2008

Toward the synthesis of polycyclic aromatic compounds as nano-carbon cages

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Toward the Synthesis of Polycyclic Aromatic Compounds as Nano-carbon Cages

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Thesis

Submitted to the Eberly College of Arts and Sciences

at

West Virginia University

In partial fulfillment of the requirements for the degree of

Master of Science

in Organic Chemistry

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2008

ABSTRACT

Toward the Synthesis of Polycyclic Aromatic Compounds as Nano-carbon Cages

Ruoxin Zhang

Under mild conditions, a key intermediate, diketone **51,** for synthesis of buckybaskets was successfully synthesized through methylation of diketone **52**. The Diels-Alder reaction between 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone **(57)** and 5,6-dimethoxy-2-norbornene **(58)** provided diester **56**. Decarbonylation of **56** furnished diester **55,** which on hydrolysis afforded diacid **54**. Intramolecular acylation of diacid **54** furnished diketone **52**.

Dedicated to

my husband and my parents

ACNOWLEDGEMENTS

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Toward the Synthesis of Polycyclic Aromatic Compounds as Nano-carbon Cages

1. Introduction

In 1985, the first buckyball composed of 60 carbon atoms, C_{60}, was discovered by H. W. Kronto (University of Sussex, UK), R. F. Curl and R.E. Smalley (both from Rice University, USA).[1] This uniquely structured molecule was named "buckminsterfullerene", from an architect Buckminster Fuller, who conceived of geodesic dome to resemble the hollow and extremely stable molecule. Since then buckminsterfullerene and other higher fullerenes have attracted a considerable attention for the exploration of their chemical reactivates and physical properties.[2] New synthesis approaches to these molecules have also been explored. Until now, chemists use gas phase chemistry to replicate the environment of interstellar space to produce buckyballs. Unfortunately, the reaction happens at high temperatures which make the reaction hard to control and only affords very small amount of products. It is still a challenge for chemists to finding a way to synthesize buckyballs. One of the most prevalent synthetic strategies to meet the challenge is to develop a practical method of producing fragments having the curved carbon frameworks represented on the surface of buckyball. Subsequent assembly of these fragments could then lead to buckyballs.

Interestingly, if a buckyball is taken apart, the piece wouldn't be stable because it would have dangling bonds, but if hydrogen atoms are put on the dangling bonds, the structure is stabilized. This bowl shaped molecule is called buckybowl or buckybasket.[2,5] The first synthesis of the smallest buckybowl corannulene ($C_{20}H_{10}$, **1**), was reported by Barth and Lawton in 1966.[3,4,5b] Corannulene is the minimal structural subunit on the surface of C_{60} that processes a curvature. Later several other examples of buckybowls, such as, semibuckminsterfullerene ($C_{30}H_{12}$, **2**),[5c,6] dibenzo[a,g]corannulene ($C_{28}H_{14}$, **3**)[5a,5b,7a,7b] and tribenzo[a,d,j]corannulene ($C_{32}H_{16}$, **4**),[5a,7c,7d] were synthesized and characterized.

C$_{20}$H$_{10}$, **1**   C$_{30}$H$_{12}$, **2**   C$_{28}$H$_{14}$, **3**   C$_{32}$H$_{16}$, **4**
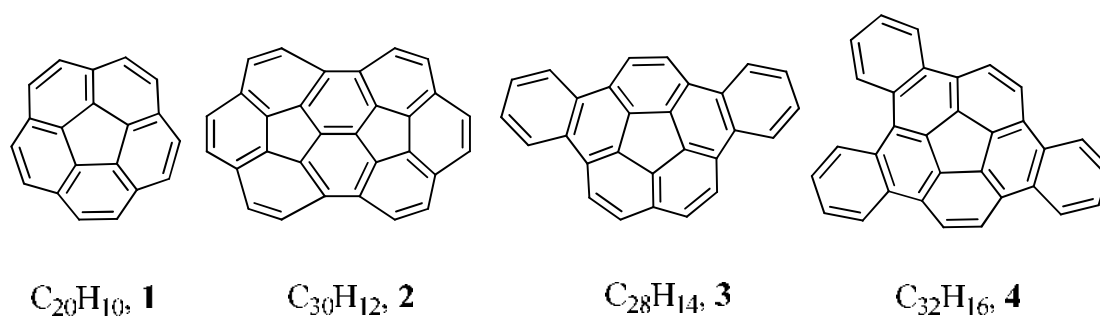
Figure 1. Representative Examples of Buckybowls

The hydrogen atoms on the edge or rim of the carbon atoms of buckybowls could be used for coordination, and the bowl shape also provide enough space for binding metal ions. Therefore, much effort has been directed toward the synthesis of metal complexes of buckminsterfullerene which may ultimately allow the preparation of

endohedral metal complexes of C_{60}. In, 1997, Seiders *et al.* reported the first transition metal complex of corannulene **5** and the first example of η^6-coordination to a curved polynuclear aromatic hydrocarbon (PAH) surface.[8] After that, more corannulene transition-metal complexes have been reported, such as Fe-corannulene complex, Ni-corannulene complex and Pt-corannulene complex.[9] In 2004, Vecchi *et al.* characterized the first corannulene complex with two η^6-coordinated {Cp*Ru} units **6** which bind to non-adjacent arene rings on opposite sides of corannulene.[10]
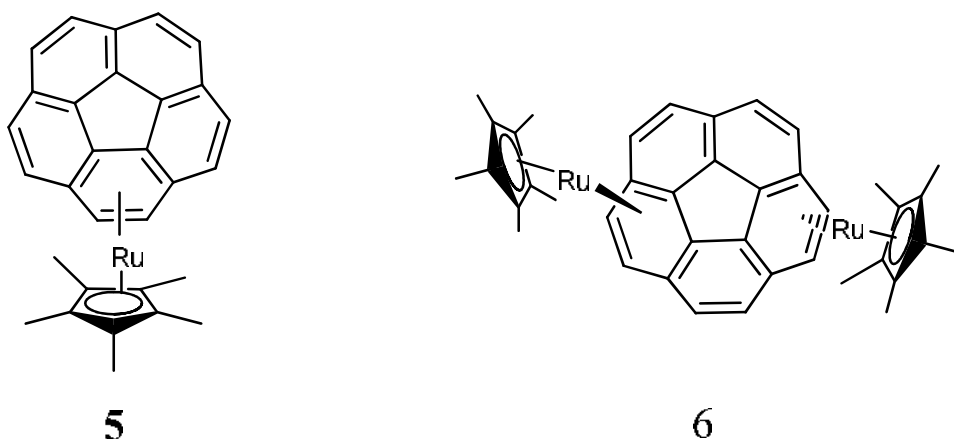
Figure 2. Structure of Ru-corannulene Complex

Due to the intrinsic curvature, the buckybowl has two curved surfaces, convex (or *exo*) and concave (or *endo*). The metal ion intereations with surfaces are much more complicated because of two sides and different sites on each side where the metal ions can attach.[11] Many studies show a preference for *exo*-metal binding. It is worth noting that *exo*-metal binding can assist the activation of the surface carbon atoms and make them more accessible to further reactions.[8]

exo-complex, 7   endo-complex, 8
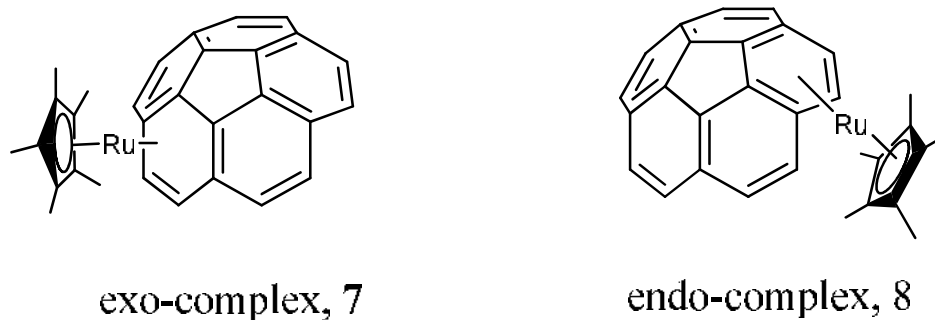
Figure 3. Structure of Exo- and Endo-corannulene Metal Complex

Similarly, buckybowls can also be synthesized through flash vacuum pyrolysis (FVP) method, which require high temperatures and the yields are low.[2,5] Our interests are focused on the synthesis of curved polycyclic aromatic hydrocarbons using solution-phase chemical reactions.

2. Research Objective

Based on our previous research on the synthesis of polycyclic aromatic hydrocarbons involving condensation of benzannulated enediynes and aryldiketones to produce benzannulated enediynyl propargylic diols for subsequent reduction and a sequence of cascade cyclization reactions,[12] we believe that a variety of other curved polycylic aromatic hydrocarbons could also be synthesized by using different diketones with benzannulated enediynes.

3. Literature Survey

In 2001, Dr. Hongbin Li in our group reported the use of thionyl chloride to induce an $S_N i'$ reaction of the benzannulated enediynyl propargylic alcohol (Scheme **1**).[12d] The alcohol **12** was obtained from condensation of 9-fluorenone (**10**) with the lithium acetylide **11**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne with n-butyllithium followed by hydrolytic workup. Treatment of **12** with thionyl chloride promoted a sequence of reactions with an initial formation of the cholorosulfite **13** followed by an $S_N i'$ reaction[13] to produce in situ the chlorinated benzoenyne-allene **14**. A Schmittel cyclization reaction then generated the biradical **15**, which in turn underwent a radical-radical coupling to afford the formal Diels-Alder adduct **16** and, after tautomerization, gave chloride **17**. The chloride **17** was prone to hydrolysis and, on exposure to water/silica gel, afforded **18** in 74% yield.
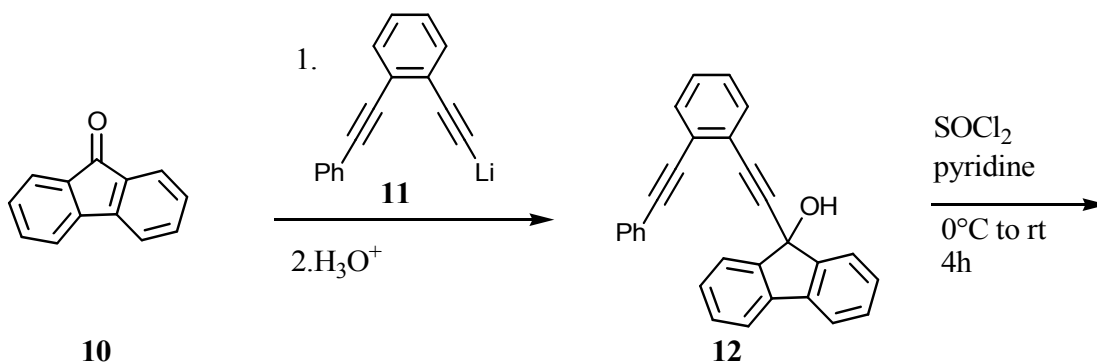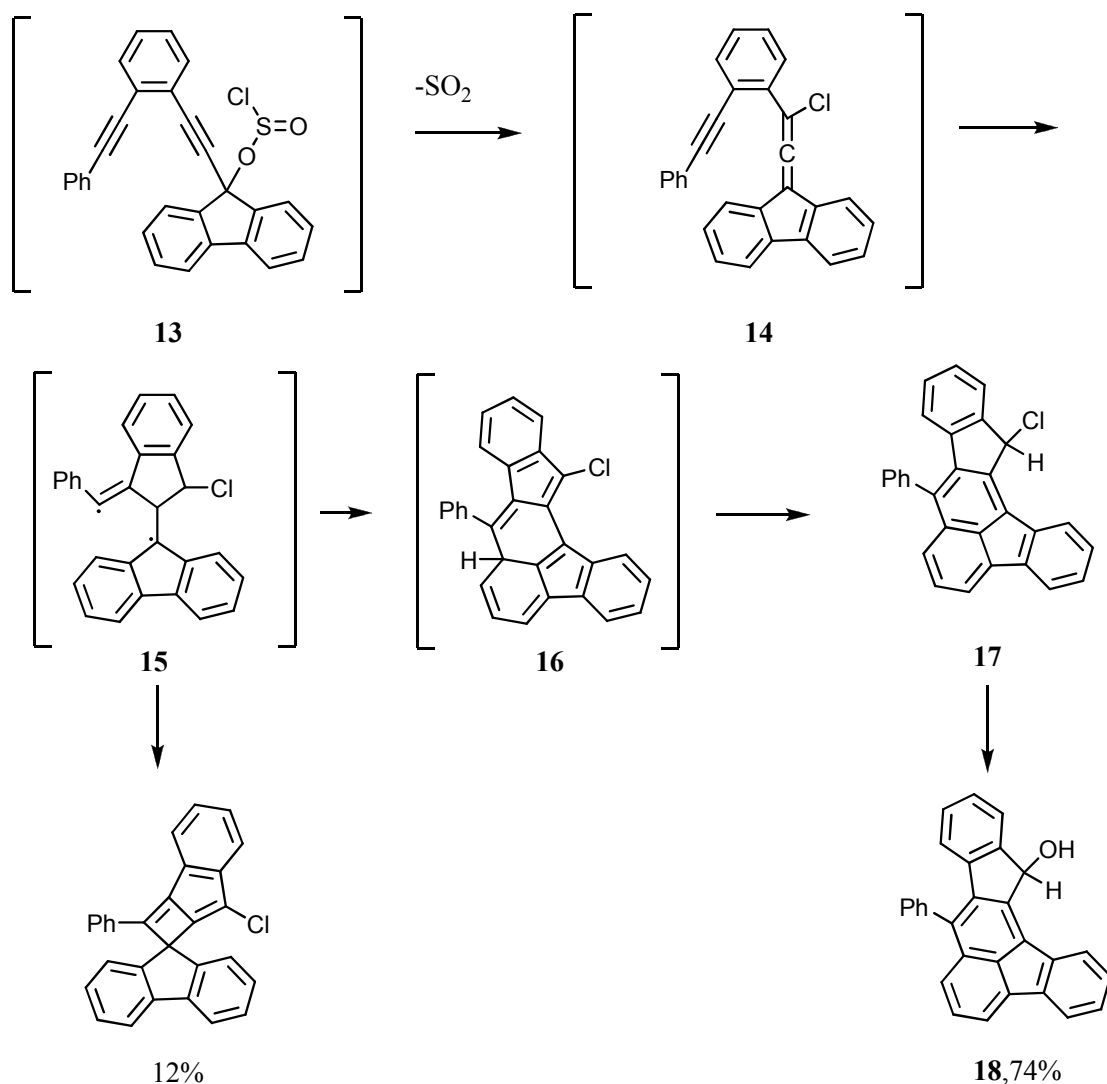
Scheme 1 Thionyl Chloride Induced Cascade Cyclization Reactions

In 2003, Dr. Yonghong Yang studied the use of molecules have two benzannulated enyne-allene units for the synthesis of polycyclic aromatic compounds.[14] The intermediate diketone **21** was synthesized by treatment of diester **19** with 4-octyne to form **20** followed by two intramolecular acylation reactions. The diol **22** was synthesized form condensation between diketone **21** and 2 equivalents of lithium acetylide **11**. It was

assumed that the Schimttel cyclization reaction of **22** would produce the desired hydrocarbon **24**. Unexpectedly, cleavage of the central benzene ring occurred during the course of cyclization, leading to highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes **23**. It is worth noting that hydrocarbon **24** has a 52-carbon framework represented on the surface of C_{60}.
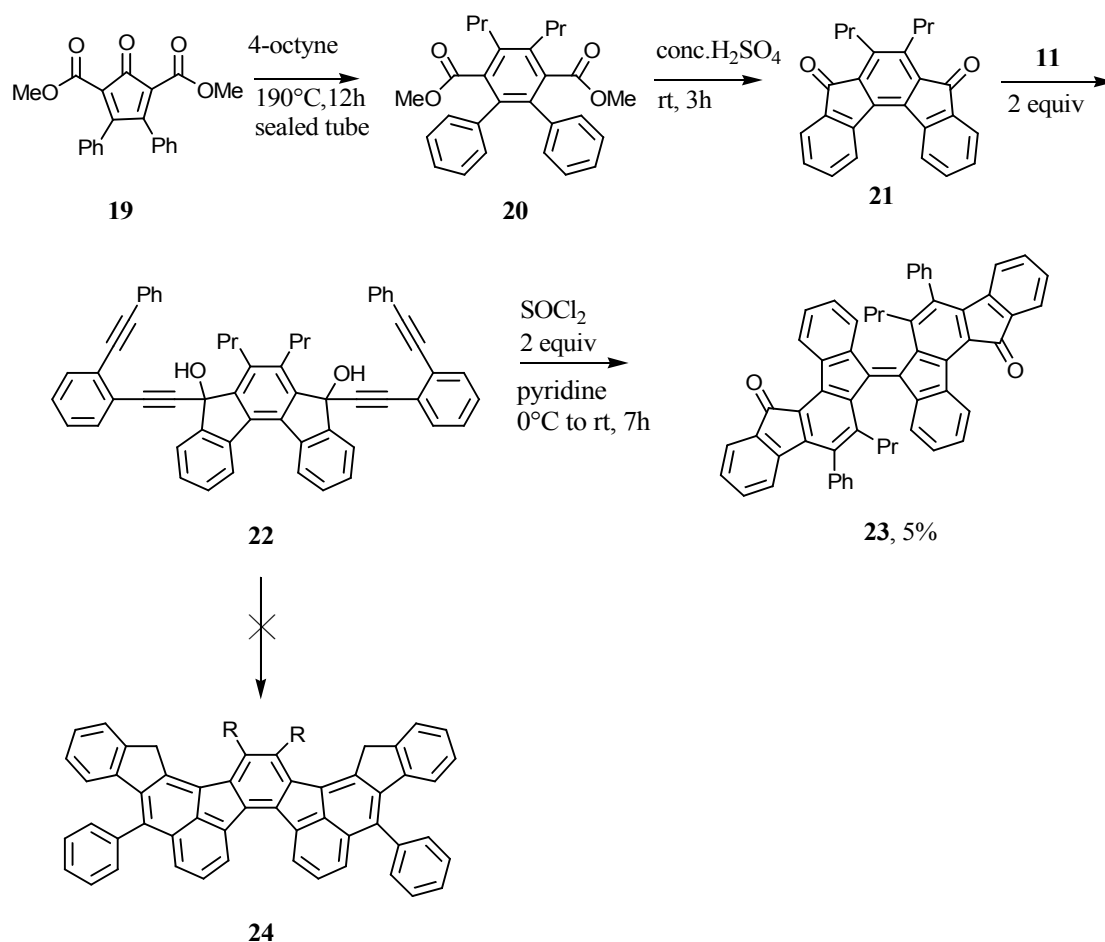
Scheme 2 Thionyl Chloride Induced Cascade Radical Cyclization of Benzannulated Enyne-Allenes

In 2004, Xiaoqing Han and Dr. Yanzhong Zhang reported the synthesis of 4*H*-cyclopenta[*def*]phenanthren-4-ones. Condensation of 1,3-

indandiones **25**, **26** with lithium acetylide **27**, **28** gave diols **29-31**.[15] Treatment of propargylic diols **29-31** with thionyl chloride promoted a cascade sequence of reactions leading to dichlorides **34-36**. Reduction of **34-36** with tributyltin hydride generated the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrenes **37-39**. Hydrolysis of **37** and **38** furnished **40** and **41**, respectively. Air oxidation of an alkaline solution of dichloride **35** produced diketone **42**. It is worth noting that the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrenes have a 41-carbon framework, 38 carbons on the aromatic rings and three carbons on the three five-membered rings, that is represented on the surface of C_{60}.

29: R = OMe, Ar = Ph
30: R = OMe, Ar = 4-t-Oct-Ph
31: R = Me, Ar = Ph

32   **33**

27: Ar = Ph
28: Ar = 4-t-Oct-Ph
t-Oct = -C(CH₃)₂CH₂C(CH₃)₃

25: R = OMe
26: R = Me

34: R = OMe, Ar = Ph
35: R = OMe, Ar = 4-t-Oct-Ph
36: R = Me, Ar = Ph

37: R = OMe, Ar = Ph
38: R = OMe, Ar = 4-t-Oct-Ph
39: R = Me, Ar = Ph

40: Ar = Ph, 97%
41: Ar = 4-t-Oct-Ph, 89%

42: Ar = 4-t-Oct-Ph
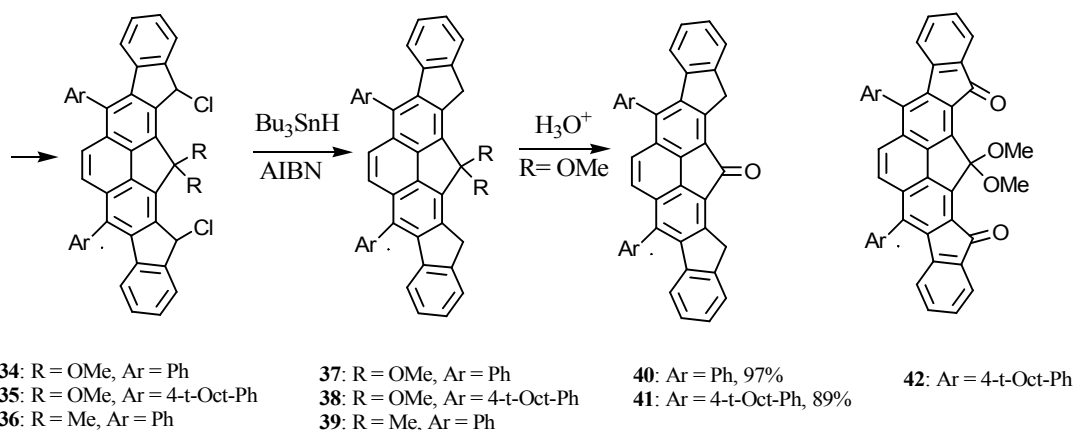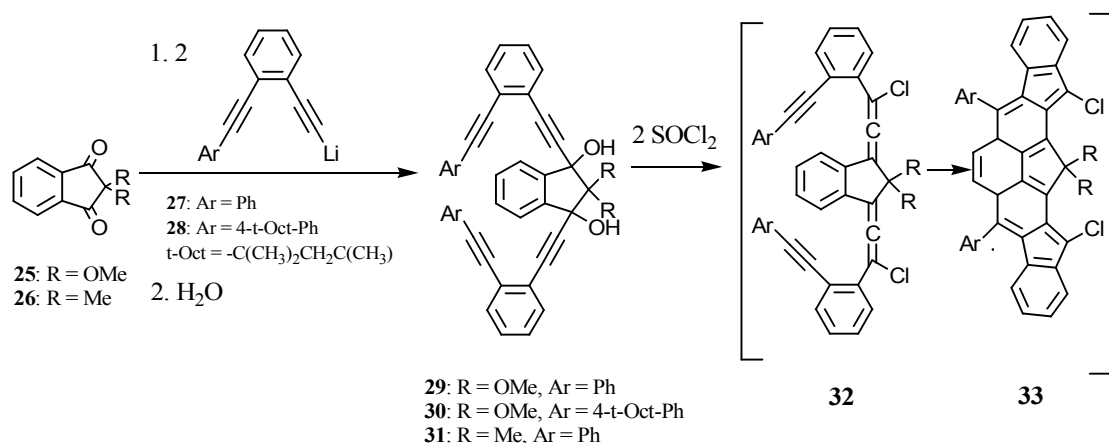
Scheme 3 Synthesis of Diindeno-Fused

4*H*-cyclopenta[*def*]phenanthrenes

In 2006, Dr. Hua Yang studied the cyclization of diol with two benzannulated enyne-allene units induced by the thionyl chloride.[16] Several methods were tried to synthesize a suitable key intermediate diketone. Finally, the diester **43** was obtained from the Diels-Alder reaction between diester **19** and 2,5-dihydrofuran, followed by decarbonylation to give **44**. Intromolecular acylation followed by methylation afforded the desired diketone **46**. Condensation between **46** and 2.6 equivalents of lithium acetylide **11** provided the benzannulated enediynyl propagylic diol **47**. Treatment of diol **47** with thionyl chloride followed by silica gel chromatography directly led to diketone **48**. The diketone **48** has a 54-carbon framework represented on the surface of C_{60} and may eventually lead to the formation of bowl-shaped polycyclic aromatic hydrocarbons (buckybowls). However, attempts to open the furan ring with trimethysilyl iodide and other methods were unsuccessful.
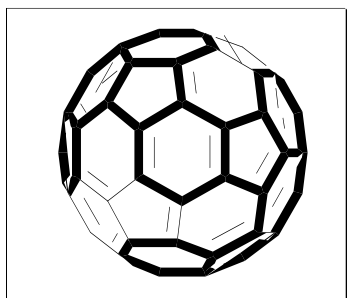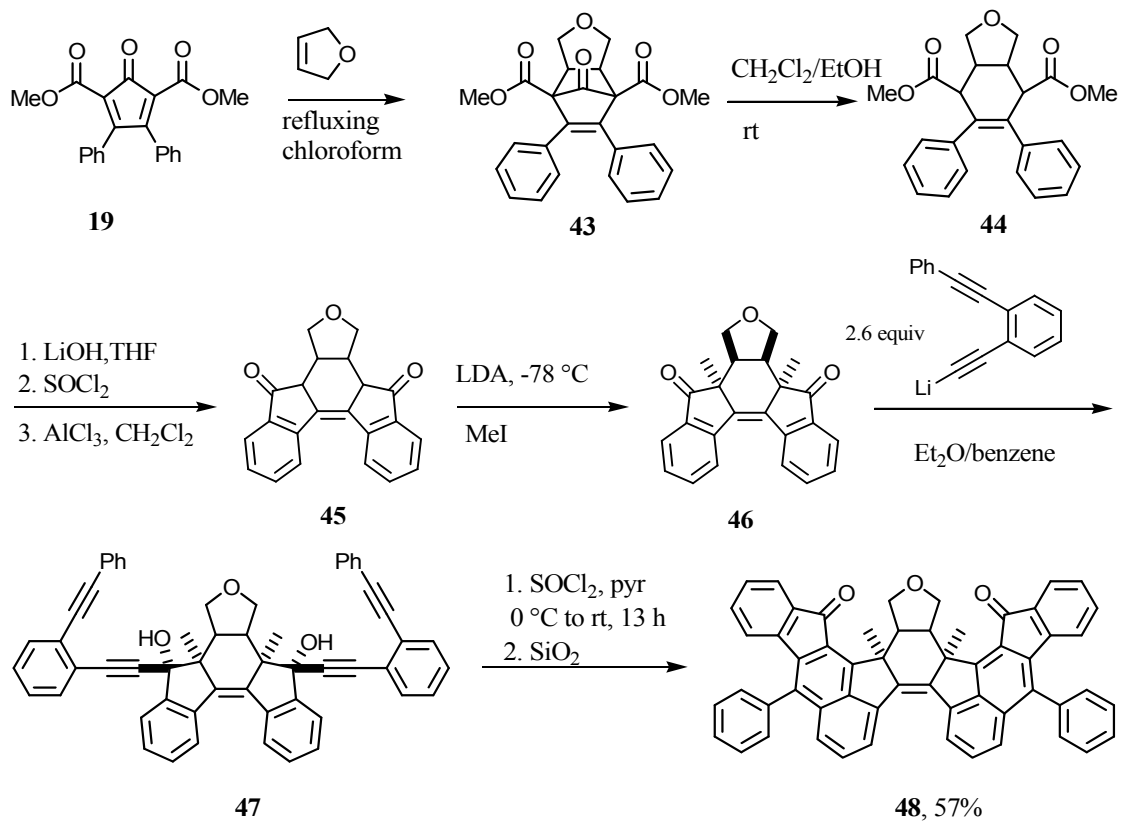
Scheme 4

4. Results and Discussion

With our ongoing interest in the synthesis of polycyclic aromatic hydrocarbons, we envisioned a retrosynthetic sequence outlined in Scheme 5 for the synthesis of polycyclic aromatic hydrocarbon **49**. It was anticipated that unlike diketone **48** with furan ring folded inside the two benzofluorenone units preventing it from cleavage by trimethysilyl iodide. The two methoxyl groups in diketone **49** could be easily demethylated to form the corresponding diol. The diol then could be oxidatively cleaved for subsequent intramolecular connections with the carbon atoms of the two ketone groups.

49   **50**

51   **52**

53   **54**   **55**
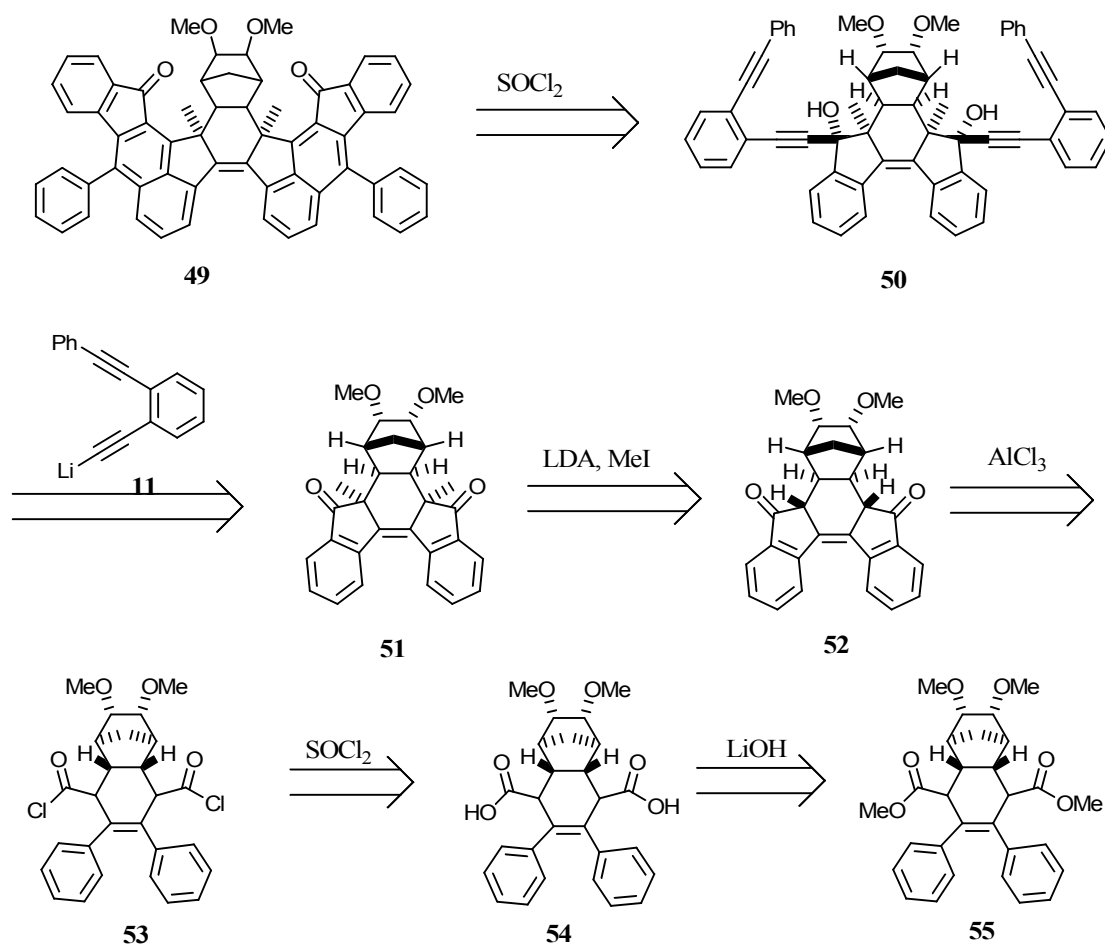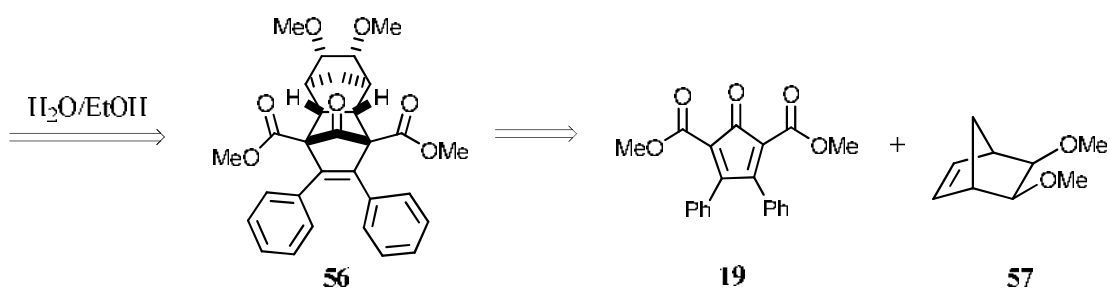
Scheme 5: Retrosynthetic analysis

The polycyclic aromatic hydrocarbon **49** could be synthesized by condensation of diketone **51** with lithium acetylide **11** followed by cascade cyclizations. The diketone **51** could be obtained from methylation of diketone **52**. The diketone **52** could be produced from intramolecular acylation of diacid **54**, which could be obtained from diester **55** followed by hydrolysis. The diester **55** could be obtained by decarbonylation of diester **56**. The diester **56** could be synthesized through the Diels-Alder reaction between diester **19** and dimethoxy norbornene **57**. The precursor **57** could be obtained through methylation of diol **58**, which was prepared from oxidation of norbornadiene **59**.

As outlined in Scheme 6, the precursor diol **58** was obtained through oxidation of norbornadiene as reported previously. The dimethoxy norbornene **57** was synthesized from diol **58** by deprotonation using sodium hydride in N,N-dimethylformamide followed by methylation with iodomethane to produce **57** in 39% yield.[17] The Diels-Alder reaction between 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (**19**) [18] and dimethoxy norbornene **57** provided diester **56** in 82% yield, with the *endo*-cycloadduct as the major product and the *exo*-cycloadduct as the

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minor product in a 3:1 ratio. The structure of the *endo*-cycloadduct was confirmed by X-ray structure analysis (Figure **4**). The X-ray structure of the *endo*-cycloadduct shows that the two carboxylate groups and the methylene bridge of the norboryl ring are on the same side of the cyclohexene ring. Dissolving diester **56** in a small amount of methylene chloride followed by decarbonylation in a mixed solvent of water and ethanol at 50°C for 15 hours afforded diester **55** in 63% yield. This procedure discovered by Lily Wang greatly improved the efficiency of the decarbonylation, as compared to an earlier reaction condition of using only ethanol, which under former condition usually takes more than two weeks. The diester **55** was treated with an excess amount of aqueous lithium hydroxide solution in THF at 60°C for 13 hours followed by acidification with 1 M hydrochloric acid to give the corresponding diacid **54** in 94% yield. The diacid **54** was refluxed in thionyl chloride to provide the corresponding diacid chloride, which underwent two Friedel-Crafts reactions by treating with aluminum chloride in anhydrous methylene chloride to afford diketone **52** in 32% yield.
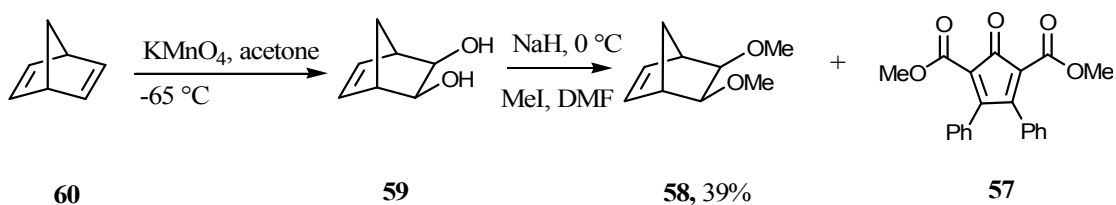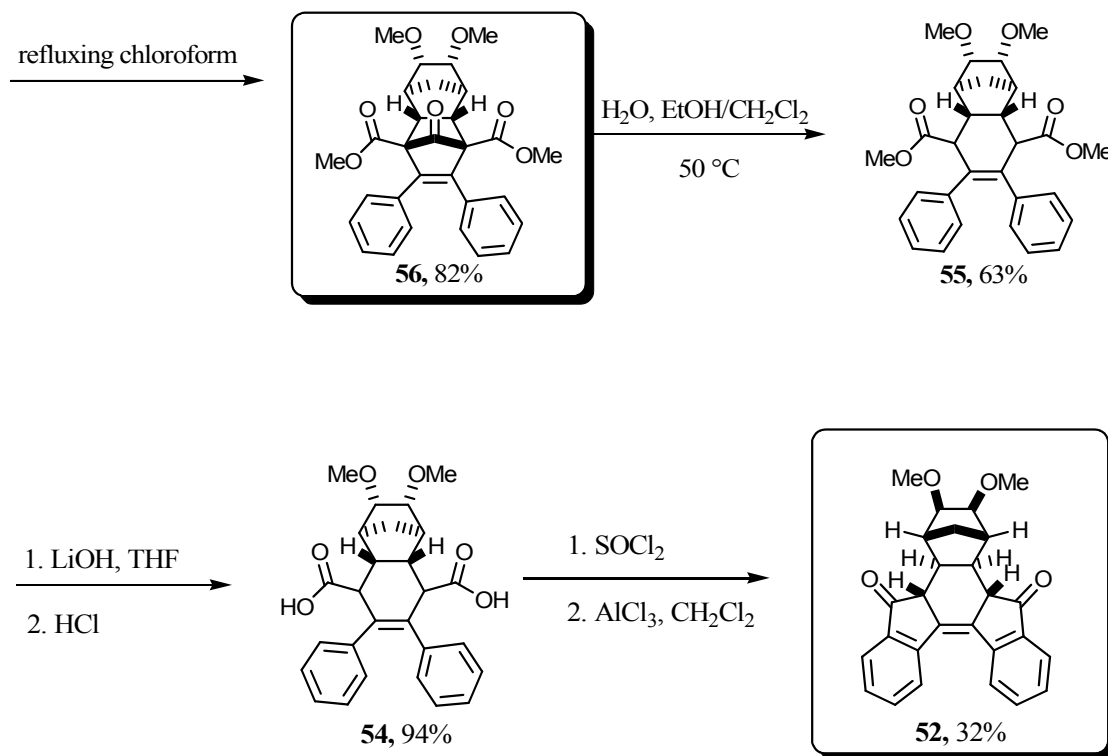
Scheme 6: Preparation of diketone **52**
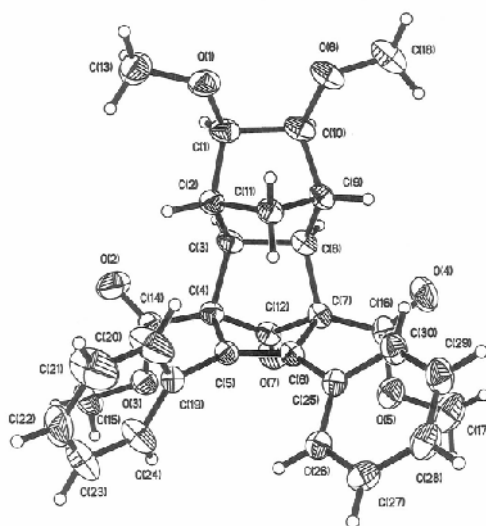
Figure 4: ORRTEP Drawing of the Crystal structures of **56**

The stereochemistry of diketone **52** was confirmed by the NOSEY experiment. The six hydrogens on the norboryl ring still have the same orientations as diester **56**. In the NOESY spectrum of diketone **52** (Figure

14

5), the two α –hydrogens adjacent to the carbonyl groups (H_1 and H_7) at 2.97 ppm showed strong nOes to H_3 and H_9 protons at 3.11 ppm, and to H_6 proton at 1.69 ppm. But, there are no nOes between H_1 and H_2 or between H_1 and H_4 protons, indicating that H_1 and H_7 protons are on the same side with the methylene bridge of norboryl ring.

Figure 5: nOe of diketone **52**
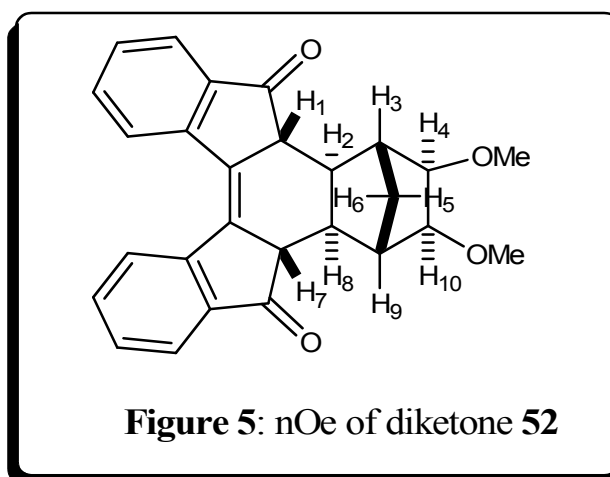
Diketone **52** was treated with 1 M lithium diisoproprylamide followed by iodomethane to afford diketone **51** in 41% yield. The stereochemistry of **51** was confirmed by NOSEY experiment.

Scheme 7: Preparation of diketone **51**
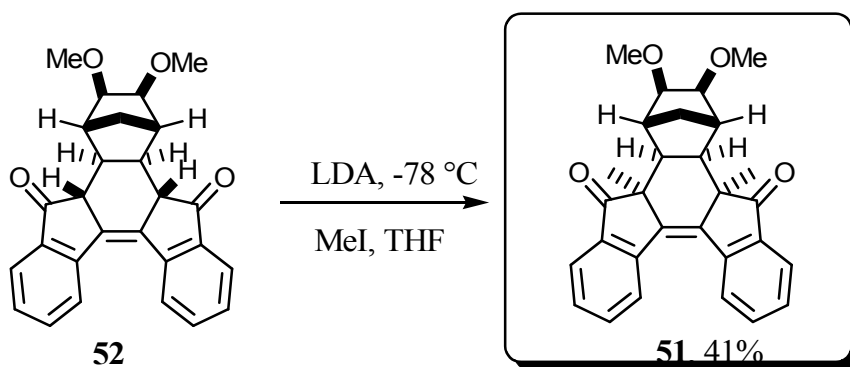
In the NOESY spectrum of diketone **51** (Figure **6**), the six protons of the two methyl groups on the α –carbons adjacent to the carbonyl groups at 1.58 ppm showed strong nOes to H_2 and H_8 protons at 2.24 ppm, and to

the H_3 and H_9 protons at 2.36 ppm. But, there are no nOes between the protons of the methyl groups and H_6 proton. Therefore, the two methyl groups are on the opposite side with the methylene bridge of the norboryl ring.

Figure 6: nOe of diketone **51**
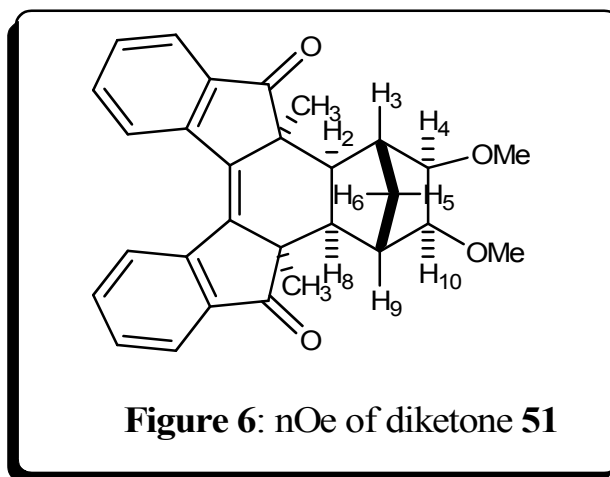
The condensation between diketone **51** and 3 equiv of **11** in distilled diethyl ether and benzene failed to afford diol **50**. Presumably, due to steric crowding caused by the norboryl ring and two methyl groups, the lithium acetylide **11** was unable to attack the two carbonyl groups to give the product **50**. A different synthetic strategy is needed to promote the reaction.
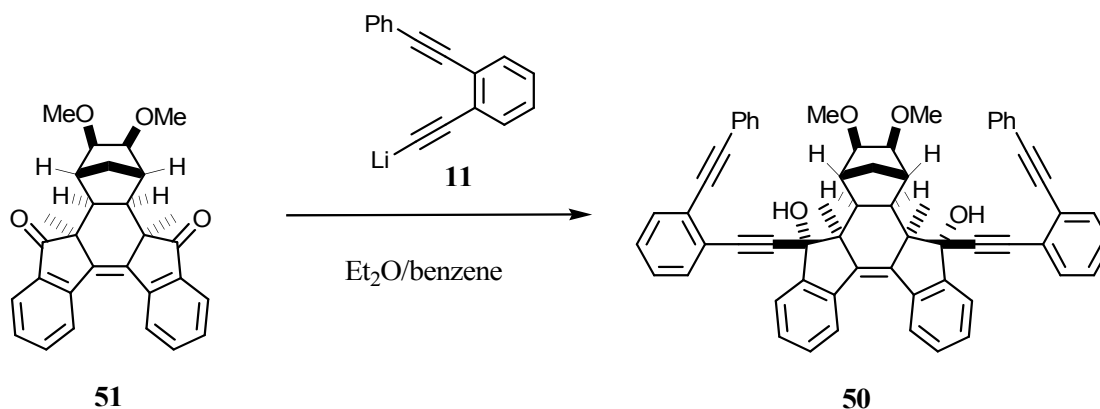
Scheme 8: Condensation Between Diketone **51** and Acetylide **11**

5. Conclusions

A simple and efficient pathway to synthesize novel nonplanar polycyclic aromatics was explored, and the key intermediate diketone **51** was successfully prepared. The diketone with a norboryl ring which could be easily opened in further steps could become a potential precursor for making a novel buckybasket.

Part Ⅱ

Experimental Section

General Methods and Materials. ^{1}H and ^{13}C NMR spectra were recoreded on a Varian VXR-600 (600 MHz) spectrometer. Chemical shifts are reported relative to CDCl$_3$ (δ 7.26 ppm) for ^{1}H and CDCl$_3$ (δ 77.0 ppm) for ^{13}C. Infrared (IR) Spectra were obtained on a FT-IR spectrometer. Melting Points were determined with Eledtrothermal Mel-Temp apparatus and are uncorrected. Flash column chromatagraphy 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 254nm. R$_f$ values are obtained by elution in the stated solvent ratios (v/v). Diethyl ether, THF, benezene and triethylamine were dried by passing through activated alumina column with argon gas pressure. Anhydrous diethyl ether, THF and benzene were distilled from benezephenone ketyl prior to use. Methylene Chloride was distilled from CaH$_2$. Commercial regents 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.

***Exo-cis*-5,6-dimethoxy-2-Norbornene (57).** To a vigorously stirred solution of sodium hydride (60% in mineral oil, 2.51 g, 62.9 mmol) in DMF (50 mL) at 0 °C was added dropwise 1.98 g of *exo-cis*-5-norbornene-2,3-diol **59** (15.7 mmol) in dry *N,N*-dimethyl--formamide (DMF, 20 mL). After the addition, the mixture was allowed to warm to room temperature and stirred vigorously until a homogeneous solution was obtained. After 30 minutes, the solution was cooled to 0 °C and 15.06 mL of iodomethane (78.5 mmol) was added dropwise with stirring. After additional 7 hours at room temperature, 80 mL of water was introduced slowly and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate and diethyl ether was evaporated by rotary evaporator. The residue was further purified by distillation at 190 °C to give *exo-cis*-2,3-dimethoxy-5-norbornene (58, 0.95g) as a clear yellow oil (6.2 mmol, 39%): ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.03 (2H, t, *J*=1.8 Hz), 3.44 (6H, s), 3.34 (2H, d, *J*=1.8Hz), 2.85 (2H, t, *J*=1.2 Hz), 1.95 (1H, d, *J*=8.4 Hz), 1.61 (1H, dt, J_d=9 Hz, J_t=1.8 Hz); ^{13}C NMR δ (150 MHz, CDCl$_3$) δ 136.7, 79.4, 58.3, 44.3, 43.3.

Diels-Alder Adduct 56. A mixture of 0.25 g of 2,5-dicarbomethoxy-3,4--diphenylcyclopentadienone **57** (0.72 mmol) and 0.15 g of *exo-cis*-5,6-dimethoxy-2-norbornene **58** (0.97 mmol) in 15 mL of

chloroform was heated under reflux for 15 hours. The solvent was removed in vacuo. The residue was purified by recrystallization from methylene chloride and hexanes to afford 0.25 g of diester **56** as a white solid (0.50 mmol, 82%): mp 176.9-178.5 °C; IR (thin film, cm^{-1}) 2922, 1737, 1456, 1092, 699; ^{1}H NMR (600M Hz, CDCl$_3$) δ 7.24-7.22 (6H, m), 7.14-7.13 (4H, m), 3.56 (6H, s), 3.45 (6H, s), 2.79 (2H, s), 2.56 (2H, s), 1.99 (2H, s), 1.92 (1H, d, *J*=11.4 Hz), 1.70 (1H, d, *J*=11.4 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 1896.2, 167.8, 136.1, 133.5, 128.4, 128.3, 128.2, 86.3, 67.9, 58.8, 52.2, 42.7, 41.6, 29.7; CIHRMS: calculated for [C$_{30}$H$_{30}$O$_7$+H]$^+$: 503.2070, found [C$_{30}$H$_{30}$O$_7$+H]$^+$: 503.20698; calculated [C$_{30}$H$_{30}$O$_7$+Na]$^+$: 525.18883; found [C$_{30}$H$_{30}$O$_7$+Na]$^+$: 525.18892.

Diester 55. To a solution of 0.427 g of diester **56** (0.90 mmol) in 3 mL of methylene chloride was added 15 mL of ethanol and 10 mL of water. The mixture was stirred at 50 °C for 15 hours. The resulting solution was extracted three times with methylene chloride. The combined organic layers were washed with brine, water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/ethyl acetate:methylene chloride:hexanes = 3:5:5) to provide 0.27 g of diester **55** as a white solid(0.57 mmol, 63%): IR (thin film, cm^{-1}) 1731, 1265, 1198, 1120, 700; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.10-7.04 (6H, m), 6.88-6.86 (4H, m), 3.70(2H, q, *J*=2.4 Hz), 3.45 (6H, s),

3.42 (2H, s), 3.39 (2H, s), 3.35(6H, s), 2.99 (2H, s), 1.94-1.91 (1H, d, J=11.4 Hz), 1.74-1.72 (1H, d, J=11.4 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 172.4, 139.8, 135.9, 128.6, 127.5, 126.3, 86.1, 58.5, 51.4, 48.9, 42.9, 40.8, 30.9.

Diacid 54. To a solution of 0.26 g of diester **55** (0.571 mmol) in 8 mL of THF was added an aqueous lithium hydroxide solution (4.7 mL, 1.0 M). The resulting solution was stirred at 60 °C for 13 hours and then concentrated under reduced pressure. The residue was neutralized with 1 M hydrochloric acid and extracted with methylene chloride. The organic layer was washed with brine, water, dried over sodium sulfate, and concentrated to afford 0.24 g of diacid **54** as white solid (0.537 mmol, 94%): mp 192.6-193.4 °C; IR (thin film, cm^{-1}) 2932, 1703, 1095, 697; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.16-7.13 (10H, m), 3.66 (2H, s), 3.50 (2H, s), 3.42 (6H, s), 2.67 (2H, s), 2.28 (2H, s), 1.98 (1H, d, J=10.2 Hz), 1.71 (1H, d, J=10.2 Hz), 1.57 (1H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 179.8, 141.8, 135.8, 129.1, 128.0, 126.9, 58.6, 52.0, 47.4, 39.9, 30.4; CIHRMS: calculated for [C$_{27}$H$_{28}$O$_6$+H]$^+$: 449.1964, found [C$_{27}$H$_{28}$O$_6$+H]$^+$: 449.19642; calculated for [C$_{27}$H$_{28}$O$_6$+Na]$^+$: 471.17823, found [C$_{27}$H$_{28}$O$_6$+Na]$^+$: 471.17836

Diketone 52. A solution of 0.482 g of acid (1.07 mmol) in 4 mL thionyl

chloride was heated under reflux for 12 hours. Then thionyl chloride was removed in vacuo. The residue was dissolved in 40 mL of anhydrous methylene chloride at 0 °C and 0.43 g of anhydrous aluminum chloride (3.22 mmol) was added slowly. After 2 hours at 0 °C, the reaction mixture was allowed to warm to room temperature. After an additional 5 hours at room temperature, 15 mL of a saturated ammonium chloride solution was introduced slowly and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine, water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/ethyl acetate:methylene chloride:hexane = 2:5:5) to provide 0.140 g of diketone **52** as yellow solid (0.34 mmol, 32%): mp 278.8-280.1 °C; IR (thin film, cm^{-1}) 1702, 1090, 761; ^{1}H NMR (600 M Hz, CDCl$_3$) δ 8.35 (2H, d, *J*=7.8 Hz), 7.91 (2H, d, *J*=7.8 Hz), 7.77 (2H, t, *J*=7.8 Hz), 7.53 (2H, t, *J*=7.8 Hz), 3.50 (6H, s), 3.38 (2H, d, *J*=1.2 Hz), 3.11 (2H, s), 2.97 (2H, dd, J_d=10.2 Hz, J_d=2.4 Hz), 1.96 (1H, d, *J*=12 Hz), 1.68 (1H, d, *J*=12 Hz), 1.65 (2H, d, *J*=9 Hz); ^{13}C NMR (600 M Hz, CDCl$_3$) δ 203.2, 145.7, 138.1, 135.2, 132.4, 129.6, 124.8, 124.6, 84.9, 58.6, 51.8, 43.7, 42.6, 27.1; CIHRMS: calculated for [C$_{27}$H$_{24}$O$_4$+H]$^{+}$: 413.1753., found [C$_{27}$H$_{24}$O$_4$+H]$^{+}$: 413.17529, calculated for [C$_{27}$H$_{24}$O$_4$+Na]$^{+}$: 435.15713., found [C$_{27}$H$_{24}$O$_4$+Na]$^{+}$: 435.15723.

Diketone 51. To a solution of 0.140 g (0.35 mmol) of diketone **52** in 30 mL of anhydrous THF under a nitrogen atmosphere at -78 °C was added 1.05 mL of a 1 M solution of lithium diisopropylamide (1.05 mmol) in THF/*n*-heptane. After 30 minutes of stirring, 0.12 mL of iodomethane was added. After an additional 13 h, 30 mL of a saturated ammonium chloride solution was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/ethyl acetate:methylene chloride:hexanes= 1:2:2) to provide 0.064 g of diketone **51** as a red-brown oil (0.145 mmol, 41%): IR (thin film, cm^{-1}) 1712, 1264, 734; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.40 (2H, d, *J*=7.8 Hz), 7.92 (2H, d, *J*=7.2 Hz), 7.73 (2H, t, *J*=7.2 Hz), 7.53 (2H, t, *J*=7.2 Hz), 3.39 (2H, d, *J*=1.2 Hz), 3.36 (6H, s), 2.37 (2H, s), 2.25 (2H, s), 1.59 (6H, s), 1.11 (1H, d, *J*=10.8 Hz), 0.58 (1H, d, *J*=10.8 Hz); ^{13}C NMR (600 M Hz, CDCl$_3$) δ 206.9, 146.4, 138.4, 135.9, 134.8, 129.8, 125.3, 124.9, 85.0, 58.4, 54.9, 46.4, 43.8, 29.5, 27.9; CIHRMS: calculated for [C$_{29}$H$_{28}$O$_4$+H]$^+$: 441.2076, found: [C$_{27}$H$_{28}$O$_6$+H]$^+$: 441.20659; calculated for [C$_{29}$H$_{28}$O$_4$+Na]$^+$: 463.18943, [C$_{27}$H$_{28}$O$_6$+Na]$^+$: 463.18853.

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APPENDIX

57

OMe
OMe

7.260

6.034
6.031
6.028

3.437
3.346
3.343

2.854
2.852
2.849

2.170
2.169
1.961
1.947

1.544

13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm

28

3.707
3.703
3.700
3.696

3.450
3.428
3.419
3.409
3.401
3.390
3.388

3.345

3.309

2.998

55

MeO

O

MeO

OMe

H

OMe

H

O

OMe

3.7   3.6   3.5   3.4   3.3   3.2   3.1   3.0   ppm

33

200 180 172.373 160 140 139.775 135.877 128.623 127.541 126.313 120 100 86.105 80 77.211 77.000 76.789 60 58.470 51.376 48.910 42.924 40.807 30.897 40 20 0 ppm

55

34

200

180

179.798

160

140

141.794
135.830
130.157

129.108
128.036
127.785
127.577
126.914

120

100

85.376

80

77.211
77.000
76.789

60

58.623

52.021

47.423

40

39.889

30.398

20

0

ppm

54

HO
O
H
MeO
OMe
O
OH

203.156

145.656

138.059
135.156
132.438
129.647
124.772
124.557

84.910

77.211
77.000
76.789

58.550

51.832

43.754
42.617

27.115

200 180 160 140 120 100 80 60 40 20 0 ppm

52

MeO OMe

OMe

51

206.960

146.414

138.446
135.965
134.827
129.827
125.273
124.908

85.015

77.212
77.000
76.788

58.374
54.925

46.356
43.849

29.492
27.984

51

MeO   OMe

40

c:\pel_data\spectra\d-a.002

%T

4000.0   3000   2000   cm-1   1500   1000   650.0

105.8
104
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
71.1

2922.22
2853.26
1790.95
1737.34
1594.02
1573.97
1456.47
1362.82
1320.34
1279.36
1267.94
1247.56
1215.30
1157.58
1126.74
1108.03
1092.77
1072.86
1025.93
991.07
949.65
918.22
861.88
845.77
834.35
820.05
767.92
751.68
733.30
699.59
659.75

MeO

O

H

H

MeO

OMe

56

O

O

OMe

O

55

2952.34
2829.63

1790.01
1731.06
1597.44
1492.93
1436.09
1265.17
1198.45
1120.76
977.37
841.56
735.32
700.56

4000.0   3000   2000   cm-1   1500   1000   650.0

101.4
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72.4

%T

c:\pel_data\spectra\diester.002

42

%T

4000.0

3000

2000

cm-1

1500

1000

650.0

103.5
102
100
98
96
94
92
90
88
86
84
82
80
78
76
73.7

3078.28
2970.89
2924.11
2821.00
2060.31
1702.49
1592.90
1572.42
1469.43
1454.55
1389.27
1370.92
1346.09
1318.87
1296.91
1276.63
1228.88
1195.21
1173.58
1130.97
1090.40
1068.19
1054.17
1025.72
1015.90
976.65
940.46
919.31
891.11
844.25
805.03
761.65
735.32
673.46

51

MeO OMe