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

Ruoxin Zhang
West Virginia University

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

Ruoxin Zhang

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

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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
ACKNOWLEDGEMENTS

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Part I

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Part I

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. Kroto (University of Sussex, UK), R. F. Curl and R.E. Smalley (both from Rice University, USA). 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 reactives and physical properties. 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 buckybowls or buckybasket. The first synthesis of the smallest buckybowls corannulene \((C_{20}H_{10})\), was reported by Barth and Lawton in 1966. 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 \((C_{30}H_{12})\), dibenzo[a,g]corannulene \((C_{28}H_{14})\) and tribenzo[a,d,j]corannulene \((C_{32}H_{16})\) were synthesized and characterized.

\[
\begin{align*}
\text{C}_{20}\text{H}_{10} & : 1 \\
\text{C}_{30}\text{H}_{12} & : 2 \\
\text{C}_{28}\text{H}_{14} & : 3 \\
\text{C}_{32}\text{H}_{16} & : 4
\end{align*}
\]

**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 C₆₀. In, 1997, Seiders et al. reported the first transition metal complex of corannulene 5 and the first example of η⁶-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 η⁶-coordinated {Cp*Ru} units 6 which bind to non-adjacent arene rings on opposite sides of corannulene.¹⁰

![Structure of Ru-corannulene Complex](image)

**Figure 2.** Structure of Ru-corannulene Complex

Due to the intrinsic curvature, the buckybowel 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
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 polycyclic 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).\textsuperscript{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 chlorosulfite 13 followed by an $S_{N-i}$’ reaction\textsuperscript{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.

\begin{center}
\includegraphics[width=\textwidth]{scheme}
\end{center}
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. 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 4H-cyclopenta[def]phenanthren-4-ones. Condensation of 1,3-
indandiones 25, 26 with lithium acetylide 27, 28 gave diols 29-31.\textsuperscript{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 4H-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 4H-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\textsubscript{60}.
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 propagyllic 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 trimethylsilyl 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 trimethylsilyl 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.
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. The Diels-Alder reaction between 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (19) and dimethoxy norbornene 57 provided diester 56 in 82% yield, with the *endo*-cycloadduct as the major product and the *exo*-cycloadduct as the
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 norbornyl 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.

\[
\begin{align*}
  \text{KMnO}_4, \text{acetone, } -65 ^\circ C & \rightarrow \text{59, 39\%} \\
  \text{NaH, 0 } ^\circ C & \rightarrow \text{58, 39\%} \\
  \text{MeI, DMF} & \rightarrow \text{57}
\end{align*}
\]
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
the two \( \alpha \)-hydrogens adjacent to the carbonyl groups \((H_1\text{ and } H_7)\) 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 norbornyl ring.

Diketone 52 was treated with 1 M lithium diisopropropylamide followed by iodomethane to afford diketone 51 in 41% yield. The stereochemistry of 51 was confirmed by NOSEY experiment.

In the NOESY spectrum of diketone 51 (Figure 6), the six protons of the two methyl groups on the \( \alpha \)-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 \( \text{H}_3 \) and \( \text{H}_9 \) protons at 2.36 ppm. But, there are no nOes between the protons of the methyl groups and \( \text{H}_6 \) 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](image)

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](image)
5. Conclusions

A simple and efficient pathway to synthesize novel nonplanar polycyclic aromatics was explored, and the key intermediate diketone \textbf{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 recorded on a Varian VXR-600 (600 MHz) spectrometer. Chemical shifts are reported relative to CDCl$_3$ ($\delta$ 7.26 ppm) for $^1$H and CDCl$_3$ ($\delta$ 77.0 ppm) for $^{13}$C. Infrared (IR) Spectra were obtained on a 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 254nm. R$_f$ values are obtained by elution in the stated solvent ratios (v/v). Diethyl ether, THF, benzene and triethylamine were dried by passing through activated alumina column with argon gas pressure. Anhydrous diethyl ether, THF and benzene were distilled from benzezphenone 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%): ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR δ (150 MHz, CDCl₃) 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; ¹H NMR (600M Hz, CDCl₃) 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); ¹³C NMR (150 MHz, CDCl₃) δ 189.6, 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 [C₃₀H₃₀O₇+H]⁺: 503.2070, found [C₃₀H₃₀O₇+H]⁺: 503.20698; calculated [C₃₀H₃₀O₇+Na]⁺: 525.18883; found [C₃₀H₃₀O₇+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; ¹H NMR (600 MHz, CDCl₃) 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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; ¹H NMR (600 M Hz, CDCl₃) 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, Jd=10.2 Hz, Jd=2.4 Hz), 1.96 (1H, d, J=12 Hz), 1.68 (1H, d, J=12 Hz), 1.65 (2H, d, J=9 Hz); ¹³C NMR (600 M Hz, CDCl₃) 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 [C₂₇H₂₄O₄+H]⁺: 413.1753, found [C₂₇H₂₄O₄+H]⁺: 413.17529, calculated for [C₂₇H₂₄O₄+Na]⁺: 435.15713, found [C₂₇H₂₄O₄+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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.


Reference:


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APPENDIX