2007

Synthesis of polycyclic aromatic hydrocarbons via benzannulated enediynyl alcohols

Elbin Sehnaz Parbin
West Virginia University

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Parbin, Elbin Sehnaz, "Synthesis of polycyclic aromatic hydrocarbons via benzannulated enediynyl alcohols" (2007). *Graduate Theses, Dissertations, and Problem Reports*. 2539.
<https://researchrepository.wvu.edu/etd/2539>

This Thesis is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Thesis has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

Synthesis of Polycyclic Aromatic Hydrocarbons via Benzannulated Eneidyryl Alcohols

Elbin Sehnaz Parbin

Dissertation

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 Science

in Organic Chemistry

Kung K. Wang, Ph. D., Advisor

George A. O'Doherty, Ph. D.

Jeffrey L. Petersen, Ph. D.

C. Eugene Bennett Department of Chemistry

Morgantown, West Virginia

2007

Keyword: Schmittel Cyclization, Enyne–Allenenes, Biradical

ABSTRACT

Synthesis of Polycyclic Aromatic Hydrocarbons via Benzannulated Enediynyl Alcohols

Elbin Sehnaz Parbin

Under mild conditions, a derivative of 11*H*-benzo[*b*]fluorine **76**, was successfully synthesized through tandem cyclization of the corresponding enediynyl propargylic alcohol, **69**. Condensation of the substituted indanone **67** with the lithium acetylide **23** furnished benzannulated enediynyl propargylic alcohol **69** in 1:1 diastereomeric ratio. Reduction of propargylic alcohol **69** with triethylsilane in the presence of trifluoroacetic acid gave benzannulated enediynes **70**. Treatment of **70** with potassium *tert*-butoxide in refluxing toluene furnished alkene **74**. Hydroboration of alkene **74** followed by iodination in the presence of base produced alkyl iodide **75**. The alkyl iodide **75** with treatment of potassium *tert*-butoxide in THF underwent intramolecular cyclization, producing the polycyclic aromatic hydrocarbon **76** in 18% overall yield from substituted indanone **67**.

DEDICATED TO

My husband, my brother, and my parents

ACKNOWLEDGEMENTS

It gives me an immense pleasure and pride to express my sincere gratitude and respect for my advisor, Dr. Kung K. Wang, for his support, patience, constant encouragement and practical suggestions throughout my graduate studies. His mentorship was essential to the completion of this dissertation.

I take this opportunity to thank my research committee members, Dr. George A. O'Doherty and Dr. Jeffrey L. Petersen for their valuable comments and suggestions that improved the contents of this dissertation.

My special thanks go to Dr. Novruz Akhmedov for his help with the NMRs and nOe structure analysis of my compounds.

My very special appreciation goes to Sanjeeva Rao Guppi and Daehwan Kim for their help, suggestions and discussions.

I would also like to thank the former and present group members, Dr. Weixiang Dai, Dr. Hua Yang, Lily Wang, Hu Cui, Bo Wen, and Ruoxin Zhang for their help and support.

I take the opportunity to thank the entire faculty, staff, and graduate students for their encouragement and help in a variety of ways.

I feel fortunate to have my husband Dr. Mohammed M. Ahmed, who always stood by me during the period of crisis and made me to realize my strength to face trouble and difficulties.

Special appreciation and gratitude are due to my parents, in-laws, brother, and my cute daughter Mehreen for their constant support and love.

Financial support from the C. Eugene Bennett Department of Chemistry at West Virginia University is gratefully acknowledged.

TABLE OF CONTENTS

Title Page	i
Abstract	ii
Dedications	iii
Acknowledgements	iv
Table of Contents	v
Experimental Section	vi
List of Figures	vii

Part I

Synthesis of Polycyclic Aromatic Hydrocarbons via Benzannulated Ene-diynyl Alcohols

1. Introduction	1
2. Research Objective	4
3. Literature Survey for the Synthesis of 11 <i>H</i> -Benzo(<i>b</i>)fluorenes and Its Derivatives	4
4. Result and Discussion	15
5. Conclusions	22

Part II

Experimental Section

General Methods and Materials	23
References	33
Appendix (¹ H NMR, ¹³ C NMR and IR Spectra)	37
¹ H NMR and ¹³ C NMR of 2-Methoxy-1-iodoethane 59	38-39
¹ H NMR and ¹³ C NMR of 2,3-dihydro-3-(2-methoxyethyl)- inden-1-one 62	40-41
¹ H NMR, ¹³ C NMR and IR Spectra of 2,3-dihydro-2,2-dimethyl -3-(2-methoxyethyl)inden-1-one/2,3-dihydro-2-methyl-3- (2-methoxyethyl)inden-1-one 64/63	42-47
¹ H NMR, ¹³ C NMR and IR Spectra of 2-allyl-2,3-dihydro-2-methyl- inden-1-one 67	48-50
¹ H NMR, ¹³ C NMR and IR Spectra of propargylic alcohol 69	51-53
¹ H NMR, ¹³ C NMR and IR Spectra of diacetylenic hydrocarbon 70	54-56
¹ H NMR, ¹³ C NMR and IR Spectra of alkene 74	57-59
¹ H NMR, ¹³ C NMR and IR Spectra of 11 <i>H</i> -benzo[<i>b</i>]fluorene iodide 75	60-62
¹ H NMR, ¹³ C NMR and IR Spectra of polycyclic aromatic hydrocarbon 76	63-65

LIST OF FIGURES

Figure 1. Several examples of these bowl-shaped hydrocarbons	2
Figure 2. Comparison of 11 <i>H</i> -benzo[<i>b</i>]fluorene (7) with other buckybowls	3
Figure 3. nOe drawing of 62	17
Figure 4. nOe drawing of 63	18
Figure 5. nOe drawing of 64	18
Figure 6. nOe drawing of 76	22

Part I

Synthesis of Polycyclic Aromatic Hydrocarbons via Benzannulated Enediynyl Alcohols

1. Introduction:

In 1985, C₆₀ (buckyball), buckminsterfullerene¹ was discovered by H. W. Kroto (University of Sussex, UK), R. F. Curl and R. E. Smalley (both from Rice University, USA) and the Nobel Prize in Chemistry for the year 1996 was awarded to them. The C₆₀ (buckyball) was named as “Molecule of the Year” by *Science* in 1991². Since then there has been an extensive research activities going on to explore its chemical reactivities and physical properties and to develop new synthetic routes for C₆₀ (buckyball). It is astonishing that buckyball and the related fullerene family have attracted this kind of attention from physicists, material scientists, and inorganic as well as organic chemists.³ Buckminsterfullerene and other higher fullerenes were isolated from soot produced by the vaporization of graphite in macroscopic quantity, access to this molecules facilitated the research activities. It is still remain a challenge for chemist to synthesize buckminsterfullerene and other higher fullerenes.

One of the most prevalent 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} Interestingly more than two decades prior to the discovery of C₆₀ (buckyball),⁵ in 1966, Barth and Lawton first reported the synthesis of corannulene (C₂₀H₁₀) **1**,^{4b,6} the minimal structural subunit with a curvature of a fullerene. Later on several other examples of these bowl-shaped hydrocarbons, for instance benzo[*a*]acorannulene (C₂₄H₁₂) **2**,^{4a,4b,4d} semibuckminsterfullerene (C₃₀H₁₂) **3**,^{4d,6d,8} benzo[*g*]acecorannulene (C₂₆H₁₂) **4**,^{4a,4d} dibenzo[*a,g*]corannulene (C₂₈H₁₄) **5**^{4a,4b,7a,7b} and tribenzo[*a,d,j*]corannulene (C₃₂H₁₆) **6**,^{4a,6d,7c,7d} have been synthesized and characterized (figure 1).

Figure 1

Recently, the flash vacuum pyrolysis (FVP) method has been successful in providing more direct access to corannulene and several other buckybowls. However, FVP normally requires heating the precursors to 1000 °C or higher and the yields of highly strained buckybowls are very low, usually below 5% and sometimes even below 1%.^{3,4} Presumably at this high temperature, buckybowls with more delicate structures and higher energies may not survive. More recently, several synthetic efforts were reported in the literature^{6b-c,8d,9a-c} by using non-pyrolytic pathways to prepare buckybowls. To synthesize buckybowls which have five-membered rings surrounded by six-membered rings, it is not hard to imagine that benzo[fluorene], **7** and its derivatives can be used as potential precursors by comparing their structures with corannulenes and other buckybowls (figure 2).^{3,4,9}

Figure 2

2. Research Objective

Based on our previous discovery about the synthesis of 11*H*-benzo[*b*]fluorene derivatives involving condensation of benzannulated enediynes and arylketones to produce benzannulated enediynyl propargylic alcohols followed by reduction and a sequence of cascade cyclization reactions,¹⁰ we envisioned that by using different combinations of benzannulated enediynes and arylketones for condensations, it is possible that a variety of other polycyclic aromatic hydrocarbons could also likewise be synthesized. We also hypothesized that by introducing sp³-hybridized carbons into the skeleton of the substrate the structure of bucky bowl would be less strained, allowing the connection of properly situated carbon atoms.

3. Literature Survey for the Synthesis of 11*H*-Benzo[*b*]fluorene and Its Derivatives

11*H*-Benzo[*b*]fluorene (**7**) and its derivatives attracted our interest because of their potentiality to be used as precursors for the synthesis of polycyclic aromatic hydrocarbons with carbon frameworks represented on the surface of C₆₀.

Our group reported several novel synthetic pathways for the synthesis of several derivatives of 11*H*-Benzo[*b*]fluorenes and the synthetic route relied on the enyne-allene cyclizations.¹⁰ Enyne-allenes can undergo either

Myers-Saito cyclizations¹¹ (C2-C7) or Schmitt cyclizations¹² (C2-C6). In a simple system such as enyne-allene **8**, the cyclization pathway depends on the alkynyl terminus substituent R (Scheme 1). When R is a proton or a 1° alkyl group, such as the methyl group or the ethyl group, the enyne-allene favors the Myers-Saito cyclization pathway to produce the $\alpha,3$ -didehydrotoluene/naphthalene biradical **9**; when R is an aryl group or a sterically demanding group, such as the *tert*-butyl group or the trimethylsilyl group, the enyne-allene favors the Schmitt cyclization pathway to produce the fulvene/benzofulvene biradical **10**.

Scheme 1

Our group studied Myers-Saito cyclizations of (*Z*)-1,2,4-heptatrien-6-ynes **11** (Scheme 2).¹³ If we compare to the parent (*Z*)-1,2,4-heptatrien-6-yne, the rate of cycloaromatization of **11a** is increased because of the formation of a more stable tertiary benzylic radical center in **12a**, but in case of **11b** the rate of cycloaromatization is slow because of increased steric interactions due to tertiary butyl group although it forms more stable tertiary benzylic radical center in **12b**.

Scheme 2

Our group also studied the Schmitt cyclizations of **14** with a benzene tether connecting the alkyne and the allene moiety to produce the benzofulvene biradicals **15** (Scheme 3).^{10f} The aryl groups at the allenic terminus of the enyne-allene system could further participate in an intramolecular radical-radical coupling to form the formal Diels-Alder adducts **16**, and subsequently after tautomerization, gave the tetracyclic hydrocarbon **17**.

Scheme 3

Dr. Hai-Ren Zhang first reported the synthesis of 5,10-diphenyl-11*H*-benzo[*b*]fluorene in 1999 and the synthesis relied on enyne-allene Schmitt cyclization (Scheme 4).^{10c,10f} The synthetic sequence involved Horner olefination of aldehyde **18** with phosphinoxy carbanion in THF at -78 °C to room temperature to produce benzoenyne-allenes **19**, which then underwent a facile C2-C6 cyclization at room temperature to form the biradical **20**. The subsequent intramolecular radical-radical coupling produced **21**, leading to

the 5,10-diphenyl-11*H*-benzo[*b*]fluorene **7** through tautomerization in 51% yield. There are ample precedents in the literature to support the formation of the formal Diels-Alder adduct **21** through a 2 steps C2-C6 cyclization involving a biradical intermediate **20**.¹²

Scheme 4

In 2001, Dr. Hongbin Li reported the synthesis of 5,10-diphenyl-11*H*-benzo[*b*]fluoren-11-ol (Scheme 5).^{10d} It was obtained from condensation of benzophenone (**22**) with the lithium acetylide **23**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne with *n*-butyllithium, followed by hydrolytic workup to furnish the propargylic alcohol **24**. Treatment of **24** with thionyl chloride promoted a sequence of reactions with an initial

formation of chlorosulfite **25** followed by an S_Ni' reaction¹⁴ to produce in situ the chlorinated benzoenyne-allene **26**.

Scheme 5

A Schmittel (C2-C6) cyclization reaction generated the biradical **27**, which in turn underwent a radical-radical coupling to afford the formal Diels-Alder adduct **28** and subsequently after tautomerization gave chloride **29**. The chloride **29** was prone to hydrolysis and, on exposure to water/silica gel, the chloride **29** was converted to the 5,10-diphenyl-11*H*-benzo[*b*]fluoren-11-ol **30** in 85% overall yield from alcohol **24**.

Dr. Hongbing Li also developed a new synthetic pathway for the synthesis of 10-(1,1-dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluorene **37** (Scheme 6).^{10d} The synthetic sequence involved condensation of 2,2-dimethylpropiophenone (**31**) with the lithium acetylide **23**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne with *n*-butyllithium, followed by hydrolytic workup to furnish the propargylic alcohol **32**. Treatment of alcohol **32** with triethylsilane followed by trifluoroacetic acid¹⁵ produced hydrocarbon **33** in 96% yield. Prototropic isomerization, promoted by potassium *tert*-butoxide in refluxing toluene,¹⁶ produced the benzoenyne-allene **34** in situ, which in turn underwent a formal [4 + 2] cycloaddition reaction to furnish **36** and, after tautomerization, 10-(1,1-dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluorene **37** in 90% yield.

Scheme 6

In 2003, Dr. Yonghong Yang studied the cyclization of diol **39** with two benzannulated enyne-allene units induced by the thionyl chloride (Scheme 7).¹⁷ The diol **39** was synthesized from condensation between diketone **38** and 2 equivalents of lithium acetylide **23**. It was assumed that the Schmitt cyclization reaction of **39** would produce the desired

hydrocarbon **41**. Unexpectedly, cleavage of the central benzene ring occurred during the course of cyclization, leading to the highly twisted 1,1'-dialkyl-9,9'-bifluorenylidene **40**.

Scheme 7

It is worth noting that hydrocarbon **41** has a 52-carbon framework represented on the surface of C₆₀ (Scheme 7) and may eventually lead to the formation of bowl-shaped polycyclic aromatic hydrocarbons (buckybowls).

Recently, Daehwan Kim of our group reported the synthesis of bowl-shaped polycyclic aromatic hydrocarbons **52** via palladium-catalyzed intramolecular arylation reactions (Scheme 8).¹⁸ In his reaction sequence the benzannulated enediyne **45** was obtained in good yield via a Sonogashira coupling between (2,6-dibromophenyl)ethyne **42** and (trimethylsilyl)ethyne **43** followed by desilylation.¹⁹ Condensation of **45** with pivalophenone produced enediynyl propargylic alcohol **46**, which upon treatment with triethyl silane in the presence of trifluoroacetic acid afforded benzannulated endiyne **47**. On exposure of **47** with *t*-BuOK in refluxing toluene for 12h produced 5-(2,6-dibromophenyl)-10-(1,1-dimethylethyl)-11H-benzo[*b*]fluorene **51** in a single operation with good yield. Presumably, the transformation from **47** to **51** proceeded through an initial 1,3-prototropic rearrangement to form the corresponding benzannulated enyne-allen **48**. The enyne-allen **48** underwent a Schemittel cyclization reaction to generate biradical **49** followed by an intramolecular radical-radical coupling to afford, in situ, **50**. A second prototropic rearrangement to regain aromaticity then gave **51**. Treatment of **51** with 10 mol% of Pd(PPh₃)₂Br₂ in the presence of DBU at 150 °C²⁰ for 72h furnished bulkybowl **52**.

Scheme 8

4. Results and Discussion

With our ongoing interest in the synthesis of polycyclic aromatic hydrocarbons, we envisioned a retrosynthetic sequence outlined in Scheme 9 for the synthesis of polycyclic aromatic hydrocarbon **53**. The polycyclic aromatic hydrocarbon **53** could be synthesized from alkyl iodide **54** via intramolecular alkylation. Alkyl iodide **54** could be achieved from deprotection of methyl ether **55** followed by iodination. The methyl ether **55** could be obtained from the propargylic alcohol **56** via reduction and cascade cyclization.

Scheme 9: Retrosynthetic analysis

The propargylic alcohol **56** could be synthesized from condensation of lithium acetylide **23** and the substituted indanone **57**, which could be achieved from alkylation of indanone (**58**).

As outlined in Scheme 10, the alkyl iodide **59** was synthesized from 2-methoxy ethanol via mesylation using methanesulfonylchloride in dichloromethane and triethylamine followed by iodination with lithium iodide producing **59** in 70% yield over 2 steps.²¹

Scheme 10

Unexpectedly, the alkylation of indanone with lithium diisopropylamine

(LDA)/2-methoxy-1-iodoethane yielded the β -alkylated product **62** instead of the desired α -alkylated product **61**. This is presumably via the formation of dianion **58a**. By proton NMR it was very difficult to distinguish the α -alkylated or β -alkylated product **61/62**. Then, we proceed for second alkylation by using LDA/methyl iodide giving mono and dimethylated product **63** and **64** in 90% yield with 1:1.2 ratio. By proton NMR of **63**, we concluded that the monomethylated product **63** was not our required product **57**. Furthermore, NOESY spectrum of all three alkylated products **62**, **63** and **64** revealed that the first alkylation of indanone occurred at the β -position and the second methylation at α -position of indanone (figure 3-5).

In the NOESY spectrum of **62** (figure 3), H₃ proton at 3.51 ppm shows strong nOes to H₁ and H₂ proton at 2.91 and 2.42 ppm respectively. In addition, H₃ proton also shows strong nOes to H₄ proton at 7.50 ppm. But, there are no nOes between H₁ and H₄ or H₂ and H₄ proton.

Again, in the NOESY spectrum of **63** (figure 4), H₂ proton at 3.08 ppm shows strong nOes to alpha methyl protons at 1.33 and H₃ proton at 7.50 ppm. In addition to that, when we irradiate the alpha methyl protons at 1.33 ppm shows strong nOes to H₁ and H₂ proton at 2.43 and 3.08 ppm respectively. But, there are no nOes between H₃ and alpha methyl protons.

Similarly, in the NOESY spectrum of **64** (figure 5), H₁ proton at 3.15 ppm shows strong nOes to alpha methyl protons at 1.23 and 1.13 ppm respectively. In addition, H₁ proton also shows strong nOes to H₂ proton at 7.50 ppm. But, there are no nOes between H₂ and alpha methyl protons. From above three experiments we confirmed, the 2-methoxyethyl group was at the beta position of indanone.

Having difficulties in alkylation, we tried methylation of indanone first using LDA/MeI followed by the second alkylation using LDA/1-iodo-2-methoxyethane (Scheme 11). That is to say, treatment of commercially available indanone with LDA/MeI in THF at -78 °C gave monomethyl indanone **65** and dimethyl indanone **66** in 90% yield with 1:1.2 ratio and separated by column chromatography.²² Unfortunately, the second alkylation failed to produce the desired product **57**. Instead, we recovered the starting material methyl indanone **65**. Auspiciously, the second alkylation underwent smoothly with LDA/allylbromide in THF at -78 °C to afford the substituted indanone **67** in 85% yield.

Scheme 11

Condensation of **67** with the lithium acetylide **23**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne **68**²³ with *n*-butyllithium,

followed by hydrolytic workup furnished the propargylic alcohol **69** in 75% yield with a 1:1 diastereomeric ratio (Scheme 12). Reduction of propargylic alcohol **69** with triethylsilane followed by trifluoroacetic acid¹⁵ produced hydrocarbon **70** in 80% yield.

Scheme 12

Treatment of **70** with potassium *t*-butoxide under refluxing toluene produced alkene **74** in a single operation.¹⁶ The transformation from **70** to **74** presumably involved prototropic acetylene to allene rearrangements of the

internal acetylenic moieties followed by formal intramolecular Diels–Alder reaction and subsequent prototropic rearrangement of the resulting Diels–Alder adduct **73**. Hydroboration of alkene **74** with disiamylborane followed by iodination in the presence of sodium hydroxide afforded alkyl iodide **75** in 65% yield (Scheme 13).²⁴ Treatment of alkyl iodide **75** with potassium *t*-butoxide in THF at 40 °C furnished the polycyclic aromatic hydrocarbon **76** in 60% yield.

Scheme 13

The structure of **76** was confirmed by ¹HNMR, ¹³CNMR and supported by CIHRMS which showed [M+H]⁺ peak at *m/z* 373.1951. The stereochemistry was confirmed by NOESY experiments of **76** (figure 6).

In the NOESY spectrum of **76** (figure 6), H₁ proton at 4.20 ppm shows strong nOes to H₂' proton at 2.57 ppm and H_{Ar} proton at 7.42 ppm. In addition, H₁ proton also shows strong nOes to CH₃ proton at 1.60 ppm and H₃' protons at 2.42 ppm. Similarly, CH₃ proton at 1.60 ppm shows strong nOes to H₁ proton, H₆' protons at 3.34 ppm and H₄' protons at 2.42 ppm. Therefore, the angular CH₃ group is cis to H₁.

5. Conclusions

A simple and efficient pathway employing Schmitt cyclization reaction to synthesize novel polycyclic aromatic hydrocarbon **76**, having six fused rings was successfully developed. Using different combinations of benzoenediynes and substituted indanones for condensation, it is possible that a variety of other polycyclic aromatic hydrocarbons could likewise be synthesized.

Part II

Experimental Section

General Methods and Materials. ^1H and ^{13}C NMR spectra were recorded on Varian VXR-600 (600 MHz) spectrometers. Chemical shifts are reported relative to CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Melting points were determined with Electrothermal Mel-Temp apparatus and are uncorrected. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60Å, F_{254}) and visualized by UV-lamp at 254 nm. R_f values are obtained by elution in the stated solvent ratios (v/v). Diethylether, THF, methylene chloride and triethylamine were dried by passing through activated alumina column with argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven-dried glassware and standard syringe/septa techniques.

1-Iodo-2-methoxyethane (59).²¹ A solution of methanesulfonyl chloride (900 mg, 7.8 mmol) in dichloromethane (50 mL) was added over 10 min to a solution of 2-methoxy ethanol (500 mg, 6.5 mmol) and Et₃N (1.052 g, 10.4 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 1 hr and was quenched with aq satd. NaHCO₃ and organic phase was dried over Na₂SO₄ and evaporated. The crude mesylate was dissolved in THF (80 mL), Lithium iodide (2.6 g, 19.5 mmol) was added and the resulting mixture was stirred for 4 hr at room temperature. After evaporation of all the volatile components, the residue was suspended in hexane, and the suspension was vigorously stirred for 5 min. The crude product was filtered off through a short pad of silica, and the filtrate was evaporated. The residue was dried *in vacuo* to give 1-Iodo-2-methoxyethane (**59**) as sticky oil in 80% yield: ¹H NMR (600 MHz, CDCl₃) δ 3.66 (t, *J* = 6.6 Hz, 2H), 3.40 (s, 3H), 3.26 (t, *J* = 6.6 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 73.1, 58.4, 2.6.

2,3-Dihydro-3-(2-methoxyethyl)inden-1-one (62). 1-Indanone (200 mg, 1.5 mmol) was dissolved in 100 mL of THF under nitrogen, to which was added 1M solution of lithium diisopropylamine (1.8 mL, 1.8 mmol) at -78 °C and stirred for 30 min and lastly 1-Iodo-2-methoxyethane (**59**) (0.36 g, 1.95 mmol) was then added via syringe. The reaction was allowed to stir for 2 hr at room temperature, and then the reaction was quenched by adding 100

mL of satd. NH_4Cl and 200 mL of diethyl ether. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether (3 x 100 mL). The organic layers were combined and washed with 200 mL of brine, dried using Na_2SO_4 , and the solvent was removed under reduced pressure. Crude product was purified by silica gel chromatography with 5% EtOAc/hexane to afford pure 2,3-dihydro-2-(2-methoxyethyl)inden-1-one (**62**, 185 mg, 65% yield): R_f (30% EtOAc/Hexanes) = 0.24; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, J = 7.8, 1H), 7.60 (dd, J = 8.4, 7.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 8.4, 7.8, 1H), 3.54-3.50 (m, 2H), 3.48-3.44 (m, 1H), 3.36 (s, 3H), 2.89 (dd, J = 18.6, 7.8 Hz, 1H), 2.45 (dd, J = 18.6, 3.6 Hz, 1H), 2.25-2.20 (m, 1H), 1.75-1.70 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 206.1, 158.4, 136.7, 134.6, 127.5, 125.6, 123.6, 70.8, 58.7, 43.1, 35.9, 35.3.

2,3-Dihydro-2,2-dimethyl-3-(2-methoxyethyl)inden-1-one/2,3-Dihydro-2-methyl-3-(2-methoxyethyl)inden-1-one (64/63). 2,3-dihydro-3-(2-methoxyethyl) inden-1-one **62** (100 mg, 0.52 mmol) was dissolved in 25 mL of THF and cooled to -78°C . To the solution was added 1M solution of lithium diisopropylamine (0.78 mL, 0.78 mmol) via cannula under nitrogen atmosphere and stirred for 30 min. Methyl iodide (0.04 mL, 0.78 mmol) was added and allowed to stir at room temperature for 2 hr the reaction was then quenched by adding 100 mL saturated NH_4Cl and 100 mL

of diethyl ether. The organic layer was separated and the aqueous layer was back extracted with diethyl ether (3 x 50 mL). The organic layers were combined and washed with 100 mL of brine, dried over Na₂SO₄, and the solvent removed under reduced pressure. Crude product was purified by silica gel chromatography with 10% EtOAc/hexane to give pure 2,3-dihydro-2,2-dimethyl-3-(2-methoxyethyl)inden-1-one/2,3-dihydro-2-methyl-3-(2-methoxyethyl)inden-1-one (**64/63**) in 50% and 40% yield respectively.

2,3-dihydro-2,2-dimethyl-3-(2-methoxyethyl)inden-1-one (**64**): R_f (30% EtOAc/Hexanes) = 0.35; ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, J = 7.8, 1H), 7.60 (dd, J = 8.4, 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 8.4, 7.8, 1H), 3.59-3.53 (m, 2H), 3.40 (s, 3H), 3.15 (dd, J = 7.8, 7.2 Hz, 1H), 2.06-2.00 (m, 1H), 1.94-1.89 (m, 1H), 1.23 (s, 3H), 1.13 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 210.8, 155.8, 134.6, 134.5, 127.5, 125.7, 124.2, 71.1, 58.7, 49.7, 46.8, 31.1, 25.8, 20.6.

2,3-dihydro-2-methyl-3-(2-methoxyethyl)inden-1-one (**63**): R_f (30% EtOAc/Hexanes) = 0.41; ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, J = 7.8, 1H), 7.61 (dd, J = 8.4, 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 8.4, 7.8, 1H), 3.59-3.50 (m, 2H), 3.37 (s, 3H), 3.08 (td, J = 8.4, 2.4 Hz, 1H), 2.42 (qd, J = 7.8, 2.4 Hz, 1H), 2.31-2.25 (m, 1H), 1.82-1.77 (m, 1H), 1.32 (d, J = 7.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 208.6, 156.8, 135.9, 134.8,

127.6, 125.4, 123.8, 70.7, 58.7, 48.9, 44.1, 35.3, 16.1.

2,3-Dihydro-2-methyl-2-(2-propenyl) inden-1-one (67): 2,3-Dihydro-2-methylinden-1-one (**65**) (800 mg, 5.5 mmol) was dissolved in 250 mL of THF and cooled to -78 °C. To the solution was added 1M solution of lithium diisopropylamine (6.1 mL, 6.1 mmol) via cannula under a nitrogen atmosphere. The reaction mixture was stirred for 30 min before allyl bromide (0.53 mL, 6.1 mmol) was added. After 2h room temperature, the reaction was quenched by adding 100 mL of saturated NH₄Cl and 200 mL of diethyl ether. The organic layer was separated and aqueous layer was back extracted with diethyl ether (3 x 150 mL). The organic layers were combined and washed with 300 mL of brine, dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography with 10% EtOAc/hexane to give pure **67** (870 mg, 85% yield): *R_f* (30% EtOAc/Hexanes) = 0.86; IR (thin film, cm⁻¹) 2923, 2852, 1742, 1455, 1436, 1346, 1114, 1027, 754; ¹H NMR (600 MHz, CDCl₃) δ 7.76-7.74 (m, 1H), 7.60-7.57 (m, 1H), 7.43-7.41 (m, 1H), 7.38-7.35 (m, 1H), 5.69-5.62 (m, 1H), 5.09-5.05 (m, 1H), 5.02-5.00 (m, 1H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.85 (d, *J* = 16.8 Hz, 1H), 2.40-2.37 (m, 1H), 2.32-2.28 (m, 1H), 1.22 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 210.7, 152.5, 135.9, 134.8, 133.8, 127.4, 126.5, 124.2, 118.3, 48.8, 42.5, 39.4, 23.7.

Propargylic Alcohol 69. To 1-(2-ethynylphenyl)-2-phenylethyne (**68**, 600 mg, 2.96 mmol) in 100 mL of THF under a nitrogen atmosphere at $-78\text{ }^{\circ}\text{C}$ was added a 1.6 M solution of *n*-butyllithium (2.0 mL, 3.25 mmol) in hexanes. After 30 min of stirring, a solution of **67** (610 mg, 3.25 mmol) in 50 mL of THF was charged via cannula, and the reaction mixture was allowed to warm at room temperature. After an additional 2 hr, the reaction mixture was quenched with 50 mL of satd. NH_4Cl , and the reaction mixture was extracted with diethyl ether (3 x 100 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4 , and concentrated. Purification using silica gel chromatography (5% EtOAc/hexane) provided propargylic alcohol **69** (810 mg, 2.0 mmol) in 70% yield as a 1:1 diastereomeric mixture: R_f (30% EtOAc/Hexanes) = 0.59; IR (thin film, cm^{-1}) 3447, 3465, 2971, 2930, 1736, 1638, 1598, 1494, 994, 913, 755; ^1H NMR (600 MHz, CDCl_3 , 1:1 diastereomeric mixture) δ 7.67 and 7.61 (two doublets, $J = 7.8\text{ Hz}$, $J = 7.2\text{ Hz}$, 1H, 1:1 ratio), 7.55-7.50 (m, 2H), 7.43-7.41 (m, 2H), 7.33-7.22 (m, 6H), 7.18-7.10 (m, 2H), 6.04 and 5.82 (two multiplets, 1H, 1:1 ratio), 5.12-5.06 (m, 1H), 4.96-4.87 (m, 1H), 3.10 (d, $J = 15.6\text{ Hz}$, 1H), 2.78 (d, $J = 15.6\text{ Hz}$, 1H), 2.59 and 2.56 (two doublets, $J = 7.2\text{ Hz}$, $J = 7.2\text{ Hz}$, 1H, 1:1 ratio), 2.24-2.19 (m, 2H), 1.26 and 1.21 (two singlets, 3H, 1:1 ratio); ^{13}C NMR (150 MHz, CDCl_3 , 1:1 diastereomeric

mixture) δ 145.8, 142.4, 135.9, 132.4, 132.2 (2C), 131.9, 129.1, 128.6, 128.4 (2C), 128.3, 128.1, 127.1 (2C), 126.1, 125.3, 124.3, 123.2, 117.8, 93.5, 93.1, 88.3, 86.6, 82.1, 52.4, 43.0, 41.2, 29.9.

Diacetylenic Hydrocarbon 70. To a mixture of propargylic alcohol **69** (700 mg, 1.8 mmol) and triethylsilane (520 mg, 4.5 mmol) in 80 mL of dichloromethane was added trifluoroacetic acid (820 mg, 7.2 mmol). After 10 min of stirring at room temperature, sodium carbonate (760 mg, 7.2 mmol) was added followed by 20 mL of water and 70 mL of diethyl ether. The organic layer was separated, washed with brine and water, dried over Na_2SO_4 , and concentrated. Flash column chromatography (5% EtOAc/hexane) provided diacetylenic hydrocarbon **70** (0.50 g, 1.3 mmol, 75%) as a 1:1 mixture of diastereomers: R_f (30% EtOAc/Hexanes) = 0.65; IR (thin film, cm^{-1}) 2985, 1737, 1373, 1234, 1043, 938, 847; ^1H NMR (600 MHz, CDCl_3 , 1:1 dr) δ 7.55-7.46 (m, 3H), 7.43-7.41 (m, 2H), 7.32-7.26 (m, 5H), 7.18-7.14 (m, 2H), 7.11-7.08 (m, 1H), 5.95 and 5.78 (two multiplets, 1H, 1:1 ratio), 5.09 (m, 1H), 4.93 and 4.86 (two multiplets, 1H, 1:1 ratio), 4.15 and 4.10 (two singlets, 1H, 1:1 ratio), 2.96 and 2.91 (two doublets, $J = 15.6$ Hz, $J = 15$ Hz, 1H, 1:1 ratio), 2.64 and 2.62 (two doublets, $J = 15$ Hz, $J = 15.6$ Hz, 1H, 1:1 ratio), 2.49 (dd, $J = 13.8, 7.8$ Hz, 1H), 2.21 (dd, $J = 13.8, 7.8$ Hz, 1H), 1.29 and 1.13 (two singlets, 3H, 1:1 ratio); ^{13}C NMR (150 MHz, CDCl_3 ,

1:1 diastereomeric mixture) δ 142.9, 141.8, 135.5, 132.1, 131.9 (2C), 131.7, 128.2 (2C), 127.8, 127.4 (2C), 126.9, 126.5, 126.1 (2C), 124.7, 124.5, 123.3, 117.4, 92.9, 92.7, 88.4, 83.9, 49.4, 48.2, 45.0, 42.7, 24.9.

Alkene 74. To a mixture of diacetylenic hydrocarbon **70** (500 mg, 1.3 mmol) in 50 mL of anhydrous toluene under a nitrogen atmosphere were added a solution of potassium *tert*-butoxide (180 mg, 1.56 mmol) in THF and 0.5 mL of 2-methyl-2-propanol. The reaction mixture was heated under reflux for 2 hr. After the reaction mixture was allowed to cool to room temperature, 20 mL of water and 50 mL of dichloromethane were added. The organic layer was separated, dried over Na₂SO₄, and concentrated. Flash column chromatography on silica gel (5% EtOAc/hexanes) provided substituted alkene **74** (370 mg, 1.0 mmol) as a brown solid in 76% yield: mp 55-60 °C; *R_f* (30% EtOAc/Hexanes) = 0.85; IR (thin film, cm⁻¹) 2955, 2908, 1736, 1604, 1441, 1376, 1238, 1028, 913, 773, 754, 727, 703; ¹H NMR (600 MHz, CDCl₃) δ 7.60-7.52 (m, 4H), 7.46-7.42 (m, 2H), 7.35-7.33 (m, 1H), 7.26-7.21 (m, 3H), 7.02 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.66 (m, 1H), 5.11 (m, 1H), 4.98 (m, 1H), 4.19 (d, *J* = 21.0, 1H), 4.15 (d, *J* = 21.0, 1H), 3.56 (d, *J* = 16.8 Hz, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 2.85-2.81 (m, 1H), 2.73-2.69 (m, 1H), 1.63 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 145.7, 144.2, 142.9, 141.6, 138.8, 137.0, 135.2, 133.2, 131.0, 130.7, 130.2, 130.1, 128.9

(2C), 127.5 (2C), 127.3, 126.8, 126.4, 124.8, 123.7, 121.4, 119.0, 117.5, 47.7, 44.6, 44.5, 34.0, 26.6.

11*H*-benzo[*b*]fluorene iodide 75. A solution of alkene **74** (100 mg, 0.26 mmol) in THF (10 mL) was added over 5 min to a solution of disiamylborane (1 equiv, 0.26 mmol,) at 0 °C. After the reaction mixture was stirred at rt for 2 hr iodine (151 mg, 1.2 mmol) was added all at once followed by a solution of NaOH (50 mg, 1.2 mmol) in 2 mL of methanol. The reaction mixture was stirred for another 30 min, and then quenched with aq. satd. NH₄Cl. Diethyl ether was added and the organic phase was separated, dried over Na₂SO₄, and concentrated. Silica gel column chromatography (2% EtOAc/hexanes) provided 11*H*-benzo[*b*]fluorene iodide **75** (87 g, 0.17 mmol) as a yellow liquid in 65% yield: *R_f* (30 % EtOAc/Hexanes) = 0.69; IR (thin film, cm⁻¹) 2827, 1698, 1601, 1263, 1027, 908, 725; ¹H NMR (600 MHz, CDCl₃) δ 7.60-7.54 (m, 4H), 7.53-7.42 (m, 2H), 7.35 (dd, *J* = 8.4, 6.6, 1H), 7.26-7.21 (m, 3H), 7.02 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.19 (d, *J* = 21.0, 1H), 4.15 (d, *J* = 21.0, 1H), 3.48 (d, *J* = 16.8 Hz, 1H), 3.26 (d, *J* = 16.8 Hz, 1H), 3.15 (t, *J* = 6.6 Hz, 2H), 2.26-2.21 (m, 1H), 2.07-2.02 (m, 1H), 1.81-1.69 (m, 2H), 1.64 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 145.1, 144.1, 141.5, 142.6, 139.7, 138.2, 138.7, 133.3, 131.0, 130.8, 130.1 (2C), 129.0 (2C), 127.6, 127.3, 126.9, 126.4,

124.9, 123.7, 121.5, 119.0, 47.5, 45.3, 41.1, 33.9, 29.3, 27.3, 7.7.

Polycyclic Aromatic Hydrocarbon 76. To a solution of alkyl iodide **75** (90 mg, 0.18 mmol) in THF (50 mL) was added a solution of *t*-BuOK (30 mg, 0.27 mmol) in THF. The reaction mixture was heated to 40 °C for 2 hr and quenched with aq satd. NH₄Cl. The reaction mixture was extracted with Et₂O, and the organic phase was dried over Na₂SO₄ and concentrated. Silica gel column chromatography (2% EtOAc/hexanes) provided the polycyclic aromatic hydrocarbon **76** (40 mg, 0.10 mmol) as a yellow liquid in 60% yield: *R_f* (30% EtOAc/Hexanes) = 0.71; IR (thin film, cm⁻¹) 2924, 2852, 1698, 1602, 1442, 1377, 1265, 1158, 1070, 1027, 914, 774, 751, 731, 706; ¹H NMR (600 MHz, CDCl₃) δ 7.60-7.40 (m, 6H), 7.35 (dd, *J* = 8.4, 6.6, 1H), 7.28-7.21 (m, 3H), 7.02 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.20 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.35 (d, *J* = 16.8 Hz, 1H), 3.29 (d, *J* = 16.8 Hz, 1H), 2.58 (m, 1H), 2.42 (m, 1H), 2.25 (m, 1H), 2.17 (m, 1H), 1.89 (m, 1H), 1.60 (s, 3H), 1.33 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 148.6, 147.1, 143.3, 141.4, 139.5, 138.7, 137.8, 136.2, 130.8, 130.4, 130.1, 129.9, 128.9, 128.8, 127.5, 127.3, 126.9, 126.6, 124.0, 123.5, 121.4, 119.2, 48.9, 47.3, 47.1, 40.3, 33.4, 26.6, 25.1; CIHRMS: Calculated for [C₂₉H₂₄+H]⁺: 373.1956, Found: 373.1951.

References:

- 1 Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature*. **1985**, *318*, 162.
- 2 Culotta, E.; Koshland, D. E. *Science*. **1991**, *254*, 1706.
- 3 Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235 and references therein.
- 4 (a) Vikki, M. T.; Lawrence, T. S. *Chem. Rev.* **2006**, *106*, 4868. (b) Scott, L. T. *Pure and Appl. Chem.* **1996**, *68*, 291 and references therein. (c) McComas, C. C.; B.S. Thesis, Boston College, Chestnut Hill, MA, **1997**. (d) Mehta, G.; Rao, H. S. P. *Tetrahedron*. **1998**, *54*, 13325. (e) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082.
- 5 Barth, W. E.; Lowton, R. G.; *J. Am. Chem. Soc.* **1966**, *88*, 380.
- 6 (a) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339. (b) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800. (c) Seiders, T. J.; Elliott, E. L.; Grube, G. H. *J. Am. Chem. Soc.* **1999**, *121*, 7804.
- 7 (a) Meyer, D. T. M.S. Thesis, University of Nevada, Reno, **1991**. (b) Bratcher, M.S. Ph. D. Dissertation, Boston College, Chestnut Hill, MA, **1996**. (c) McMahan, B.J. B. S. Thesis, Boston College, Chestnut Hill, MA,

1997. (d) Mehta, G.; Srirama Sarma, P. V. V. *Chem. Commun.* **2000**, 19

8 (a) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1994**, *116*, 7891. (b) Clayton, M. D.; Marcinow, Z. Rabideau, P. W. *J. Org. Chem. Soc.* **1996**, *61*, 6052. (c) Mehta, G. *Chem. Commun.* **1997**, 2081. (d) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666.

9 (a) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1071. (b) Harvey, R. G.; Abu- Shaqara, E.; Yang, C. *J. Org. Chem.* **1993**, *58*, 5866. (c) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.

10 (a) Zhang, H. R.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 7996. (b) Zhang, H. R.; Ph. D. Dissertation, West Virginia University, 2000, (c) Seiders, T. J.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754. (d) Hongbin, Li.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662-6668. (e) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207-222. (f) Wang, K. K.; Zhang, H.-R.; Petersen, J. L. *J. Org. Chem.* **1999**, *64*, 1650-1656.

11 (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057-8059. (b) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 9130-9132. (c) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995-4998. (d) Nagata, R.; Yamanaka, H.; Murahashi, E.; Saito, I. *Tetrahedron Lett.* **1990**, *31*, 2907-2910.

- 12 (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, 36, 4975-4978. (b) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, 37, 999-1002. (c) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1843-1845. (d) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, 37, 7691-7694. (e) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem.-Eur. J.* **1997**, 3, 807-816. (f) Schmittel, M.; Steffen, J.-P.; Maywald, M.; Engels, B.; Helten, H.; Musch, P. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1331-1339.
- 13 Wang, K. K.; Wang, Z.; Sattsangi, P. D. *J. Org. Chem.* **1996**, 61, 1516-1518.
- 14 Jacobs, T. L.; Fenton, D. M. *J. Org. Chem.* **1965**, 30, 1808-1812.
- 15 Carey, F. A.; Hsu, C. L. W. *J. Organomet. Chem.* **1969**, 19, 29-41.
- 16 (a) Landor, P. D. in *The Chemistry of the Allenes*; Landor, S. R. Ed.; Academic Press: London 1982, Vol. 1, pp 44-47. (b) Kuhn, R.; Rewicki, D. *Chem. Ber.* **1965**, 98, 2611-2618.
- 17 Yonghong, Y.; Wang, K. K.; Petersen, J. L. *J. Org. Chem.* **2003**, 68, 5832-5837.
- 18 Kim, D.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2006**, 8, 2313-2316.
- 19 Bradshaw, J. D.; Guo, L.; Tessier, C. A.; Youngs, W. J. *Organometallics*. **1996**, 15, 2582-2584.

- 20 Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, 2, 1427-1430.
- 21 Seidel, G.; Laurich, D.; Furstner, A. *J. Org. Chem.* **2004**, 69, 3950–3952.
- 22 Maciej, A.; Watt, D. S. *J. Org. Chem.* **1984**, 49, 4226-4227.
- 23 Hongbin, Li.; Wang, K. K. *J. Org. Chem.* **2001**, 66, 7804-7810.
- 24 (a) Brown, H. C.; Moerikofer, A. W. *Organic and Biological Chemistry*. **1961**, 83, 3417-3422. (b) Brown, H. C.; Rathke, M. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, 90, 5038-5040.

Appendix
(¹H NMR, ¹³C NMR and IR Spectra)

¹H NMR

600 MHz, CDCl₃

59

¹³C NMR
150 MHz, CDCl₃
67

77.210
76.996
76.785

135.867
134.859
133.875
127.399
126.565
124.254
118.300

152.560

23.776

42.525
39.441

48.827

210.715

ppm
20
40
60
80
100
120
140
160
180
200

¹H NMR
600 MHz, CDCl₃
69

¹³C NMR
150 MHz, CDCl₃
69

¹H NMR
600 MHz, CDCl₃
70

¹³C NMR
150 MHz, CDCl₃
70

^1H NMR
600 MHz, CDCl_3
74

¹³C NMR
150 MHz, CDCl₃
74

**^1H NMR
600 MHz, CDCl_3
75**

¹³C NMR
150 MHz, CDCl₃
75

¹H NMR
600 MHz, CDCl₃
76

¹³C NMR
150 MHz, CDCl₃
76

77.211
77.000
76.789

148.651
147.182
143.371
141.473
139.535
138.730
137.801
136.263
130.867
130.459
130.091
129.913
128.907
128.791
127.486
127.362
126.936
126.674
124.047
123.526
121.475
119.234

48.859
47.306
47.139
40.300
33.443
26.685
25.169

ppm