration, the organic layer was seperated, dried over Na_2SO_4, and concentrated to afford the crude product of **73**. To the crude product of **73** in 40 mL of diethyl ether were added 20 mL of a 10% NaOH solution and 30 mL of methanol. After 8 h at rt, the organic solvents were removed in vacuo. Water (30 mL) and diethyl ether (50 mL) were added. The organic layer was separated, washed with 2 M HCl and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to afford 2.342 g (10.94 mmol, 93% yield from **72**) of **74** as a yellow oil: R_f 0.45 (hexanes); IR (neat) 3306, 2109, 834 cm^{-1}; ^{1}H NMR δ 7.39 (4 H, dd, *J* = 23.7 and 8.7 Hz), 3.04 (1 H, s), 1.76 (2 H, s), 1.37 (6 H, s), 0.73 (9 H, s); ^{13}C NMR δ 151.21, 131.60, 126.14, 118.79, 83.91, 76.44, 56.74, 38.68, 32.33, 31.78, 31.39; MS m/z 214 (M^+), 143, 115.

1-(2-Bromophenyl)-2-(4-*tert*-octylphenyl)ethyne (75). To a flask containing 0.22 g of dichlorobis(triphenylphosphine)palladium (0.32 mmol) and 0.06 g of CuI (0.32 mmol) was added via cannula a solution of 2.985 g of 1-bromo-2-iodobenzene (10.55 mmol) in 20 mL of triethylamine followed by a solution of 2.258 g of **74** (10.55 mmol) in

20 mL of triethylamine. The resulting mixture was heated at 45 °C. After 10 h, the mixture was allowed to cool to rt and concentrated. A saturated aqueous ammonium chloride solution (100 mL) was then added. After filtration, the filtrate was extracted with hexanes. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 3.786 g (10.26 mmol, 97% yield) of **75** as a yellow solid: mp 81−83.5 °C; R_f 0.34 (hexanes); IR 2220, 834, 753 cm^{-1}; ^{1}H NMR δ 7.63-7.50 (4 H, m), 7.40-7.36 (2 H, m); 7.28 (1 H, td, *J* = 7.7 and 1.2 Hz), 7.16 (1 H, td, *J* = 7.7 and 1.7 Hz), 1.77 (2 H, s), 1.37 (6 H, s), 0.74 (9 H, s); ^{13}C NMR δ 151.15, 133.13, 132.38, 131.18, 129.12, 126.97, 126.23, 125.62, 125.53, 94.28, 87.40, 56.74, 38.74, 32.34, 31.79, 31.42; MS m/z 370 (M^+), 368, 299, 297.

1-(4-*tert*-Octylphenyl)-2-[2-(trimethylsilylethynyl)phenyl]ethyne (77). A 2.5 M solution of *n*-butyllithium (4.81 mL, 12.0 mmol) in hexanes was added dropwise to a solution of 3.696 g of **75** (10.02 mmol) in diethyl ether (25 mL) at -78 °C. After 2 h of stirring at -78 °C, 3.31 g of I_2 (13.0 mmol) in 100 mL of diethyl ether was added via cannula at -78 °C and the mixture was then allowed to warm to room temperature. After 12 h, 30 mL of a 5% $Na_2S_2O_3$ solution was added, and the organic layer was separated, washed with water, dried with Na_2SO_4, and concentrated to furnish **76** as a yellow solid. It was used for the next step without further purification. To a flask containing 0.21 g of dichlorobis(triphenylphosphine)palladium (0.30 mmol) and 0.06 g of CuI (0.32 mmol) was added via cannula a solution of the crude product of **76** in 40 mL of triethylamine followed by a solution of 1.18 g of (trimethylsilyl)acetylene in 15 mL of triethylamine. The resulting mixture was heated at 45 °C. After 16 h, the mixture was allowed to cool to

rt and concentrated. A saturated aqueous ammonium chloride solution (100 mL) was then added. After filtration, the filtrate was extracted with diethyl ether. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 2.963 g (7.676 mmol, 77% yield from **75**) of **77** as a yellow solid: R_f 0.20 (hexanes); IR 2217, 2158, 874, 843, 757 cm^{-1}; ^1H NMR δ 7.52–7.46 (4 H, m), 7.38–7.35 (2 H, m), 7.31–7.21 (2 H, m), 1.76 (2 H, s), 1.37 (6 H, s), 0.72 (9 H, s), 0.27 (9 H, s); ^{13}C NMR δ 150.78, 132.20, 131.60, 131.20, 128.16, 127.60, 126.35, 126.16, 125.50, 119.96, 103.55, 98.48, 93.81, 87.51, 56.84, 38.71, 32.35, 31.75, 31.42, 0.03; MS m/z 386 (M^+), 315.

1-(2-Ethynylphenyl)-2-(4-*tert*-octylphenyl)ethyne 78. To 2.931g of 1-(4-*tert*-octylphenyl)-2-[2-(trimethylsilylethynyl)phenyl]ethyne (**77**) (7.593 mmol) in 40 mL of diethyl ether were added 40 mL of methanol and 25 mL of a 10% NaOH solution. After 30 min at rt, the organic solvents were removed in vacuo. Water (30 mL) and diethyl ether (50 mL) were then added. The organic layer was separated, washed with 2 M HCl and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to give 2.219 g (7.067 mmol, 93% yield) of **78** as a yellow solid: mp 80.5–82 °C; R_f 0.31 (hexanes); IR 3291, 2218, 834, 758 cm^{-1}; ^1H NMR δ 7.55–7.48 (4 H, m), 7.39–7.24 (4 H, m), 3.38 (1 H, s), 1.77 (2 H, s), 1.38 (6 H, s), 0.74 (9 H, s); ^{13}C NMR δ 150.96, 132.52, 131.69, 131.25, 128.48, 127.66, 126.55, 126.17, 124.47, 119.81, 93.90, 87.22, 82.26, 81.02, 56.75, 38.71, 32.35, 31.78, 31.41; MS m/z 314 (M^+), 243.

Propargylic Alcohols 80a and 80b. The same procedure was repeated as described for **56a** and **56b** except that 2.126 g 1-(2-ethynylphenyl)-2-(4-*tert*-

octylphenyl)ethyne (**78)** (6.772 mmol) and 0.634 g of **54** (3.078 mmol) were used to afford 1.887 g (2.263 mmol, 74% yield) of the *trans* propargylic alcohol **80a** and 0.251 g (0.301 mmol, 10% yield) of the *cis* propargylic alcohol **80b** as white solids. **80a**: mp 136–139 °C; R_f 0.20 (hexanes/CH_2Cl_2 = 1:1); IR 3519, 2216, 834, 757 cm^{-1}; ^1H NMR δ 7.71–7.68 (2 H, m), 7.53–7.47 (4 H, m), 7.40–7.37 (4 H, m), 7.32–7.21 (10 H, m) 3.87 (2 H, s), 3.81 (6 H, s), 1.73 (4 H, s), 1.34 (12 H, s), 0.70 (18 H, s); ^{13}C NMR δ 150.76, 142.27, 132.20, 131.85, 131.26, 129.78, 128.30, 127.60, 126.25, 126.13, 124.75, 124.32, 119.70, 109.68, 93.70, 91.74, 87.39, 86.46, 77.14, 56.77, 53.17, 38.68, 32.34, 31.77, 31.41; MS m/z 857 (MNa^+), 817, 785; HRMS calcd for $C_{59}H_{62}O_4Na$ (MNa^+) 857.4546, found 857.4587. **80b**: R_f 0.04 (hexanes/CH_2Cl_2 = 1:1); IR 3501, 2216, 834, 758; ^1H NMR δ 7.84–7.78 (2 H, m), 7.55–7.49 (4 H, m), 7.43–7.40 (4 H, m), 7.34–7.25 (8 H, m), 7.23–7.18 (2 H, m), 3.89 (3 H, s), 3.66 (3 H, s), 3.64 (2 H, s), 1.73 (4 H, s), 1.34 (12 H, s), 0.70 (18 H, s); ^{13}C NMR δ 150.84, 142.73, 132.14, 131.89, 131.29, 130.11, 128.36, 127.62, 126.39, 126.14, 124.96, 124.75, 119.70, 109.16, 93.79, 90.83, 87.39, 86.96, 78.13, 56.72, 52.97, 52.30, 38.67, 32.32, 31.76, 31.46, 31.39; MS m/z 857 (MNa^+), 817, 785; HRMS calcd for $C_{59}H_{62}O_4Na$ (MNa^+) 857.4546, found 857.4586.

Ketal 86. The same procedure was repeated as described for **62** except that 1.625 g of the *trans* propargylic alcohol **80a** (1.948mmol) was used to afford 0.731 g (0.911mmol, 47% yield from **80a**) of **86** as a yellow solid: compound turns dark at 268 °C and becomes black without melting at 273 °C; R_f 0.23 (hexanes/CH_2Cl_2 = 1:1); IR 2951, 822, 780, 748, 715 cm^{-1}; ^1H NMR δ 7.63–7.60 (6 H, m), 7.40 (4 H, d, *J* = 8.4 Hz), 7.38 (2 H, s), 7.29–7.24 (2 H, m), 7.02 (2 H, t, *J* = 7.5 Hz), 6.86 (2 H, d, *J* = 7.9 Hz); 4.33 (4 H, s), 3.33 (6 H, s), 1.91 (4 H, s), 1.52 (12 H, s), 0.89 (18 H, s); ^{13}C NMR δ 149.69,

143.99, 141.65, 139.79, 137.98, 135.15, 134.68, 133.66, 129.14, 126.85, 126.75, 127.72, 126.27, 125.01, 123.68, 123.62, 114.72, 57.10, 52.69, 38.64, 34.60, 32.56, 31.87, 31.82.

Ketone 87. To a mixture of 0.705 g of **86** (0.879 mmol), 30 mL of CH_2Cl_2, and 60 mL of acetone was added 35 ml of a 5% HCl solution. The progress of the reaction was monitored by TLC. After 19 h, the reaction mixture was concentrated in vacuo, and 50 mL of CH_2Cl_2 was added. The organic layer was separated, washed with a saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/ 33% hexanes in CH_2Cl_2) to afford 0.592 g (0.783 mmol, 89% yield) of **87** as a yellow solid: compound turns dark at 305 °C and becomes black without melting at 314 °C; R_f 0.33 (hexanex:CH_2Cl_2 = 1:2); IR (KBr) 1709 cm^{-1}; ^{1}H NMR δ 7.50 (4 H, d, *J* = 8.2 Hz), 7.34 (2 H, d, *J* = 7.4 Hz), 7.27 (4 H, d, *J* = 8.2 Hz), 7.11 (2 H, t, *J* = 7.3 Hz), 6.89 (2 H, t, *J* = 7.4 Hz), 6.69 (2 H, d, *J* = 7.9 Hz), 3.99 (4 H, s), 1.88 (4 H, s), 1.49 (12 H, s), 0.88 (18 H, s); ^{13}C NMR δ 193.60, 149.87, 143.76, 140.98, 140.62, 138.29, 137.13, 133.97, 128.73, 127.33, 126.90, 126.78, 126.37, 126.06, 124.93, 123.36, 57.07, 38.62, 34.54, 32.55, 31.88, 31.78; MS m/z 756 (M^+), 685, 570; HRMS calcd for $C_{57}H_{56}O$ 756.4331 found 756.4348.

Diester 88. The same procedure was repeated as described for **70** except that 0.220 g of **87** (0.291 mmol) was used. Purification by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) afforded 0.129 g (0.148 mmol, 51% yield) of **88** as a red solid: compound turns dark at 275 °C and becomes black without melting at 294 °C; R_f 0.08 (hexanes:CH_2Cl_2 = 1:1); IR (KBr) 1720 cm^{-1}; ^{1}H NMR δ 7.60 (4 H, d, *J* = 8.2 Hz), 7.49 (2 H, d, *J* = 7.4 Hz), 7.35 (4 H, d, *J* = 8.16 Hz), 7.32 (2 H, s), 7.21 (2 H, t, *J* = 7.4 Hz), 6.94 (2 H, t, *J* = 7.7 Hz), 6.70 (2 H, d, *J* = 7.9 Hz), 4.18 (6 H, s), 4.01 (4 H, s),

1.89 (4 H, s), 1.49 (12 H, s), 0.88 (18 H, s); ^{13}C NMR δ 167.09, 149.98, 148.93, 143.24, 140.92, 140.74, 136.73, 136.06, 134.50, 131.65, 128.99, 127.26, 126.91, 126.72, 126.20, 125.93, 124.22, 123.60, 123.38, 57.03, 53.58, 38.67, 37.42, 32.57, 31.88, 31.84.

Dichloride 90. To 0.114 g of **88** (0.131 mmol) in 10 mL of THF was added 0.80 mL of a 1.0 M solution of lithium triethylborohydride in THF (0.80 mmol). After 12 h, water (10 mL) was introduced, and reaction mixture was concentrated to remove THF. Chloroform (15 mL) was added and the organic layer was separated, dried over Na_2SO_4, and concentrated to furnish a yellow solid. To this yellow solid in 10 mL of THF was added 0.80 mL of a 1.0 M solution of lithium triethylborohydride in THF (0.80 mmol). After 12 h, water (10 mL) was introduced, and the reaction mixture was concentrated to remove THF. Chloroform (15 mL) was added, and the organic layer was separated, dried over Na_2SO_4, and concentrated to furnish a white solid (the crude product of **89)**. To a solution of the crude product **89** in 10 mL of pyridine at 0 °C was added dropwise 0.5 mL (0.3 g, 2.6 mmol) of thionyl chloride. The reaction mixture was then allowed to warm to room temperature. After 12 h, the reaction mixture was then poured into a flask containing 20 mL of water and 30 mL of chloroform. The organic layer was separated, washed with water and a 5% HCl solution, dried over Na_2SO_4, and concentrated. The solid was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to afford 0.054 g (0.059 mmol, 45% yield from **88**) of **90** as a white solid: R_f 0.09 (hexanes:CH_2Cl_2 = 1:2); ^{1}H NMR δ 7.63–7.56 (6 H, m), 7.47–7.40 (4 H, m), 7.31–7.20 (4 H, m), 6.99 (2 H, t, *J* = 7.6 Hz), 6.82 (2 H, d, *J* = 7.9 Hz), 5.29 (1 H, d, *J* = 1.7 Hz), 4.38–4.15 (4 H, m), 4.01–3.86 (2 H, m), 3.82–3.71 (2 H, m), 3.47–3.42 (1 H, m), 1.90 (4 H, s), 1.50 (12 H, d, *J* =1.5 Hz), 0.88 (18 H, s); ^{13}C NMR δ 149.60, 143.37, 143.18,

141.99, 139.41, 139.29, 138.25, 138.07, 137.04, 136.73, 136.63, 136.48, 134.95, 134.91, 132.76, 132.62, 129.35, 127.32, 127.18, 126.82, 126.53, 126.39, 126.33, 124.82, 123.74, 62.90, 57.09, 48.89, 46.57, 45.74, 38.64, 36.17, 35.50, 32.58, 31.88, 31.78.

Chloride 92. To 0.032 g of **90** in 10 mL of THF was added 4 drops of *tert*-butanol and 0.3 mL of a 1.0 M solution of potassium *tert*-butoxide in THF. The resulting mixture was heated to reflux for 18 h before it was allowed to cool to rt. Water (10 mL) was introduced, and the reaction mixture was concentrated to remove THF. Chloroform (10 mL) was added, and the organic layer was separated, dried over Na_2SO_4, and concentrated to furnish a yellow solid: ^{1}H NMR (crude product) δ partial 7.63–7.52 (6 H, m), 7.48–7.40 (4 H, m), 7.35–7.29 (2 H, m), 7.21 (2 H, t, *J* = 7.3 Hz), 6.97 (2 H, t, *J* = 7.5 Hz), 6.83 (1 H, d, *J* = 7.4 Hz), 6.80 (1 H, d, *J* = 7.4 Hz), 4.40–4.12 (6 H, m), 3.08–3.03 (1 H, m), 2.67–2.62 (1 H, m), 2.51–2.47 (1 H, m). Although additional spectral data will be needed to elucidate unequivocally the structure of the product, the ^{1}H NMR spectrum of the crude residue appeared to support the formation of **92** as the major product.

Diketone 93. To a solution of the crude product of the chloride **85** (prepared from 0.701 g (0.841 mmol) of the propargylic alcohol **80a**) in 30 mL of THF was added 8 mL of a 2 N sodium hydroxide aqueous solution at 0 °C. The resulting mixture was stirred while a stream of air bubbled into the solution for 24 h at room temperature. The reaction mixture was concentrated in vacuo and then extracted with methylene chloride. The organic layer was washed with saturated NH_4Cl and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (silica gel/25% CH_2Cl_2 and 25% Et_2O in hexanes) to afford 0.315 g of **93** (0.380 mmol, 45% yield from **80a**) as a yellow solid: compound turns dark at 315 °C and becomes black without melting at 331

°C; R_f 0.14 (hexanes:CH_2Cl_2:diethyl ether = 1:1:1); IR (KBr) 1715, 752 cm^{-1}; ^1H NMR δ 7.74 (2 H, d, *J* = 6.7 Hz), 7.61 (4 H, d, *J* = 8.4 Hz), 7.36 (2 H, s), 7.34 (2 H, d, *J* = 8.4 Hz), 7.22 (2 H, td, *J* = 7.4 and 0.7 Hz), 7.10 (2 H, td, *J* = 7.6 and 1.2 Hz), 6.55 (2 H, d, *J* = 7.7 Hz), 3.68 (6 H, s), 1.88 (4 H, s), 1.48 (12 H, s), 0.85 (18 H, s); ^{13}C NMR δ 191.55, 150.69, 145.22, 139.65, 139.54, 137.43, 135.67, 135.06, 134.29, 133.00, 131.89, 129.58, 128.80, 128.67, 127.18, 127.02, 124.20, 123.92, 113.62, 57.01, 53.76, 38.72, 32.58, 31.86, 31.76; MS m/z 853 (MNa^+), 807, 795; HRMS calcd for $C_{59}H_{58}O_4Na$ (MNa^+) 853.4233, found 853.4259.

Propargylic alcohols 94a, 94b and 95. To a solution of 0.338 g of 1-(2-ethynylphenyl)-2-(4-*tert*-octylphenyl)ethyne (**79)** (1.007 mmol) in 15 mL of THF was added 0.36 mL of a 2.5 M solution of *n*-butyllithium (0.90 mmol) in hexanes at 0 °C. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 0.298 g of **73** (0.359 mmol) in 15 mL of THF was added via cannula, and the mixture was stirred at room temperature for 12 h. Water (20 mL) was introduced, and reaction mixture was concentrated. Chloroform (30 mL) was then added, and the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a yellow solid. The solid was purified by flash column chromatography (silica gel/10% diethyl ether and 25% CH_2Cl_2 in hexanes) to afford 0.226 g (0.155 mmol, 44% yield) of **94a**, 0.096 g (0.066 mmol, 18% yield) of **94b**, and 0.107 g (0.094mmol, 26% yield) of **95** as yellow solids. **94a**: R_f 0.34 (hexanes:CH_2Cl_2:diethyl ether = 6:2:1); IR 3486, 2218, 755 cm^{-1}; ^1H NMR δ 7.86 (2 H, d, *J* = 7.4 Hz), 7.66–7.54 (6 H, m), 7.48 (2 H, s), 7.44–7.33 (6 H, m), 7.30–7.22 (4 H, m), 7.16 (2 H, t, *J* = 7.5 Hz), 7.03 (4 H, d, *J* = 8.4 Hz), 6.96 (2 H, t, *J* = 7.7 Hz), 6.88 (4 H, d,

J = 8.2 Hz), 6.67 (2 H, d, *J* = 7.9 Hz), 4.76 (2 H, s), 3.34 (6 H, s), 1.88 (4 H, s), 1.65 (4 H, s), 1.49 (6 H, s), 1.48 (6 H, s), 1.26 (12 H, s), 0.86 (18 H, s), 0.66 (18 H, s); ^{13}C NMR δ 150.35, 150.26, 147.00, 142.92, 139.18, 137.54, 136.28, 135.87, 133.58, 133.10, 132.44, 131.61, 130.89, 129.40, 129.01, 128.93, 128.80, 128.16, 128.07, 127.68, 126.97, 126.94, 126.04, 125.79, 125.00, 124.92, 124.76, 123.63, 119.57, 116.28, 93.62, 93.35, 87.57, 82.45, 73.53, 57.08, 56.74, 53.11, 39.69, 38.61, 32.58, 32.32, 31.87, 31.80, 31.52, 31.36; MS m/z 1482 (MNa^+), 1443, 1084; HRMS calcd for $C_{107}H_{110}O_4Na$ (MNa^+) 1481.8296, found 1481.8367. **94b**: R_f 0.04 (hexanes:CH_2Cl_2:diethyl ether = 6:2:1); IR 3514, 2218, 753 cm^{-1}; ^{1}H NMR δ 7.88 (2 H, d, *J* = 7.4 Hz), 7.65–7.54 (6 H, m), 7.45–7.35 (8 H, m), 7.24–7.10 (10 H, m), 7.04–6.95 (6 H, m), 6.70 (2 H, d, *J* = 7.7 Hz), 4.51 (2 H, s), 3.45 (3 H, s), 3.16 (3 H, s), 1.90 (4 H, s), 1.69 (4 H, s), 1.50 (12 H, s), 1.31 (12 H, s), 0.88 (18 H, s), 0.68 (18 H, s) ; ^{13}C NMR δ 150.40, 150.22, 146.90, 142.81, 139.29, 137.49, 136.31, 135.81, 133.67, 133.08, 132.27, 131.48, 131.08, 129.35, 129.05, 128.93, 128.80, 128.20, 127.89, 127.44, 126.99, 126.92, 126.05, 125.99, 125.11, 124.98, 124.74, 123.60, 119.67, 116.18, 93.78, 93.46, 87.46, 82.41, 73.48, 57.09, 56.77, 53.14, 52.54, 38.69, 38.63, 32.58, 32.32, 31.87, 31.79, 31.42; MS m/z 1482 (MNa^+), 1443, 1084; HRMS calcd for $C_{107}H_{110}O_4Na$ (MNa^+) 1481.8296, found 1481.8403. **95**: R_f 0.10 (hexanes:CH_2Cl_2:diethyl ether = 6:2:1); IR 3486, 2217, 1710, 752 cm^{-1}; ^{1}H NMR δ 7.90 (1 H, d, *J* = 7.4 Hz), 7.74–7.70 (2 H, m), 7.65–7.51 (5 H, m), 7.45–7.33 (6 H, m), 7.30–7.19 (4 H, m), 7.14–6.96 (4 H, m), 6.85 (2 H, d, *J* = 8.4 Hz), 6.69 (1 H, d, *J* = 7.9 Hz), 6.57 (1 H, d, *J* = 7.7 Hz), 5.17 (1 H, s), 3.69 (3 H, s), 3.42 (3 H, s), 1.89 (4 H, s), 1.66 (2 H, s), 1.50 (12 H, s), 1.27 (6 H, s), 0.88 (9 H, s), 0.86 (9 H, s), 0.67 (9 H, s); ^{13}C NMR δ 191.91, 150.62, 150.27, 150.21, 147.40, 145.39, 142.44, 139.00, 138.88, 138.29, 137.11, 137.06, 136.48,

136.15, 135.70, 135.41, 135.06, 134.42, 133.55, 133.01, 132.51, 131.63, 131.44, 130.85, 130.57, 129.35, 128.92, 128.84, 128.72, 128.62, 128.52, 127.84, 127.61, 127.16, 127.04, 126.95, 125.96, 125.66, 125.39, 124.94, 124.76, 124.18, 123.89, 123.62, 119.72, 114.73, 93.76, 93.46, 87.70, 82.13, 73.24, 57.04, 56.72, 54.00, 53.09, 38.69, 38.58, 32.56, 32.29, 31.85, 31.78, 31.49, 31.31; MS m/z 1168 (MNa^+), 1084; HRMS calcd for $C_{83}H_{84}O_4Na$ (MNa^+) 1167.6262, found 1167.6221.

Chlorides 97a and 97b. To 0.074 g of the *trans* propargylic alcohol **94a** (0.051 mmol) in 10 mL of THF at 0 °C was added via cannula a solution of 0.075 g of thionyl chloride (0.63 mmol) and 0.130 g of anhydrous pyridine (1.65 mmol) in 5 mL of THF. The reaction mixture was then allowed to warm to rt. After 11 h, the reaction mixture was concentrated, and 15 mL of water and 25 mL of chloroform were added. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a light brow solid. The solid was purified by flash column chromatography (silica gel/25% CH_2Cl_2 in hexanes) to afford 0.032 g (0.022 mmol, 42% yield) of **97a** and 0.010 g (0.007 mmol, 13% yield) of **97b** as yellow solids. The same procedure was repeated with the use of 0.183 g of the *cis* propargylic alcohol **94b** (0.126 mmol) to afford 0.060 g (0.040 mmol, 32% yield) of **97a** and 0.052 g (0.035 mmol, 28% yield) of **97b** as yellow solids. **97a**: compound turns dark at 162 °C and becomes black without melting at 174 °C; R_f 0.52 (hexanes:CH_2Cl_2 = 3:1); IR 833, 751 cm^{-1}; ^{1}H NMR δ 7.76–7.73 (2 H, m), 7.66–7.57 (8 H, m), 7.47 (6 H, d, *J* = 8.7 Hz), 7.36–7.33 (4 H, m), 7.18 (2 H, t, *J* = 7.4 Hz), 7.06–6.99 (6 H, m), 6.86 (4 H, d, *J* = 7.7 Hz), 6.79 (2 H, b s), 1.91 (4 H, s), 1.69 (4 H, s), 1.65 (6 H, s), 1.52 (12 H, s), 1.26 (6 H, s), 1.22 (6 H, s), 0.89 (18 H, s), 0.67 (18 H, s); ^{13}C NMR δ 152.19, 149.83, 149.37, 149.08, 146.98, 146.19, 141.82, 141.23, 140.34,

137.46, 135.79, 135.64, 134.52, 134.44, 130.01, 129.72, 129.47, 129.27, 128.02, 127.67, 127.54, 127.26, 126.97, 126.75, 126.09, 124.92, 124.25, 124.18, 123.99, 123.73, 118.96, 115.07, 108.33, 62.78, 57.11, 56.28, 51.63, 38.80, 38.67, 32.58, 32.28, 31.90, 31.58, 31.50; MS m/z 1496 (MH^+), 1466, 1426; HRMS calcd for $C_{107}H_{108}O_2Cl_2H$ (MH^+) 1495.7799, found 1495.7838. **97b**: compound turns dark at 228 °C and becomes black without melting at 247 °C; R_f 0.33 (hexanes:CH_2Cl_2 = 3:1); IR 832, 751 cm^{-1}; ^1H NMR δ 7.65 (4 H, d, *J* = 8.7 Hz), 7.59 (2 H, d, *J* = 7.2 Hz), 7.48 (4 H, t, *J* = 8.5 Hz), 7.39 (2 H, s), 7.35–7.31 (4 H, m), 7.26–7.10 (10 H, m), 7.01–6.95 (6 H, m), 6.82 (2 H, d, *J* = 7.7 Hz), 2.61 (3 H, s), 1.91 (4 H, s), 1.60 (2 H, s), 1.59 (2 H, s), 1.52 (12 H, s), 1.41 (3 H, s), 1.20 (6 H, s), 1.14 (6 H, s), 0.89 (18 H, s), 0.59 (18 H, s); ^{13}C NMR δ 151.92, 149.88, 148.68, 148.66, 147.25, 146.46, 141.82, 140.37, 140.00, 137.91, 136.14, 135.80, 134.65, 134.51, 129.86, 129.44, 129.24, 128.97, 128.32, 127.57, 127.32, 127.03, 126.81, 126.02, 124.78, 124.33, 124.11, 123.62, 123.19, 118.98, 115.74, 108.96, 62.77, 57.11, 56.51, 53.31, 50.88, 38.72, 38.68, 32.58, 32.27, 31.90, 31.71, 31.59, 31.01; MS m/z 1495 (M^+), 1466, 1446; HRMS calcd for $C_{107}H_{108}O_2Cl_2$ 1494.7721, found 1494.7899.

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