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Development of New Synthetic Methods for Carbon Nanohoops

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Development of New Synthetic Methods for Carbon Nanohoops

Merfat Aljhdli

Dissertation submitted to the Eberly College of Art and Sciences
at West Virginia University

In partial fulfillment of the requirements
for the degree of Doctoral of Philosophy
in
Organic Chemistry

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ABSTRACT

Development of New Synthetic Methods for Carbon Nano hoops

Merfat Aljhdli

Carbon nanotubes have received much attention from the material chemists after the synthesis and structure analysis by Iijima in 1991. It was envisioned that cycloparaphenylenes (CPPs), which comprise a sequence of benzene units connected at *para* position to make a cyclic ring structure, are possible templates for growing carbon nanotubes of a single chirality and single diameter for nanotechnology application. Recently, chemists turned their attention to synthesizing aromatic carbon nanobelts proposed as a general term for carbon molecules composed of fused benzene rings in cylindrical structure shape. Cyclophenacenes (CPAs) as carbon nanobelts are expected to be more suitable candidates for growing carbon nanotubes because it is anticipated that CPAs would be thermally more robust.

In this investigation, an alternative and efficient pathway of preparing 4,4'-dibromo-3,3'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic acid was developed, leading to 2,7-dibromo-1,8-bis(bromomethyl)phenanthrene containing suitable functional groups as a potential building block for CPAs. The presence of the functional groups provides the opportunity to connect multiple phenanthrene units together to form macrocycles bearing the carbon frameworks of CPAs.

A synthetic pathway was developed using 2,7-dibromo-1,8-bis(bromomethyl)phenanthrene as a building block to form a macrocycle bearing two 2,7-dibromophenanthrene units connected via two dibenzylamine linkages at C1 and C8 positions. The structure of the macrocycle having two dibenzylamine linkages is not planar and the two phenanthrene units are nonequivalent on the NMR time scale at 25 °C. The DFT calculations and

temperature-dependent NMR studies indicate that the two phenanthrene units preferred a conformation with one phenanthrene unit oriented perpendicular to the other unit.

DEDICATED TO

My Parents, Othman Aljhdli & Manawer Aljhdli
My husband, Yaser Alansary, My sons, Battal Alansary & Ammar
Alansary

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List of publications

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Chapter 1. Synthesis and Structure of Cycloparaphenylenes and Cyclophenacenes

1.1 Introduction

Carbon nanotubes (CNTs) have received much attention from the material chemists after the synthesis and structure analysis by Iijima in 1991.¹ CNTs are considered to be promising candidates in emerging new technologies due to their outstanding mechanical, electrical, and thermal properties. CNTs are used in different applications such as electrical wiring,² sensor arrays,³⁻⁷ biomaterials,⁸ sensing,⁹ field-effect transistors,¹⁰⁻¹² interconnect,¹³ and other various nanoscale applications. CNTs are formed by wrapping a graphene sheet into a hollow cylindrical structure in the type of CNTs typically referred to as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (Figure 1.1).¹⁴ Single-wall carbon nanotubes are made by wrapping a one-atom-thick layer of graphene into a cylindrical shape. In contrast, multi-wall carbon nanotubes consist of multiple rolled layers of a concentric nanotube of graphene inside another nanotube.

Figure 1.1. Different types of CNTs, A) single-wall CNTs, and B) multi-wall CNTs

1.2 Structure and Properties of CNTs

CNTs have three possible types depending on how the graphene is rolled up: armchair carbon nanotubes, zigzag carbon nanotubes, and chiral carbon nanotubes (Figure 1.2).¹⁵ CNTs have different electrical properties based on their molecular structure and diameter. Single wall carbon nanotubes can be either conducting or semiconducting depending on their chirality. In the armchair CNTs, the hexagons are arranged parallel to the axis of the nanotube; thus, this type has electrical properties that are similar to metals. The structure arrangement is different in Zigzag and chiral CNTs, but they are similar in electrical properties; both have semiconductors properties.¹⁶ A slight change in chirality will shift the electrical properties in CNTs from metallic to semiconducting.¹⁷

Figure 1.2. Armchair, Zigzag and Chiral CNTs

Different methods are known for the synthesis CNTs; the three primary methods for synthesizing CNTs are arc discharge,¹⁸ laser ablation,¹⁹ and chemical vapor deposition.²⁰ Carbon nanotubes obtained by these methods contain very different chiralities and diameters. Unfortunately, there is no efficient purification method that allows the isolation of carbon nanotube with single chirality and single diameter. Still, the door is open for the chemists to explore more to address this issue.

1.3 Cycloparaphenylenes (CPPs)

1.3.1 Background

Cycloparaphenylenes (CPPs) is a possible template for growing single chirality single-wall carbon nanotubes. It is also called carbon nanorings, which is the smallest cyclic repeating unit in carbon nanotubes (Figure 1.3).²¹ CPPs comprise a sequence of benzene units connected at *para* position to make a cyclic ring structure. CPPs have received considerable attention because of their interesting electrochemical and photophysical properties, intriguing structures, and potential applications in materials science.

Figure 1.3. [6]CPP represent the shortest-possible cyclic unit of a (6,6) CNT

1.3.2 Synthetic Attempts for the Preparation of CPPs

Early Synthetic Attempts of Cycloparaphenylenes

The history of synthesizing cycloparaphenylene began with the first attempt reported in 1934 by Parekh and Guha (Scheme 1.1).^{22b} Parekh and Guha provided an approach to synthesis the most straightforward and smallest [2]CPP by connecting two benzene rings with a sulfide bridge. Thermal desulfination in the presence of copper was employed to remove the sulfide from **I-1** and

attach the two rings failed. [2]CPP is too strained to exist under anything but an extreme condition.

Scheme 1.1. Parekh and Guha's Attempted Synthesis of [2]CPP

In 1993, the chemistry of CPP significantly advanced further when Vögtle and co-workers published their paper entitled “On the way to macrocyclic paraphenylenes”.^{23a} Although they did not successfully synthesis CPPs, their work opened the way for many later successes in the CPPs field. Vögtle applied different methods for the synthesis of CPPs. The first attempt targeted larger CPPs following Parekh and Guha’s strategy, which seems to be more plausible targets than [2]CPP. Unfortunately, the transformation of precursors to [6]CPP and [8]CPP via the desulfination failed. Other proposed approaches by Vögtle, including the Diels-Alder reaction, cyclooligomerisation, and the McMurry reaction all failed (Scheme 1.2).^{23b,c,d}

Scheme 1.2. Vögtle Attempts for the Preparation of CPPs

A. Pyrolysis Approach

B. Diels-Alder Reaction Approach

C. Cyclooligomerisation Approach

D. McMurry Reaction Approach

Bertozzi and Jasti's Approach for the Synthesis of Cycloparaphenylenes

In 2008, Bertozzi, Jasti and co-workers reported the first successful synthesis of cycloparaphenylenes (Scheme 1.3).²⁴ In their strategy they utilized 1,4-*cis*-dimethoxy-2,5-cyclohexadiene unit **I-5** to build strain-free CPP precursor macrocycles. The L-shaped structure in compound **I-5** was a result of the presence of sp^3 hybridized carbons, that give the compound the

flexibility that is necessary to form the macrocycle.²⁵ The synthesis starts by the formation of compound **I-5** from the monolithiated 1,4-diiodobenzene and 1,4-benzoquinone followed by the subsequent borylation of **I-5** to yield **I-6** in 82% yield. The palladium-catalyzed cross-coupling reaction of diiodo **I-5** and the diborylated **I-6** produces three different macrocycles, [9]CPP precursor **I-7**, [12]CPP precursor **I-8** and [18]CPP precursor **I-9** in 2%, 10%, 10% yield, respectively.

Scheme 1.3. First Successful Synthesis of CPPs by Bertozzi and Jasti

The last step toward the preparation of the three cycloparaphenylenes involved the reductive aromatization reaction of the cyclohexadiene moieties in macrocycles. This conversion was successfully achieved upon using lithium naphthalenide to produce [9]CPP **I-10**, [12]CPP **I-11**, and [18]CPP **I-12** in 43%, 52%, and 36% yield, respectively (Scheme 1.4).

Scheme 1.4. Reductive Aromatization and Proposed Mechanism

Itami's Approach for the Synthesis of [12]CPP

The community quickly recognized the importance of the Bertozzi group's work. One year later, Itami and co-workers published their first contribution in synthesizing CPPs by reporting their selective synthesis of [12]CPP (Scheme 1.5).²⁶ Like Bertozzi, Itami utilizes a precursor containing non-aromatic rings to undergo macrocyclization and produce macrocycle **I-17**. Dehydration and aromatization of macrocycle **I-17** provide the desired cycloparaphenylene [12]CPP in a good yield.

Scheme 1.5. The Synthesis of [12]CPP Reported by Itami and Co-worker

Yamago's Approach for the Synthesis of [8]CPP

One year after reporting the synthesis of [12]CPP by Itami, Yamago and co-workers reported the third original synthetic route to cycloparaphenylenes (Scheme 1.6).²⁷ The critical strategy relied on the synthesis of a tetraplatinum precursor, which is a strain-free macrocycle due to the square-planar geometry of $\text{Pt}(\text{II})$. Transmetalation between 4,4'-bis(trimethylstannyl)biphenyl and $[\text{PtCl}_2(\text{cod})]$ (cod = 1,5-cyclooctadiene) afforded the less strained square-shaped precursor **I-18**. Following ligand exchange to give **I-19** (L = dppf), reductive elimination with bromine as an oxidant led to the formation of transient $\text{Pt}(\text{IV})$ species. Those species undergo reductive elimination, depending on the ligand,²⁸ can either form Ar-Br bond or Ar-Ar bond, and in this case, four-fold Ar-Ar bonds were formed, producing the smallest cycloparaphenylene at that time, which is [8]CPP in 37% yield. With the same strategy, Yamago and co-workers successfully prepared a variety of CPPs with different sizes.

Scheme 1.6. The Synthesis of [8]CPP by Yamago

Wang's Approach for the Synthesis of a Functionalized [9]CPPs

In 2014, Wang's group reported the synthesis of a functionalized [9]CPP. The strategy's critical step was utilizing the Diels-Alder reaction to form the CPP precursor (Scheme 1.7).²⁹ The formation of the Diels-Alder adduct **I-21** was achieved from the Diels-Alder reaction between diene **I-20** and 1,4-benzoquinone in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a catalyst. Methylation of **I-21** produces **I-22** in 91 % over two steps. The Diels-Alder reaction provided **I-21** precursor exclusively in *cis* conformation, which is necessary for the subsequent macrocyclization ring formation.

Scheme 1.7. Preparation of the [9]CPP Precursor via the Diels-Alder Reaction

Homocoupling reaction³⁰ of precursors **I-22** utilizing Ni(cod)_2 in the presence of 2,2'-bipyridyl (bpy) produces a mixture of macrocycles, including macrocyclic dimers, *syn*-**I-23**

and *anti*-**I-24**, and macrocyclic trimers, *syn*-**I-25** *anti*-**I-26** (Scheme 1.8). All isomers were identified by X-ray structure analysis and ^1H NMR spectroscopy.

Oxidative aromatization was the final step for the formation of the functionalized [9]CPP and functionalized [6]CPP. Treating the mixture of the dimers and the trimers with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)³¹ produced the fully aromatized [9]CPP, while the fully aromatized [6]CPP was not obtained even under harsher reaction conditions. Wang's group successfully prepared a range of CPPs by using different combinations of dienes and dienophiles to produce CPP precursors from the Diels-Alder reaction.

Scheme 1.8. Synthetic Strategy for the Preparation of Functionalized [9]CPP

1.4 Cyclophenacenes (CPAs)

1.4.1 Background

Aromatic carbon nanobelts were proposed as a general term for carbon molecules that composed of fused benzene rings in cylindrical structure shape.³² Constructing two units of cycloparaphenylene (CPP), which is a cyclic structure where the benzene units are connected at *para* positions to each other, can form cyclophenacenes (CPAs). In CPAs, each set of CPP in CPAs has two connections between the adjacent benzene rings.³³ Itami also proposed a definition to distinguish between carbon nanorings and carbon nanobelts. In carbon nanobelts at least two C-C bonds need to be cleaved to open their cyclic structure, while in carbon nanorings only one C-C bond needs to be cleaved (Figure 1.4).³⁴

Figure 1.4. Definition of carbon nanobelts and carbon nanorings.

While the discovery of carbon nanotubes occurred in 1991,¹ carbon nanobelts have received much attention from the synthetic communities for more than half a century not only due to their special optical and electrical properties, but also their preparation could open the way to chemical synthesis of carbon nanotubes.¹ Moreover, unlike benzene units in carbon nanorings,

benzene units in carbon nanobelts cannot rotate and the sidewall of benzene rings are essentially parallel to one another.³⁵ Chemists expected that CPAs are suitable candidates for growing carbon nanotubes because it is anticipated that CPAs would be thermally more robust.³⁶

However, there have been no effective syntheses of the π -conjugated carbon nanobelts and two main obstacles still remain: high strain energy and high reactivity of the resulting carbon nanobelts. High strain energy is the major problem facing the synthesis of highly bent carbon nanobelts which accrue at the last step during the arene skeleton building.¹ In addition, $[n]$ cyclacenes that related to zigzag-edged carbon nanobelts have not yet been synthesized due to their instability comparing to armchair-edged carbon nanobelts, $[n]$ cyclophenacenes.¹

Another aspect of analyzing the polycyclic system's stability and properties, such as polycyclic aromatic hydrocarbons (PAHs), is the Clar's rule.³⁷ Clar's rule states that the Kekulé resonance structure with the most significant number of disjoint aromatic π -sextets, i.e., benzene-like moieties, is critical for the characterization of the properties of PAHs. The definition of the aromatic π -sextets is that six π -electrons localized in a single benzene-like ring isolated from adjacent rings by formal CC single bonds. The analysis of the Clar Structure,³⁷ in $[n]$ cyclacene shows that there are no isolated sextets that can be identified, which is presented in the Clar structure of $[n]$ cyclophenacene, thus underlining the higher stability of $[n]$ cyclophenacenes (Figure 1.5).¹

Figure 1.5. Clar structures for $[n]$ cyclacene (A) and $[n]$ cyclophenacene (B).

In order to overcome those obstacles, chemists have developed two main conceptual approaches to synthesize carbon nanobelts.¹ The first strategy is to synthesize a partially saturated double-stranded macrocycle followed by the attempt to fully aromatize the macrocycle.³⁸ The second reported strategy focuses on constructing a single-stranded conjugated macrocycle following by closing up the fjord regions by dehydrogenation cyclization reactions.³⁹

1.4.2 Synthetic Attempts for the Preparation of CPAs

Early Synthetic Attempts of Cyclophenacenes

The first attempt for synthesizing of zigzag-edged carbon nanobelt [12]cyclacene was reported by Stoddart and co-workers in 1987 (Scheme 1.9).⁴⁰ Their strategy relied upon reducing the strain energy by designing a double-stranded partially saturated macrocyclic precursor via the Diels-Alder reactions following by the aromatization step through deoxygenation and dehydration. Different dehydrogenation reagents have been used to aromatize the precursor in order to achieve the targeted carbon nanobelt. However, all attempts were unsuccessful because of the high strain energy and intrinsic high reactivity of [12]cyclacenes.⁴⁰

Scheme 1.9. Stoddart's Attempts for the Synthesis of [12]Cyclacene

In 1996, Cory reported the synthetic strategy for macrocyclic belt [8]cyclacene.⁴¹ Cory also applied the idea of using a bifunctional monomer for a double Diels–Alder macrocyclization

reaction (Scheme 1.10). Unlike Stoddart's rigid monomers, Cory employed a flexible monomer that allowed the curvature to be more natural with low strain energy and theoretically more susceptible to aromatization.⁴² Different attempts in the final aromatization step of the precursor were reported, but unfortunately only with partial success without the formation of the final [8]cyclacene.

Scheme 1.10. Cory's Attempts for the Synthesis of [8]Cyclacene

The second reported strategy focuses on constructing a single-stranded, conjugated macrocycle, followed by closing up the fjord regions by dehydrogenative cyclization.¹ Wittig and Lehman reported the first attempted chemical synthesis of carbon nanobelts in 1957.⁴³ They were able to successfully synthesize an all-cis-hexabenzo[12]annulene that could serve as a precursor leading to the (3,3)armchair carbon nanotube. However, the intramolecular cyclodehydrogenation reaction of the precursor only afforded products that derived from C-C bond cleavage (Scheme 1.11).

Scheme 1.11. Wittig and Lehman's Attempts for the Synthesis of (3,3) Armchair Carbon Nanobelt.

In 2002, Iyoda and his colleagues provided an evidence that armchair-edged carbon nanobelts $[n]$ cyclophenacenes could be synthesized (Scheme 1.12).^{44c} The group successfully synthesized a series of *cis*-benzannulenes as carbon nanobelts precursors. However, converting the precursors to the final products via chemical or photochemical cyclodehydrogenation failed. The good sign was observing a peak correlated to the cation of $[8]$ cyclophenacene by laser-desorption mass spectrum which confirms that $[n]$ cyclophenacenes could be synthesized and also isolated.

Scheme 1.12. Iyoda's Attempts for the Synthesis of $[n]$ Cyclophenacenes

In 2003, Nakamura and his research group reported the first cyclophenacene derivative by multistep, site-selective addition reactions starting from $[60]$ fullerene (Scheme 1.13).⁴⁵ The strategy began with a highly strained precursor, $[60]$ fullerene, in order to avoid the necessity of building up strain during the synthesis. They were able to isolate the conjugated belt $[10]$ cyclophenacene around the equator of the fullerene. However, no further chemical modification can be done due to the limited space on this doubly capped $[10]$ cyclophenacene derivative.

Scheme 1.13. Synthesis of a Fullerene-Derived $[10]$ Cyclophenacene by Nakamura

First Carbon Nanobelt Synthesized by Itami

In 2017, Itami's group ultimately reported the successful synthesis and characterization of a parent carbon nanobelt, which can be regarded as a segment of an armchair carbon nanotube (Scheme 1.14).⁴⁶ There are two key reasons that contributed to the success of this synthesis. The first reason involved the synthesis of an all cis-benzannulene macrocycle precursor, which is similar to Iyoda's precursor reported in 2002, with two bromine atoms attached to each benzene ring. The functionalized benzene ring in Itami's precursor allowed the use of nickel-mediated homocoupling reaction for ring cyclization instead of applying chemical or photo-chemical oxidative dehydrogenation reactions. The second reason for success was due to the presence of two bromine atoms attached to each benzene ring, which induced the Z-selectivity in the Wittig reaction and facilitated the synthesis of all-Z-benzannulene precursor. Although the yield was only 7%, the final cyclization step afforded the targeted carbon nanobelt.

Scheme 1.14. Itami's Successful Synthesis of Carbon Nanobelt

1.5 Our Synthetic Approach to [n]Cyclophenacene

With the success of synthesizing carbon nanobelts by Itami and coworkers, it suggested that other carbon nanobelts can be further investigated and explored. This success also encouraged

other chemists to synthesize carbon nanobelt with different sizes, different functional groups and eventually carbon nanotube. Here we are attempting to develop a synthetic pathway for the construction of armchair carbon nanobelts relying on previously accumulated knowledge, strategies and developed methods.

Our synthetic pathway has two main stages. The first stage involved the preparation of 2,7-dibromo-1,8-bis(bromomethyl)phenanthrene and 2,7-dibromo-1,8-bis(hydroxymethyl)phenanthrene, starting from the homocoupling reaction of 6-amino-3-bromo-2-methylbenzoic acid hydrochloric salt (Scheme 1.15).

Scheme 1.15. The First Stage of Our Synthetic Approach

The second stage of the synthetic sequence involved the investigation of different methods to convert 2,7-dibromo-1,8-bis(bromomethyl)phenanthrene and 2,7-dibromo-1,8-bis(hydroxymethyl)phenanthrene into dimer, trimer or tetramer macrocycles bearing the carbon framework of cyclophenacenes.

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Chapter 2. Synthesis of 2,7-Dibromo-1,8-bis(hydroxymethyl)phenanthrene

2.1 Introduction

To achieve large, structurally well-defined aromatic molecules and conjugated polymer, phenanthrenes represent useful intermediates due to its stability, accessible to characterize, no conformational rotation, and potentially synthetically approachable.¹ In particular, our attention was focused on designing and synthesizing phenanthrene derivatives that can be used for macrocyclization toward our desired cyclophenacenes (CPAs).

Here, we have developed a synthetic pathway leading to a macrocycle bearing the carbon framework of [16]cyclophenacene, which is the shortest macrocyclic belt-like structure of an (8,8)armchair carbon nanotube. Our developed synthetic pathway has two main stages. The first stage involved the preparation of 2,7-dibromo-1,8-bis(hydroxymethyl)phenanthrene (**II-3**), starting from the homocoupling reaction of 6-amino-3-bromo-2-methylbenzoic acid hydrochloride salt (**II-1**) (Scheme 2.1). The next stage of the synthetic sequence involved converting 2,7-dibromo-1,8-bis(hydroxymethyl)phenanthrene into a macrocycle bearing the carbon framework of cyclophenacenes.

Scheme 2.1. The First Stage of Our Synthesis

2.2 Development of a Pathway for the Synthesis of 4,4'-Dibromo-3,3'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic Acid (II-2).

2.2.1 Introduction

Conjugated π systems are of particular interest due to their delocalized electrons which are expected to favor electronic transport through their structures.² Molecules with π conjugated systems, single-molecule wires³⁻⁵ or polymers,⁶⁻⁹ have received much interest as potential functional subunits, for instance, in molecular electronics,¹⁰ photovoltaics,¹¹⁻¹² or light-emitting systems.¹³

Biphenyls is the smallest structure that comprises two adjacent benzene rings as individual π systems. Biphenyls have attracted considerable attention from chemists and have been synthesized¹⁴⁻¹⁵ through the diazonium salts of the corresponding anthranilic acids followed by the coupling of the radicals generated *in situ* (Scheme 2.2).

Scheme 2.2. Examples of Reported Syntheses of Biphenyls Compounds

2.2.2 Oh's Synthesis of 4,4'-Dibromo-3,3'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic Acid (**II-2**).

Our targeted compound diphenic dicarboxylic acid **II-2** was reported in 2014 by Oh (Scheme 2.3).¹⁶ In Oh's strategy, diphenic dicarboxylic acid **II-5** was prepared via the formation of the diazonium salt from the commercially available 2-amino-6-methylbenzoic acid (**II-4**), followed by coupling of the radical generated *in situ*. The following step was the bromination of the resulting diphenic dicarboxylic acid **II-5** using dibromoisocyanuric acid (DBI) as a brominating agent in the presence of concentrated sulfuric acid and an inert solvent, affording the desired product **II-2**. Although it was not mentioned in the paper, brominated isomers were expected.

Scheme 2.3. Oh's Synthetic Approach to **II-2**

2.2.3 Problems

Following Oh's synthetic approach, we started our synthesis by preparing diphenic dicarboxylic acid **II-5** from the diazonium salt prepared from 2-amino-6-methyl benzoic acid (**II-4**). The diazonium salt then went through the homocoupling reaction to afford **II-5** in 64% yield (Scheme 2.4).

Scheme 2.4 Preparation of Diphenic Carboxylic Acid II-5

However, in our hands treatment of **II-5** with dibromoisocyanuric acid in the presence of concentrated sulfuric acid produced a mixture of isomers (Scheme 2.5). We first treated **II-5** with 2.2 equivalents of DBI in the presence of concentrating sulfuric acid overnight at room temperature, affording diphenic dicarboxylic acid **II-6** as the major product, which most likely arises from the so called halogen dance reaction that will be discussed in the following section. In Oh's method, it was mentioned that an inert solvent was used without mentioning in the paper what solvent was used. It was possible that with this condition involving an inert solvent, they might be able to avoid the formation of **II-6**. We therefore used dichloromethane as an inert solvent to carry out the bromination reactions. Although the desired product diphenic dicarboxylic acid **II-2** was detected by NMR spectroscopy, other isomers were also produced.

Scheme 2.5 Different Isomers Obtained by Bromination of II-5

Compound **II-6** was detected readily by proton NMR spectroscopy (Figure 2.1). It was found that there are two singlet signals in the aromatic region. The first singlet occurred at 8.02 ppm, which corresponding to (H6). The second singlet occurred at 7.81 ppm, corresponding to (H4). Compound **II-7** also was detected by the NMR spectroscopy. The spectra show a triplet at 7.22 ppm corresponding to (H5'), two duplets at 7.68 and 7.60 ppm corresponding to (H6 and H6') and two duplets at 7.04 and 6.92 ppm corresponding to (H5 and H4').

Figure 2.1. ¹H NMR of the structures of compounds **II-6** and **II-7**

2.2.4 Halogen Dance Reaction

The halogen dance (HD) reaction was discovered by Vaitiekunas in 1951 when he isolated the unexpected tetra-bromothiophene instead of 2-ethynylthiophene upon the reaction of 2-bromothiophene with sodium acetylide in liquid ammonia. Further studies aimed to investigate the reaction of the halogenated thiophenes and sodium amide in the presence of liquid ammonia was applied (Scheme 2.6).¹⁷ It is found that dibromothiophenes generally gave tetrabromothiophene and mono-bromothiophene. The reaction represents a base induced reaction of a haloaromatic compound in which the position of the halogen atom in the product differs from its position in the starting material. The driving force behind this rearrangement process is that the migration proceeds into the direction of the most stable anion or metalated species.¹⁸

Scheme 2.6. Discovery of Halogen Dance Reaction by Vaitiekunas in 1951

The halogen dance reaction was widely studied, particularly the one that was induced by organic lithium bases, such as LAD or LTMP. However, there are also some examples of halogen migrations under neutral or acidic conditions. One example of the acid-catalyst halogen dance reaction on deactivated pyrroles was reported by Quarteri in 2010 (Scheme 2.7).¹⁹ The pyrrole derivative, which was reacted under strongly acidic conditions, ended up producing four different compounds.

Scheme 2.7. Acid-Catalyzed Halogen Migration of a Bromopyrrole System

In our case, the HD reaction was also observed when treating diphenic carboxylic acid **II-5** with DBI under highly acidic conditions. Under this condition, product **II-6** was obtained instead of the expected product **II-2** (Scheme 2.5). The proposed mechanism is shown in (Scheme 2.8). Treating diphenic **II-5** with DBU first will afford **II-2** as a kinetic product. However, because the reaction is reversible the kinetic product **II-2** can revert to the original reactant diphenic **II-5** and react again to form the thermodynamic product **II-6**. Although the methyl group is an ortho and para directing group and the carboxylic acid is a meta directing group, the product that obtained here was compound **II-6** in which the bromine is placed in the position that is meta to the methyl group. In conclusion, it seems that product **II-2** is less stable due to the higher steric hindrance, which lead to the formation of the thermodynamically more stable product **II-6**, conceivable due to less steric hindrance.

Scheme 2.8. The Proposed Mechanism of the Acid-Catalyzed Halogen Migration of II-2

The proposed mechanism:

2.2.5 Our Synthetic Approach to 4,4'-Dibromo-3,3'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic Acid (II-2**).**

To overcome the production of the undesired product **II-6** and the difficulty of defining and separating the desired product **II-2** from the other isomers, we established a new synthetic pathway leading to **II-2** as the major product. In our method, we decided to first brominate the anthranilic acid **II-4** by following the reported procedure published by Comess in 2004 (Scheme 2.9).²⁰

The first step involved the protection of the amine group in the anthranilic acid **II-4** using di-*tert*-butyl dicarbonate to afford **II-11** in 93 % yield. Bromination of **II-11** was accomplished with good yield using tetrabutylammonium tribromide to provide **II-12** in 92% yield, which then underwent deprotection of the *tert*-butoxycarbonyl (Boc) group using 4 M hydrogen chloride in dioxane at room temperature for 2 hours to produce **II-1** as a hydrochloride salt in 97% yield.

Scheme 2.9. Synthesis of the Hydrochloric Salt **II-1**

Formation of the diazonium salt from **II-1** followed by coupling of the radical generated *in situ* gave **II-2** in good yield. Due to the low solubility of acid **II-1**, aqueous sodium hydroxide solution was used to improve the solubility.²¹ It is worth noting that careful temperature control is a key factor to obtain an acceptable yield of **II-2** (Scheme 2.10). We are delighted to be able to report that selective bromination of the commercially available 2-amino-6-methylbenzoic acid **II-4** followed by the coupling reaction of the diazonium salt from **II-1** afforded diphenic carboxylic acid **II-2** as the major product.

The diphenic dicarboxylic acid **II-2** was then reduced, without any further purification, to the diol **II-13** by using sodium borohydride as the reducing agent and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the activating Lewis acid.²² Crystallization of the crude diol from methylene chloride and hexanes gave **II-13** in 53% yield over two steps from **II-1**. Oxidation of the two alcohol moieties using Swern oxidation yielded the desired dialdehyde **II-14** in 65 % yield.

Scheme 2.10. Preparation of Diphenic Carboxylic Acid **II-2, Diol **II-13**, and Dialdehyde **II-****

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Cyclization of **II-14** using hydrazine monohydrate and glacial acetic acid gave **II-15** in 93% yield (Scheme 2.11).²³ It is known that the reaction of hydrazine with diphenyl-2,2'-dialdehyde under acidic or alkaline conditions give phenanthrene in good to excellent yield. The mechanism of the addition of hydrazine to carbonyl functional group is illustrated in Scheme 2.12. Under the acidic condition, the mechanism started from the nucleophilic addition of hydrazine to the first carbonyl functional group following by deprotonated of nitrogen atom to form the hydrazone intermediate **A**. Intramolecular cyclization will occur due to the bifunctionality of hydrazine. Second nucleophilic addition with the second carbonyl group will occur resulting in the formation of cyclic azine containing a central eight-membered (1,2-diazocine) ring intermediate **B**. Upon heating, the eight-membered ring undergo ring rearrangement and finally losing nitrogen gas to produce the corresponding phenanthrene derivative **II-15**.

Scheme 2.11. Preparation of Phenanthrene II-15

Scheme 2.12. The Mechanism of Cyclization Reaction Through Hydrazine

Radical bromination of **II-15** was then performed by using *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of benzoyl peroxide (BPO) as the initiator and carbon tetrachloride as the solvent to provide **II-16** in 74% yield.²⁴ Tetrabromide **II-16** was then treated with CaCO₃/H₂O to promote nucleophilic substitution reactions to give diol **II-3** in 92% yield (Scheme 2.13).

Scheme 2.13 Preparation of II-16 & II-3

2.3 Summary

In summary, we have successfully synthesized 2,7-dibromo-1,8-bis(hydroxymethyl)phenanthrene (**II-3**) containing suitable functional groups as the starting material that could be used in the macrocyclization reaction leading to a macrocycle bearing the carbon framework of cyclophenacenes. Along the synthetic pathway, we developed an alternative and efficient pathway of preparing 4,4'-dibromo-3,3'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic acid **II-4** as the major product.

2.4 General Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under an argon atmosphere. Oil bath was used as the heating source for the reactions that required heating. 6-Amino-3-bromo-2-methylbenzoic acid hydrochloride salt II-1 was prepared according to the reported procedure.²⁰ All chemicals, including 2-amino-6-methylbenzoic acid, di-*tert*-butyl dicarbonate, copper(II) sulfate pentahydrate, hydroxylamine hydrochloride, sodium borohydride, boron trifluoride diethyl etherate, oxalyl chloride, DMSO, hydrazine monohydrate, carbon tetrachloride, *N*-bromosuccinimide, and benzoyl peroxide, were purchased from chemical suppliers and used in the synthesis directly without further purification. Infrared (IR) spectra of solid samples were recorded on a Fourier transform infrared system equipped with a diamond crystal attenuated total reflectance sampling interface. HRMS spectra were obtained on an Orbitrap mass analyzer coupled with electrospray ionization (ESI).

Experimental Procedure for 2-[(*tert*-butoxycarbonyl)amino]-6-methylbenzoic Acid (II-11). To a 500-mL flask were added 2-amino-6-methylbenzoic acid **II-4** (15.0 g, 99.2 mmol), di-*tert*-butyl dicarbonate (22.7 g, 104 mmol), anhydrous acetonitrile (150 mL), and triethylamine (15.2 mL, 109 mmol). The reaction mixture was stirred at rt for 18 h and then concentrated in vacuo at 70 °C. The residue was partitioned between water (200 mL) and dichloromethane (150 mL) and acidified with 1 M HCl (100 mL). The organic layer was separated and washed with 1 M HCl (100 mL), water, and brine, dried over Na₂SO₄, and then concentrated in vacuo. The residue

was passed through a short pad of silica gel column and eluted with 5% methanol in dichloromethane. The solvents were then evaporated in vacuo to give **II-11** (23.2 g, 92.3 mmol, 93% yield) as a white solid: ^1H NMR (400 MHz, DMSO- d_6) δ 8.94 (1 H, s), 7.56 (1 H, d, J = 8.2 Hz), 7.29 (1 H, t, J = 7.9 Hz), 6.97 (1 H, d, J = 7.6 Hz), 2.36 (3 H, s), 1.43 (9 H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 169.6, 152.9, 137.6, 130.6, 125.9, 123.9, 119.4, 79.8, 28.2, 21.5.

Experimental Procedure for 3-Bromo-6-[(*tert*-butoxycarbonyl)amino]-2-methylbenzoic Acid (II-12). To a solution of **II-11** (23.2 g, 92.3 mmol), tetrabutylammonium tribromide (47.0 g, 97.5 mmol), and DMF (250 mL) was slowly added water (250 mL), and the resulting solution was stirred at rt for 18 h. The reaction mixture was then partitioned between water (250 mL) and ethyl acetate (250 mL). The organic layer was separated, washed with water (7 $\times$ 500 mL) and brine, dried over Na_2SO_4 , and then concentrated in vacuo at 60 $^\circ\text{C}$ to provide **II-12** (28.0 g, 84.8 mmol, 92% yield) as a white solid: ^1H NMR (400 MHz, DMSO- d_6) δ 8.64 (1 H, s), 7.62 (1 H, d, J = 8.7 Hz), 7.36 (1 H, d, J = 8.8 Hz), 2.36 (3 H, s), 1.42 (9 H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 168.4, 153.0, 135.4, 135.0, 133.6, 123.0, 119.9, 79.9, 28.1, 21.0.

II-1

Experimental Procedure for 6-Amino-3-bromo-2-methylbenzoic acid hydrochloride salt (II-1). In a 1-L flask was dissolved **II-12** (28.0 g, 84.8 mmol) in 4 M HCl (200 mL) and dioxane (400 mL), and the reaction mixture was stirred at rt for 2 h. The resulting white precipitate was filtered, and the filtrate was concentrated in vacuo at 80 °C. A small amount of white precipitate appeared, which was filtered and combined with the white precipitate collected earlier. The combined white precipitates were air-dried to give **II-1** (22.0 g, 82.5 mmol, 97% yield) as a white solid: ^1H NMR (400 MHz, DMSO- d_6) δ 7.38 (1 H, d, J = 8.8 Hz), 6.69 (1 H, d, J = 8.7 Hz), 2.34 (3 H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 168.7, 142.7, 136.1, 134.4, 121.5, 117.7, 114.3, 21.3.

II-2

Experimental Procedure for 4,4'-Dibromo-3,3'-dimethyl[1,1'-biphenyl]-2,2'-dicarboxylic Acid (II-2). A solution of NaNO_2 (0.932 g, 13.5 mmol) in water (3.6 mL) was added dropwise to an ice-cold solution of **II-1** (3.00 g, 11.3 mmol) in a 2.45 M solution of NaOH (10.6 mL) and water (9 mL). The reaction mixture was stirred at 0 °C until it became homogeneous. An ice-cooled 4 M aqueous solution of HCl (14.5 mL) was added slowly at a rate such that the temperature was maintained below 5 °C. The resulting orange solution of the diazonium salt was

stirred at 0 °C for 1 h. To a 100-mL flask were added CuSO₄·5H₂O (5.62 g, 22.5 mmol) and water (20 mL), and the resulting solution was cooled in an ice bath. After the solution reached 5 °C, a 30% NH₄OH solution (10 mL) was added in one portion followed by the addition of a freshly prepared solution of NH₂OH·HCl (1.67 g, 24.0 mmol) in 6 M NaOH (4.0 mL, 24 mmol) in one portion. The resulting dark-blue solution was stirred at 0 °C for 30 min. The diazonium salt was then introduced to the copper solution in portions to maintain the temperature below 7 °C. The resulting solution was then stirred at 25 °C for 15 min and then heated at 70 °C for 1 h. The mixture was then allowed to cool to rt and acidified with concentrated HCl (20 mL). The brown precipitate was collected by filtration, washed with water, and air-dried to give 2.10 g of the crude **II-2** as a brown powder. An analytical sample of **II-2** was prepared by recrystallization of a sample of the crude **II-2** from hot ethanol by adding drops of water to induce the formation of pale brown crystals: mp = 186–187 °C ; IR 3200–2750 (br), 1723, 1257 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.69 (2 H, d, *J* = 8.2 Hz), 7.03 (2 H, d, *J* = 8.3 Hz), 3.39 (2 H, br s), 2.37 (6 H, s); ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 169.8, 137.5, 134.8, 134.0, 129.2, 128.1, 127.1, 19.5; HRMS (ESI) *m/z* [M – H]⁻ calcd for C₁₆H₁₁Br₂O₄ 424.9030, 426.9009, 428.8989; found 424.9044, 426.9015, 428.8976.

II-13

Experimental Procedure for 4,4'-Dibromo-3,3'-dimethyl-[1,1'-Biphenyl]-2,2'-dimethanol (II-13). To a 100-mL flask under argon were added the crude **II-2** (1.94 g) and 40 mL

of anhydrous THF. Sodium borohydride (0.685 g, 18.1 mmol) was added slowly in small portions to keep the temperature below 30 °C, and the solution was then stirred at rt for 1 h before BF₃·Et₂O (3.5 mL, 28 mmol) was added dropwise. The reaction mixture was then stirred at 45 °C for 12 h, quenched with a solution of 5% HCl (2.5 mL) in ethyl acetate (47.5 mL), and filtered through a Celite pad. The brown filtrate was washed with a saturated Na₂CO₃ solution, water, and brine, and then dried over Na₂SO₄. The solvents were evaporated in vacuo at 60 °C, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 30:70) to produce **II-13** (1.10 g, 2.75 mmol, 53% yield) as a pale-brown solid: mp = 138–139 °C; IR 3253 (br), 1004 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (2 H, d, *J* = 8.2 Hz), 6.81 (2 H, d, *J* = 8.2 Hz), 4.51 (2 H, d, *J* = 11.8 Hz), 4.18 (2 H, d, *J* = 11.7 Hz), 3.35 (2 H, br s), 2.58 (6 H, s); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 140.1, 138.3, 138.2, 131.9, 128.2, 125.7, 59.9, 19.3; HRMS (ESI) *m/z* [M – H]⁻ calcd for C₁₆H₁₅Br₂O₂ 396.9444, 398.9424, 400.9403; found 396.9436, 398.9393, 400.9384.

II-14

Experimental Procedure for 4,4'-Dibromo-3,3'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxaldehyde (II-14). A solution of oxalyl chloride (0.29 mL, 3.4 mmol) in 10 mL of dichloromethane was cooled at –78 °C in a dry ice/acetone bath under argon. DMSO (0.34 mL, 4.8 mmol) was then added carefully by using a syringe. After 15 min of stirring, a solution of **II-13** (0.500 g, 1.25 mmol) in 5 mL of dichloromethane was added via cannula, and the reaction

mixture was stirred for 1.5 h. Triethylamine (1.08 mL, 7.75 mmol) was added, and the reaction mixture was allowed to warm to rt. The reaction mixture was then transferred into a separatory funnel, washed with 5% HCl (30 mL), saturated NaHCO₃, and brine, and then dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo at 40 °C, and the residue was purified by crystallization from hot diethyl ether to produce **II-14** (0.322 g, 0.813 mmol, 65% yield) as pale-yellow crystals: mp = 107–108 °C; IR 1692, 1396, 1153, 829 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.96 (2 H, s), 7.77 (2 H, d, *J* = 8.1 Hz), 6.95 (2 H, d, *J* = 8.1 Hz), 2.74 (6 H, s); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 192.2, 141.2, 139.8, 136.2, 134.8, 129.9, 127.7, 19.7; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₆H₁₃Br₂O₂ 394.9277, 396.9256, 398.9236; found 394.9271, 396.9250, 398.9230.

II-15

Experimental Procedure for 2,7-Dibromo-1,8-dimethylphenanthrene (II-15). To a 100-mL two-neck flask were added **II-14** (0.800 g, 2.02 mmol) and glacial acetic acid (15 mL). The flask was then attached with a reflux condenser, and the reaction mixture was heated at reflux for 10 min. Hydrazine monohydrate (0.14 mL, 2.89 mmol) in glacial acetic acid (4 mL) was introduced to the reaction mixture dropwise by using a syringe. The reaction mixture was then stirred for an additional 2.5 h before it was allowed to cool to rt. The acetic acid was evaporated in vacuo at 50 °C, and the residue was washed with water and dried in vacuo. Purification of the residue by flash column chromatography (silica gel/hexanes) produced **II-15** (0.680 g, 1.87 mmol,

93% yield) as a white solid: mp = 134–135 °C; IR 1449, 817, 792 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (2 H, d, *J* = 9.1 Hz), 8.05 (2 H, s), 7.79 (2 H, d, *J* = 9.0 Hz), 2.87 (6 H, s); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 133.9, 131.2, 130.7, 129.4, 123.9, 123.8, 122.1, 19.1; HRMS (ESI) *m/z* [M – H]⁻ calcd for C₁₆H₁₁Br₂ 360.9233, 362.9213, 364.9192; found 360.9245, 362.9222, 364.9162.

II-16

Experimental Procedure for 2,7-Dibromo-1,8-di(bromomethyl)phenanthrene (II-16).

To a 100-mL flask were added **II-15** (1.50 g, 4.12 mmol), benzoyl peroxide (0.020 g, 0.083 mmol), and CCl₄ (15 mL). NBS (1.47 g, 8.24 mmol) was then added in one portion, and the reaction mixture was heated at reflux for 20 h before it was allowed to cool to rt. The reaction mixture was then filtered, and the white solid was washed with water and cold toluene, and then air-dried to produce **II-16** (1.60 g, 3.07 mmol, 74% yield) as a white solid: mp = 180–181 °C; IR 1584, 1447, 818, 800, 793 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (2 H, d, *J* = 9.1 Hz), 8.24 (2 H, s), 7.85 (2 H, d, *J* = 9.0 Hz), 5.19 (4 H, s); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 133.0, 131.5, 130.8, 129.9, 124.95, 124.88, 124.1, 30.1; anal. calcd for C₁₆H₁₀Br₄: C, 36.82; H, 1.93; Br, 61.24; found: C, 37.02; H, 1.94; Br, 61.41.

II-3

Experimental Procedure for 2,7-Dibromo-1,8-bis(hydroxymethyl)phenanthrene (II-3). To a 100-mL flask were added **II-16** (0.600 g, 1.15 mmol) and dioxane (20 mL). A slurry of CaCO_3 (0.253 g, 2.53 mmol) in H_2O (10 mL) was added to the reaction mixture, and the reaction mixture was heated at reflux for 48 h. Dioxane and water were evaporated in vacuo at 80 °C, and the residue was treated with 6 M HCl until acidic. The reaction mixture was filtered, and the white solid was washed with water and then air-dried to give **II-3** (0.423 g, 1.07 mmol, 92% yield) as a white solid: mp = 184–185 °C; IR 3313 (br), 1006, 793 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.74 (2 H, d, $J = 9.1$ Hz), 8.32 (2 H, s), 7.87 (2 H, d, $J = 9.0$ Hz), 5.47 (4 H, t, $J = 5.1$ Hz), 5.14 (2 H, d, $J = 5.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{DMSO}-d_6$) δ 136.4, 131.5, 130.8, 129.4, 125.0, 124.9, 123.6, 60.4. Recrystallization of **II-3** from hexanes and dichloromethane produced a single crystal suitable for X-ray structure analysis.

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Chapter 3. Development of Synthetic Pathways Leading to Carbon Nanobelts

3.1 Cyclophanes and Related Macrocyclic Compounds

3.1.1 Introduction

After the first synthesis of anti-[2.2]metacyclophane by Pellegrin in 1899¹ and [2.2]paracyclophane by Cram in 1951,² cyclophanes have received much attention from the material chemists in terms of their essential role in host-guest chemistry³⁻⁷ and supermolecular assembly.⁸⁻¹¹ Cyclophanes are strained organic molecules consisting of aromatic rings, that provided the rigidity to the structure, as well as aliphatic chain that provided the flexibility to the overall structure.¹² The aliphatic chain connected two aromatic rings to form a bridge-like structure (Figure 3.1). When X in structure A is only CH₂ it is called cyclophanes, and it is calixarene when X is longer than CH₂ in one or more sites of the macrocyclic structure.¹³⁻¹⁶ Also, X can contain hetero analogs with X = CH₂OCH₂, CH₂SCH₂ or CH₂NRCH₂. In the cases of the oxygenated analogues, the macrocycles are named as homooxacalixarenes.¹³

Figure 3.1. A General Structure of Cyclophanes

Although a vast number of cyclophanes has been reported, only a very small proportion of them contain polycyclic aromatic systems. Here are some examples of macrocycles that were synthesized with an ether linkage between the aromatic units.

In 1998, Masci and coworkers reported the synthesis of *p*-*tert*-butylhomooxacalix[4]arene compounds with various combinations of CH₂ and CH₂OCH₂ units that connect between the aromatic rings (Scheme 3.1).¹³ For example, macrocycle **III-3** has CH₂OCH₂ bridge in all sites connecting the four aromatic rings, while macrocycle **III-6** has one CH₂ bridge in addition to three CH₂OCH₂ bridges to attach the four aromatic rings. Their method consists of a Williamson ether synthesis between a variety of hydroxymethylated and analogous bromomethylated phenylethers using powdered KOH in dioxane.

Scheme 3.1. Synthesis of Macrocycle III-3 & III-6 by Masci

In 2005, Georghiou reported the synthesis of macrocyclic molecules that are formed by a cyclic array having naphthalene ring-connecting units (Scheme 3.2).¹⁵ The synthesis of **III-11** was started by the base-mediated alkylation of diol **III-7** to produce di-*O*-alkylated **III-8**. Double bromoethylation of **III-8** afforded the corresponding bis-bromoethylated naphthyl ether **III-9**, which then underwent hydrolysis using CaCO_3 in aqueous dioxane leading to the bishydroxymethyl **III-10**. Several methods were applied to form the macrocyclic ether but was not successful, due to the steric hindrance resulting from the alkoxy groups on the naphthalene rings. Finally, macrocyclic **III-11** was observed in 12-18 % yield following Masci's methodology by applying Williamson ether synthesis using powdered KOH in dioxane.¹³

Scheme 3.2. Synthesis of Macrocyclic **III-11** by Georghiou

In 2008, Masci's group reported the synthesis of macrocyclic **III-14** (Scheme 3.3).¹⁷ They developed a synthetic pathway leading to a cyclophane featuring two opposite anthracene units. The cyclization step using NaH as a base in DMF or powdered KOH in dioxane was unsuccessful.^{16&18} However, using the heterogeneous Me_4NOH -dioxane system yielded **III-14** in 19 % yield.

Scheme 3.3. Synthesis of Macrocyclic **III-14** by Masci

Last but not least, Levine's research group synthesized macrocycle **III-19** in 2013 (Scheme 3.4).²⁰ The synthesis started with a double Williamson ether synthesis between **III-15** and **III-16**, affording **III-17** in 81 % yield. The linear precursor **III-18** then was achieved via double Suzuki reactioin in 94 % yield. The key macrocyclization step was accomplished via a double etherification reaction to provide macrocycle **III-19** in 24% yield.

Scheme 3.4. Synthesis of Macrocycle **III-19** by Levine

3.2 Our Attempts in Synthesizing Macrocyclic Dimer, Trimer, and Tetramer of II-3

Ethers have been prepared by the different protocols such as Williamson ether synthesis, the Mitsunobu reaction, biomolecular dehydration, the Ullmann method, the Cu(II)-catalyzed synthesis, a transition metal-free coupling reaction between aliphatic alcohols and unsymmetrical diaryliodonium salts, and more.²¹ After the success in the first stage of our synthetic pathway described in Chapter 2, which included the synthesis of both monomers **II-3** and **II-16** as essential fragments for the construction of macrocycles, the next stage involved the investigation of methods to convert monomer diol **II-3** into macrocyclic dimer **III-20**, macrocyclic trimer **III-21**, and macrocyclic tetramer **III-22**. It was anticipated that macrocyclic tetramer **III-22** could undergo intramolecular homocoupling reactions to give the desired macrocyclic **III-23** bearing the carbon framework of [16]cyclophenacene (Scheme 3.5).

Scheme 3.5. The Second Stage of Our Synthetic Pathway

3.2.1 Attempts for the Preparation of Macrocyclic Tetramer **III-22**

The Williamson ether synthesis was widely used in the synthesis of ethers using an organohalide and deprotonated alcohol (alkoxide). Here, the first method that was investigated was the Williamson ether synthesis of monomer **II-16** and **III-25** to produce the desired macrocycle. The first step involved the monosilylation of monomer diol **II-3**, and the reagents that were used here were TBS-Cl and imidazole with DCM as the solvent (Scheme 3.6).²² Under the condition shown in Scheme 3.6, part A, it was observed that only the di-protected monomer **III-24** was obtained along with unreacted monomer diol **II-3**. This problem occurred due to the low solubility of the monomer diol **II-3** in the DCM solvent. To overcome this problem, the DCM solvent was replaced by DMF to enhance the solubility of diol **II-3**, and heating was required to push the reaction toward the desired product **III-25** (Scheme 3.6 B). However, the desired product was produced in low yield.

Scheme 3.6. Monosilylation of Monomer Diol **II-3 With TBS-Cl and Imidazole**

Another way that we tried to obtain the mono silyl ether **III-25** in a better yield was the deprotection of one side of the silyl groups in di-protected monomer **III-24**. It is known that Lewis acid in acetonitrile can be used to cleave silyl ether effectively at room temperature.²³ Treatment of di-protected monomer **III-24** with 0.5 equivalent of FeCl₃ unfortunately was too harsh a condition, and silyl ether **III-24** was cleaved on both sides to give the monomer diol **II-3** after only 5 minutes of reaction (Scheme 3.7).

Scheme 3.8. Monosilylation of Monomer Diol II-3 With TBSOTf and 2,6-Lutidine

The use of Williamson ether synthesis between **II-16** and **III-25** yielded the acyclic trimer **III-26** in 24% yield. Desilylation of **III-26** with TBAF gave acyclic trimer diol **III-27** in 81% yield (Scheme 3.9).²⁵ However, the use of Williamson ether synthesis between acyclic trimer diol **III-27** and monomeric tetrabromide **II-16** was not successful due most likely to the extremely low solubility of the acyclic trimer diol **III-27** in DMF.

Scheme 3.9. Our First Attempt to Prepare Macrocyclic Tetramer **III-22**

3.2.2 Attempts for the Preparation of Macrocyclic Trimer **III-21**

Since the acyclic trimer **III-27** cannot be used further due to its low solubility, it was essential to find a reaction condition that could allow the use of the more soluble acyclic TBS-trimer **III-26** for direct macrocyclization to produce the macrocyclic trimer **III-21**.

It was reported that benzylation of benzene and benzene derivatives, such as toluene and anisole, with benzyl alcohol or benzyl chloride could be catalyzed by ion-exchange resins (Lewatit and Amberlyst-15).²⁶ Particularly, we were interested in learning that benzylation of benzene with benzyl alcohol using Amberlyst-15 afforded dibenzyl ether **III-30** in good yield (Scheme 3.10).

Scheme 3.10. Ion-exchange Resins-Catalyzed Benzylation of Benzene with Benzyl Alcohol

The use of Amberlyst-15 as a catalyst for the benzylation reaction was investigated on 2-bromobenzyl alcohol for a model study. Benzyl alcohol **III-31** was first silylated with a trimethylsilyl group and a *tert*-butyldimethylsilyl group to produce **III-32** and **III-33**, respectively (Scheme 3.11).

Scheme 3.11. Silylation of Alcohol III-31

Treatment of **III-32** with Amberlyst-15 produced dibenzyl ether **III-34** in 20% yield and alcohol **III-31** as the major product. Treatment of **III-33** with an increasing amount of Amberlyst-

15 and under a higher concentration enhanced the yield of dibenzyl ether **III-34** up to 75% yield (Scheme 3.12).

Scheme 3.12. Benzylation Reaction in the Presence of Amberlyst-15

To better understand the reaction illustrated in Scheme 3.12, we did further investigation to explain how alcohol **III-31** was obtained along with the desired product. Benzyl alcohol **III-31** can be generated either from hydrolysis of the starting materials **III-32** and **III-33** or from the ether cleavage in the product **III-34**. It is known that hydrolysis of ether usually achieved in the presence of a large surplus of water, which drives the reaction towards alcohol by Le Chatelier's principle. So, treating **III-33** with Amberlyst-15 and 0.1% of H₂O, benzyl alcohol was found to be the major product. In the presence of a water molecule, the reaction shifted to the left, forming benzyl alcohol as the major product (Scheme 3.13).

Scheme 3.13. Hydrolysis of **III-34**

Unfortunately, macrocyclic trimer **III-21** was not obtained using Amberlyst-15 as a catalyst. Treatment of **III-26** with Amberlyst-15 in dilute condition did not produce the desired macrocyclic trimer **III-21**, and only starting material was observed after 18 hours of stirring at 80 °C (Scheme 3.14). Repeating the reaction at a higher concentration and stirring over two days at 80 °C produced only trimer diol **III-27**.

Scheme 3.14. An Attempt for the Preparation of Macrocyclic Trimer III-21

3.2.3 Attempts for the Preparation of Macrocyclic Dimer III-20

The reductive etherification reaction is a direct and straightforward method for the synthesis of symmetrical ether. It was reported that aldehydes and ketones can smoothly undergo reductive etherification under a mild condition using polymethylhydrosiloxane (PMHS) in the presence of molecular iodine as a catalyst to produce an excellent amount of the corresponding symmetrical ether.²⁷ The sterically hindered mesitylaldehyde produced the corresponding dibenzyl ether in 82% isolated yield at room temperature in 45 minutes.

To examine the use of PMHS, monomer diol **II-3** was first oxidized to monomer dialdehyde **III-35**. Treatment of monomer diol **II-3** with PCC afforded dialdehyde **III-35** in 91 % yield. Monomer dialdehyde **III-35** was then treated with PMHS and a catalytic amount of (2.5 mol%) molecular iodine for reductive etherification. The desired macrocycle **III-20** was not obtained under this condition (Scheme 3.15). Upon increasing the amount of molecular iodine approximately to 1 eq, monomer diiodide **III-36** was obtained in 52 % yield.

Scheme 3.15. Attempt to produce Macrocyclic Dimer III-20 From Dialdehyde III-35

Moreover, reductive etherification reaction using PMHS in presence of molecular iodine was employed using acyclic dimer dialdehyde **III-39**. Acyclic dimer **III-37** was prepared by Williamson ether synthesis *in situ* by coupling the alkoxide with sulfonate ester (Scheme 3.15). Treating mono-silylated **III-25** with sodium hydride and 4-butylbenzenesulfonyl chloride in THF

provided dimer **III-37** in 65 % yield. Desilylation of dimer **III-37** was accomplished by using 1% of HCl in methanol solution, providing dimer diol **III-38** in 85% yield. Treatment of acyclic dimer diol **III-37** with PCC in DCM gave dimer dialdehyde **III-39** in 72% yield.

Scheme 3.16. Preparation of Acyclic Dimer Dialdehyde III-39

Treatment of dialdehyde **III-39** with PMHS and a catalytic amount of (2.5 mol%) molecular iodine for reductive etherification did not afford the desired macrocycle **III-20** (Scheme 3.17). Upon increasing the amount of molecular iodine also monomer diiodide **III-36** was obtained.

Scheme 3.17. Attempt to produce Macrocyclic Dimer III-20 From Dialdehyde III-39

3.3 Investigations of Different Synthetic Methods for Dibenzyl Ether

3.3.1. Reductive Etherification of Carbonyl Compounds with Alkoxytrimethylsilanes

With the unsuccessful attempts of using Williamson ether synthesis and Amberlyst-15 for macrocyclization, other methods to prepare macrocyclic ethers were investigated. In 1994, Nishizawa and coworkers reported that TMSOTf efficiently catalyzed the synthesis of ether from ketones or aldehydes and alkoxytrimethylsilanes via triethylsilane reduction (Scheme 3.18).²⁸

Scheme 3.18. Reductive Etherification of Carbonyl Compounds by Nishizawa in 1994

Reductive etherification of 2-bromobenzaldehyde **III-40** with alkoxytrimethylsilanes **III-32** or alkoxy-*tert*-butyldimethylsilane **III-33**, catalyzed by TMSOTf followed by reduction with Et_3SiH , afforded dibenzyl ether **III-34** and benzyl alcohol **III-31** (Scheme 3.19).

Scheme 3.19. Reductive Etherification of Aldehyde III-40

Applying this condition for macrocyclization in our cases required the use of both **III-35** and silylation of monomer diol **II-3** (Scheme 3.20). The silylation reaction of monomer diol **II-3** with hexamethyldisilazane (HMDS) in the presence of a catalytic amount of iodine produced **III-41** in 96% yield. However, attempts to use the reductive etherification condition was unsuccessful, and only monomer **III-41** was hydrolyzed to give monomer diol **II-3**. The primary drawback of this method is that the TMS group in compound **III-41** is less reactive due to the steric hindrance resulting in significant hydrolysis leading to the recovery of only diol **II-3**.

Scheme 3.20. Our Attempt in Reductive Etherification of Dialdehyde III-35

3.3.2. Benzylolation of Alcohols Using Benzyl Trichloroacetimidates

In 1993, Schmeck and coworkers reported that primary, secondary, and tertiary alcohols that are sensitive under basic or acidic reaction conditions can be *O*-benzylated under mild acidic conditions using benzyl 2,2,2-trichloroacetimidate as the benzylation agent (Scheme 3.21).²⁹ A variety of alcohols for benzylolation were investigated using benzyl trichloroacetimidate and

trimethylsilyl trifluoromethanesulfonate (TMSOTf) or trifluoromethanesulfonic acid (TFMSA) as an acidic catalyst. It was observed that best results were obtained upon using TMSOTf as an acidic catalyst, producing desired products in good yield, whereas only moderate yields were obtained with TFMSA.

Scheme 3.21. *O*-Benzylation of Alcohols Under Mild Acidic Condition

In order to use this condition of benzylation, we first synthesized 2-bromobenzyl 2,2,2-trichloroacetimidate **III-42** and use it for reactions with **III-32** and **III-33**. Treatment of 2-bromobenzyl alcohol **III-31** with trichloroacetonitrile and DBU yielded the corresponding **III-42** in 80% yield.³⁰ Benzyl trichloroacetimidate **III-42** was then employed for the benzylation reaction with either **III-32** or **III-33**. In both cases the reactions were complete at rt in 3 h, giving only the desired benzyl ether **III-34**. It was observed that when the reaction was allowed to continue for a longer time, benzyl ether **III-34** slowly hydrolyzed to give benzyl alcohol **III-31** (Scheme 3.22)

Scheme 3.22. Preparation of Benzyl Trichloroacetimidate **III-42 and Dibenzyl Ether **III-34****

Attempts to synthesis the acyclic trimer **III-26** by using the benzyl trichloroacetimidate as a benzylation agent was not successful (Scheme 3.23). Trichlororacetimidate **III-43** was prepared from monomer diol **II-3** using trichloroacetonitrile and DBU that produced trichloroacetimidate **III-43** in 76% yield. Reaction between the trichlororacetimidate **III-43** and compound **III-25** in the presence of a catalytic amount of TMSOTf for 5 h showed, by ^1H NMR spectroscopy, only unreacted starting materials. Unfortunately, after 17 hours of reaction both of the starting materials were hydrolyzed to monomer diol **II-3**.

Scheme 3.23. Our Attempt to Synthesis Trimer III-26 Using Schmeck's Approach

3.3.3. Alkylation Using Sulfonate Ester

The first step toward the investigation was to activate both, monomer diol **II-3** and acyclic dimer diol **III-38** by converting them to the corresponding sulfonate ester (Scheme 3.24). Treatment both monomer diol **II-3** and acyclic dimer diol **III-38** with an excess amount of 4-butylbenzenesulfonyl

chloride in the presence of NaH in THF produced **III-44** and **III-45** in 83% yield and 72% yield respectively. In the case of acyclic dimer diol **III-38**, the reaction required heating at 45 °C to drive the reaction to completion.

Scheme 3.24. Preparation of III-44 and III-45

The next step involved the synthesis of macrocyclic trimer **III-21** by reacting monomer di-sulfonate ester **III-44** with acyclic dimer diol **III-38**, and for the synthesis of macrocyclic tetramer **III-22** by reacting acyclic dimer di-sulfonate ester **III-45** with acyclic dimer diol **III-38** (Scheme 3.25). Unfortunately, none of macrocycles was produced. In both reactions we only observed the hydrolysis products in the ^1H NMR spectrum.

Scheme 3.25. Our Attempts to Synthesis **III-12** and **III-22** via Alkylation of Sulfonate Ester

3.4 The Nitrogen-Containing Macrocycles

Due to the high reactivity of acyclic dimer bissulfonate **III-45** and the low solubility of the acyclic trimer diol **III-27**, all the macrocyclization steps were unsuccessful. Unfortunately, our desired products including macrocyclic dimer **III-20**, macrocyclic trimer **III-21** and macrocyclic tetramer **III-22** could not be obtained. Here we turned our attention to synthesis nitrogen-containing macrocycles as it is anticipated that the alkane chain in the amine should enhance the solubility of our compounds.

One example of a nitrogen-containing macrocycle was published in 1993 from Kyusyu University in Japan.³¹ The group successfully synthesized tetraaza[3.3.3.3]cyclophanes **III-48** in 21% yield (Scheme 3.26). The synthesis started with the alkylation of *N*-substituted trifluoroacetamide **III-46** with dibromide **III-47** followed by the removal of the trifluoroacetyl groups and *N*-methylation of the resulting amines.

Scheme 3.26. Synthesis of Cyclophanes III-48 by Alkylation of N-Substituted Trifluoroacetamide

3.4.1 Alkylation of Amides and Amines

To explore this area, different amides and amines were employed. The first choice was 4-butylbenzamide. The dialkylation of 4-butylbenzamide was investigated by reacting 1 mol of 4-butylbenzamide with 2 mol of monomer **III-49** to try to produce acyclic dimer **III-50** (Scheme 3.27). The first step involved the preparation of monomer **III-49** by treating monomer **III-25** with an excess amount of 4-butylbenzenesulfonyl chloride in the presence of NaH in THF to

produce **III-49** in 77% yield. The reaction of 4-butylbenzamide with monomer **III-49** resulted in producing only monoalkylated adduct **III-51**. The second alkylation to produce acyclic dimer **III-50** did not occur, conceivable due to the steric hindrance.

Scheme 3.27 Alkylation of 4-Butylbenzamide

Obtaining monomer **III-51** leads us to explore more and investigate the possibility of producing acyclic trimer **III-52** (Scheme 2.28). Again, the second alkylation of the corresponding amide under this reaction condition did not occur. The monobenzamide **III-51** was desilylated as it was observed in the ^1H NMR spectrum.

Scheme 3.28. Attempt to Prepare Acyclic Trimer III-52

Dialkylation of 4-butylbenzamide did not occur, possibly because the amide is too hindered and obstructs the second alkylation of the selected amide. For this reason, 1-dodecanamine was chosen to investigate the alkylation step in the presence of K_2CO_3 as an acid scavenger. Acyclic dimer **III-53** is an excellent candidate for synthesizing cyclic tetramer (Scheme 3.29). Unfortunately, the second alkylation to obtain acyclic dimer **III-53** did not occur. Instead, monomer diamine **III-54** was produced as the primary product. One reason that the second alkylation of 1-dodecanamine may be too slow could be due to slow deprotonation of the first alkylating product of ammonium bromide by K_2CO_3 . The second alkylation of monomer diamine **III-54** may occur if the monomer is not in the form of the corresponding ammonium bromide.

Scheme 3.29. Attempt to Produce Acyclic Dimer III-53

To overcome the slow deprotonation of the first alkylating products *N,N*-diisopropylethylamine (DIPEA or Hünig's base) was used as a hindered base. It is reported that DIPEA was used as a selective reagent in the alkylation of secondary amines to give tertiary amines by alkyl halides without the formation of the undesired quaternary ammonium salt.³² Reacting monomer tetrabromide **II-16** with monomer diamine **III-54** in the presence of Hünig's base successfully produced macrocyclic dimer **III-55** in 40% yield with an interesting NMR spectrum which will be discussed in a separated section (Scheme 3.30).

Scheme 3.30. Synthesis of Macrocyclic III-55

With the success of synthesizing macrocycle **III-55**, we attempt to synthesis larger macrocyclic from acyclic trimer **III-56** (Scheme 3.31). Reacting monomer **III-49** with monomer diamine **III-54** in the presence of Hünig's base and potassium carbonate followed by desilylation with TBAF successfully produced acyclic trimer **III-56** in 59% yield.

Scheme 3.31 Preparation of Acyclic Trimer III-56

Unfortunately, with the enhanced solubility of **III-56**, the use of Williamson ether synthesis between monomer tetrabromide **II-16** and acyclic trimer **III-56** did not afford the expected cyclic tetramer **III-57**, and only polymers were obtained (Scheme 3.32)

Scheme 3.32. Our Attempt to Synthesis Macrocycle III-57

3.4.2 Synthesis and Structure of Nitrogen-Containing Macrocyclic Dimer III-59

After our success in the dialkylation step of 1-dodecanamine in producing macrocyclic dimer **III-55**, we decided to synthesize the same dimer using isoamylamine. The proton NMR spectrum of isoamylamine shows clear signals in the aliphatic region and a distinctive doublet

signal at 0.9 ppm. The clear spectrum of isoamylamine facilitates tracing the amine's fate during the reaction.

The first step of the synthesis of macrocyclic dimer **III-59** involved the reaction of isoamylamine with monomer tetrabromide **II-16** to afford **III-58** in 90 % yield. Treatment of **III-58** with one equivalent of monomer tetrabromide **II-16** successfully produced **III-59** in 48 % isolated yield (Scheme 3.33). It was found that the high-resolution mass spectroscopy of macrocycle **III-59** contained ca. 1% of the corresponding cyclic tetramer **III-60**.

Scheme 3.33. Synthesis of Macrocycle **III-59**

Both macrocycles **III-55** and **III-59** exhibited impressive ^1H NMR spectra that indicated the two phenanthrene units are nonequivalent on the NMR time-scale at room temperature. One phenanthrene unit is perpendicular to the other phenanthrene unit. As a result, one set of the central aromatic hydrogens are shifted upfield to δ 5.76 ppm while the other set occurred at δ 8.00 ppm as a singlet in toluene- d_8 . Also, all four benzylic hydrogens are in different magnetic environments showing four signals at δ 4.32, 4.23, 4.10, and 3.50 ppm with large coupling constants of 12.9 and 13.3 Hz respectively. The methylene hydrogens attached to the nitrogen atom are diastereotopic due to the nonplanar conformation showing two signals with one occurred at δ 2.50 ppm, and the other one occurred at δ 2.22 ppm. The two methyl groups are also diastereotopic, showing two signals with one doublet occurring at δ 0.67 ppm, and an additional doublet appearing at δ 0.30 ppm.

Figure 3.2 (A) DFT-optimized structure and ^1H NMR chemical shifts (δ) in toluene- d_8 of macrocycle **III-59** bearing two 2,7-dibromophenanthrene units with carbons (gray), hydrogens

(white), nitrogens (blue), and bromines (red). **(B)** Temperature-dependent 600 MHz ^1H NMR spectra of macrocycle **III-59** in toluene- d_8 .

DFT calculations and temperature-dependent NMR spectra (Figure 3.2) supported the preference of the conformer with one phenanthrene units oriented perpendicular to the other unit. Temperature-dependent NMR studies with different temperature also indicated the equilibrating behavior of conformers. At 90 °C, in the aliphatic region, the four doublets of the benzylic hydrogens become a broad singlet at δ 4.2, and the methylene hydrogens and methyl groups all collapsed to give a broad singlet peaks at δ 2.4 and 0.5, respectively. In the aromatic region, the four doublets became two broad peaks at δ 7.6 and 7.9, and the two singlets at δ 5.76 and 8.00 formed two broad peaks (Figure 3.2 (B)).

3.4.3 Synthesis of Nitrogen-Containing Macroacyclic Trimer **III-63**

With improved solubility of diamine **III-58** in common organic solvents, synthetic pathways leading to trimer macrocycle via reductive etherification reaction was investigated. Reacting monomer **III-49** with monomer diamine **III-58**, in the presence of DIPEA and K_2CO_3 afforded **III-61** in 61% yield. Desilylation of **III-61** with TBAF gave acyclic trimer diol **III-62** in 93% yield. The next step involved the oxidation of **III-62**. The swern oxidation of **III-62** afforded **III-63** in 37% yield. An attempt was made to treat dialdehyde **III-63** with PMHS and a catalytic amount (2.5 mol%) of molecular iodine for reductive etherification to afford macrocyclic trimer **III-64**. Unfortunately, the products obtained had low solubility in common organic solvents which cannot be further purified and analyzed (Scheme 3.34). However, it is envisioned that acyclic trimer dialdehyde **III-63** could be employed for the synthesis of macrocyclic tetramer, which is now under investigation in our laboratory.

Scheme 3.34. Synthesis of Macrocycle **III-63**.

3.5 Summary

A variety of methods were investigated for synthesizing trimer and tetramer macrocycles with ether linkage to connect phenanthrene units. Unfortunately, several synthetic pathways were unsuccessful due to the low solubility of the liner precursors. However, macrocyclic dimer **III-20** with two ether linkages between the two phenanthrene units was successfully achieved via reductive etherification reaction of the corresponding monomer dialdehyde **III-35**. Also, macrocycle dimer **III-59** having two dibenzylamine linkages was successfully synthesized. The molecular was found to show an interesting conformation based on NMR studies. All studies including ^1H and ^{13}C NMR spectra, temperature-dependent NMR, and DFT calculations supported a preferred conformation with one of the phenanthrene units oriented essentially perpendicular to

the other unit. With the enhanced solubility of compound **III-58** in most common organic solvents, new synthetic pathways leading to larger macrocycle could be developed.

3.6 General Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under an argon or nitrogen atmosphere. Oil bath was used as the heat source for the reactions that required heating. Chemicals, including, polymethylhydrosiloxane (trimethylsilyl terminated), isopentylamine, *tert*-butyldimethylsilyl trifluoromethanesulfonate, tetrabutylammonium fluoride, trichloroacetonitrile were purchased from chemical suppliers and were used as received.

Experimental Procedure for III-25. To a 50-mL flask was added 0.300 g of monomer diol **II-3** (0.76 mmol). The flask was flushed with argon before 20 mL of DMF was introduced via cannula. 0.174 mL of TBSOTf (0.76 mmol) was introduced by a syringe followed by adding 0.13 mL of 2,6-lutidine (1.14 mmol). The reaction mixture was then stirred at rt for 2 h. The reaction mixture was then partitioned between water (30 mL) and dichloromethane (30 mL). The organic layer was separated, washed with water (4 X 30 mL) and brine, dried over Na₂SO₄, and then evaporated in vacuo at 40 °C to provide a mixture of monomer diol **II-3**, mono-silylated **III-25**, and di-silylated **III-24**. 3.0 mL dichloromethane was added to the crude to separate the unreacted monomer diol **II-3** by filtration to give (0.014 g) of recovered diol **II-3**. The residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 10:90) to afford **III-25** (0.160 g, 0.31 mmol, 45% yield) as a white solid: IR 3250 (br), 2927, 1252, 1067, 835, 792, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (2 H, d, *J* = 9 Hz), 8.45 (2 H, d, *J* = 9 Hz), 8.35, 8.26 (2 H,

ABq, $J = 9.6$ Hz), 7.8 (2 H, t, $J = 8$ Hz), 5.37 (2 H, s), 5.36 (2 H, s), 0.91 (9 H, s), 0.13 (6 H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ 135.7, 135.2, 132.1, 131.6, 131.0, 130.7, 129.9, 129.8, 125.6, 124.7, 124.2, 123.7, 123.6, 63.0, 62.0, 25.9, 18.3, -5.0 ; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{Br}_2\text{O}_2\text{Si}$ 506.9996, 508.9976, 510.9955; found 506.9998, 508.9971, 510.9951. Di-silylated **III-24** was obtained (0.110 g, 0.176 mmol, 23% yield) as a pale yellow solid: IR 2954, 2928, 2857, 1257, 1059, 835, 807, 774 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (2 H, d, $J = 10.7$ Hz), 8.31 (2 H, s), 7.77 (2 H, d, $J = 9$ Hz), 5.38 (4 H, s), 0.89 (18 H, s), 0.11 (12 H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ 135.7, 132.2, 130.7, 129.8, 124.9, 124.2, 123.4, 63.0, 25.8, 18.3, -5.0 .

III-26

Experimental Procedure for III-26. To a 50-mL flask were added **II-16** (0.092 g, 0.18 mmol) and **III-25** (0.197 g, 0.39 mmol). The flask was flushed with argon before 20 mL of DMF was introduced via cannula. The reaction mixture was cooled to 0 °C before (0.012 g, 0.48 mmol) of NaH was added. The reaction mixture was allowed to warm to rt and stirred for 18 h before it passed through a short column of celite pad. The solution was then transferred into a separatory funnel, (50 mL) of water was added and the organic layer was extracted by dichloromethane (50 mL). The organic layer was separated, washed with water (4 X 50 mL), brine, and dried over Na_2SO_4 . The solvent was then evaporated by vacuo at 40 °C and the residue was purified by flash

column chromatography (silica gel/ethyl acetate:hexanes = 5:95) produced **III-26** (0.060 g, 0.043 mmol, 24% yield) as a white solid; ^1H NMR (400 MHz, CDCl_3) δ 8.49 (2 H, d, $J = 9.7$ Hz), 8.20 (2 H, d, $J = 9.0$ Hz), 8.18 (2 H, s), 8.12 (2 H, d, $J = 9.7$ Hz), 7.83 (2 H, d, $J = 8.8$ Hz), 7.73 (4 H, d, $J = 9.3$ Hz), 7.60 (2 H, d, $J = 9.0$ Hz), 7.56 (2 H, d, $J = 10.1$ Hz), 5.42 (4 H, s), 5.24 (4 H, s), 4.70 (4 H, s), 0.77 (9 H, s), -0.01 (6 H, s).

III-27

Experimental Procedure for III-27. To a solution of **III-26** (0.060 g, 0.043 mmol) in THF (5 mL) cooled to 0 °C, was added a solution of TBAF (1.0 M in THF, 0.103 mL, 0.103 mmol). The reaction mixture was then warmed to rt and stirred for 14 h. The resulting white solid was collected by filtration, washed with water, and air dried to give **III-27** (0.039 g, 0.034 mmol, 81% yield) as a white solid; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.73 (2 H, d, $J = 9.0$ Hz), 8.64 (2 H, d, $J = 9.0$ Hz), 8.58 (2 H, d, $J = 9.0$ Hz), 8.07 (2 H, s), 7.96 (4 H, s), 7.88 (2 H, d, $J = 9.6$ Hz), 7.83 (2 H, d, $J = 8.4$ Hz), 7.79 (2 H, d, $J = 8.4$ Hz), 5.34 (4 H, s), 5.31 (4 H, s), 4.98 (4 H, s).

III-35

Experimental Procedure for 2,7-Dibromo-1,8-phenanthrenedicarboxaldehyde III-35.

To a 50-mL flask were added 0.100 g of **II-3** (0.252 mmol) and 0.20 g of PCC (0.93 mmol). The flask was flushed with argon before 20 mL of dichloromethane was introduced via cannula. The resulting dark-orange reaction mixture was then stirred vigorously at rt for 2 h. The reaction mixture was then filtered through a short pad of Celite and silica gel. Solvents were removed in vacuo at 40 °C to give, without further purification, **III-35** (0.090 g, 0.230 mmol, 91% yield) as a yellow solid: IR 2887, 1683, 1140, 825, 809 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 10.79 (2 H, s), 9.11 (2 H, s), 8.70 (2 H, d, $J = 8.9$ Hz), 7.94 (2 H, d, $J = 9.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.5, 132.0, 131.1, 130.0, 129.4, 129.2, 129.0, 126.1; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_9\text{Br}_2\text{O}_2$ 390.8964, 392.8943, 394.8923; found 390.8948, 392.8931, 394.8909.

III-36

Experimental Procedure for III-36. To a 50-mL flask were added 0.100 g of **III-35** (0.255 mmol) and 0.298 g polymethylhydrosiloxane (ca. 4.6 mmol of hydride). The flask was flushed with argon before 3.0 mL of dichloromethane was introduced by a syringe. Excess amount of Iodine was added to the reaction mixture at 0 °C before it was allowed to warm to rt and stirred

for 30 min. The reaction mixture was then filtered, and the resulting yellow solid was washed with an aqueous solution of Na₂S₂O₃, water, and hexanes, and then air-dried to give (0.087 g, 0.133 mmol, 52% yield) of **III-36** as a yellow solid: mp = 136.6 °C (decomposition); IR 1583, 1445, 1147, 831, 799 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (4 H, d, *J* = 9.2 Hz), 8.22 (4 H, s), 7.80 (4 H, d, *J* = 9.2 Hz), 5.09 (8 H, s); HRMS (EI) calcd for C₁₆H₁₀Br₂I₂ 613.7239; found 613.7256.

Experimental Procedure for III-37. To a 100-mL flask containing of 0.250 g of **III-25** (0.490 mmol) and 0.118 g of sodium hydride (4.90 mmol) in 50 mL of anhydrous tetrahydrofuran under nitrogen atmosphere was added 0.048 mL of 4-butylbenzenesulfonyl chloride (0.245 mmol) by using a syringe. The reaction mixture was then stirred at rt for 12 h before it is pass through a short celite column (5 cm high). The column was further eluted with 50 mL of THF and solvent was then evaporated in vacuo at 60 °C, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 2:98) to produce **III-37** (0.160 g, 0.160 mmol 65% yield) as a white solid; ¹H NMR (600 MHz, CDCl₃) δ 8.45 (2 H, d, *J* = 8.8 Hz), 8.41 (2 H, d, *J* = 8.8 Hz), 8.13, 8.11 (4 H, ABq, *J* = 9.8 Hz) 7.79 (2 H, d, *J* = 8.9 Hz), 7.76 (2 H, d, *J* = 8.9 Hz), 5.40 (4 H, s), 5.27 (4 H, s), 0.85 (18 H, s), 0.07 (12 H, s); ¹³C{¹H} NMR (600 MHz, CDCl₃) δ 135.7, 132.7, 132.3, 132.1, 130.9, 130.7, 129.8, 129.7, 125.4, 125.3, 124.8, 124.2, 124.1, 123.6, 69.1, 63.0, 25.9, 18.3, -5.1.

III-38

Experimental Procedure for III-38. In 100-mL flask containing 0.160 g of **III-37** (0.160 mmol) was added a solution of 1% of hydrochloric acid in methanol (40 mL). The reaction mixture was then stirred at rt for 30 h. the resulting white solid was then collected by filtration, washed with water, and then air-dried to give **III-38** (0.105 g, 0.135 mmol 85% yield) as a white solid: ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.76 (2 H, d, $J = 9.2$ Hz), 8.70 (2 H, d, $J = 9.2$ Hz), 8.24 (4 H, s), 7.88 (2 H, d, $J = 8.9$ Hz), 7.85 (2 H, d, $J = 8.9$ Hz), 5.40 (2 H, t, $J = 5.4$ Hz), 5.37 (4 H, s), 5.10 (4 H, d, $J = 5.4$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{DMSO}-d_6$) δ 136.4, 132.7, 131.7, 131.4, 131.0, 130.7, 129.3, 129.2, 125.8, 125.2, 125.0, 124.9, 124.3, 123.7, 68.6, 60.3.

III-41

Experimental Procedure for III-41. To a 25-mL flask were added diol **II-3** (0.050 g, 0.126 mmol), I_2 (0.0006 g, 0.00252 mmol) and 5 mL DCM. The reaction mixture was stirred and then HMDS (0.042 mL, 0.202 mmol in 1 mL DCM) was added dropwise. The reaction mixture was stirred at rt for 5 h. Powdered $\text{Na}_2\text{S}_2\text{O}_3$ (20 mg) was added, reaction mixture was then stirred

for additional 30 min. the resulting mixture was filtered, washed with NaHCO₂, dried over sodium sulfate. DCM was evaporated in vacuo, and the crude residue was purified by flash column chromatography (silica gel/ hexanes:ethylacetate = 5:95) to produce **III-41** (0.065 g, 0.120 mmol, 96% yield) as a yellow solid: ¹H NMR (400 MHz, CDCl₃) δ 8.42 (2 H, d, *J* = 9.0 Hz), 8.27 (2 H, s), 7.76 (2 H, d, *J* = 8.9 Hz), 5.33 (4 H, s).

III-43

Experimental Procedure for III-41. To a 50-mL flask was added diol **II-3** (0.100 g, 0.25 mmol) and dry DCM (10 mL). The reaction mixture was cooled to 0 °C before 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.008 mL, 0.05 mmol) and trichloroacetonitrile (0.50 mL, 5.05 mmol) was added by syringe. The reaction mixture then was stirred at rt for 3 h before the DCM was removed by vacuo at 40 °C. the residue was then purified by recrystallization from DCM and hexanes to give **III-43** (0.130 g, 0.189 mmol, 76% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.58 (2 H, d, *J* = 9.1 Hz), 8.09 (2 H, s), 7.89 (2 H, d, *J* = 9.0 Hz), 5.98 (4 H, s).

III-44

Experimental Procedure for III-44. To a 50-mL flask was added diol **II-3** (0.100 g, 0.25 mmol) and NaH (0.12 g, 5.05 mmol), before the flask was flushed with argon and (20 mL) of THF was added. 4-butylbenzenesulfonyl chloride (0.15 mL, 0.76 mmol) was then added by syringe and the reaction mixture was stirred at rt for 12 h. The reaction mixture was then filtered through a short column of celite and THF was evaporated in vacuo at 60 °C. Recrystallization of the resulting solid from DCM and hexanes afforded **III-44** (0.164 g, 0.21 mmol, 83% yield) as a white solid; ^1H NMR (400 MHz, CDCl_3) δ 8.46 (2 H, d, $J = 9.2$ Hz), 7.96 (2 H, s), 8.36 (4 H, d, $J = 8.4$ Hz), 7.78 (2 H, d, $J = 9.0$ Hz), 7.32 (4 H, d, $J = 8.6$ Hz), 5.76 (4 H, s), 2.67 (4 H, t, $J = 7.7$ Hz), 1.59 (4 H, overlapped with water peak), 1.35 (4 H, m, $J = 7.7$ Hz), 0.94 (6 H, t, $J = 7.3$ Hz).

III-45

Experimental Procedure for III-45. To a 50-mL flask was added **III-37** (0.055 g, 0.071 mmol) and NaH (0.050 g, 2.13 mmol), before the flask was flushed with argon and (20 mL) of THF was added. 4-butylbenzenesulfonyl chloride (0.04 mL, 0.213 mmol) was then added by

syringe and the reaction mixture was stirred at 45 °C for 12 h. The reaction mixture was then filtered through a short column of celite and THF was evaporated in vacuo at 60 °C. Recrystallization of the solid from DCM and hexanes afforded **III-45** (0.060 g, 0.051 mmol, 72% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.44 (2 H, d, *J* = 9.0 Hz), 8.42 (2 H, d, *J* = 8.9 Hz), 8.07 (2 H, d, *J* = 9.5 Hz), 7.83 (2 H, d, *J* = 9.0 Hz), 7.79 (2 H, d, *J* = 9.5 Hz), 7.76 (4 H, d, *J* = 8.5 Hz), 7.73 (2 H, d, *J* = 9.0 Hz), 7.19 (4 H, d, *J* = 8.7 Hz), 5.68 (4 H, s), 5.39 (4 H, s), 2.60 (4 H, t, *J* = 7.1 Hz), 1.52 (4 H, m, *J* = 7.7 Hz), 1.30 (4 H, m, *J* = 7.4 Hz), 0.91 (6 H, t, *J* = 7.3 Hz).

III-49

Experimental Procedure for III-49. To a 50-mL flask were added **II-25** (100 g, 0.294 mmol), NaH (0.071 g, 2.94 mmol). The flask was flushed by argon and THF (15 mL) was introduced by canula. 4-Butylbenzenesulfonyl chloride (0.143 mL, 0.735 mmol) was then introduced by using a syringe (0.143 mL, 0.735 mmol) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was then filtered through a short column of celite and THF was evaporated in vacuo at 60 °C. Recrystallization of the solid from DCM and hexanes afforded **III-49** (0.160 g, 0.226 mmol, 77% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (1 H, d, *J* = 9.0 Hz), 8.39 (1 H, d, *J* = 9.7 Hz), 8.32 (1 H, d, *J* = 9.8 Hz), 7.98 (1 H, d, *J* = 9.7 Hz), 7.83 (2 H, d, *J* = 8.3 Hz), 7.79 (1 H, d, *J* = 8.9 Hz), 7.73 (1 H, d, *J* = 9.1 Hz), 7.25 (2 H, d, *J* = 6.9 Hz), 5.79 (2 H, s), 5.36 (2 H, s), 2.63 (2 H, t, *J* = 8.0 Hz), 1.50 (2 H, overlapped with H₂O peak), 1.33 (2 H, m, *J* = 7.9 Hz), 0.93 (3 H, t, *J* = 7.1 Hz), 0.92 (9 H, s), 0.15 (6 H, s).

III-58

Experimental Procedure for III-58. To a 50-mL flask were added **II-16** (0.300 g, 0.575 mmol) and potassium carbonate (0.119 g, 0.862 mmol). The flask was flushed with nitrogen before 16 mL of THF was introduced via cannula. Isopentylamine (0.27 mL, 2.3 mmol) was then introduced by a syringe, and the reaction mixture was stirred at 50 °C for 3 h before it was cooled to rt. The reaction mixture was then passed through a short column of Celite pad, and the THF was evaporated in vacuo. Then 10 mL of hexanes was added to the residue, and the mixture was stirred at rt for 5 min. The white solid was then removed by filtration, and the filtrate was collected and dried in vacuo to afford **III-58** (0.276 g, 0.516 mmol, 90% yield) as a brown solid: mp = 49–50 °C; IR 2952, 2867, 1583, 1365, 1465 1107, 797 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.30 (2 H, d, *J* = 9.1 Hz), 8.13 (2 H, s), 7.71 (2 H, d, *J* = 8.9 Hz), 4.36 (4 H, s), 2.80 (4 H, t, *J* = 7.5 Hz), 1.67 (2 H, septet, *J* = 6.7 Hz), 1.46 (4 H, q, *J* = 6.9 Hz), 0.91 (12 H, d, *J* = 6.7 Hz); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 135.7, 131.5, 130.8, 129.7, 124.3, 124.2, 123.5, 50.2, 48.1, 39.1, 26.0, 22.6; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₂₆H₃₅Br₂N₂ 533.1162, 535.1141, 537.1121; found 533.1140, 535.1116, 537.1100.

III-59

Experimental Procedure for III-59. To a 50-mL flask were added **II-16** (0.121 g, 0.232 mmol), **III-58** (0.124 g, 0.232 mmol), and potassium carbonate (0.128 g, 0.928 mmol). The flask was flushed with nitrogen before 15 mL of THF was introduced via cannula. Diisopropylethylamine (0.162 mL, 0.928 mmol) was then introduced by a syringe. The reaction mixture was stirred at 70 °C for 40 h before it was cooled to rt. The reaction mixture was then filtrate, the white solid was washed with water and air-dried afforded **III-59** in 48 % yield (0.100 g, 0.112 mmol) containing ca. 1% yield of **II-60** : mp = 215 °C (decomposition); IR 1581, 1443, 807, 793, 744, 717 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.55 (2 H, d, *J* = 8.9 Hz), 8.17 (2 H, d, *J* = 8.8 Hz), 8.16 (2 H, s), 7.90 (2 H, d, *J* = 8.9 Hz), 7.59 (2 H, d, *J* = 8.8 Hz), 6.10 (2 H, s), 4.60 (2 H, d, *J* = 13.2 Hz), 4.41 (2 H, d, *J* = 13.2 Hz), 4.11 (2 H, d, *J* = 13.2 Hz), 3.79 (2 H, d, *J* = 13.2 Hz), 2.55 (2 H, ddd, *J* = 13.2, 8.6, 6.2 Hz), 2.32 (2 H, ddd, *J* = 13.2, 8.0, 4.9 Hz), 1.4088 (2 H, dddd, *J* = 12.5, 8.0, 7.1, 6.2 Hz), 1.4075 (2 H, dddd, *J* = 12.5, 8.6, 6.6, 4.9 Hz), 1.20 (2 H, m), 0.72 (6 H, d, *J* = 6.6 Hz), 0.32 (6 H, d, *J* = 6.6 Hz); ¹H NMR (600 MHz, toluene-*d*₈, less concentrated sample) δ 8.06 (2 H, d, *J* = 8.9 Hz), 8.05 (2 H, s), 7.71 (2 H, d, *J* = 8.9 Hz), 7.60 (2 H, d, *J* = 8.7 Hz), 7.39 (2 H, d, *J* = 8.7 Hz), 5.92 (2 H, s), 4.35 (2 H, d, *J* = 12.9 Hz), 4.26 (2 H, d, *J* = 12.9 Hz), 4.15 (2 H, d, *J* = 13.3 Hz), 3.61 (2 H, d, *J* = 13.3 Hz), 2.54 (2 H, ddd, *J* = 13.2, 9.0, 6.3 Hz), 2.24 (2 H, ddd, *J* = 13.2, 8.2, 4.8

Hz), 1.27 (4 H, m), 1.11 (2 H, m), 0.70 (6 H, d, $J = 6.7$ Hz), 0.33 (6 H, d, $J = 6.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 134.8, 134.0, 132.8, 131.7, 130.8, 130.0, 129.6, 129.0, 126.3, 125.9, 124.7, 124.5, 124.1, 123.3, 55.7, 52.2, 51.6, 35.1, 26.0, 23.1, 21.5; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{42}\text{H}_{43}\text{Br}_4\text{N}_2$ 891.0154, 893.0134, 895.0113, 897.0093, 899.0072; found 891.0157, 893.0129, 895.0101, 897.0079, 899.0057; **III-60** : HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{84}\text{H}_{85}\text{Br}_8\text{N}_4$ 1781.0236, 1783.0215, 1785.0195, 1787.0174, 1789.0154, 1791.0133, 1793.0113, 1795.0180, 1797.0160; found 1781.0182, 1783.0205, 1785.0203, 1787.0202, 1789.0186, 1791.0189, 1793.0185, 1795.0164, 1797.5567.

III-61

Experimental Procedure for III-61. To a 50-mL flask were added **III-58** (0.073 g, 0.137 mmol), **III-49** (0.194, 0.274 mmol), and potassium carbonate (0.076 g, 0.548 mmol). The flask was then attached with a reflux condenser and flushed with nitrogen. THF (15 mL) was then introduced by a syringe followed by the addition of N,N-diisopropylethylamine (0.095 mL, 0.548 mmol) by a syringe. The reaction mixture was heated to reflux at 70 °C and stirred for 3 days. The reaction mixture was then allowed to cool to rt, passed through short pad of celite, and THF was evaporated in vacuo at 60 °C. The residue was purified by flash column chromatography (silica

gel/hexanes) to produce **III-61** (0.127 g, 0.082 mmol 61% yield) as a white solid; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (2 H, d, J = 8.8 Hz), 8.16 (4 H, d, J = 9.4 Hz), 7.84 (2 H, d, J = 9.5 Hz), 7.78 (2 H, d, J = 9.2 Hz), 7.66 (2 H, d, J = 8.9 Hz), 7.62 (2 H, d, J = 9.2 Hz), 7.59 (2 H, d, J = 8.4 Hz), 7.53 (2 H, s), 5.09 (4 H, s), 4.21 (4 H, s), 4.17 (4 H, s), 2.56 (4 H, t, J = 7.6 Hz), 1.40 (4 H, q, J = 6.6 Hz), 1.33 (2 H, m), 0.71 (18 H, s), 0.53 (12 H, s), -0.05 (12 H, s).

III-62

Experimental Procedure for III-62. To a solution of **III-61** (0.127 g, 0.083 mmol) in THF (5 mL) cooled to 0 °C, was added a solution of TBAF (1.0 M in THF, 0.199 mL, 0.199 mmol). The reaction mixture was then warmed to rt and stirred for 18 h. A saturated aqueous NaHCO_3 solution (5.0 mL) was added, and the mixture was poured into water (10 mL) and extracted with dichloromethane (10 mL $\times$ 3). The combined organic layers were dried over sodium sulfate. Solvents were evaporated in vacuo at 40 °C, and the crude residue was purified by flash column chromatography (silica gel/hexanes) to produce **III-62** (0.101 g, 0.079 mmol, 93% yield) as a white solid: ^1H NMR (400 MHz, CDCl_3) δ 8.48 (2 H, d, J = 9.2 Hz), 8.15 (4 H, d, J = 8.9 Hz), 7.92 (2 H, s), 7.86 (2 H, d, J = 9.0 Hz), 7.70 (2 H, d, J = 8.2 Hz), 7.62 (2 H, d, J = 9.5 Hz), 7.59 (2 H, d, J = 9.9 Hz), 7.16 (2 H, d, J = 9.2 Hz), 4.76 (4 H, d, J = 5.2 Hz), 4.36 (4 H, s), 4.20 (4 H, s),

3.75 (2 H, t, $J = 6.6$ Hz), 2.60 (4 H, t, $J = 7.6$ Hz), 1.85 (4 H, m), 1.50 (2 H, m), 0.64 (12 H, d, $J = 6.5$ Hz).

III-63

Experimental Procedure for III-63. A solution of oxalyl chloride (0.017 mL, 0.199 mmol) in 3 mL of dichloromethane was cooled at -78 °C in a dry ice/acetone bath under argon. DMSO (0.02 mL, 0.28 mmol) was then added carefully by using a syringe. After 15 min of stirring, a solution of **III-62** (0.095 g, 0.074 mmol) in 3 mL of dichloromethane was added via cannula, and the reaction mixture was stirred for 1.5 h. Triethylamine (0.64 mL, 0.46 mmol) was added, and the reaction mixture was allowed to warm to rt. The reaction mixture was then transferred into a separatory funnel, washed with 3% HCl (4 mL), saturated NaHCO_3 , and brine, and then dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo at 40 °C, and the residue was purified by crystallization from DCM and hexanes to produce **III-63** (0.035 g, 0.0272 mmol, 37% yield) as a white solid: ^1H NMR (400 MHz, CDCl_3) δ 10.23 (2 H, s), 8.48 (2 H, d), 8.22 (2 H, d), 8.14 (2 H, d), 8.07 (2 H, d), 7.86 (2 H, d), 7.79 (4 H, d), 7.72 (2 H, d), 7.56 (2 H, d), 4.46 (4 H, s), 4.23 (4 H, s), 2.62 (4 H, t), 1.45 (4 H, m), 1.25 (2 H, m), 0.67 (12 H, d).

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Appendix Chapter-II

II-1

II-1

II-14

II-14

II-15

II-15

II-16

II-16

II-3

II-3

The structure of 2,7-Dibromo-1,8-phenanthrenedimethanol (**II-3**). All non-hydrogen atoms are drawn with 50% thermal probability ellipsoids. All hydrogen atoms except those on heteroatoms are omitted for clarity.

The asymmetric unit of 2,7-Dibromo-1,8-phenanthrenedimethanol (**II-3**). All non-hydrogen atoms are drawn as 50% thermal probability ellipsoids. All hydrogen atoms except those on heteroatoms are omitted for clarity.

Description of the X-ray Structural Analysis of 2,7-Dibromo-1,8-phenanthrenedimethanol (**II-3**).

Table 1 Crystal data and structure refinement for 2,7-Dibromo-1,8-phenanthrenedimethanol (II-3).

Identification code	kw44_a
Empirical formula	C _{17.33} H _{14.67} Br ₂ O _{2.33}
Formula weight	420.11
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	10.3356(3)
b/Å	13.9547(3)
c/Å	16.7653(4)
$\alpha/^\circ$	104.8520(10)
$\beta/^\circ$	93.3620(10)
$\gamma/^\circ$	97.1140(10)
Volume/Å ³	2308.96(10)
Z	6
$\rho_{\text{calc}}/\text{cm}^3$	1.813
μ/mm^{-1}	5.271
F(000)	1244.0
Crystal size/mm ³	0.249 × 0.093 × 0.058
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	5.396 to 56.716
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	81412
Independent reflections	11528 [R_{int} = 0.0529, R_{sigma} = 0.0301]
Data/restraints/parameters	11528/0/610
Goodness-of-fit on F ²	1.022
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0294, wR_2 = 0.0558
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.0600
Largest diff. peak/hole / e Å ⁻³	0.64/-0.60

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for II-3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Br5	8900.4(2)	9399.3(2)	6362.4(2)	18.64(6)
Br3	6529.2(2)	10009.7(2)	9419.9(2)	16.31(5)
Br2	1299.0(2)	1873.8(2)	8226.5(2)	19.45(6)

Br4	7022.7(2)	2151.3(2)	8830.9(2)	18.43(6)
Br1	574.2(2)	9700.9(2)	8886.7(2)	18.58(6)
Br6	9684.1(3)	1569.2(2)	5736.3(2)	19.50(6)
O6	6382.5(17)	2127.6(14)	5197.6(11)	15.0(4)
O1	3257.8(17)	8413.6(14)	7484.3(11)	17.1(4)
O4	6134.0(17)	2940.8(15)	6809.1(12)	21.1(4)
O5	5724.2(17)	7307.2(15)	5454.6(12)	19.1(4)
O2	3629.2(19)	3423.5(15)	7036.1(11)	21.8(4)
O3	5688.2(19)	7963.3(15)	7098.4(11)	20.5(4)
O7	3252.0(19)	171.4(15)	7102.5(12)	25.0(4)
C34	8074(2)	7280.8(18)	5653.3(14)	11.3(4)
C1	893(2)	8384.3(17)	8877.1(15)	13.4(5)
C39	8498(2)	3154.9(18)	5320.6(14)	11.7(4)
C18	6632(2)	7991.9(18)	8471.3(14)	11.6(4)
C15	3123(2)	8672.7(18)	8361.6(14)	13.6(5)
C40	9526(2)	2920.9(18)	5763.0(14)	12.9(5)
C14	-90(2)	7800.4(18)	9161.1(15)	13.9(5)
C24	6871(2)	3503.5(17)	8853.4(15)	12.2(4)
C36	7233(2)	5467.3(19)	5082.5(14)	14.1(5)
C25	6623(2)	4109.4(18)	9619.2(14)	12.3(4)
C38	8399(2)	4188.2(17)	5421.3(14)	11.1(4)
C4	3185(2)	6543.2(18)	8173.0(14)	11.8(4)
C44	9244(2)	5991.5(17)	6024.2(14)	10.7(4)
C17	6497(2)	8605.6(17)	9241.8(15)	12.0(4)
C6	2262(2)	4905.9(17)	8309.4(13)	9.8(4)
C33	8995(2)	8006.2(17)	6176.5(14)	13.4(5)
C2	2001(2)	8019.6(17)	8585.1(14)	11.6(4)
C23	7019(2)	3865.0(18)	8166.4(14)	11.9(4)
C8	1342(2)	3280.9(17)	8417.1(14)	12.7(4)
C29	6367(2)	7235.6(18)	9861.4(14)	12.9(5)
C46	10043(2)	7759.1(18)	6620.1(14)	14.1(5)
C11	1172(2)	5317.5(17)	8661.7(14)	10.6(4)
C9	275(2)	3680.1(18)	8786.0(15)	14.6(5)
C47	6966(2)	7539.9(19)	5159.4(15)	15.5(5)
C27	6639(2)	5518.3(17)	9020.0(14)	10.6(4)
C7	2360(2)	3871.0(17)	8197.4(14)	11.5(4)
C13	11(2)	6815.5(18)	9108.5(15)	13.5(5)
C43	9353(2)	4944.3(17)	5934.4(14)	10.4(4)
C37	7325(2)	4493.2(18)	5008.7(14)	13.7(5)
C35	8192(2)	6256.6(18)	5586.0(14)	11.2(4)
C5	3262(2)	5561.5(18)	8071.1(14)	12.3(4)
C41	10483(2)	3655.4(19)	6272.9(14)	14.5(5)

C3	2092(2)	6989.1(17)	8517.1(14)	10.4(4)
C12	1086(2)	6374.3(17)	8766.6(14)	10.8(4)
C48	7489(2)	2347.6(18)	4762.4(14)	13.4(5)
C19	6666(2)	6956.0(17)	8400.0(14)	10.1(4)
C30	6348(2)	8230.0(18)	9940.8(15)	14.0(5)
C20	6858(2)	6280.8(18)	7622.8(14)	13.8(5)
C32	7315(2)	3225.0(18)	7350.4(14)	13.8(5)
C10	198(2)	4678.4(18)	8908.7(14)	13.0(5)
C45	10167(2)	6773.6(18)	6537.7(14)	12.9(5)
C42	10398(2)	4646.8(18)	6352.2(14)	12.6(4)
C16	3581(2)	3471.9(19)	7890.9(15)	14.6(5)
C26	6519(2)	5096.0(17)	9697.0(14)	11.4(4)
C21	6960(2)	5310.7(18)	7550.8(14)	13.2(5)
C22	6870(2)	4889.5(17)	8246.7(14)	11.0(4)
C31	6767(2)	8381.7(19)	7715.3(15)	15.9(5)
C28	6541(2)	6566.6(17)	9098.9(14)	10.3(4)
C49	2807(3)	449(2)	6372.3(17)	22.3(6)
C50	3959(3)	421(2)	5834.5(18)	25.5(6)
C52	4618(3)	555(2)	7239.6(19)	30.0(7)
C51	5105(3)	281(2)	6392(2)	28.6(6)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for II-3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Br5	23.51(13)	11.39(12)	22.13(13)	5.77(10)	6.58(10)	1.83(9)
Br3	21.15(12)	10.29(11)	18.00(12)	4.47(9)	2.25(9)	2.50(9)
Br2	22.08(13)	10.44(11)	25.58(14)	4.76(10)	0.89(10)	2.14(9)
Br4	21.02(12)	10.05(11)	24.61(13)	5.83(10)	2.58(10)	0.91(9)
Br1	21.56(12)	12.92(12)	23.90(13)	7.06(10)	4.45(10)	6.85(9)
Br6	25.03(13)	14.48(12)	22.23(13)	8.82(10)	3.22(10)	6.42(10)
O6	12.2(8)	19.3(9)	13.4(8)	4.9(7)	1.2(7)	0.7(7)
O1	18.3(9)	20.0(10)	15.9(9)	9.1(8)	4.4(7)	3.2(7)
O4	15.1(9)	30.9(11)	11.4(9)	-4.6(8)	2.1(7)	2.6(8)
O5	13.1(9)	30.6(11)	13.3(9)	3.4(8)	0.4(7)	7.4(7)
O2	18.0(10)	36.6(12)	11.6(9)	3.9(8)	3.9(7)	11.2(8)
O3	21.1(10)	30.8(11)	13.8(9)	8.9(8)	4.0(7)	13.0(8)
O7	31.7(11)	24.4(10)	23.3(10)	11.7(8)	4.4(8)	8.5(8)
C34	10.9(10)	14.7(11)	9.4(10)	4.3(9)	3.7(8)	2.4(9)
C1	14.5(11)	9.1(11)	16.1(12)	2.5(9)	-1.8(9)	2.9(9)
C39	11.4(11)	14.4(11)	9.6(11)	3.0(9)	4.1(8)	1.7(9)

C18	7.6(10)	15.6(12)	13.1(11)	6.0(9)	2.3(8)	2.3(8)
C15	14.6(11)	13.0(11)	13.8(11)	4.3(9)	1.8(9)	2.1(9)
C40	14.8(11)	13.6(11)	13.1(11)	5.9(9)	5.8(9)	6.1(9)
C14	10.3(11)	15.3(12)	17.0(12)	4.2(10)	2.7(9)	4.6(9)
C24	9.4(10)	9.9(11)	17.6(12)	4.8(9)	-0.8(8)	0.8(8)
C36	12.4(11)	18.6(12)	10.2(11)	2.7(9)	-2.3(8)	2.0(9)
C25	11.0(11)	14.8(12)	11.2(11)	5.5(9)	-1.4(8)	-0.6(9)
C38	10.7(10)	13.7(11)	8.9(10)	2.7(9)	2.2(8)	1.8(9)
C4	6.9(10)	15.1(11)	13.5(11)	5.0(9)	1.1(8)	-0.3(8)
C44	9.6(10)	13.9(11)	8.8(10)	3.0(9)	3.0(8)	1.6(8)
C17	9.5(10)	10.7(11)	16.3(11)	5.2(9)	-0.8(8)	0.9(8)
C6	9.6(10)	12.5(11)	6.7(10)	2.3(9)	-2.3(8)	1.4(8)
C33	17.1(12)	10.9(11)	13.1(11)	3.8(9)	6.1(9)	2.2(9)
C2	12.0(11)	12.4(11)	10.3(11)	4.0(9)	-1.6(8)	0.8(9)
C23	7.0(10)	14.3(11)	13.6(11)	2.5(9)	-0.2(8)	0.9(8)
C8	16.0(11)	10.0(11)	11.5(11)	2.4(9)	-2.8(9)	2.2(9)
C29	15.6(11)	14.6(12)	9.3(11)	5.1(9)	1.5(8)	0.7(9)
C46	11.6(11)	16.4(12)	11.9(11)	1.2(9)	1.6(8)	-1.3(9)
C11	10.1(10)	12.2(11)	9.0(10)	3.3(9)	-2.7(8)	0.6(8)
C9	12.3(11)	14.1(12)	17.4(12)	6.3(10)	-0.6(9)	-1.8(9)
C47	16.9(12)	17.0(12)	15.2(12)	6.7(10)	1.2(9)	6.6(9)
C27	7.5(10)	12.4(11)	11.6(11)	4.0(9)	-0.9(8)	-0.6(8)
C7	10.4(11)	13.6(11)	9.8(11)	2.4(9)	-2.4(8)	1.9(9)
C13	10.6(11)	13.0(11)	17.1(12)	5.0(9)	2.6(9)	-0.4(9)
C43	10.4(10)	13.1(11)	8.0(10)	3.1(9)	2.0(8)	1.6(8)
C37	10.6(11)	15.5(12)	13.2(11)	2.3(9)	-1.9(8)	-0.2(9)
C35	11.0(10)	14.1(11)	9.3(10)	4.2(9)	2.6(8)	2.2(9)
C5	9.0(10)	16.1(12)	12.2(11)	4.3(9)	0.6(8)	2.2(9)
C41	13.0(11)	21.2(13)	11.3(11)	6.5(10)	1.1(9)	5.4(9)
C3	9.7(10)	12.3(11)	9.0(10)	3.7(9)	-2.7(8)	0.3(8)
C12	9.1(10)	12.0(11)	11.3(11)	4.0(9)	-1.8(8)	1.1(8)
C48	15.2(11)	14.0(11)	10.1(11)	1.5(9)	2.0(8)	1.5(9)
C19	6.9(10)	13.1(11)	10.5(10)	4.3(9)	0.0(8)	0.7(8)
C30	16.3(11)	14.5(12)	11.2(11)	3.5(9)	1.9(9)	1.9(9)
C20	15.6(11)	17.7(12)	10.4(11)	6.8(9)	3.2(9)	3.9(9)
C32	13.2(11)	14.1(12)	12.9(11)	1.1(9)	2.0(9)	2.5(9)
C10	9.7(10)	15.0(12)	14.6(11)	4.4(9)	2.3(8)	1.2(9)
C45	10.9(11)	16.6(12)	10.1(11)	2.8(9)	-1.2(8)	0.7(9)
C42	11.2(11)	16.6(12)	9.7(11)	3.7(9)	0.3(8)	1.2(9)
C16	14.3(11)	15.6(12)	14.8(12)	3.8(10)	2.3(9)	5.8(9)
C26	11.9(11)	11.9(11)	9.9(11)	2.9(9)	0.4(8)	-0.4(9)
C21	12.5(11)	15.9(12)	10.7(11)	1.9(9)	3.3(8)	2.5(9)

C22	8.2(10)	13.7(11)	10.8(11)	3.5(9)	-0.4(8)	0.0(8)
C31	19.1(12)	17.5(12)	14.6(12)	9.0(10)	4.8(9)	4.9(10)
C28	7.8(10)	12.9(11)	10.5(11)	4.3(9)	0.1(8)	0.6(8)
C49	25.4(14)	20.0(13)	22.8(14)	7.2(11)	-2.2(11)	7.0(11)
C50	29.4(15)	25.4(15)	24.1(14)	10.3(12)	4.6(11)	4.1(12)
C52	36.6(16)	19.7(14)	32.1(16)	8.5(12)	-11.9(13)	0.9(12)
C51	21.3(14)	23.7(15)	45.0(18)	16.6(14)	3.2(12)	3.8(11)

Table 4 Bond Lengths for II-3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br5	C33	1.904(2)	C4	C3	1.436(3)
Br3	C17	1.901(2)	C44	C43	1.449(3)
Br2	C8	1.901(2)	C44	C35	1.416(3)
Br4	C24	1.904(2)	C44	C45	1.416(3)
Br1	C1	1.902(2)	C17	C30	1.410(3)
Br6	C40	1.903(2)	C6	C11	1.419(3)
O6	C48	1.436(3)	C6	C7	1.425(3)
O1	C15	1.441(3)	C6	C5	1.437(3)
O4	C32	1.427(3)	C33	C46	1.405(3)
O5	C47	1.432(3)	C2	C3	1.428(3)
O2	C16	1.421(3)	C23	C32	1.501(3)
O3	C31	1.431(3)	C23	C22	1.430(3)
O7	C49	1.443(3)	C8	C9	1.402(3)
O7	C52	1.430(4)	C8	C7	1.381(3)
C34	C33	1.382(3)	C29	C30	1.362(3)
C34	C47	1.507(3)	C29	C28	1.412(3)
C34	C35	1.426(3)	C46	C45	1.369(3)
C1	C14	1.405(3)	C11	C12	1.454(3)
C1	C2	1.376(3)	C11	C10	1.413(3)
C39	C40	1.379(3)	C9	C10	1.368(3)
C39	C38	1.425(3)	C27	C26	1.412(3)
C39	C48	1.512(3)	C27	C22	1.419(3)
C18	C17	1.380(3)	C27	C28	1.451(3)
C18	C19	1.425(3)	C7	C16	1.507(3)
C18	C31	1.509(3)	C13	C12	1.416(3)
C15	C2	1.510(3)	C43	C42	1.415(3)
C40	C41	1.400(3)	C41	C42	1.370(3)
C14	C13	1.372(3)	C3	C12	1.416(3)
C24	C25	1.402(3)	C19	C20	1.440(3)
C24	C23	1.380(3)	C19	C28	1.418(3)

C36	C37	1.349(3)	C20	C21	1.346(3)
C36	C35	1.436(3)	C21	C22	1.437(3)
C25	C26	1.368(3)	C49	C50	1.533(4)
C38	C43	1.415(3)	C50	C51	1.528(4)
C38	C37	1.439(3)	C52	C51	1.508(4)
C4	C5	1.349(3)			

Table 5 Bond Angles for II-3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C52	O7	C49	104.2(2)	C10	C11	C6	118.3(2)
C33	C34	C47	122.2(2)	C10	C11	C12	121.8(2)
C33	C34	C35	118.0(2)	C10	C9	C8	119.8(2)
C35	C34	C47	119.7(2)	O5	C47	C34	112.03(19)
C14	C1	Br1	115.90(17)	C26	C27	C22	118.2(2)
C2	C1	Br1	121.79(18)	C26	C27	C28	121.9(2)
C2	C1	C14	122.3(2)	C22	C27	C28	119.9(2)
C40	C39	C38	117.7(2)	C6	C7	C16	119.6(2)
C40	C39	C48	121.4(2)	C8	C7	C6	117.9(2)
C38	C39	C48	120.8(2)	C8	C7	C16	122.5(2)
C17	C18	C19	118.1(2)	C14	C13	C12	121.1(2)
C17	C18	C31	122.5(2)	C38	C43	C44	120.2(2)
C19	C18	C31	119.4(2)	C42	C43	C38	118.2(2)
O1	C15	C2	112.47(19)	C42	C43	C44	121.6(2)
C39	C40	Br6	121.25(18)	C36	C37	C38	121.8(2)
C39	C40	C41	122.4(2)	C34	C35	C36	120.8(2)
C41	C40	Br6	116.29(17)	C44	C35	C34	120.9(2)
C13	C14	C1	119.5(2)	C44	C35	C36	118.3(2)
C25	C24	Br4	115.37(17)	C4	C5	C6	121.9(2)
C23	C24	Br4	122.21(18)	C42	C41	C40	119.5(2)
C23	C24	C25	122.4(2)	C2	C3	C4	120.9(2)
C37	C36	C35	121.9(2)	C12	C3	C4	118.3(2)
C26	C25	C24	119.5(2)	C12	C3	C2	120.8(2)
C39	C38	C37	121.1(2)	C13	C12	C11	121.8(2)
C43	C38	C39	120.9(2)	C3	C12	C11	119.9(2)
C43	C38	C37	118.1(2)	C3	C12	C13	118.3(2)
C5	C4	C3	121.9(2)	O6	C48	C39	110.93(18)
C35	C44	C43	119.8(2)	C18	C19	C20	121.0(2)
C35	C44	C45	118.0(2)	C28	C19	C18	120.8(2)
C45	C44	C43	122.2(2)	C28	C19	C20	118.2(2)
C18	C17	Br3	121.62(17)	C29	C30	C17	119.3(2)

C18	C17	C30	122.0(2)	C21	C20	C19	122.0(2)
C30	C17	Br3	116.39(17)	O4	C32	C23	108.36(18)
C11	C6	C7	120.7(2)	C9	C10	C11	121.1(2)
C11	C6	C5	118.1(2)	C46	C45	C44	121.3(2)
C7	C6	C5	121.2(2)	C41	C42	C43	121.2(2)
C34	C33	Br5	122.18(18)	O2	C16	C7	110.36(19)
C34	C33	C46	121.9(2)	C25	C26	C27	121.5(2)
C46	C33	Br5	115.88(18)	C20	C21	C22	121.7(2)
C1	C2	C15	122.5(2)	C23	C22	C21	121.0(2)
C1	C2	C3	117.9(2)	C27	C22	C23	120.6(2)
C3	C2	C15	119.6(2)	C27	C22	C21	118.3(2)
C24	C23	C32	122.6(2)	O3	C31	C18	111.8(2)
C24	C23	C22	117.7(2)	C29	C28	C27	122.3(2)
C22	C23	C32	119.7(2)	C29	C28	C19	117.9(2)
C9	C8	Br2	116.03(17)	C19	C28	C27	119.8(2)
C7	C8	Br2	121.85(17)	O7	C49	C50	106.3(2)
C7	C8	C9	122.1(2)	C51	C50	C49	104.1(2)
C30	C29	C28	122.0(2)	O7	C52	C51	104.6(2)
C45	C46	C33	119.7(2)	C52	C51	C50	102.5(2)
C6	C11	C12	119.9(2)				

Table 6 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for II-3.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H15A	2980	9381	8545	16
H15B	3947	8606	8662	16
H14	-820	8085	9388	17
H36	6514	5636	4793	17
H25	6527	3837	10080	15
H4A	3873	6951	8013	14
H29	6260	6985	10333	16
H46	10662	8273	6976	17
H9	-393	3259	8950	17
H47A	7123	8264	5192	19
H47B	6947	7164	4570	19
H13	-651	6423	9305	16
H37	6662	3995	4675	16
H5A	3998	5296	7835	15
H41	11186	3468	6562	17
H48A	7195	2572	4276	16

H48B	7891	1732	4559	16
H30	6236	8666	10462	17
H20	6914	6528	7146	17
H32A	7986	3604	7108	17
H32B	7657	2621	7431	17
H10	-523	4946	9164	16
H45	10887	6611	6831	15
H42	11054	5144	6694	15
H16A	4362	3914	8214	18
H16B	3589	2795	7973	18
H26	6362	5507	10219	14
H21	7095	4894	7027	16
H31A	6819	9120	7881	19
H31B	7591	8215	7477	19
H49A	2556	1130	6526	27
H49B	2039	-28	6069	27
H50A	3773	-145	5328	31
H50B	4146	1054	5671	31
H52A	5075	242	7621	36
H52B	4757	1290	7478	36
H51A	5285	-420	6239	34
H51B	5909	733	6363	34
H4	6300(30)	2760(20)	6390(20)	21(9)
H2	4330(30)	3300(30)	6940(20)	35(10)
H3	5090(40)	8120(30)	7240(20)	43(12)
H1	3140(30)	8910(30)	7320(20)	40(10)
H5	5770(30)	7510(30)	5940(20)	37(10)
H6	5810(30)	2320(30)	5030(20)	35(10)

Appendix Chapter-III

III-27

III-36

III-38

III-51

III-54

III-55

III-58

III-58

135.6567
131.4792
130.7810
129.7357
124.3106
124.1924
123.4942

77.2136
77.0000
76.7901

50.2144
48.0550
39.0553

26.0421
22.6200

III-59

¹H and ¹³C NMR chemical shifts (δ/ppm) for **III-59**

Coupling constants (J/Hz) in Toluene-*d*₈; (aromatic solvent induced shifts - ASIS): $\Delta\delta_{\text{H}}^* = \delta_{\text{CDCl}_3} - \delta_{\text{Toluene-d}_8}$

Proton	CDCl ₃	Toluene- <i>d</i> ₈	$\Delta\delta_{\text{H}}^*$	H _m ---	J/ Hz	Carbon	δ/ppm
H3	7.58	7.39	0.19	H _n		C1	a
H4	7.90	7.60	0.30	³ J _{3,4}	8.7	C2	a
H8a	4.10	4.15	-0.05	² J _{8a,8b}	-13.3	C3	129.47
H8b	3.77	3.61	0.16	² J _{9a,9b}	-12.9	C4	123.33
H12	8.16	7.71	0.45	³ J _{12,13}	8.9	C5	a
H13	8.55	8.06	0.49	² J _{17a,17b}	-13.2	C6	a
H17a	2.32	2.24	0.08	³ J _{17a,18a}	4.8	C7	124.66
H17b	2.54	2.54	0.00	³ J _{17a,18b}	8.2	C8	52.26
H18a	1.40	1.27	0.13	³ J _{17b,18a}	9.0	C9	55.72
H18b	1.40	1.27	0.13	³ J _{17b,18b}	6.3	C10	a
H19	1.20	1.11	0.09	² J _{18a,18b}	-12.5	C11	a
H20	0.32	0.33	-0.01	³ J _{18a,19}	6.6	C12	130.75
H21	0.72	0.70	0.02	³ J _{18b,19}	7.2	C13	125.99
				³ J _{19,20}	6.7	C14	a
				³ J _{20,21}	6.7	C15	a
						C16	124.12
						C17	51.69
						C18	35.09
						C19	25.92
						C20	21.34
						C21	22.54

**DFT B3LYP/6-31g(d)
optimized structure**

Ball and Bond type of representation

Tube type of representation

DFT B3LYP/6-31G(d)
optimized structure

Figure 1. DFT calculations illustrating an energetically feasible pathway for interconversion of inequivalent phenanthrene rings (**2•syn**) through an intermediate (**2•anti**) possessing co-planar phenanthrene rings (*top*). Intermediates identified along the pathway to **2•anti** (*bottom*). Hydrogen atoms have been removed for clarity.

Computational methods.

Spin-restricted density functional theory (RDFT) calculations were performed with the Gaussian 16 (G16) program.¹ Gas-phase geometry optimization and normal mode analyses were performed using the M06 functional and the 6-31+G(d) basis set to identify ground state geometries.² The identified stationary points met or exceeded all default G16 convergence criteria including predicted changes in energy upon further optimization less than 0.002 kcal/mol. Using the same functional-basis set, normal-modes were calculated for each optimized structure and thermochemical corrections were determined.

References:

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; K. Toyota; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford CT, 2004.
2. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2006**, *120*, 215.

Computational Coordinates and Energetic Details

2•syn

Calculation results at DFT-optimized geometry:

Total Energy: -7542041.4 kcal/mol

SCF Convergence: 0.41D-08

Enthalpy (298 K): -7541549.7 kcal/mol

Entropy (298 K): 264.95 eu

Free Energy (298 K): -7541628.7 kcal/mol

Three lowest frequencies (cm^{-1}): 12.3, 17.5, 22.6

C	-3.523983	-2.511500	-1.479095
C	-2.851275	-1.348074	-1.150332
C	-1.479209	-3.671279	-1.991473
C	-1.431438	-1.347937	-1.302172
C	-2.851870	-3.663729	-1.917254
C	-0.726532	-2.523141	-1.671570
C	-0.677955	-0.154280	-1.087132
H	-3.424754	-4.552772	-2.171649
H	0.986837	-4.590816	-2.299500
H	-0.986836	-4.590816	-2.299500
C	0.677955	-0.154280	-1.087132
H	-1.199697	0.780098	-0.907117
H	1.199697	0.780099	-0.907117
C	1.431438	-1.347936	-1.302172
C	2.851275	-1.348074	-1.150332
C	0.726533	-2.523141	-1.671570
C	3.523983	-2.511499	-1.479094
C	2.851870	-3.663729	-1.917254
H	3.424754	-4.552771	-2.171648

C	1.479210	-3.671279	-1.991473
Br	-5.421481	-2.665840	-1.352026
Br	5.421481	-2.665840	-1.352024
C	3.530671	-0.133001	-0.566635
H	4.626360	-0.225510	-0.667440
H	3.257390	0.761397	-1.147243
C	-3.530671	-0.133001	-0.566634
H	-3.257391	0.761397	-1.147243
H	-4.626360	-0.225511	-0.667440
N	-3.115231	0.095769	0.819386
N	3.115231	0.095770	0.819386
C	3.426380	-1.002373	1.729493
H	3.022238	-1.926760	1.285459
C	4.903990	-1.204695	2.069756
H	2.845388	-0.832050	2.651708
C	-3.426380	-1.002373	1.729493
C	-4.903989	-1.204694	2.069759
H	-3.022239	-1.926761	1.285459
H	-2.845386	-0.832050	2.651708
C	3.512535	3.454794	-0.128118
C	2.848143	2.542228	0.672469
C	1.471322	4.578978	-0.710576
C	1.432539	2.681991	0.803243
C	2.839304	4.487369	-0.798246
C	0.726334	3.667695	0.065663
C	0.678635	1.805212	1.647710
H	3.404274	5.190126	-1.406608
H	-0.974297	5.366171	-1.272059
H	0.974296	5.366171	-1.272059
C	-0.678636	1.805212	1.647710
H	1.201392	1.079131	2.263964
H	-1.201392	1.079131	2.263963
C	-1.432539	2.681991	0.803243
C	-2.848144	2.542227	0.672469
C	-0.726334	3.667695	0.065663
C	-3.512535	3.454793	-0.128118

C	-2.839305	4.487368	-0.798246
H	-3.404275	5.190126	-1.406607
C	-1.471322	4.578978	-0.710576
Br	5.394343	3.371901	-0.418230
Br	-5.394343	3.371901	-0.418230
C	-3.545197	1.387427	1.346166
H	-4.638821	1.522461	1.280374
H	-3.306412	1.393608	2.421755
C	3.545197	1.387428	1.346166
H	3.306412	1.393608	2.421755
H	4.638821	1.522461	1.280373
C	5.219472	-2.599515	2.606338
H	5.514713	-1.032509	1.168226
H	5.232581	-0.454018	2.811493
C	4.480563	-2.887616	3.908293
H	4.885866	-3.330122	1.845589
C	6.720928	-2.764749	2.795784
H	4.750096	-3.875302	4.307272
H	4.743559	-2.138971	4.673062
H	3.389211	-2.870207	3.784684
H	6.974570	-3.773932	3.148968
H	7.265089	-2.588014	1.857081
H	7.098775	-2.047356	3.541296
C	-5.219473	-2.599515	2.606338
H	-5.232578	-0.454018	2.811499
H	-5.514714	-1.032505	1.168231
C	-6.720928	-2.764746	2.795788
H	-4.885870	-3.330120	1.845586
C	-4.480561	-2.887620	3.908290
H	-4.750094	-3.875307	4.307267
H	-3.389209	-2.870212	3.784679
H	-4.743554	-2.138977	4.673062
H	-6.974571	-3.773930	3.148970
H	-7.098772	-2.047354	3.541302
H	-7.265092	-2.588009	1.857087

syn•N^{sp2}

Calculation results at DFT-optimized geometry:

Total Energy: -7542032.6 kcal/mol

SCF Convergence: 0.35D-08

Enthalpy (298 K): -7541541.1 kcal/mol

Entropy (298 K): 265.72 eu

Free Energy (298 K): -7541620.3 kcal/mol

Three lowest frequencies (cm⁻¹): 12.3, 15.8, 21.6

C	-5.180777	-0.144356	1.027554
N	-4.035488	0.493559	0.417517
C	-3.662963	0.140012	-0.937239
C	-2.959032	-1.196624	-1.164419
C	-1.531405	-1.310941	-1.123163
C	-0.696380	-0.158163	-0.991120
C	0.658521	-0.240846	-0.931401
C	1.347110	-1.489096	-1.011924
C	0.567132	-2.657837	-1.216565
C	-0.882520	-2.570309	-1.265328
C	-1.682429	-3.711106	-1.468932
C	-3.048139	-3.607990	-1.571095
C	-3.666682	-2.357277	-1.436555
Br	-5.559765	-2.380429	-1.693607
C	1.243636	-3.883776	-1.383341
C	2.615027	-3.948804	-1.354217
C	3.366612	-2.786913	-1.119669
C	2.773527	-1.552353	-0.920049
Br	5.258446	-3.035822	-1.098274
H	3.127338	-4.896869	-1.502416

H	0.693216	-4.805824	-1.551495
H	-1.234824	-4.696406	-1.569513
H	-3.656876	-4.489280	-1.762179
H	-1.147760	0.828518	-0.944440
H	1.229639	0.676566	-0.825562
H	-3.050452	0.954028	-1.348175
H	-4.585617	0.148261	-1.536045
C	-4.892371	-1.450568	1.766131
C	-3.102070	1.116061	1.324571
H	-3.664465	1.337411	2.248003
H	-2.293871	0.425709	1.622254
C	-2.645833	4.435397	-0.543577
C	-2.493233	2.397777	0.785502
C	-3.244201	3.361387	0.131685
Br	-5.146412	3.336565	0.116328
H	-0.715613	1.170901	2.468333
C	-1.084359	2.609531	0.863811
C	-0.255831	1.822694	1.729847
H	-0.838061	5.340226	-1.184964
C	-1.274899	4.530216	-0.605432
C	-0.455477	3.614536	0.082629
C	0.991705	3.618888	-0.042693
H	1.679541	1.244626	2.330621
C	1.097088	1.874006	1.664575
C	1.765490	2.684477	0.691666
C	1.660177	4.468210	-0.947689
H	1.109319	5.209545	-1.521820
C	3.013519	4.354572	-1.161464
H	3.823649	1.544388	2.220005
C	3.158413	2.520419	0.436603
C	3.899343	1.405583	1.129078
C	3.745785	3.363511	-0.490170
H	3.517799	5.002491	-1.875051
Br	5.587280	3.227625	-0.959335
H	4.975593	1.465750	0.891680

H	3.228604	-0.605058	2.771296
N	3.340030	0.092004	0.823913
C	3.708658	-0.905535	1.824174
H	3.234897	-1.857735	1.536394
C	5.206017	-1.124601	2.046562
H	4.634740	-0.478864	-0.784050
C	3.564355	-0.316171	-0.564137
H	3.257213	0.521970	-1.208030
H	-3.276010	5.168845	-1.042305
C	5.533177	-2.450582	2.730521
H	5.728626	-1.092188	1.076571
H	5.627201	-0.300162	2.650259
C	7.040845	-2.651149	2.796849
C	4.920260	-2.538051	4.123763
H	5.105336	-3.259176	2.108871
H	7.299893	-3.615542	3.255456
H	7.494216	-2.619927	1.795803
H	7.511009	-1.859290	3.401067
H	5.202159	-3.475716	4.622456
H	5.277780	-1.707857	4.754182
H	3.822849	-2.494482	4.104010
C	-6.145241	-2.189130	2.233743
H	-4.307973	-2.111105	1.105664
H	-4.245062	-1.249501	2.640705
C	-5.792670	-3.611848	2.646567
C	-6.847077	-1.457298	3.372187
H	-6.840111	-2.245213	1.375465
H	-5.639327	0.586148	1.718278
H	-5.928842	-0.323980	0.239061
H	-6.678868	-4.169187	2.981233
H	-5.337488	-4.166218	1.812570
H	-5.069793	-3.605964	3.477826
H	-7.744282	-1.999976	3.701192
H	-6.176661	-1.368655	4.242029
H	-7.161472	-0.443714	3.088782

anti-N^{sp2}

Calculation results at DFT-optimized geometry:

Total Energy: -7542028.0 kcal/mol

SCF Convergence: 0.45D-08

Enthalpy (298 K): -7541536.4 kcal/mol

Entropy (298 K): 262.64 eu

Free Energy (298 K): -7541614.7 kcal/mol

Three lowest frequencies (cm⁻¹): 13.8, 21.0, 23.0

C	-5.416738	-0.291637	-0.318627
N	-4.032686	-0.504177	0.093821
C	-3.507700	0.350281	1.162890
C	-3.007912	1.722195	0.722347
C	-1.606148	1.978159	0.564815
C	-0.616381	1.211872	1.264461
C	0.710996	1.488520	1.174129
C	1.213662	2.468295	0.258867
C	0.270948	3.248604	-0.457522
C	-1.148631	3.082841	-0.204597
C	-3.421697	3.891141	-0.332071
C	-2.095715	4.012444	-0.673517
C	-3.860948	2.760031	0.370620
Br	-5.681768	2.836108	0.943818
H	-4.136629	4.666173	-0.599770
H	-1.782436	4.887838	-1.237631
C	0.747233	4.161458	-1.420679
H	0.051826	4.751602	-2.013333
C	2.091754	4.292136	-1.670724
H	2.450394	4.976689	-2.436243
C	3.013210	3.527655	-0.938318
Br	4.847025	3.794917	-1.387583
C	2.616817	2.629173	0.036980
H	3.368225	2.035248	1.936276

C	3.603173	1.853925	0.874481
H	4.618757	2.257443	0.717771
N	3.538597	0.414424	0.671479
C	4.090941	-0.329357	1.799597
H	3.475508	-0.082149	2.681368
H	3.925776	-1.402533	1.609690
C	5.568259	-0.087806	2.109873
C	4.003855	-0.037170	-0.642123
H	5.102697	-0.001727	-0.742152
C	3.486597	-1.432747	-0.884948
C	2.076709	-1.622099	-1.009619
C	1.209589	-0.529018	-1.309353
C	-0.140217	-0.658710	-1.308057
C	-0.786296	-1.885340	-0.948512
C	0.047817	-3.027242	-0.765161
C	1.492434	-2.901643	-0.847934
C	2.356971	-4.012939	-0.748573
H	1.959201	-5.021885	-0.670491
C	3.722264	-3.855150	-0.769698
H	4.380762	-4.719635	-0.719748
C	4.275523	-2.564374	-0.807314
Br	6.177964	-2.470936	-0.701641
C	-0.559844	-4.260894	-0.470231
H	0.041658	-5.151694	-0.307274
H	-2.391179	-5.331215	-0.162184
C	-1.925536	-4.371081	-0.373836
C	-2.731552	-3.240193	-0.553492
C	-2.207024	-1.981354	-0.808787
C	-3.124468	-0.785746	-1.012268
H	-2.544267	0.108413	-1.282781
H	-3.741129	-0.999440	-1.897544
H	-5.605134	-1.001377	-1.134451
H	-5.585168	0.714313	-0.751292
C	-6.428857	-0.566215	0.780826
H	-4.293189	0.457087	1.920621
H	-2.696164	-0.204484	1.648439
H	-0.926875	0.409508	1.929257
H	1.414238	0.881673	1.737872

H	-0.730814	0.215801	-1.566507
H	1.634468	0.440618	-1.557004
H	3.615838	0.663689	-1.394230
Br	-4.602821	-3.580510	-0.505894
C	6.185817	-1.160845	3.004741
H	6.137845	-0.048692	1.166436
H	5.701536	0.898432	2.590662
C	7.687369	-0.942821	3.128955
C	5.533260	-1.196438	4.382078
H	6.019924	-2.137786	2.513773
H	8.158371	-1.719591	3.747222
H	8.176007	-0.951850	2.144061
H	7.900776	0.030250	3.598850
H	6.014866	-1.941899	5.029885
H	5.627611	-0.216945	4.878064
H	4.464480	-1.445511	4.334228
C	-7.875787	-0.412866	0.309696
H	-6.266872	-1.587831	1.166911
H	-6.269407	0.114292	1.630559
C	-8.813404	-0.351024	1.508534
H	-7.954502	0.544792	-0.238188
C	-8.293913	-1.540200	-0.628552
H	-9.862409	-0.246077	1.198384
H	-8.734194	-1.271944	2.107560
H	-8.568468	0.495351	2.166538
H	-9.334496	-1.416265	-0.959299
H	-7.668107	-1.597332	-1.529653
H	-8.223266	-2.511244	-0.112506

^1H NMR chemical shifts in Toluene- d_8 (dilute solution)

^1H NMR chemical shifts in CDCl_3

Experimental (a) and calculated (b) ^1H NMR spectra in Toluene- d_8

Experimental (a) and calculated (b) ^1H NMR spectra in Toluene- d_8

Variable-temperature ^1H NMR spectrum in Toluene- d_8

gCOSY spectrum in Toluene- d_8

Expanded regions of the gCOSY spectrum

Expanded regions of the zTOCSY spectrum

Expanded regions of the gHSQCAD spectrum

DEPT 135 with suppression of Quaternary carbons
(expanded region)

DEPT 135 with suppression of Quaternary carbons

Number of scans --8192

Calculation of free energy of activation ($\Delta G^\ddagger$ / kcal mol⁻¹)

$$\Delta G^\ddagger = RT \left[23.76 - \ln \left(\frac{k}{T} \right) \right]$$

$$R = 1.9872 \text{ cal mol}^{-1}$$

$$T = 75 + 273.15 = 348.15 \text{ K}$$

$$k_{\text{rate}} = 2.22 \delta v$$

$$k_{\text{rate}} = 2.22 \times (2.50 - 2.22) \times 599.6707 = 2.22 \times (0.28 \times 599.6707)^\dagger = 372.8 \text{ s}$$

$$\Delta G^\ddagger = 1.9872 \times 348.15 \times [23.76 - \ln(372.8/348.15)]$$

$$\Delta G^\ddagger = 691.84 [23.76 - 1.07] = 15697 \text{ cal mol}^{-1} = 15.7 \text{ kcal mol}^{-1}$$

¹H NMR (600 MHz) and ¹³C NMR (150 MHz) Spectra of Macrocycle **III-59**

¹H and ¹³C NMR chemical shifts (δ/ppm) and coupling constants (J/Hz) in CDCl₃

Proton	δ/ppm	H _m --- H _n	J/Hz	Carbon	δ/ppm
H3	7.59	³ J _{3,4}	8.8	C1	134.80
H4	8.17	² J _{8a,8b}	-13.2	C2	124.69
H7	6.10	² J _{9a,9b}	-13.2	C3	129.62
H8a	4.11	³ J _{12,13}	8.9	C4	125.92
H8b	3.79	² J _{17a,17b}	-13.2	C5	130.03
H9a	4.60	³ J _{17a,18a}	4.9	C6	131.69
H9b	4.41	³ J _{17a,18b}	8.0	C7	124.54
H12	7.90	³ J _{17b,18a}	8.6	C8	52.19
H13	8.55	³ J _{17b,18b}	6.2	C9	55.74
H16	8.16	² J _{18a,18b}	-12.5	C10	134.03
H17a	2.32	³ J _{18a,19}	6.6	C11	126.32
H17b	2.55	³ J _{18b,19}	7.1	C12	130.83
H18a	1.4075	³ J _{19,20}	6.6	C13	124.14
H18b	1.4088	³ J _{20,21}	6.6	C14	130.82
H19	1.20			C15	132.77
H20	0.32			C16	123.27
H21	0.72			C17	51.56
				C18	35.05
				C19	25.95
				C20	21.46
				C21	23.07

**DFT B3LYP/6-31G(d)
optimized structure**

Selective decoupled ^1H - $\{^1\text{H}\}$ NMR spectra (a - d)

Irradiation of H18, ^1H NMR spectrum (b)

Control ^1H NMR spectrum (a)

Exchange between proton pairs:

H8a - H9a

H8b - H9b

Selective decoupled $^1\text{H} - \{^1\text{H}\}$ NMR spectra (b-g)

Control ^1H NMR spectrum (a)

Exchanging between proton pairs:

H3 - H12

H4 - H13

H7 - H16

Experimental and calculated
¹H NMR spectra
 Back to back and
 overlapping representations

gCOSY spectrum (a)
and expanded portions
(b-d)

zTOCSY

Spin system
identification

zTOCSY spectrum (a)
and expanded portions
(b-c)

Exchanging between proton pairs:

H3 - H12

H4 - H13

H7 - H16

H8a - H9a

H8b - H9b

Expanded portion of the gHMBCAD spectrum

Expanded portion of the gHMBCAD spectrum

The top ^1H NMR spectrum (600 MHz) of macrocycle **3** in $\text{toluene-}d_8$ was obtained from a less concentrated sample. The bottom ^1H NMR spectrum of macrocycle **3** in $\text{toluene-}d_8$ was obtained from a more concentrated sample.

09/08/20

09/07/20

The top ^1H NMR spectrum of macrocycle **3** in $\text{toluene-}d_8$ was obtained from a less concentrated sample. The bottom ^1H NMR spectrum of macrocycle **3** in $\text{toluene-}d_8$ was obtained from a more concentrated sample.

HRMS of III-36

SAMPLE2-FMS #58 RT: 0.51 AV: 1 NL: 3.73E7
T: FTMS + p ESI Full ms [150.0000-2000.0000]

Wide Mass Range for HRMS ($[M + H]^+$) of Macrocycles **III-59** and **III-60**

HRMS ($[M + H]^+$) of Macrocycle **III-59**

NL:
1.88E7
SAMPLE2_202009211
03656#8-11 RT:
0.07-0.10 AV: 4 T:
FTMS + p ESI SIM ms
[884.9000-905.1000]

NL:
2.36E5
 $C_{42}H_{42}Br_4N_2 + H$:
 $C_{42}H_{43}Br_4N_2$
pa Chrg 1

HRMS ($[M + H]^+$) of Macrocycle **III-60**

NL:
1.17E6
SAMPLE2-FMS#1-58
RT: 0.01-0.51 AV: 58
T: FTMS + p ESI Full
ms
[150.0000-2000.0000]

NL:
1.08E5
C₈₄H₈₄Br₈N₄+H:
C₈₄H₈₅Br₈N₄
pa Chrg 1