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## Syntheses and Structures of Functionalized Carbon Nanohoops

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# Syntheses and Structures of Functionalized Carbon Nanohoops

Shuangjiang Li

Dissertation submitted to the Eberly College of Arts 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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Keywords: Diels–Alder Reaction, Cycloparaphenylenes, Homocoupling Reaction, Stille  
Coupling Reaction, Oxidative Aromatization, Friedel–Crafts reaction, ...

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## ABSTRACT

### Syntheses and Structures of Functionalized Carbon Nano hoops

Shuangjiang Li

Functionalized [9]cycloparaphenylenes ([9]CPPs) bearing nine aromatic units in the macrocyclic structures were synthesized. The macrocyclic structures were substituted with carbomethoxy or *N*-phenylphthalimido groups. The Diels–Alder reaction of (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene or a related diene with dimethyl acetylenedicarboxylate followed by the nickel-mediated homocoupling reactions and oxidative aromatization produced the functionalized [9]CPPs. Treatment of a resultant [9]CPP with aniline or 1,4-diaminobenzene gave the corresponding *N*-phenylphthalimides. The X-ray structure of a [9]CPP bearing six carbomethoxy groups was obtained.

A synthetic pathway to a functionalized [9]cycloparaphenylene bearing three indeno[2,1-*a*]fluorene-11,12-dione-2,9-diyl units in the macrocyclic ring structure ([3]CIFO) has been developed. The <sup>1</sup>H and <sup>13</sup>C NMR spectra show that only the *anti* rotamer (*anti*-[3]CIFO) is produced. DFT calculations indicate that the *anti* rotamer is thermodynamically more stable than the *syn* rotamer by 4.3 kcal/mol, and the rotational barrier from the *anti* to *syn* rotamer is estimated to be 23.3 kcal/mol. The UV/Vis and fluorescence spectra and cyclic voltammogram of *anti*-[3]CIFO were investigated.

A synthetic pathway for the construction of an armchair carbon nanobelt was designed, which represents a belt segment of (8,8) carbon nanotube and is a tetramethylated [16]cyclophenacene. The corresponding belt precursor has been successfully synthesized. We are developing reaction conditions for the transformation to the tetramethylated [16]cyclophenacene.

**DEDICATED TO**

**My Family and My Girlfriend**

## Acknowledgment

I would like to express my heartfelt appreciation to my advisor Prof. Kung K. Wang for the unconditional support of my Ph.D. study. Your immense knowledge, integral view and enthusiasm for chemistry have made a deep impression on me. In research, you gave me enough freedom and continuing to contribute valuable feedback, advice, and encouragement. During the last five and a half years, I have learned extensively from you. I have been so lucky to have such a tremendous advisor as you. I would miss those enjoyable moments talking about chemistry with you.

Besides my advisor, I would like to thank my committee members, Prof. Brian V. Popp, Prof. Bjorn C. G. Soderberg, Prof. Jessica Hoover, and Prof. Yon Rojanasakul, for your insightful comments and encouragement. I would also like to give special thanks to Prof. Jeffrey L. Petersen for your great help in X-ray structure analysis, Prof. Brian V. Popp for your important contribution in DFT calculations, Prof. Carsten Milsmann and Yu Zhang for your help in the analysis of cyclic voltammetry, Dr. Novruz Akhmedov for your tremendous contribution in NMR experiments.

My sincere thanks to my lab mates, Dr. Changfeng Huang, Dr. Haresh Thakellapalli, Dr. Behzad Farajidizaji and Merfat Aljhdli for your help and support. Special thanks to Dr. Changfeng Huang for the great help in my first year, for the stimulating discussions, for the sleepless nights in the lab.

Last, I would like to thank my father Deliang Li, my mother Zongai Li, and my girlfriend Xiaojun Li for your unconditional love, support, and sacrifices. I owe a lot to my parents, who encouraged and helped me at every stage in my life, and longed to see this achievement come true. I wish to give special thanks to my beloved girlfriend Xiaojun Li, for your continuous support and

love since in high school. And thank you for your suggestion on studying abroad, which totally changed my life. Finally, I dedicate this thesis to the memory of my grandparents, whose role in my life was, and remains, immense.

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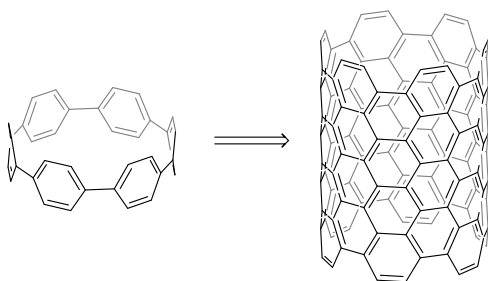


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# Chapter 1. Syntheses and Structures of Cycloparaphenylenes

## 1.1 Introduction

Connecting benzene units in *para* positions in a cyclic array produces cycloparaphenylenes (CPPs), which are the shortest repeating hooplike structures of the corresponding armchair carbon nanotubes (CNTs).<sup>1</sup> It was envisioned that CPPs could serve as templates for growing carbon nanotubes of a single chirality and diameter for nanotechnology applications (Figure 1.1).<sup>2</sup> In addition, CPPs are inherently interesting because they have been shown to exhibit unique size-dependent optoelectronic and redox properties.<sup>3</sup> The presence of well-defined cavity space provides opportunity to investigate host-guest interactions.<sup>4</sup> Furthermore, the unusual alignments of the radially  $\pi$ -conjugated systems in these molecules present a platform for the study of the effect of pyramidalization of  $sp^2$ -hybridized carbons on aromaticity<sup>5</sup> and ring size on strain energy.<sup>6</sup>

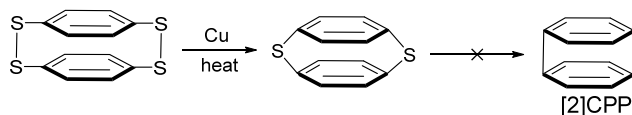


**Figure 1.1.** The shortest-possible unit of a (6,6) CNT is [6]CPP.

## 1.2 Synthetic Attempts for the Preparation of CPPs

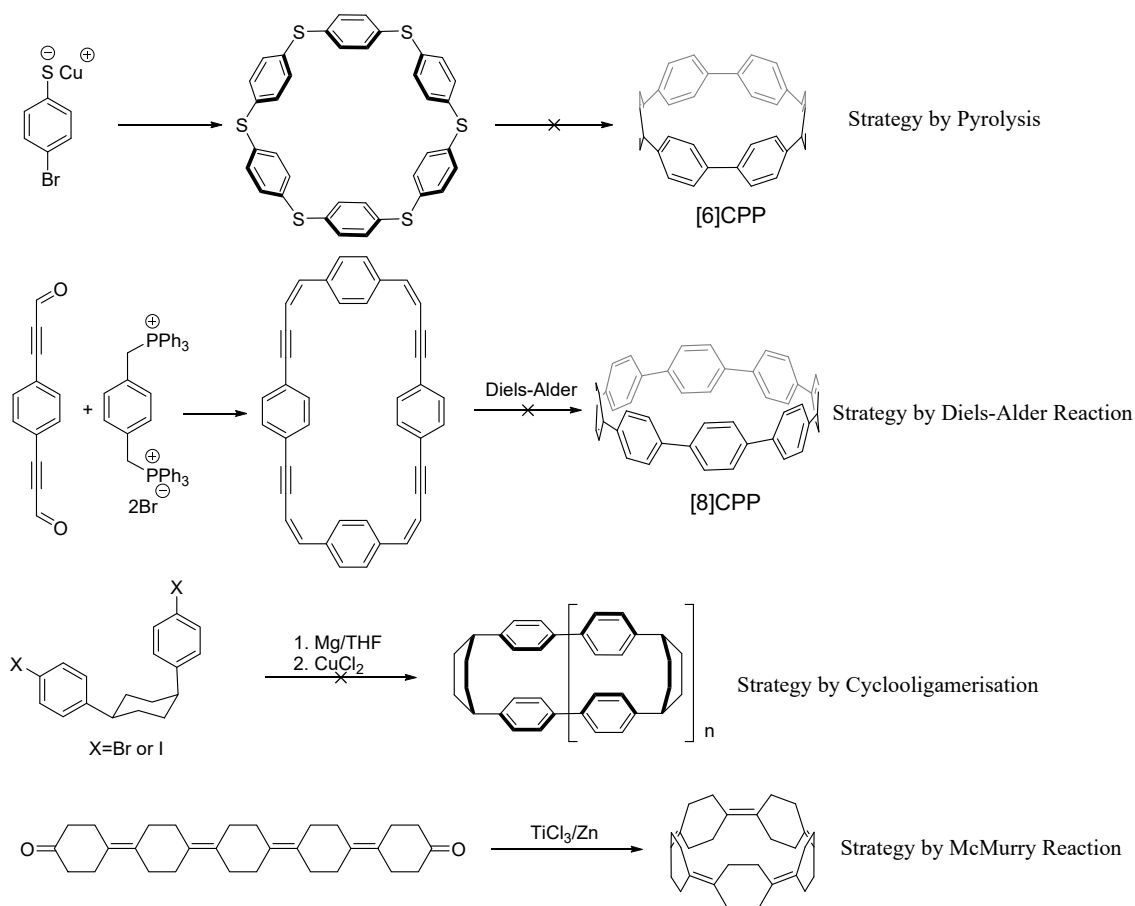
The earliest attempts to synthesize cycloparaphenylenes were reported in 1934 by Parekh and Guha (Scheme 1.1).<sup>8b</sup> The authors introduced a Cu-mediated pyrolysis method to try to promote the synthesis of [2]CPPs over two steps. However, the structure of [2]CPP is far too strained to be constructed. Nevertheless, the chapter of attempts for the synthesis of CPPs was opened.

### Scheme 1.1. Early Work by Parekh and Guha in 1934



After almost 60 years since the first attempt to the synthesize CPPs, the most comprehensive exploration of CPP chemistry was conducted by Vögtle and co-workers.<sup>9</sup> There were several strategies proposed to accomplish the synthetic challenge of CPPs by Vögtle and co-workers (Scheme 1.2). Even though those strategies were not successful, they exerted significant influence on the accomplishment of rational synthesis of CPPs fifteen years later.

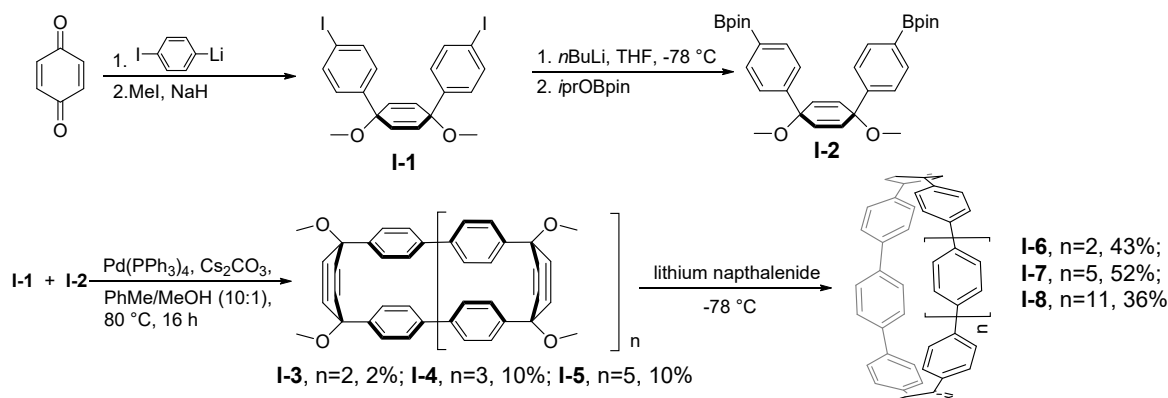
### Scheme 1.2. Vögtle's Strategies for the Synthesis of CPPs



## Bertozzi and Jasti's Strategy for the Synthesis of CPPs

After almost 80 years since the first attempt for the synthesis of the strained carbon nanohoops, Bertozzi, Jasti, and co-workers reported the successful construction of CPPs in 2008 (Scheme 1.3).<sup>7a</sup> Their key strategy was to build up ring strain sequentially through the synthesis of a strain-free macrocyclic CPP precursor. For the synthesis of the macrocyclic CPP precursor, a borylated L-shaped unit **I-2** was synthesized from the parent L-shaped structure **I-1**, which was prepared from *p*-benzoquinone and 4-iodophenyllithium. Subsequently, three different CPP precursors, **I-3**, **I-4**, and **I-5**, were produced in 22% combined yield via the Suzuki-Miyaura cross-coupling reactions of **I-1** and **I-2**. Finally, three CPPs, **I-6** ([9]CPP), **I-7** ([12]CPP), and **I-8** ([18]CPP), were synthesized from the corresponding precursors, **I-3**, **I-4**, and **I-5**, respectively, via reductive aromatization reactions. Later, Jasti's group was able to selectively synthesize [5]- to [12]CPPs in a similar manner.<sup>1a, 4b, 7f, 7g, 7m</sup>

### Scheme 1.3. Bertozzi and Jasti's First Synthesis of CPPs in 2008

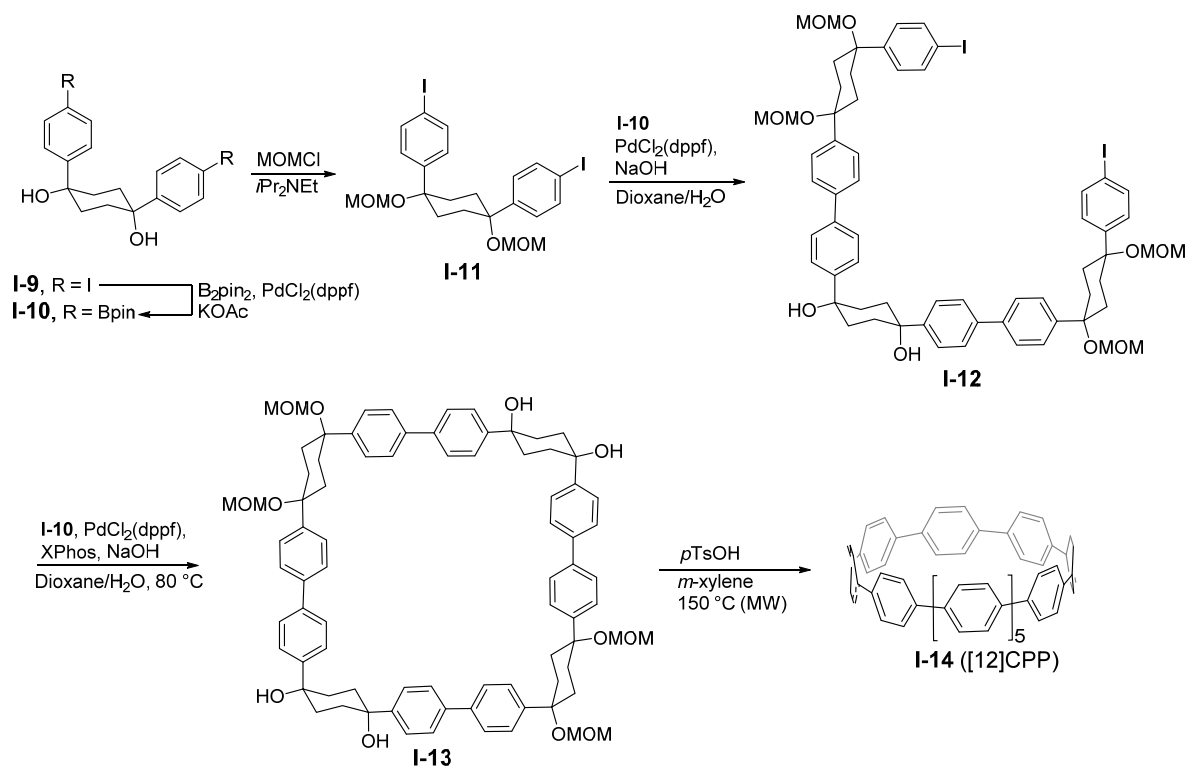


## Itami's Strategy for the Synthesis of CPPs

Shortly after the first successful synthesis of CPPs, Itami's group was able to selectively prepare [12]CPP in 2009 (Scheme 1.4).<sup>7b</sup> The key idea of this strategy was to introduce a cyclohexyl unit between 4-halogenated as an L-shaped precursor as shown in **I-9** for macrocyclization. The corresponding

fully aromatized [12]CPP (**I-14**) was produced by dehydration and aromatization of macrocycle **I-13**. By using cyclohexyl unit as a lynchpin, Itami's group developed similar approaches for the synthesis of [7]- to [16]CPPs.<sup>1b,3e,7d,7e</sup>

### Scheme 1.4. Itami's Approach for Selective Synthesis of [12]CPP

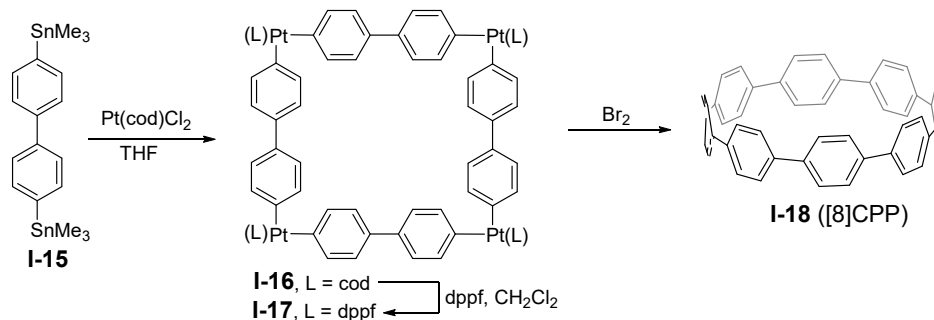


### Yamago's Strategy for the Synthesis of CPPs

In 2010, Yamago's group reported a distinctly different strategy for the synthesis of CPPs through a platinum-mediated approach (Scheme 1.5).<sup>7c</sup> As the key intermediate in Yamago's approach, a tetraplatinum-containing cyclic square shaped structure **I-16** was synthesized via the reaction of  $Pt(cod)Cl_2$  with 4,4'-bis(trimethylstannyl)biphenyl (**I-15**). Subsequently, complex **I-17** was obtained by ligand exchange replacing 1,5-cyclooctadiene (COD) to the much more electron-rich ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf). The formation of [8]CPP (**I-18**) was

achieved by a bromine induced reductive elimination reaction of the platinum-containing macrocyclic complex. One year after the selective synthesis of [8]CPP, Yamago and co-workers successfully prepared [12]CPP selectively<sup>6b</sup> and [8]- to [13]CPP randomly via a similar strategy.<sup>7i,7u</sup>

### Scheme 1.5. Yamago's Strategy for the Selective Synthesis of [8]CPP



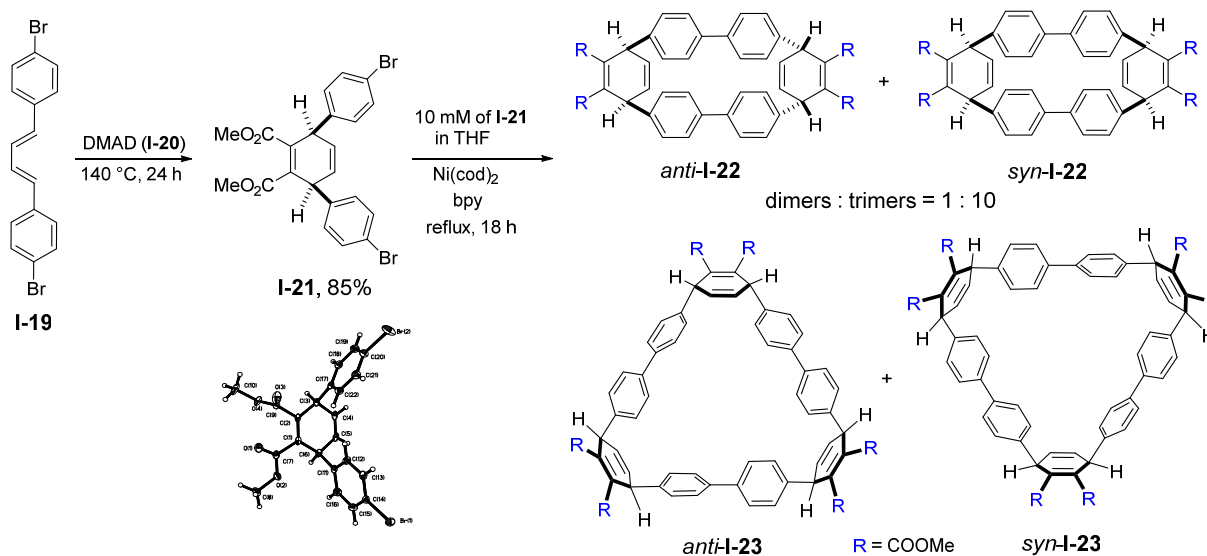
### 1.3 Synthesis of Functionalized [9]Cycloparaphenylenes

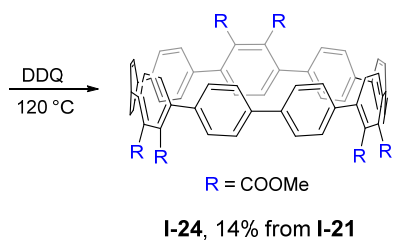
Several synthetic pathways to CPPs have been developed,<sup>7</sup> allowing the construction of various ring sizes ranging from the smallest with five benzene units, [5]CPP,<sup>7l,m,q</sup> to the largest with 20 units.<sup>7a</sup> Previously, we reported the use of the Diels–Alder reaction as a key step in producing a CPP precursor for the synthesis of a functionalized [9]CPP<sup>7o</sup> and thiophene-containing CPPs.<sup>8a</sup> In this project, we have further extended this strategy to the construction of other functionalized [9]CPPs by using different combinations of dienes and dienophiles for the Diels–Alder reaction to form CPP precursors.<sup>12</sup>

Condensation between (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene (**I-19**) and dimethyl acetylenedicarboxylate (**I-20**) at 140 °C produced the Diels–Alder adduct **I-21** in 85% yield (Scheme 1.6).<sup>10</sup> It is worth noting that due to the high stereoselectivity of the Diels–Alder reaction the two 4-bromophenyl groups in **I-21** are *cis* to each other exclusively, which is essential for the subsequent macrocyclic ring formation. The X-ray structure of **I-21** showed that the included angle

between the two 4-bromophenyl groups is  $73.5^\circ$  in the crystal lattice. Treatment of **I-21** with  $\text{Ni}(\text{cod})_2$  (cod: 1,5-cyclooctadiene) in the presence of 2,2'-bipyridyl (bpy) promoted the homocoupling reactions<sup>7e</sup> to give the macrocyclic dimers, *syn*-**I-22** and *anti*-**I-22** (1:1), and the macrocyclic trimers, *syn*-**I-23** and *anti*-**I-23** (1:3). Small fractions of the four macrocyclic products were isolated for structural elucidation. The ratio between the dimers and the trimers was determined by NMR spectroscopy to be 1:10. This is in contrast to the earlier report that the homocoupling reactions of the precursor derived from **I-19** and 1,4-benzoquinone followed by methylation gave the corresponding macrocyclic dimers predominantly.<sup>7o</sup> We found that it was operationally simpler to treat the mixture of the dimers and the trimers, without further purification, with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to produce the fully aromatized [9]CPP **I-24** bearing six carbomethoxy groups in 14% yield from **I-21** over two steps. The corresponding fully aromatized [6]CPP was not obtained. Oxidative aromatization of the isolated *anti*-**I-23** with DDQ gave **I-24** in 80% yield. A similar result was also obtained from the isolated *syn*-**I-23** in producing **I-24**.

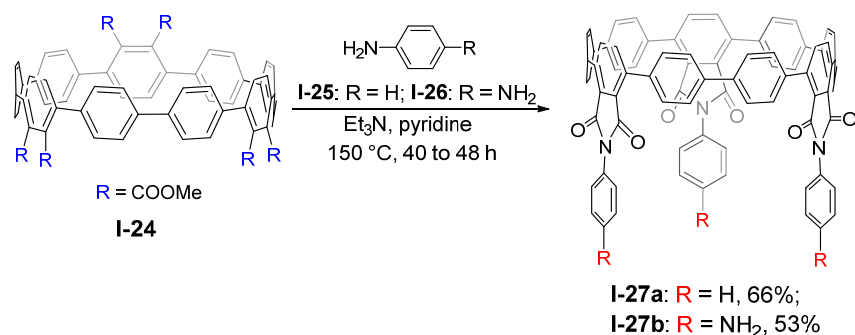
### Scheme 1.6. Synthesis of the Functionalized [9]CPP **I-24** Bearing Six Carbomethoxy Groups





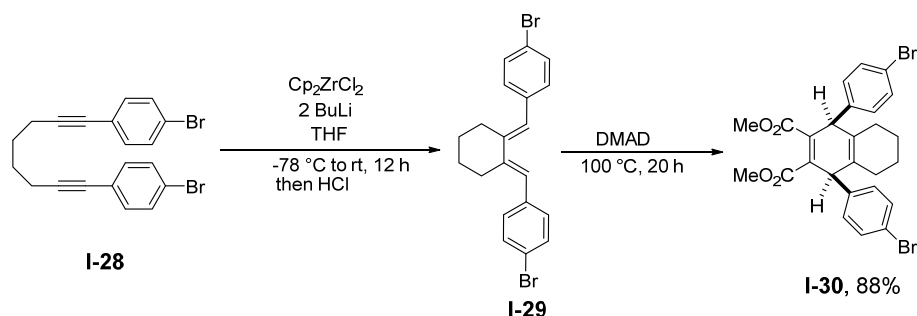
The structure of **I-24** contains six carbomethoxy groups, which on treatment with aniline (**I-25**) and 1,4-diaminobenzene (**I-26**) gave [9]CPPs **I-27a** and **I-27b** bearing three *N*-phenylphthalimido groups, respectively (Scheme 1.7).

### Scheme 1.7. Synthesis of [9]CPPs **I-27a** and **I-27b** Bearing Three *N*-Phenylphthalimido Groups



Diene **I-29**, readily prepared from **I-28** and  $\text{Cp}_2\text{ZrBu}_2$  followed by hydrolysis,<sup>11</sup> underwent the Diels–Alder reaction with DMAD to give **I-30** in 88% yield (Scheme 1.8). Compared to **I-19**, the fixed *s-cis* configuration of the 1,3-butadienyl structure in **I-29** facilitates its reaction with DMAD.

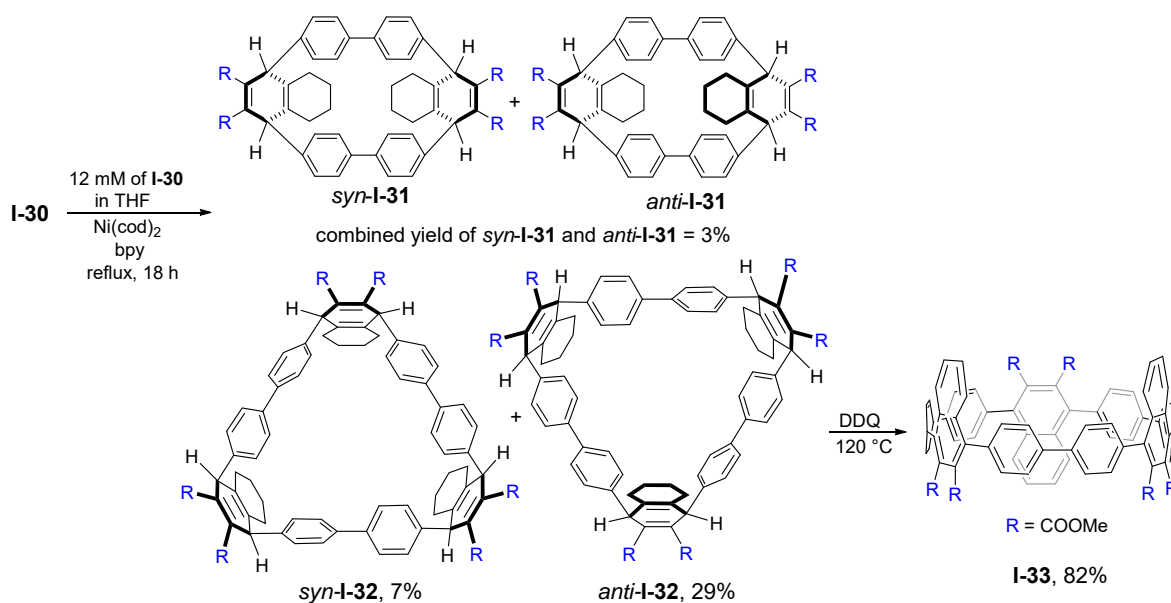
### Scheme 1.8. Synthesis of the CPP Precursor **I-30**



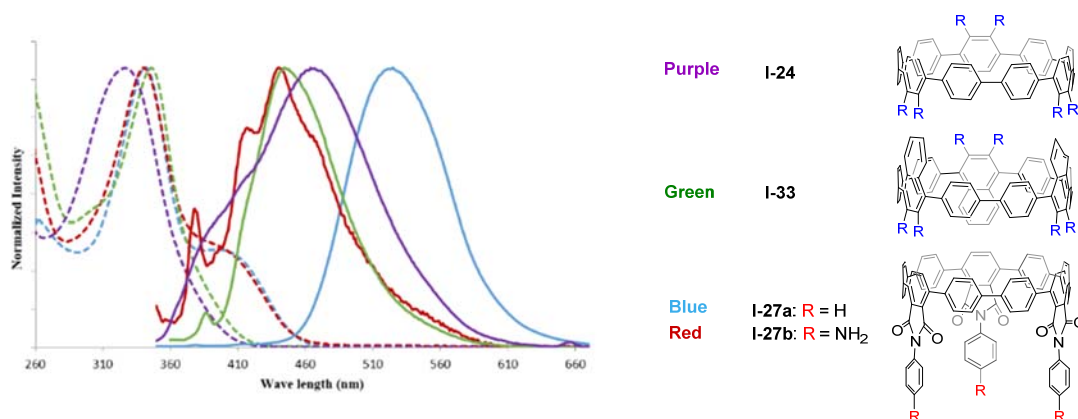


The Ni(cod)<sub>2</sub>-mediated homocoupling reactions of **I-30** produced the macrocyclic dimers, *syn*-**I-31** and *anti*-**I-31** (1:1) in 3% combined yield, and the macrocyclic trimers, *syn*-**I-32** in 7% yield and *anti*-**I-32** in 29% yield (Scheme 1.9). Treatment of *anti*-**I-32** with DDQ then produced the fully aromatized **I-33** in 82% yield. Similarly, **I-33** was also obtained from *syn*-**I-32**. It is worth noting that the tetramethylene moieties were also oxidized to form part of the naphthyl systems in **I-33**.

### Scheme 1.9. Synthesis of the Functionalized [9]CPP **I-33**

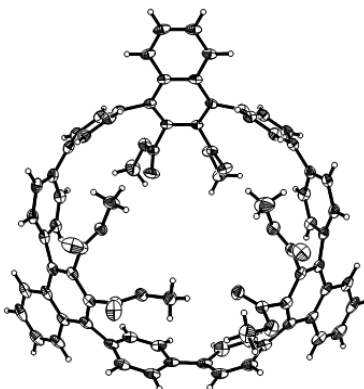


The UV-vis spectra of **I-24** and **I-33** in DMSO showed the absorption maxima ( $\lambda_{\text{abs}}$ ) at 327 nm and 346 nm, respectively (Figure 1.2). In comparison, the absorption maximum of the parent [9]CPP occurred at 340 nm<sup>7a</sup> and [9]cyclo-1,4-naphthalene occurred at 378 nm.<sup>13</sup> The fluorescence maxima ( $\lambda_{\text{em}}$ ) of **I-24** and **I-33** were observed at 464 nm and 445 nm, respectively. They are blue shifted from those of the parent [9]CPP at 494 nm and [9]cyclo-1,4-naphthalene at 491 nm. For **I-27a** and **I-27b**, the UV-vis absorption maxima occurred at 342 nm and 340 nm, respectively, and the fluorescence maxima occurred at 525 nm and 440 nm, respectively. It is worth noting that the fluorescence maximum of **I-27a** showed a significant red-shift from those of the other [9]CPPs.



**Figure 1.2.** UV-vis absorption (broken line) and fluorescence spectra (solid line) of the functionalized [9]CPPs **I-24**, **I-33**, **I-27a**, and **I-27b**.

A single crystal of **I-33** suitable for X-ray structure analysis was obtained by recrystallization from a mixture of dichloromethane and cyclohexane. The X-ray structure of **I-33** (Figure 1.3) indicates that the ester groups of the 2,3-dimethyl 2,3-naphthalenedicarboxylate units all cant toward the inner plane of the [9]CPP circle with two of them tilting above the ring while the third tilting below the ring. This arrangement is different from that of the [12]CPPhexacarboxylate, where the ester groups all cant away from the inner plan and are pointed toward the same side.<sup>7s</sup> In the crystalline state, molecules of **I-33** align to form a linear carbon nanotube-like structure with columnar assemblies all packed parallel to one another.

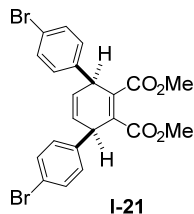


**Figure 1.3.** ORTEP drawing (solvents,  $\text{CH}_2\text{Cl}_2$  and cyclohexane, are omitted for clarity) of [9]CPP **I-33**. The thermal ellipsoids are scaled to enclose 30% probability.

In summary, functionalized [9]CPPs bearing carbomethoxy or *N*-phenylphthalimido groups have been synthesized. The high stereoselectivity of the Diels–Alder reaction provides easy access to the precursors **I-21** and **I-30** having the two 4-bromophenyl groups *cis* to each other, which is essential for the macrocyclic ring formation. Treatment of [9]CPP **I-24** with aniline or 1,4-diaminobenzene produces **I-27a** and **I-27b** bearing three *N*-phenylphthalimido groups, respectively. The X-ray structure of **I-33** indicates an interesting tubular arrangement in the crystalline state resembling that of a carbon nanotube. The presence of six carbomethoxy groups in **I-24** and **I-33** provides the potential opportunity for them to serve as hinges to connect multiple units of CPPs together in a nanotube-like arrangement. Results of this research will be presented in due course.

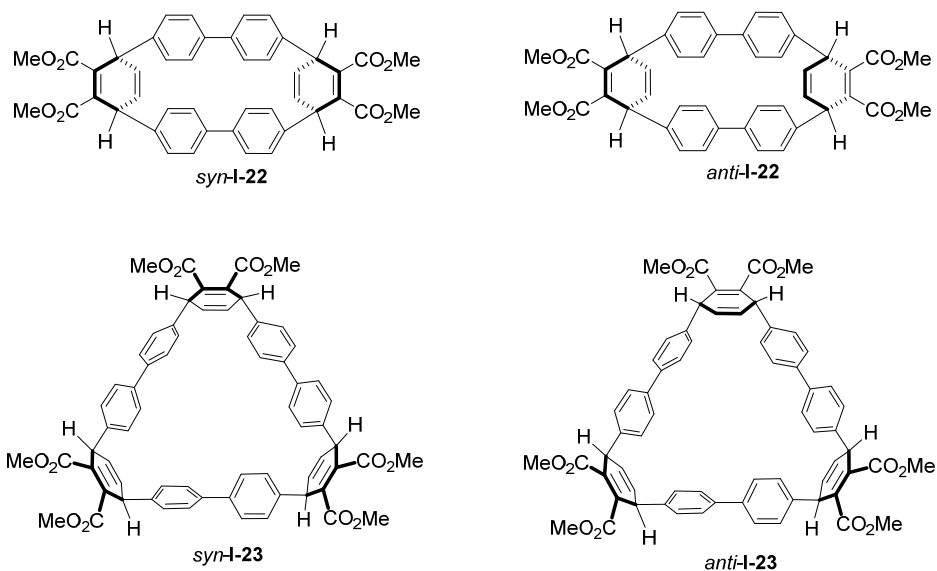
#### 1.4 Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under an argon atmosphere. (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene<sup>10</sup> and 1,8-bis(4-bromophenyl)-1,7-octadiyne<sup>11</sup> were prepared according to the reported procedures. Dimethyl acetylenedicarboxylate, ZrCp<sub>2</sub>Cl<sub>2</sub>, Ni(cod)<sub>2</sub>, 2,2'-bipyridyl, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), aniline, 1,4-diaminobenzene were purchased from chemical suppliers and were used as received. The UV-vis absorption spectrum was recorded on a Shimadzu UV-1800 spectrophotometer with a 1-nm resolution, and the baseline was corrected with a solvent filled square quartz cell. The fluorescence spectrum was recorded on a Shimadzu RF-5301PC spectrofluorophotometer with a 2-nm resolution.



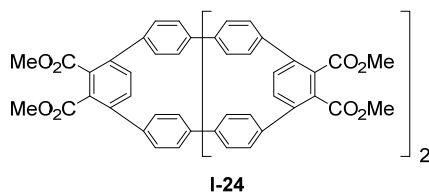
**Experimental Procedure for Dibromide I-21.** To a mixture of (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene (1.00 g, 2.74 mmol) and dimethyl acetylenedicarboxylate (0.586 g, 4.12 mmol) was added dry toluene (2 mL) under argon in a sealed tube. The reaction mixture was stirred at 140 °C for 24 h before it was allowed to cool to room temperature. Toluene was removed in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 15:85) to produce **I-21** (1.18 g, 2.33 mmol, 85% yield,  $R_f$  = 0.4) as a white solid: mp = 120–121 °C; IR 1724, 1256  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (4 H, d,  $J$  = 8.6 Hz), 7.11 (4 H, d,  $J$  = 8.2 Hz), 5.76 (2 H, d,  $J$  = 2.0 Hz), 4.43 (2 H, d,  $J$  = 2.0 Hz), 3.59 (6 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  167.48, 139.96, 135.47, 131.88, 129.85, 125.96, 121.20, 52.18, 43.33; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{18}\text{Br}_2\text{O}_4$  ( $\text{M}^+$ ) 504.9645, 506.9624, 508.9604 found 504.9650, 506.9629, 508.9609.

Recrystallization of **I-21** from a mixture of dichloromethane and hexanes produced a single crystal suitable for X-ray structure analysis.



**Experimental Procedure for Cyclic Dimers *syn-I-22* and *anti-I-22* and Cyclic Trimers *syn-I-23* and *anti-I-23*.** To a 200 mL-flask were added 0.500 g of **I-21** (0.988 mmol) and 0.370 g of 2,2'-bipyridyl (2.37 mmol). The flask was flushed with nitrogen and placed in a glovebox under a nitrogen atmosphere before 0.650 g of Ni(cod)<sub>2</sub> (2.36 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox before 100 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 18 h before it was allowed to cool to room temperature. Then the reaction mixture was passed through a short pad of silica gel column (4 cm) and eluted with a mixture of ethyl acetate and dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel/dichloromethane:diethyl ether = 97:3 to 90:10) to produce fractions containing a mixture of *syn-I-22* and *anti-I-22*, fractions containing mainly pure *anti-I-23*, and fractions containing *syn-I-23* with other unidentified materials. The ratio between **I-22** and **I-23** is estimated by NMR spectroscopy to be approximately 1:10. Further purification by preparative TLC (ethyl acetate:hexanes = 3:7) allowed the isolation of relatively pure samples of *syn-I-22*, *anti-I-22*, and *anti-I-23* and a sample of *syn-I-23* with unidentified impurities for structural

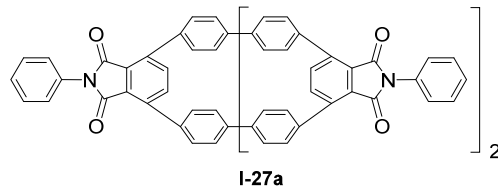
elucidation. *syn*-**I-22** and *anti*-**I-22** (sample 1, one major and one minor,  $R_f = 0.56$ , dichloromethane:diethyl ether = 95:5): IR 1716, 1272  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  6.85 (8 H, d,  $J = 7.6$  Hz), 6.78 (4 H, d,  $J = 8.2$  Hz), 6.67 (4 H, dd,  $J = 4.1, 2.9$  Hz), 4.69 (4 H, t,  $J = 3.5$  Hz), 3.90 (12 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  168.42, 141.63, 138.97, 138.27, 131.99, 127.35, 126.34, 52.68, 41.78; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{36}\text{O}_8$  ( $\text{M}^+$ ) 692.2405, found 692.2419. *syn*-**I-22** or *anti*-**I-22** (sample 2,  $R_f = 0.52$ , dichloromethane:diethyl ether = 95:5): mp  $> 250$   $^\circ\text{C}$ ; IR 1718, 1260  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  6.85 (8 H, d,  $J = 8.2$  Hz), 6.78 (8 H, d,  $J = 8.2$  Hz), 6.65 (4 H, dd,  $J = 4.4, 2.6$  Hz), 4.69 (4 H, t,  $J = 3.5$  Hz), 3.91 (12 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  168.42, 141.62, 138.96, 138.31, 131.99, 127.36, 126.35, 52.70, 41.80; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{36}\text{O}_8$  ( $\text{M}^+$ ) 692.2405, found 692.2413. *anti*-**I-23** ( $R_f = 0.39$ , dichloromethane:diethyl ether = 95:5): IR 1718, 1250  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz)  $\delta$  7.51–7.57 (12 H, m), 7.38 (12 H, d,  $J = 8.2$  Hz), 5.57–5.68 (6 H, m), 4.50–4.57 (6 H, m), 3.31 (6 H, s), 3.28 (6 H, s), 3.27 (6 H, s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.63–7.68 (12 H, m), 7.34–7.38 (12 H, m), 5.86–5.96 (6 H, m), 4.55–4.60 (6 H, m), 3.66 (6 H, s), 3.647 (6 H, s), 3.645 (6 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  168.16, 167.95, 167.74, 140.22, 139.99, 139.80, 139.07, 139.01, 138.90, 136.95, 136.00, 135.09, 128.71, 128.64, 128.53, 126.96, 126.77, 126.42, 126.04, 52.20, 52.17, 43.69, 43.52, 43.41; HRMS (ESI) calcd for  $\text{C}_{66}\text{H}_{55}\text{O}_{12}$  ( $\text{MH}^+$ ) 1039.3688, found 1039.3684. *syn*-**I-23** (sample not fully purified,  $R_f = 0.22$ , dichloromethane:diethyl ether = 95:5): IR 1724, 1253  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.66 (12 H, d,  $J = 8.2$  Hz), 7.36 (12 H, d,  $J = 8.6$  Hz), 5.89 (6 H, d,  $J = 2.8$  Hz), 4.57 (6 H, d,  $J = 2.8$  Hz), 3.66 (18 H, s).



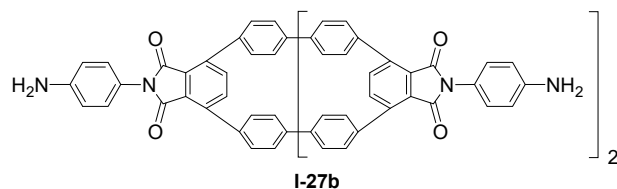
**Experimental Procedure for the Functionalized [9]CPP I-24.** To a 10-mL flask were added 0.010 g (0.0097 mmol) of *anti*-**I-23** and 0.030 g (0.13 mmol) of DDQ. The flask was flushed with argon, and then 2 mL of chlorobenzene was introduced by using a syringe. The reaction mixture was heated at 120 °C for 2 h before it was allowed to cool to room temperature. Dichloromethane (50 mL) was added, and the solution was passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 200 mL of a mixture of dichloromethane and ethyl acetate (1:1). The combined eluates were concentrated in vacuo to afford **I-24** (0.0081 g, 0.0078 mmol, 80% yield) as a white solid.

Treatment of the sample containing *syn*-**I-23** with DDQ also produced the fully aromatized **I-24**.

In a separated experiment, the crude cyclic products containing a mixture of **I-22** and **I-23**, produced from 0.500 g (0.988 mmol) of **I-21**, were not further purified and were treated directly with DDQ (0.300g, 1.32 mmol) in 5 mL of chlorobenzene at 120 °C for 3 h. Dichloromethane (50 mL) was added, and the reaction mixture was passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 100 mL of a mixture of dichloromethane and ethyl acetate (1:1). The combined eluates were concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:methylene chloride = 3:97,  $R_f$  = 0.15) to produce 0.049 g (0.047 mmol, 14% yield over two steps) of **I-24**: IR 1737, 1236  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.54 (12 H, d,  $J$  = 8.6 Hz), 7.43 (12 H, d,  $J$  = 8.6 Hz), 6.88 (6 H, s), 3.85 (18 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  168.15, 139.67, 139.08, 138.80, 135.38, 129.80, 129.64, 127.15, 52.75; HRMS (ESI) calcd for  $\text{C}_{66}\text{H}_{49}\text{O}_{12}(\text{MH}^+)$  1033.3219, found 1033.3220.



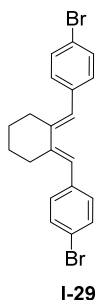
**Experimental Procedure for the Functionalized [9]CPP I-27a.** A mixture of 0.0070 g ( $6.8 \times 10^{-3}$  mmol) of **I-24**, 0.1 mL of triethylamine, 0.03 mL (0.33 mmol) of aniline and 3 mL of pyridine in a sealed tube under an argon atmosphere was heated at 150 °C for 40 h before it was allowed to cool to room temperature. The reaction was concentrated in vacuo, and the residue was purified by preparative TLC to give **I-27a** (0.0050 g,  $4.5 \times 10^{-3}$  mmol, 66% yield) as a bright yellow solid: IR 1716, 1374  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 600 MHz)  $\delta$  7.68 (12 H, d,  $J = 8.8$  Hz), 7.64 (12 H, d,  $J = 8.8$  Hz), 7.57 (6 H, t,  $J = 7.6$  Hz), 7.52 (6 H, dd,  $J = 8.8, 1.2$  Hz), 7.46 (3 H, td,  $J = 7.3, 1.2$  Hz), 7.24 (6 H, s);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 150 MHz)  $\delta$  167.33, 139.87, 138.67, 138.27, 136.72, 132.54, 130.36, 129.61, 128.72, 128.44, 127.69, 127.56; HRMS (ESI) calcd for  $\text{C}_{78}\text{H}_{46}\text{N}_3\text{O}_6$  ( $\text{MH}^+$ ) 1120.3381, found 1120.3418.



**Experimental Procedure for the Functionalized [9]CPP I-27b.** A mixture of 0.0090 g of **I-24** (0.0087 mmol), 0.1 mL of triethylamine, 0.050 g of 1,4-diaminobenzene (0.46 mmol) and 3 mL of pyridine in a sealed tube under an argon atmosphere was heated at 150 °C for 48 h before it was allowed to cool to room temperature. The reaction mixture was concentrated in vacuo, and the residue was washed with methanol and then pass through a short pad of silica gel using 100 mL of ethyl acetate as eluent. The combined eluates were concentrated in vacuo, and the residue was washed with methanol and pentane. After 2 h under high vacuum, **I-27b** (0.0050 g, 53% yield)

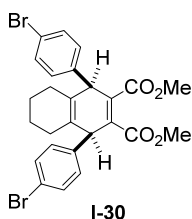


was obtained as a yellow solid: IR 3375, 1711, 1517  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ , 600 MHz)  $\delta$  7.78 (12 H, d,  $J = 8.2$  Hz), 7.72 (12 H, d,  $J = 8.2$  Hz), 7.38 (6 H, s), 7.11 (6 H, d,  $J = 8.8$  Hz), 6.66 (6 H, d,  $J = 8.8$  Hz), 5.33 (6 H, s);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 150 MHz)  $\delta$  167.07, 148.70, 138.35, 137.45, 136.18, 135.86, 129.89, 128.42, 128.32, 126.83, 119.85, 113.43; HRMS (ESI) calcd for  $\text{C}_{78}\text{H}_{49}\text{N}_6\text{O}_6$  ( $\text{MH}^+$ ) 1165.3708, found 1165.3777.

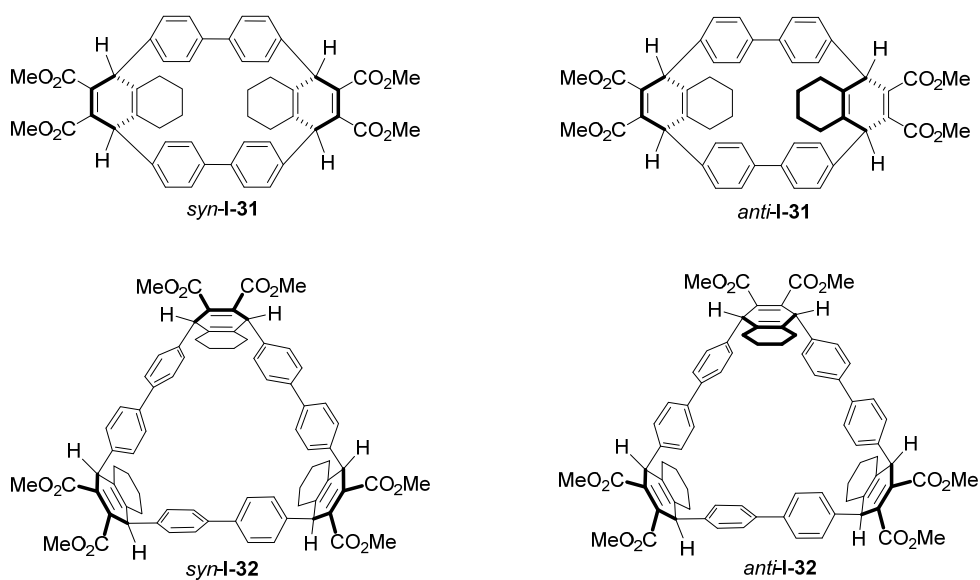


**Experimental Procedure for Diene I-29.**<sup>11a,c</sup> To a solution of  $\text{Cp}_2\text{ZrCl}_2$  (2.55 g, 8.74 mmol) in THF (30 mL) at  $-78$  °C under an argon atmosphere was added *n*-butyllithium (7.00 mL of a 2.5 M solution in hexanes, 17.5 mmol). After 1 h at  $-78$  °C, 1,8-bis(4-bromophenyl)-1,7-octadiyne (3.03 g, 7.28 mmol) in 10 mL of THF under argon was added slowly. The reaction mixture was then allowed to warm to room temperature. After 12 h, the reaction mixture was poured into 300 mL of a 3 M aqueous HCl solution. After 30 minutes of stirring, the reaction mixture was extracted with dichloromethane ( $2 \times 100$  mL). The combined organic layers were washed with a saturated  $\text{Na}_2\text{CO}_3$  solution and dried over  $\text{MgSO}_4$ . After passing through a short silica gel column, the solvent was evaporated in vacuo, and the residue was washed with cold hexanes to give **I-29** (2.50 g, 5.98 mmol, 82% yield) as a white solid: IR 2930, 1485, 1009  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.46 (4 H, d,  $J = 8.2$  Hz), 7.15 (4 H, d,  $J = 8.6$  Hz), 6.52 (2 H, s), 2.56 (4 H, m), 1.65 (4 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  145.02, 136.69, 131.19, 131.03, 123.22, 120.28, 29.91, 26.10;

HRMS (ESI) calcd for  $C_{20}H_{18}Br_2$  ( $M^+$ ) 415.9770, 417.9749, 419.9729, found 415.9788, 417.9767, 419.9742.

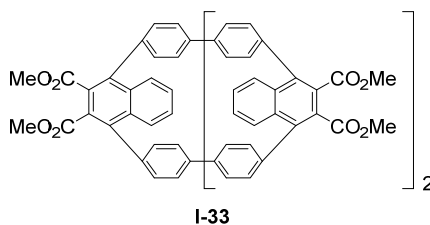


**Experimental Procedure for Dibromide I-30.** To a mixture of diene **I-29** (1.70 g, 4.07 mmol) and dimethyl acetylenedicarboxylate (0.867g, 6.10 mmol) was added 2 mL of dry toluene under argon. The reaction mixture was stirred at 100 °C for 20 h before it was allowed to cool to room temperature. Toluene was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 15:85) to afford **I-30** (2.00 g, 3.57 mmol, 88% yield) as a white solid: mp 142–143 °C; IR 1721, 1259  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.44 (4 H, d,  $J = 8.2$  Hz), 7.11 (4 H, d,  $J = 8.6$  Hz), 4.18 (2 H, s), 1.84 (4 H, t,  $J = 6.1$  Hz), 1.55–1.65 (2 H, m), 1.40–1.50 (2 H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  167.63, 139.52, 135.42, 131.62, 130.45, 128.29, 121.08, 52.11, 48.56, 27.96, 22.49; HRMS (ESI) calcd for  $C_{26}H_{25}Br_2O_4$  ( $MH^+$ ) 559.0114, 561.0094, 563.0073, found 559.0120, 561.0100, 563.0078.



**Experimental Procedure for Cyclic Dimers *syn-I-31* and *anti-I-31* and Cyclic Trimers *syn-I-32* and *anti-I-32*.** To a 250 mL-flask were added 1.00 g of **I-30** (1.79 mmol) and 0.700 g of 2,2'-bipyridyl (4.48 mmol). The flask was flushed with nitrogen and placed in a glovebox under a nitrogen atmosphere before 1.20 g of Ni(cod)<sub>2</sub> (4.36 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox before 150 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 18 h before it was allowed to cool to room temperature. Then the reaction mixture was passed through a short silica gel column (4 cm) and eluted with a mixture of ethyl acetate and dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 40:60 to 60:40) to produce a small amount (ca. 3%) of a mixture of *syn-I-31* and *anti-I-31* as a white solid, 0.205 g of *anti-I-32* (0.171 mmol, 29% yield) as a white solid, and an impure sample of *syn-I-32*. Further purification of *syn-I-32* by preparative TLC afforded 0.051 g (0.042 mmol, 7% yield) of a pure sample of *syn-I-32* as a white solid. *syn-I-31* and *anti-I-31*: mp > 330 °C; IR 1717, 1259 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 6.80 (8 H, d, *J* = 8.2 Hz), 6.751 and 6.749 (8 H, two doublets from the two isomers, *J* = 8.2 Hz), 4.35 (4 H, s), 3.90

(12 H, s), 2.58–2.61 (4 H, m), 2.31–2.35 (4 H, m), 1.85–1.94 (4 H, m), 1.77–1.85 (4 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  168.58, 142.42, 142.39, 138.98, 137.79, 137.78, 135.47, 135.45, 127.20, 126.36, 52.62, 47.86, 31.54, 22.84, 22.82; HRMS (ESI) calcd for  $\text{C}_{52}\text{H}_{48}\text{O}_8$  ( $\text{M}^+$ ) 800.3344, found 800.3364. *anti*-**I-32**: IR 1723, 1261  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.67–7.71 (12 H, m), 7.37 (12 H, d,  $J = 8.2$  Hz), 4.31 (6 H, s), 3.63 (6 H, s), 3.619 (6 H, s), 3.617 (6 H, s), 1.91–2.06 (12 H, m), 1.57–1.67 (6 H, m), 1.45–1.56 (6 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  168.11, 168.09, 139.71, 138.57, 138.51, 135.92, 135.88, 135.83, 129.29, 128.66, 128.62, 126.40, 126.36, 52.07, 52.04, 48.84, 28.00, 22.62; HRMS (ESI) calcd for  $\text{C}_{78}\text{H}_{73}\text{O}_{12}$  ( $\text{MH}^+$ ) 1201.5097, found 1201.5098. *syn*-**I-32**: IR 1725, 1262  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.69 (12 H, d,  $J = 8.8$  Hz), 7.37 (12 H, d,  $J = 8.2$  Hz), 4.31 (6 H, s), 3.63 (18 H, s), 1.91–2.04 (12 H, m), 1.57–1.65 (6 H, m), 1.44–1.52 (6 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  168.08, 139.73, 138.50, 135.87, 129.29, 128.63, 126.36, 52.08, 48.86, 28.01, 22.63; HRMS (ESI) calcd for  $\text{C}_{78}\text{H}_{73}\text{O}_{12}$  ( $\text{MH}^+$ ) 1201.5097, found 1201.5104.



**Experimental Procedure for the Functionalized [9]CPP **I-33**.** To a 20-mL flask were added 0.160 g (0.133 mmol) of *anti*-**I-32** and 0.450 g (1.98 mmol) of DDQ. The flask was flushed with argon and then 6 mL of chlorobenzene was introduced by using a syringe. The reaction mixture was heated at 120 °C for 15 h before it was allowed to cool to room temperature. Dichloromethane (10 mL) was added and the solution was passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 100 mL of dichloromethane and ethyl acetate (1:1). The combined eluates were concentrated in vacuo to afford **I-33** (0.129 g,

0.109 mmol, 82% yield) as a white solid: IR 1736, 1221  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.27 (6 H, dd,  $J = 6.5, 3.3$  Hz), 7.64 (6 H, dd,  $J = 6.4, 3.3$  Hz), 7.48 (12 H, d,  $J = 8.2$  Hz), 7.33 (12 H, d,  $J = 8.6$  Hz), 3.12 (18 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  168.57, 140.55, 136.50, 136.28, 132.12, 131.20, 131.05, 127.73, 127.60, 127.18, 52.16; HRMS (ESI) calcd for  $\text{C}_{78}\text{H}_{55}\text{O}_{12}$  ( $\text{MH}^+$ ) 1183.3688, found 1183.3692.

Treatment of *syn*-**I-32** with DDQ also produced the fully aromatized **I-33**.

Recrystallization of **I-33** from a mixture of dichloromethane and cyclohexane produced a single crystal suitable for X-ray structure analysis.

## 1.5 References

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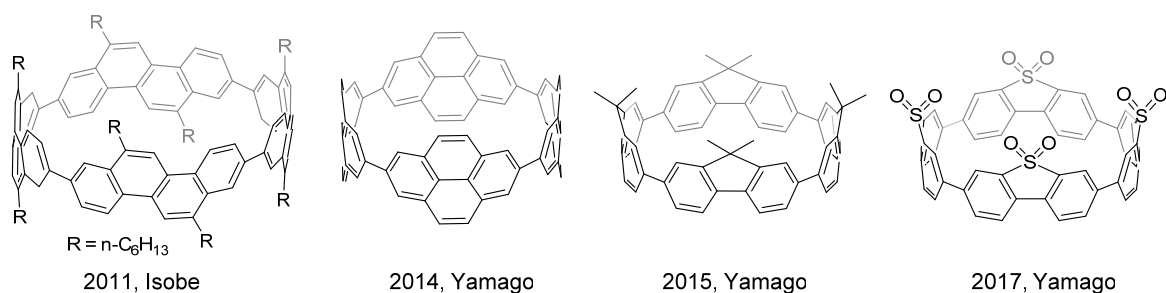
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## Chapter 2. Syntheses and Structures of Extended Carbon Nanorings

### 2.1 Introduction

Extended cycloparaphenylenes consisting of benzene units connected at para positions provide opportunities to modify their molecular structures and photo-physical and electrochemical properties.<sup>1-5</sup> *P*-extended carbon nanorings, as one type of extended cycloparaphenylenes, have gained numerous attentions from the synthetic community. Soon after the development of suitable synthetic methods for the [n]cycloparaphenylenes (CPPs), a variety of *p*-extended carbon nanorings were synthesized by various research groups (Figure 2.1).<sup>1i,1j,9,10</sup>



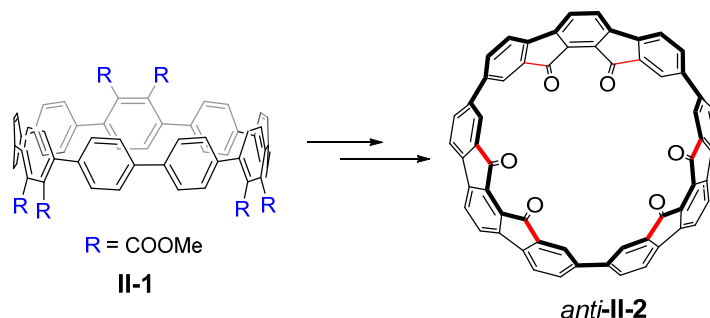
**Figure 2.1.** *P*-extended carbon nanorings.

### 2.2 Syntheses and Structures of *anti*-[3]CIFO

We reported a synthetic pathway to macrocycle **II-1**,<sup>2a</sup> which is a functionalized [9]CPP containing three di-methyl 1,1':4,1''-terphenyl-2',3'-dicarboxylate-4,4''-diyl units (Scheme 2.1). We have converted **II-1** to *anti*-**II-2** bearing three indeno[2,1-*a*]fluorene-11,12-dione-2,9-diyl (IFO) units in the macrocyclic ring structure with two of the units tilting above the macrocyclic ring and the third below the ring (*anti*-[3]CIFO).<sup>16</sup> The activation barrier ( $\Delta G^\ddagger$ ) for conversion to the *syn* rotamer (*syn*-**II-2**, *syn*-[3]CIFO) was estimated to be 23.3 kcal/mol by DFT calculations.

The properties of *anti*-**II-2** were investigated by UV/Vis and fluorescence spectroscopy and cyclic voltammetry.

### Scheme 2.1. Transformation of **II-1** to *anti*-**II-2**

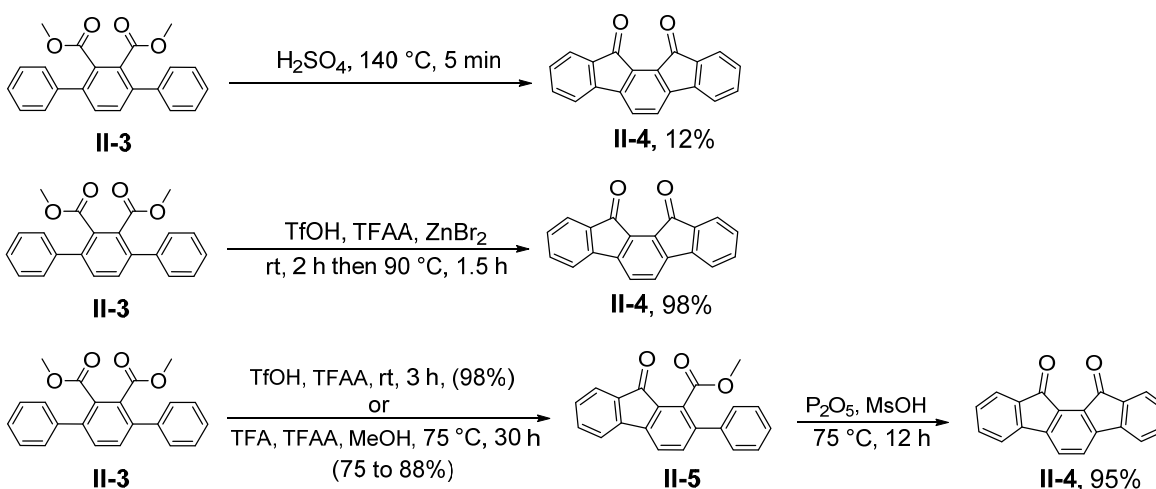


It was reported previously that exposure of dimethyl 1,1':4',1''-terphenyl-2',3'-dicarboxylate (**II-3**) to concentrated sulfuric acid at 140 °C for 5 min produced indeno[2,1-*a*]fluorene-11,12-dione (**II-4**) in only 12% isolated yield (Scheme 2.2).<sup>6</sup> Other indirect synthetic routes also produced low to moderate yields of **II-4**, ranging from 20 to 61%.<sup>6,7</sup> Upon exposure of **II-1** to concentrated sulfuric acid at 140 °C for 5 min, *anti*-**II-2** rotamer was produced only in trace amounts and *syn*-**II-2** rotamer was not observed. In addition, the reaction result was not reproducible under such a harsh reaction condition. Treatment of the corresponding carboxylic acid bearing six carboxyl groups with sulfuric acid at 140 °C for 5 to 10 min also failed to produce *anti*-**II-2** and/or *syn*-**II-2**. It was apparent that a more efficient synthetic method would be needed to produce *anti*-**II-2** and/or *syn*-**II-2** from **II-1**.

We observed that upon exposure of **II-3** to a mixture of trifluoromethanesulfonic acid (TfOH), trifluoroacetic anhydride (TFAA), and zinc bromide at rt for 2 h and then at 90 °C for 1.5 h, the acylation reactions proceeded efficiently to give **II-4** in 98% isolated yield (Scheme 2.2). On the other hand, when **II-3** was treated with a mixture of TfOH and TFAA at rt for 3 h, only monoacylation occurred to furnish 2-carbomethoxy-3-phenyl-9-fluorenone (**II-5**) in 98% isolated

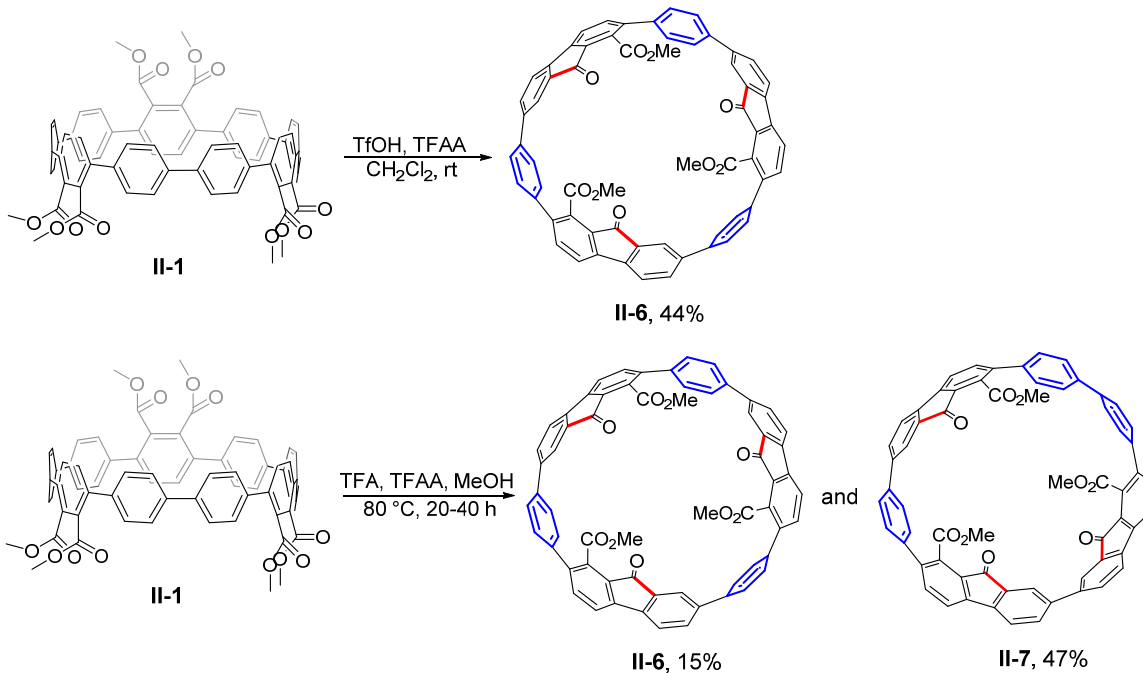
yield. Similarly, **II-5** was obtained in 75 to 88% isolated yield by subjecting **II-3** to a mixture of trifluoroacetic acid (TFA), TFAA, and a small amount of methanol at 75 °C for 30 h. Upon treatment of **II-5** with a 1:10 mixture of P<sub>2</sub>O<sub>5</sub> and methanesulfonic acid (MsOH) (Eaton's reagent)<sup>8</sup> at 75 °C for 12 h, **II-4** was obtained in 95% isolated yield.

**Scheme 2.2. Synthesis of Indeno[2,1-*a*]fluorene-11,12-dione (**II-4**) from Dimethyl 1,1':4',1''-Terphenyl-2',3'-dicarboxylate (**II-3**)**



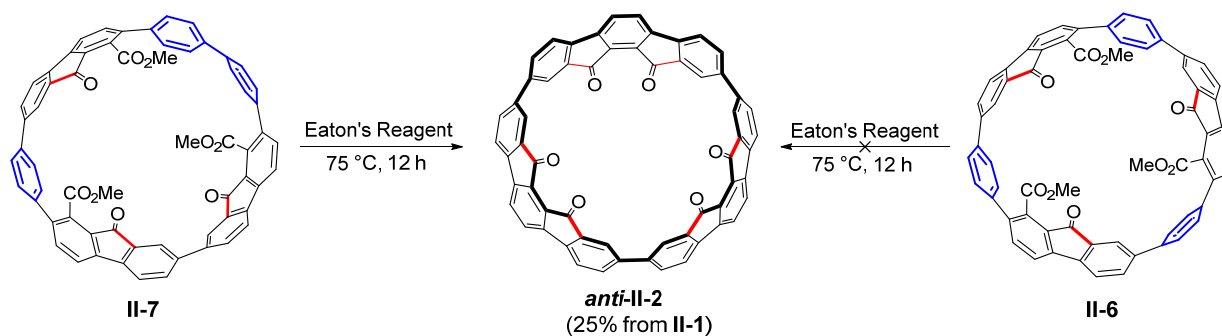
However, attempts to use the mixture of TfOH, TFAA, and ZnBr<sub>2</sub> to convert **II-1** to *anti*-**II-2** and/or *syn*-**II-2** were unsuccessful, and **II-1** decomposed upon exposure to the mixture at rt for 2 h and then at 90 °C for 1.5 h. When **II-1** was treated with the mixture of TfOH and TFAA in dichloromethane at rt for 10 h, C<sub>3</sub> symmetric **II-6** as determined by NMR spectroscopy was obtained in 44% isolated (Scheme 2.3). Interestingly, upon treatment of **II-1** with the mixture of TFA, TFAA, and a small amount of methanol at 75 °C for 30 h, **II-6** was isolated as the minor product in 15% yield and **II-7**, without a C<sub>3</sub> axis as determined by NMR spectroscopy, was isolated as the major product in 47% yield. The reason for the selectivity in producing only **II-6** by TfOH/TFAA is not clear at this time.

### Scheme 2.3. Synthesis of Intermediates II-6 and II-7 from II-1

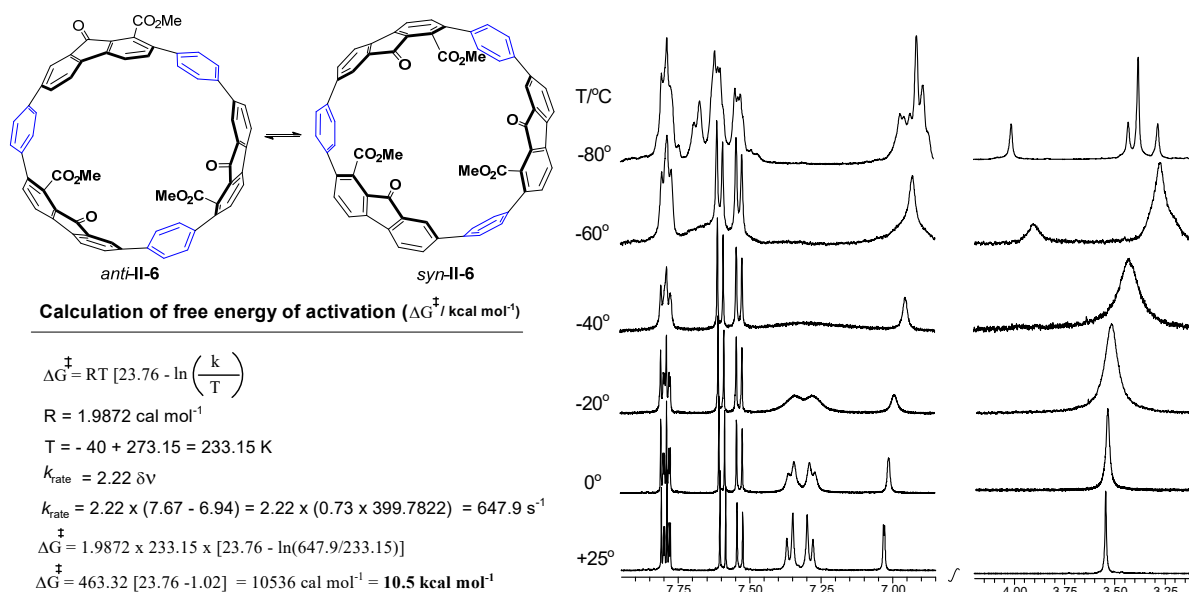


Attempts to use Eaton's reagent to convert **II-6** to *anti*-**II-2** and/or *syn*-**II-2** at 75 °C for 12 h were unsuccessful, and unreacted **II-6** was recovered (Scheme 2.4). Prolonged heating at higher temperatures resulted in decomposition. To our surprise, treatment of **II-7** with Eaton's reagent at 75 °C for 12 h was successful in producing *anti*-**II-2** in 50% isolated yield (Scheme 2.4). It was also possible and operationally simpler to treat the crude mixture of **II-6** and **II-7**, without further separation and purification, with the Eaton's reagent to produce *anti*-**II-2** from **II-1** in 25% overall yield over two steps.

### Scheme 2.4. Synthesis of *anti*-II-2 from Intermediate II-7

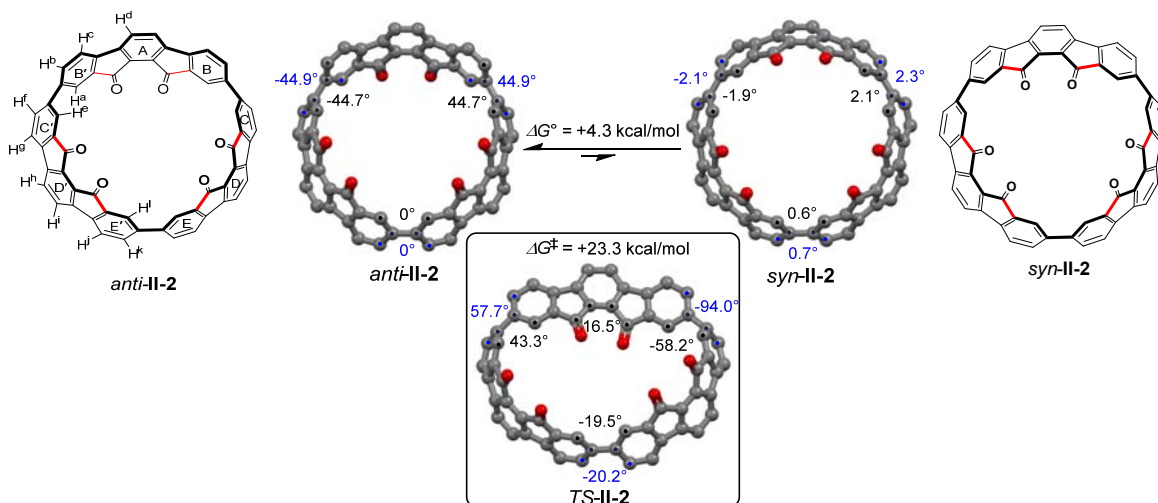


The  $^1\text{H}$  NMR spectrum of **II-6** in  $\text{CD}_2\text{Cl}_2$  at  $25\text{ }^\circ\text{C}$  exhibits a singlet at  $\delta$  3.55 for the three methoxy groups and only one set of signals for the benzene and 9-fluorenone-2,7-diyl units (Figure 2.2). At  $0\text{ }^\circ\text{C}$ , the signals of the AB pattern from the benzene units at  $\delta$  7.35 and 7.28, the isolated hydrogens of the 9-fluorenone-2,7-diyl units at  $\delta$  7.01, and the methoxy groups at  $\delta$  3.53 show the signs of line broadening, indicating slowing rotations of the benzene and 9-fluorenone-2,7-diyl units. The signals continue to broaden at lower temperatures, and at  $-60\text{ }^\circ\text{C}$  a broad peak at  $\delta$  3.90 can be clearly discerned. At  $-80\text{ }^\circ\text{C}$ , three singlets of equal intensity appear at  $\delta$  4.01, 3.42, and 3.27 and a singlet with three times the intensity also appears at  $\delta$  3.37. These observations indicate that at  $-80\text{ }^\circ\text{C}$  the rate of equilibration between the *anti* and *syn* rotamers of **II-6** with a 1:1 mole ratio between them is slower than the NMR time scale. The signal at  $\delta$  3.37 can be attributed to the three equivalent methoxy groups of the *syn* rotamer (*syn-II-6*), while the signals at  $\delta$  4.01, 3.42, and 3.27 can be attributed to the three non-equivalent methoxy groups of the *anti* rotamer (*anti-II-6*). For **II-7** at  $25\text{ }^\circ\text{C}$ , three singlets for the three non-equivalent methoxy groups were observed.



**Figure 2.2.** Temperature-dependent  $^1\text{H}$  NMR spectra of *anti-II-6* and *syn-II-6* and calculation of the rotational barrier.

The molecular structure of *anti-II-2* containing only a plane of symmetry, depicted in Figure 3 after DFT optimization, is supported by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Unlike *syn-II-2*, which has a  $C_3$  axis and can be expected to exhibit only four  $^1\text{H}$  NMR signals, *anti-II-2* without a  $C_3$  axis showed a total of twelve  $^1\text{H}$  NMR signals, including a singlet at  $\delta$  7.57 for  $\text{H}^{\text{d}}$ , a doublet at  $\delta$  7.51 for  $\text{H}^{\text{h}}$ , and a doublet at  $\delta$  7.46 for  $\text{H}^{\text{i}}$ . Three different carbonyl signals were also observed on the  $^{13}\text{C}$  NMR spectrum. Heating the NMR sample in  $\text{DMSO-}d_6$  at  $110\text{ }^\circ\text{C}$  did not show line broadening or coalescence of the  $^1\text{H}$  NMR signals, indicating that the rotation rates of the three IFO units are relatively slow on the NMR time scale. DFT calculations show that the rotational barrier ( $\Delta G^\ddagger$ ) from *anti-II-2* to *syn-II-2* is 23.3 kcal/mol, which is beyond the range for dynamic NMR studies. The rotational pathway to equilibrate *anti-II-2* and *syn-II-2* involves tilting the keto carbonyls of the IFO unit *anti* to the two other units toward the inner plane of the macrocyclic ring (Figure 2.3). The two carbon–carbon single bonds connecting the rotating unit to the two other units are more severely bent during the rotating process. DFT calculations also indicate that *anti-II-2* is thermodynamically more stable ( $\Delta G^\circ$ ) than *syn-II-2* by 4.3 kcal/mol.



**Figure 2.3.** DFT-optimized structures of *anti-II-2*, *syn-II-2*, and the transition state (*TS-II-2*) and their relative energies and torsional angles.



Yamago and coworkers recently reported the synthesis and rotational barriers of a [6]CPP derivative bearing three 9,9-dimethyl-9*H*-fluorene-2,7-diyl units ([3]CFR), an [8]CPP derivative bearing four 9,9-dimethyl-9*H*-fluorene-2,7-diyl units ([4]CFR),<sup>9</sup> and related carbazole<sup>3b</sup> and dibenzothiophene systems.<sup>10</sup> Both *anti*- and *syn*-[3]CFR were produced and separated with the ratio of *anti*:*syn* = 36:64. Only one rotamer of [4]CFR with all *anti* relationship between the adjacent FR units was isolated. DFT calculations indicate that *anti*-[3]CFR is thermodynamically more stable than *syn*-[3]CFR by 4.8 kcal/mol, and the rotational barrier from *anti*-[3]CFR to *syn*-[3]CFR is 58.4 kcal/mol. The isolation of *syn*-[3]CFR as the major product suggests that the synthetic pathway is kinetically controlled. In comparison with *anti*- and *syn*-**II-2**, the differences of thermodynamic stabilities between the *anti* and *syn* rotamers are comparable, but [3]CFR has a much higher rotational barrier. The smaller macrocyclic ring size of [3]CFR as a [6]CPP derivative causes severe bending of the single bonds connecting the three FR units together during the rotating process, which is largely responsible for the higher rotational barrier. For [4]CFR, four rotamers were calculated to be the local minima, with the rotamer having *anti* relationship between the adjacent units being thermodynamically most stable and the other three rotamers are higher in energies by 4.5, 5.3, and 7.5 kcal/mol. The rotational barrier from the all *anti* rotamer to the next most stable rotamer with one unit *anti* to the other three was calculated to be 18.2 kcal/mol, low enough to allow rapid equilibration of the rotamers at rt. It is worth noting that [4]CFR, which is an [8]CPP derivative, has a smaller macrocyclic ring size than [3]CIFO, which is a [9]CPP derivative, but [4]CFR has a lower rotational barrier. The fact that [4]CFR contains four FR units, instead of three longer IFO units in [3]CIFO, diminishes the extent of bond distortion of the single bonds connecting the units together during the rotating process, lowering the rotational barrier. The rotational barriers of several macrocycles bearing chrysenylene and anthanthrenylene units

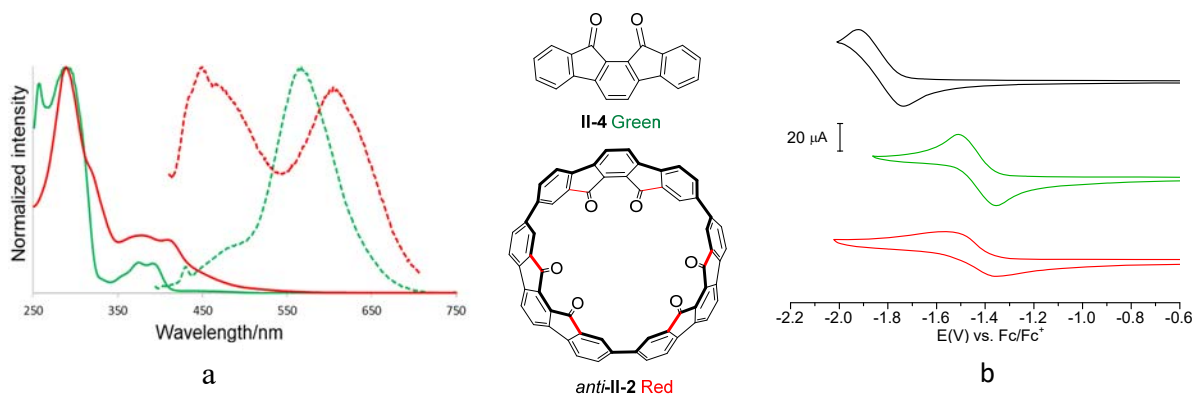
were extensively investigated by Isobe and coworkers.<sup>11</sup> The rates of rotation were found to be influenced by the chemical structures of the units and the connectivity among them. The DFT-optimized structure of *anti*-**II-2** shows that the torsional angles between benzene rings B and C, B' and C', and E and E' are approximately 44.8°, 44.8°, and 0°, respectively (Figure 2.3). On the other hand, the torsional angles between the adjacent benzene rings in *syn*-**II-2** range from 0.6 to 2.3°, substantially smaller than those between rings B and C and between rings B' and C' in *anti*-**II-2**. As a result, *syn*-**II-2** suffers from more non-bonded steric interactions between IFO units, which contribute to its lower thermodynamic stability than *anti*-**II-2**.

The IR stretching absorption of the keto carbonyls of *anti*-**2** occurs at 1730 cm<sup>-1</sup>, which is 9 cm<sup>-1</sup> higher than that of **II-4** at 1721 cm<sup>-1</sup>. The hoop-like aromatic structure of *anti*-**II-2** with a radially  $\pi$ -conjugated system diminishes the extent of its conjugation with the carbonyl  $\pi$  bonds, which is perhaps partially responsible for the higher absorption frequency.<sup>12</sup> The effect of the macrocyclic ring structure on the bond angles of the keto carbonyl groups may also contribute to the higher absorption frequency.

The UV/Vis and fluorescence spectra of *anti*-**II-2** and **II-4** in CH<sub>2</sub>Cl<sub>2</sub> (Figure 2.4a) show that the UV/Vis absorption maxima ( $\lambda_{\text{abs}}$ ) of **II-4** appear at 289 with two weaker bands at 375 and 392 nm, whereas those of *anti*-**II-2** occur at 288, 379, and 408 nm. Upon excitation of **II-4** at 380 nm, the fluorescence maximum ( $\lambda_{\text{em}}$ ) appears at 567 nm. For *anti*-**II-2**, upon excitation at 395 nm two fluorescence maxima appear at 448 and 606 nm. In comparison, the  $\lambda_{\text{abs}}$  of 9-fluorenone in CH<sub>2</sub>Cl<sub>2</sub> appears at 258 nm, which can be assigned to a  $\pi$ - $\pi^*$  transition, and a weaker band at 380 nm, which can be attributed to an n- $\pi^*/\pi$ - $\pi^*$  transition.<sup>13</sup> It is worth noting that while 9-fluorenone shows only one broad band for the n- $\pi^*/\pi$ - $\pi^*$  transition, *anti*-**II-2** and **II-4** both exhibit two absorption maxima. The  $\lambda_{\text{em}}$  of 9-fluorenone in CH<sub>2</sub>Cl<sub>2</sub> appears at 504 nm. For **II-1** in DMSO,  $\lambda_{\text{abs}}$

and  $\lambda_{em}$  appear at 327 and 464 nm, respectively.<sup>2a</sup> The parent [9]CPP exhibits  $\lambda_{abs}$  at 340 nm and  $\lambda_{em}$  at 494 nm.<sup>14</sup> The longest  $\lambda_{em}$  of *anti*-**II-2** is significantly red-shifted from those of **II-1**, **II-4**, 9-fluorenone, and the parent [9]CPP.

The cyclic voltammograms of 9-fluorenone, *anti*-**II-2**, and **II-4** in CH<sub>2</sub>Cl<sub>2</sub> (Figure 2.4b) were recorded versus the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The reduction potentials of *anti*-**II-2** and **4** at -1.47 and -1.43 V, respectively, indicate that they are more easily reduced than 9-fluorenone at -1.83 V.<sup>15</sup> The presence of one or more electron-withdrawing keto carbonyls in *anti*-**II-2** and **II-4** is responsible for the lower reduction potentials. Only one reversible redox event was observed for *anti*-**II-2** and **II-4**. The similarity of the reduction potentials of *anti*-**II-2** and **II-4** suggests that the redox event of *anti*-**II-2** is largely localized to each IFO unit.



**Figure 2.4.** (a). UV/Vis (solid lines), fluorescence (dashed lines) spectra, of *anti*-**II-2** (red) and **II-4** (green). (b). Cyclic voltammograms of 9-fluorenone (black), **II-4** (green), and *anti*-**II-2** (red) in CH<sub>2</sub>Cl<sub>2</sub> at rt (scan rate 100 mV s<sup>-1</sup>, 0.1 M of [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub>, glassy carbon working electrode).

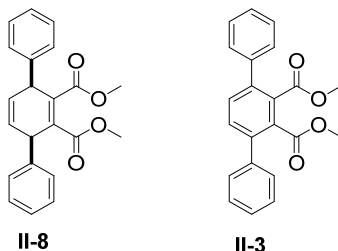
In summary, *anti*-**II-2** as a functionalized [9]CPP bearing three IFO units in the macrocyclic ring structure was synthesized. The <sup>1</sup>H and <sup>13</sup>C NMR spectra showed that the *anti* rotamer (*anti*-[3]CIFO) was the atropisomer that was isolated. DFT calculations indicate that *anti*-[3]CIFO is thermodynamically more stable than *syn*-[3]CIFO by 4.3 kcal/mol, and the rotational

barrier from the *anti* to *syn* rotamer is estimated to be 23.3 kcal/mol. The presence of six keto carbonyls in *anti*-[3]CIFO provides additional opportunities to further functionalize the macrocyclic ring structure of [9]CPP.

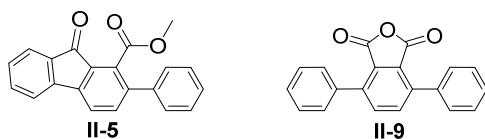
## 2.3 Experimental Methods

(*E,E*)-1,4-Diphenyl-1,3-butadiene, dimethyl acetylenedicarboxylate (DMAD), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), manganese dioxide (active), trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), trifluoromethanesulfonic acid (TfOH), methanesulfonic acid (MsOH), and phosphorus pentoxide were purchased from chemical suppliers and were used as received. The reported procedures were adopted for the synthesis of dimethyl *cis*-3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate (**II-8**)<sup>5</sup> and [9]CPP **II-1**.<sup>2a</sup> Eaton's reagent was prepared according to the reported procedure.<sup>7</sup> 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 FT-ICR mass analyzer coupled with electrospray ionization (ESI). UV/Vis absorption spectra were recorded on a spectrophotometer with a 1 nm resolution, and the baseline was corrected with a solvent filled square quartz cell. Fluorescence spectra were recorded on a spectrofluorophotometer with a 2 nm resolution. Cyclic voltammetry measurements were conducted under a nitrogen atmosphere inside a glovebox using a Gamry Interface 1000 electrochemical workstation in a single compartment cell using 1 mM sample solutions in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A three electrode setup was employed with a glassy carbon electrode as working electrode, a platinum sheet as the counter electrode, and a silver wire as a quasi-reference electrode.

Ferrocene was added as an internal standard after completion of the measurements and all potentials are referenced versus the Fc/Fc<sup>+</sup> couple.



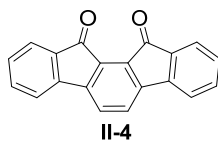
**Experimental Procedure for Compound II-3.**<sup>5</sup> A mixture of dimethyl *cis*-3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate (**II-8**)<sup>5</sup> (1.00 g, 2.87 mmol), active manganese dioxide (4.99 g, 57.4 mmol), and chlorobenzene (40 mL) was stirred at 120 °C for 20 h before it was cooled to rt. The mixture was filtered and washed with dichloromethane. Solvents were removed in vacuo to give, without further purification, **II-3** (0.89 g, 2.6 mmol, 90% yield) as a white solid: mp = 188–190 °C; IR 1742, 1723, 1236 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.52 (2 H, s), 7.45–7.35 (10 H, m), 3.61 (6 H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 168.8, 139.9, 139.7, 132.0, 131.6, 128.4, 128.2, 127.8, 52.4; HRMS (ESI/FT-ICR) *m/z* [M<sup>+</sup>] calcd for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub> 346.1200; found 346.1189.



**Experimental Procedure for Compound II-5. Method 1:** To a 20 mL vial were added 1.5 mL of trifluoroacetic acid, 1.0 mL of trifluoroacetic anhydride, and 2 drops of methanol. The vial was screwed tight with a cap and stirred at 70 °C for 15 min before it was cooled to rt. Then **II-3** (0.020 g, 0.058 mmol) was added, and the vial was again screwed tight with a cap. The mixture was

stirred at 75 °C for 30 h. Solvents were removed in vacuo, and the ratio between **II-5** and 3,6-diphenylphthalic anhydride (**II-9**)<sup>5</sup> in the crude mixture was determined by <sup>1</sup>H NMR spectroscopy to be ~6:1 in most runs, ranging from 3.5:1 to 9:1. Further separation and purification by preparative TLC (dichloromethane, *R<sub>f</sub>* = 0.52) gave **II-5** in 75 to 88% isolated yields as a yellow solid.

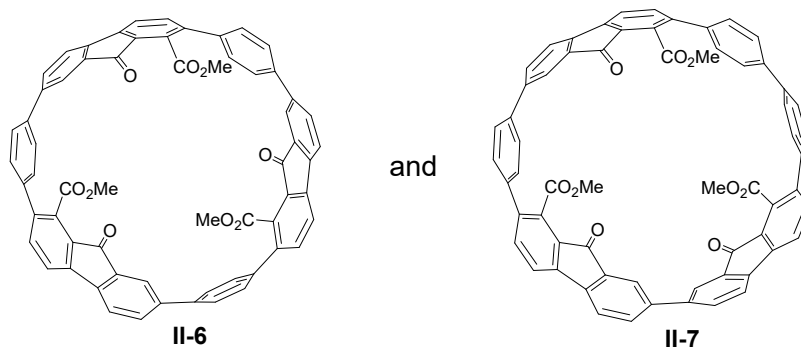
*Method 2:* To a 20 mL vial were added 1 mL of trifluoromethanesulfonic acid and 0.5 mL of trifluoroacetic anhydride. The vial was screwed tight with a cap and stirred at rt for 5 min before **II-3** (0.018 g, 0.052 mmol) was added. The vial was again screwed tight with a cap and stirred at rt for 3 h. The mixture was cooled to 0 °C, and ~10 g of ice chips was added slowly. The mixture was stirred for an additional 10 min, filtered, and washed with water. After drying in air for 20 h, compound **II-5** (0.016 g, 0.051 mmol, 98% yield) was obtained as a yellow solid: mp = 134–136 °C; IR 1733, 1714, 1606, 1283, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.65 (1 H, d, *J* = 7.4 Hz), 7.62 (1 H, d, *J* = 7.8 Hz), 7.57–7.49 (3 H, m), 7.43–7.38 (4 H, m), 7.32 (1 H, td, *J* = 1.2, 7.4 Hz), 3.84 (3 H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 191.8, 167.7, 143.4, 143.2, 140.2, 138.7, 136.0, 134.9, 134.0, 130.8, 130.6, 129.5, 128.6, 128.2, 128.1, 124.5, 121.2, 120.5, 52.6; HRMS (ESI/FT-ICR) *m/z* [MH<sup>+</sup>] calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub> 315.1016; found 315.1017.



**Experimental Procedure for Compound II-4.**<sup>5</sup> *Method 1:* To a 20 mL vial were added 3.0 g of Eaton's reagent and **II-5** (0.010 g, 0.032 mmol). The vial was screwed tight with a cap and stirred at 75 °C for 12 h before it was cooled to rt. The reaction was quenched with ice/water and extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (3 × 10

mL) and dried over sodium sulfate. The solvent was removed in vacuo to give indeno[2,1-*a*]fluorene-11,12-dione (**II-4**, 0.0086 g, 0.030 mmol, 95% yield) as a yellow solid.

*Method 2:* To a 20 mL vial were added 2 mL of trifluoromethanesulfonic acid, 1.5 mL of trifluoroacetic anhydride, and 0.100 g zinc bromide. The vial was screwed tight with a cap and stirred at rt for 5 min before **II-3** (0.217 g, 0.626 mmol) was added. The vial was again screwed tight with a cap and stirred at rt for 2 h and then at 90 °C for 1.5 h. The mixture was cooled to 0 °C and ~10 g of ice chips was added slowly. The mixture was stirred for an additional 10 min, filtered, and washed with water. After drying in air for 20 h, **II-4** (0.173 g, 0.613 mmol, 98% yield) was obtained as a yellow solid: mp >255 °C; IR 1721, 1606, 1188, 747 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.71 (2 H, dt, *J* = 7.4, 1.0 Hz), 7.62 (2 H, s), 7.53–7.48 (4 H, m), 7.33 (2 H, ddd, *J* = 8.5, 5.8, 2.6 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 190.5, 145.2, 143.6, 134.8, 133.7, 132.4, 129.6, 124.79, 124.78, 120.1; HRMS (ESI/FT-ICR) *m/z* [M<sup>+</sup>] calcd for C<sub>20</sub>H<sub>10</sub>O<sub>2</sub> 282.0675; found 282.0680.



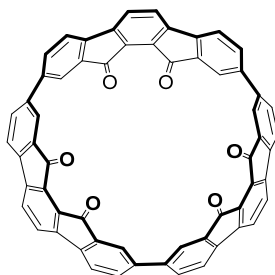
**Experimental Procedure for II-6 and II-7.** To each of five 20 mL vials were added 1.5 mL of trifluoroacetic acid, 1.0 mL of trifluoroacetic anhydride, and 2 drops of methanol. The vials were screwed tight with caps and stirred at 70 °C for 15 min before they were cooled to rt. Then ~0.007 g of **II-1** was added to each of the five vials (total 0.035 g, 0.034 mmol). The vials were again screwed tight with caps and stirred at 75 °C for 30 h. The mixtures were combined, and solvents

were removed in vacuo. The residue was purified and separated by preparative TLC (acetone:dichloromethane = 5:95) to produce **II-6** (0.005 g, 0.005 mmol, 15% yield,  $R_f$  = 0.43) as an orange solid and **II-7** (0.015 g, 0.016 mmol, 47% yield,  $R_f$  = 0.65, with small amount of impurity) as an orange solid. Compound **II-6**: IR 1732, 1463  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.76 (3 H, d,  $J$  = 7.8 Hz), 7.75 (3 H, dd,  $J$  = 7.8, 1.6 Hz), 7.54 (3 H, d,  $J$  = 7.8 Hz), 7.48 (3 H, d,  $J$  = 7.8 Hz), 7.34 (6 H, d,  $J$  = 8.6 Hz), 7.29 (6 H, d,  $J$  = 8.2 Hz), 7.04 (3 H, d,  $J$  = 1.2 Hz), 3.56 (9 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  191.4, 167.7, 143.7, 143.0, 142.2, 140.6, 138.2, 136.9, 135.6, 133.6, 132.25, 132.21, 130.5, 129.8, 129.4, 128.2, 123.07, 123.01, 52.5; HRMS (ESI/FT-ICR)  $m/z$  [ $\text{M}^+$ ] calcd for  $\text{C}_6\text{H}_3\text{O}_9$  936.2354; found 936.2382. Compound **II-7**: IR 1736, 1724, 1289, 827  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.81 (1 H, d,  $J$  = 8.0 Hz), 7.78–7.73 (5 H, m), 7.574 (1 H, d,  $J$  = 8.2 Hz) 7.566 (1 H, d,  $J$  = 8.2 Hz), 7.564 (1 H, d,  $J$  = 8.2 Hz), 7.537 (1 H, d,  $J$  = 7.9 Hz),  $\delta$  7.534 (1 H, d,  $J$  = 8.1 Hz), 7.49 (1 H, d,  $J$  = 8.1 Hz), 7.34–7.25 (12 H, m), 7.085 (1 H, d,  $J$  = 1.4 Hz), 7.076 (1 H, d,  $J$  = 1.4 Hz), 7.01 (1 H, d,  $J$  = 1.7 Hz), 3.54 (3 H, s), 3.45 (3 H, s), 3.43 (3 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  191.65, 191.63, 191.4, 167.70, 167.62, 167.51, 144.0, 143.70, 143.64, 143.17, 143.10, 142.98, 142.94, 142.92, 142.5, 140.70, 140.63, 140.55, 138.44, 138.41, 138.34, 137.0, 136.5, 136.4, 135.74, 135.67, 135.50, 133.44, 133.38, 133.2, 132.8, 132.62, 132.53, 132.42, 132.38, 132.26, 131.8, 131.5, 130.9, 129.78, 129.72, 129.3, 129.2, 128.2, 128.0, 127.8, 123.49, 123.43, 123.35, 123.32, 123.20, 123.18, 52.33, 52.30, 52.1; HRMS (ESI/FT-ICR)  $m/z$  [ $\text{M}^+$ ] calcd for  $\text{C}_6\text{H}_3\text{O}_9$  936.2354; found 936.2418.

**Experimental Procedure for Selective Synthesis of II-6.** To a 20 mL vial were added 3 mL of anhydrous dichloromethane, 1 mL of trifluoromethanesulfonic acid, and 1 mL of trifluoroacetic anhydride. The vial was screwed tight with a cap and stirred at rt for 5 min. Then **II-1** (0.010 g, 0.0097 mmol) in 3 mL of anhydrous dichloromethane was added slowly. The vial was again



screwed tight with a cap, and the reaction mixture was stirred at rt for 10 h. The mixture was cooled to 0 °C and poured into 20 mL of ice/water. The mixture was extracted by dichloromethane (2 × 10 mL) and dried over sodium sulfate. The solvent was removed in vacuo, and the residue was purified by preparative TLC (acetone:dichloromethane = 5:95) to produce **II-6** (0.0040 g, 0.0043 mmol, 44% yield) as an orange solid.



*anti-II-2*

**Experimental Procedure for *anti-II-2*.** To a 20 mL vial were added 3.0 g of Eaton's reagent, and the crude mixture containing **II-6** and **II-7** (from 0.035 g of **II-1** before preparative TLC purification and separation, 0.034 mmol). The vial was screwed tight with a cap and stirred at 75 °C for 12 h before it was cooled to rt. The reaction was quenched with ice/water and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with water (2 × 10 mL) and dried over sodium sulfate. The solvent was removed in vacuo, and the residue was purified by preparative TLC (acetone:dichloromethane = 1:10) to produce *anti-II-2* (0.0070 g, 0.0083 mmol, 25% yield,  $R_f = 0.48$ ) as a red solid: IR 1730, 1595, 1183, 1095, 775  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.10 (2 H, d,  $J = 1.9$  Hz), 7.78 (2 H, dd,  $J = 8.3, 2.0$  Hz), 7.73 (2 H, dd,  $J = 8.0, 1.7$  Hz), 7.69 (2 H, dd,  $J = 8.0, 1.8$  Hz), 7.57 (2 H, s), 7.53 (2 H, d,  $J = 8.0$  Hz), 7.51 (2 H, d,  $J = 7.9$  Hz), 7.47 (2 H, d,  $J = 7.7$  Hz), 7.46 (2 H, d,  $J = 7.8$  Hz), 7.40 (2 H, d,  $J = 8.3$  Hz), 7.17 (2 H, d,  $J = 1.8$  Hz), 7.11 (2 H, d,  $J = 1.7$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  190.5, 190.2, 190.1, 144.9, 144.72, 144.67, 143.5, 143.3, 142.9, 142.77, 142.76, 137.5, 136.4, 135.6, 135.5, 135.0,

134.8, 134.4, 132.0, 131.6, 130.7, 129.0, 128.5, 126.8, 126.6, 126.5, 122.73, 122.69, 122.59, 122.0;  
HRMS (ESI/FT-ICR)  $m/z$   $[MH^+]$  calcd for  $C_{60}H_{25}O_6$  841.1646; found 841.1633.

## 2.4 Reference

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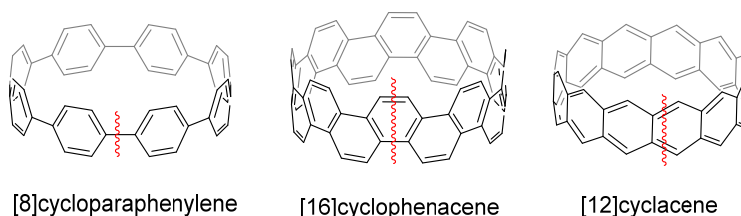
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## Chapter 3. Attempts for the Synthesis of a Carbon Nanobelt ([16]Cyclophenacene)

### 3.1 Introduction

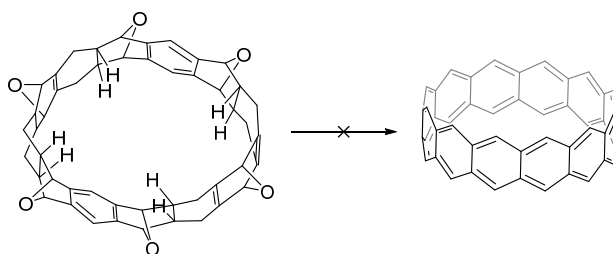
Rational syntheses of aromatic carbon nanobelts have challenged the synthetic community for more than half a century.<sup>1</sup> By Itami's definition, carbon nanobelts require the cleavage of at least two C-C bonds to form linear structure, while for carbon nanorings, only the cleavage of one C-C bond is required (Figure 3.1).<sup>2</sup> Unlike carbon nanorings, benzene units on carbon nanobelts can't rotate and sidewall thus could serve as better potential seeds for the chemical growth to form well-defined carbon nanotubes.<sup>3</sup> Carbon nanobelts themselves have also received much attention from material chemists in terms of their special optical and electronic properties.<sup>1,2</sup> However, there are two major obstacles in the design and synthesis of the  $\pi$ -conjugated carbon nanobelts: high strain energy and high reactivity.<sup>3-5</sup> Usually, the strain energy accumulates in synthetic pathways and particularly in the ring closing step because of the build-up of especially high strain energy. In addition, zigzag-edged carbon nanobelts are extremely unstable and more reactive than armchair-edged carbon nanobelts.<sup>5</sup> Therefore, it is a very challenging task for the construction of carbon nanobelts for the synthetic communities, and many research groups have tried, unfortunately, most attempts were unsuccessful.



**Figure 3.1.** Differences between carbon nanorings and carbon nanobelts.

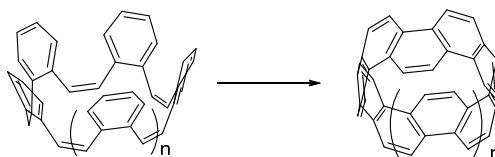
In 1987, Stoddart and his research group reported the synthetic attempts of [12]cyclacene,<sup>5</sup> which is a zigzag-edged carbon nanobelt (Scheme 3.1). The strategy was to construct a lower energy strained structure as the double-stranded macrocyclic precursor via the Diels-Alder reactions. The subsequent aromatization through deoxygenation and dehydration was thought to be possibly for reaching the targeted carbon nanobelt. However, the final aromatization step was unsuccessful due to the high strain energy and high reactivity of the [12]cyclacene.

### Scheme 3.1. Stoddart's Attempts for the Synthesis [12]Cyclacene



In 2002, Iyoda and his colleagues attempted to construct [n]cyclophenacenes, which are armchair-edged carbon nanobelts (Scheme 3.2).<sup>4d</sup> They synthesized a series of *cis*-benzannulenes as the carbon nanobelts precursors. However, attempts to convert the precursors to the final products via cyclodehydrogenation failed. Fortunately, a correlated peak to the cation of [10]cyclophenacene by MALDI-TOF was observed, providing an evidence that [n]cyclophenacenes could be synthesized and perhaps isolated.

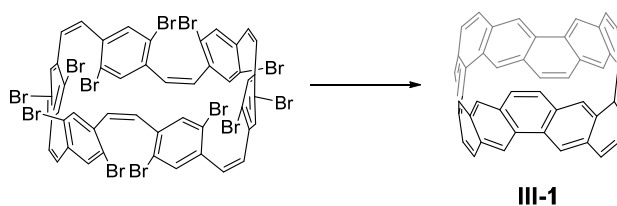
### Scheme 3.2. Iyoda's Attempts for the Synthesis of [n]cyclophenacenes



In 2017, Itami's group reported the first synthesis and characterization of a carbon nanobelt, compound **III-1**,<sup>6</sup> which can be regarded as a segment of an armchair carbon nanotube (Scheme

3.3). The key strategy in the synthesis is the construction of a brominated all-*cis*-benzannulene macrocyclic precursor, which is similar to the precursors reported by Iyoda in 2002. Instead of nonfunctionalized benzene rings in Iyoda's pathway, the brominated aryl groups allow of the use of nickel-mediated intramolecular homocoupling reactions for the carbon-carbon bond formation. The yield of the final cyclization steps was only initially reported to be 1%,<sup>6</sup> but was later optimized to be 7%.<sup>7</sup> It was estimated by DFT calculation, that the strain energy in **III-1** to be 119.5 kcal/mol.

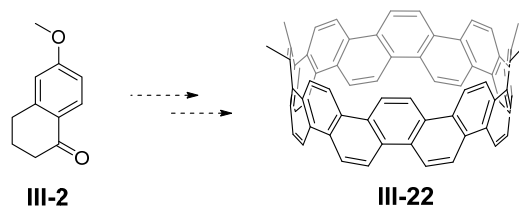
### Scheme 3.3. Itami's Successful Synthesis of Carbon Nanobelt **III-1**



### 3.2 Our Synthetic Approach to [16]Cyclophenacene

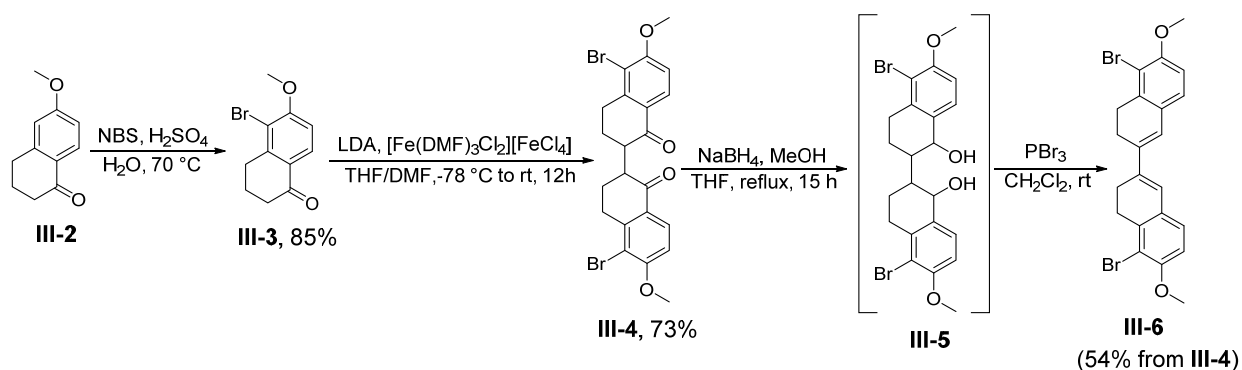
The success of synthesis of **III-1** opens the door for further investigation of carbon nanobelt chemistry. The construction of different types, sizes, and attached functional groups on carbon nanobelts is still waiting to be explored. Building on the knowledge, strategies, and methods accumulated through the previous investigation, we will attempt to develop a synthetic pathway for the construction of armchair carbon nanobelt **III-21**, which represents a belt segment of (8,8) carbon nanotube and is a tetramethylated [16]cyclophenacene (Scheme 3.4).

### Scheme 3.4. Our Proposed Construction of the Tetramethylated [16]Cyclophenacene



The synthesis started with selective bromination of the commercially available **III-2** to give **III-3** in 85% yield (Scheme 3.5).<sup>8</sup> Diketone **III-3** was successfully synthesized via an iron-promoted oxidative enolate dimerization of **III-2** in 73% yield.<sup>9</sup> It is worth noting that the enolate dimerization reaction with ferric chloride DMF complex  $[\text{Fe}(\text{DMF})_3\text{Cl}_2][\text{FeCl}_4]$  is more efficient with higher yield than using  $\text{FeCl}_3$ . In addition,  $[\text{Fe}(\text{DMF})_3\text{Cl}_2][\text{FeCl}_4]$  is stable to air and moisture, which makes the reagent easier to handle when compared to the hygroscopic  $\text{FeCl}_3$ .<sup>9</sup> Treatment of **III-4** with sodium borohydride in the presence of methanol promoted the reduction reaction to give diol **III-5**, which was used without further purification due to its limited solubility and the potential formation of various stereoisomers. Then the crude mixture of diol **III-5** was directly treated with  $\text{PBr}_3$  to provide diene **III-6** in 54% isolated yield over two steps from **III-4**. Diene **III-6** has extreme limited solubility in common organic solvents due to the possible high  $\pi$ - $\pi$  stacking effects. The proton NMR spectrum was recorded at 60 °C, which showed high product purity. However, because of the low solubility of **III-6**, the carbon NMR spectrum was not obtained.

### Scheme 3.5. Preparation of Diene **III-6**

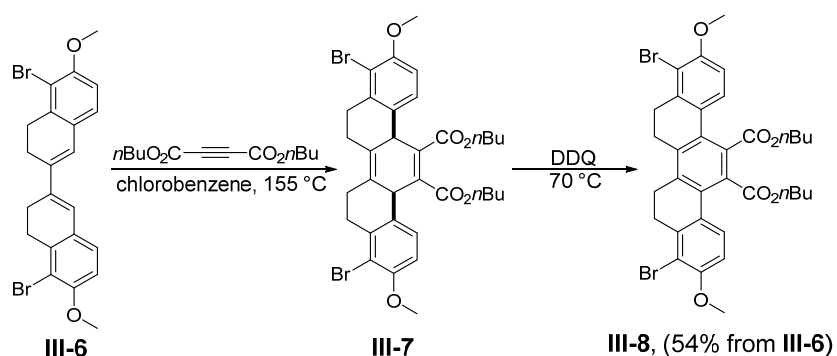


The Diels–Alder reaction between **III-6** and dibutyl acetylenedicarboxylate followed by oxidative aromatization by DDQ produced a functionalized and hydrogenated derivative of



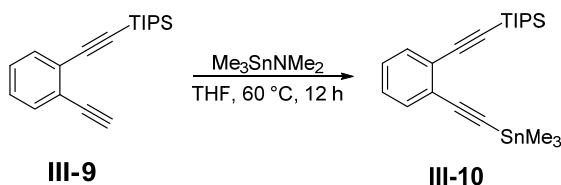
[5]phenacene **III-8** in 54% yield over two steps from **III-6** (Scheme 3.6).<sup>10</sup> It is worth noting that the Diels-Alder reaction is possibly to be reversible and the diene is also prone to aromatization and double-bond isomerization. Therefore, it is important to carefully control the reaction temperature and time to obtain the optimal yield.

**Scheme 3.6. Preparation of a Functionalized and Partially Hydrogenated Derivative of [5]phenacene III-8**



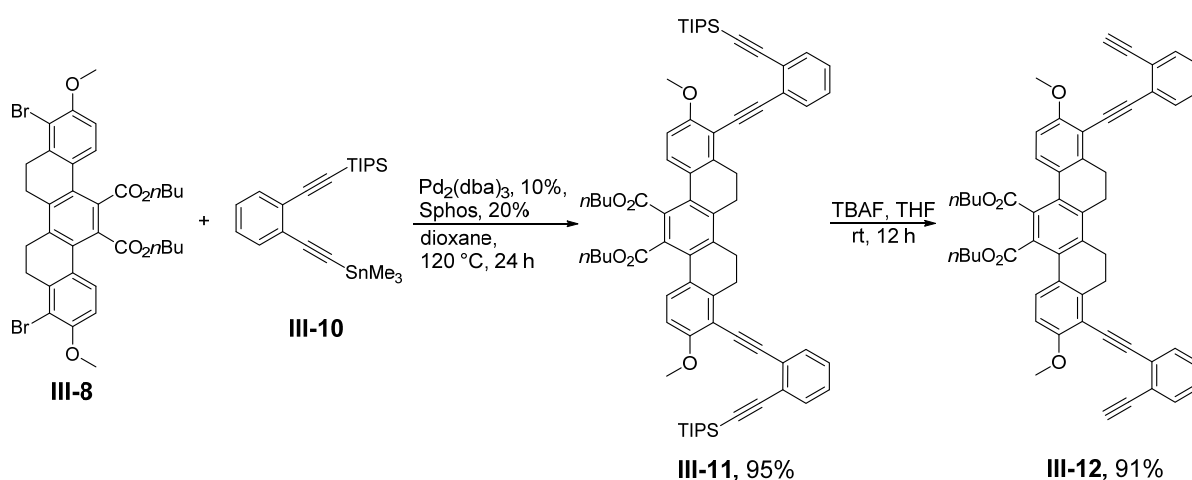
The synthetic sequence also requires the synthesis of **III-10**, which was prepared from the previously reported **III-9**<sup>11</sup> via a stannylation reaction of the terminal acetylene (Scheme 3.7). Unfortunately, utilization of  $\text{Me}_3\text{SnNMe}_2$ , an extremely toxic reagent, was necessary. In the stannylation reaction, all of the reagents and solvents are volatile and can be removed easily in vacuo, and the in situ generated stannyl product **III-10** was used without further purification for the reaction with **III-8**.<sup>12</sup>

**Scheme 3.7. In Situ Preparation of III-10**



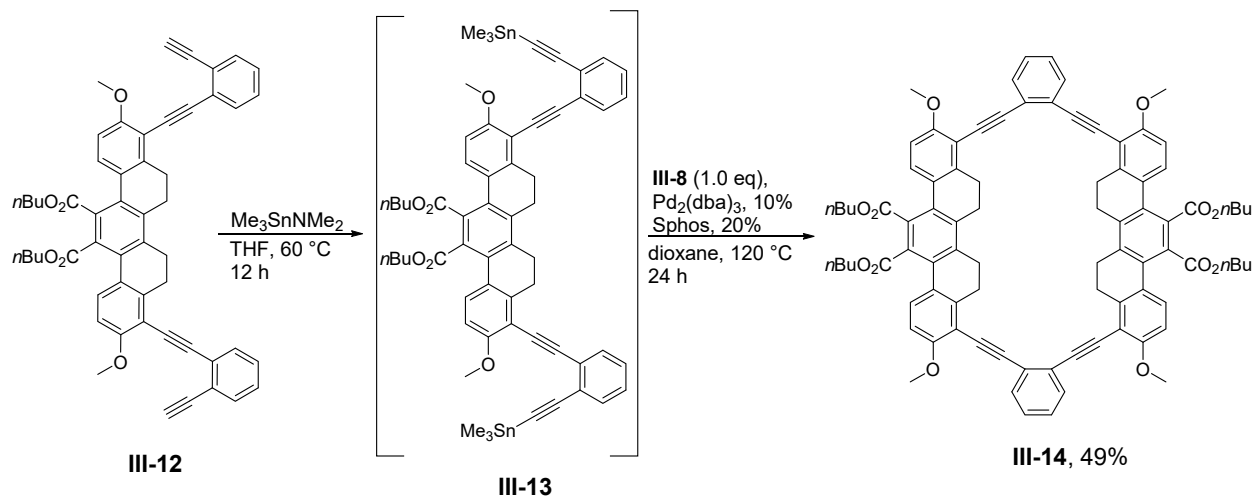
The Stille-coupling reactions between **III-8** and the in situ synthesized **III-10** then provided **III-11** in 95% yield (Scheme 3.8). The high steric hindrance of the brominated position on **III-8** is a major challenge in this reaction. After screening several palladium catalysts, ligands, and solvents, the Pd-Sphos-dioxane catalytic condition was found to be most efficient in this system.<sup>13</sup> Desilylation reaction of **III-11** with TBAF gave tetraacetylene **III-12** in 91% yield.<sup>14</sup>

### Scheme 3.8. Synthesis of Tetraacetylene **III-12**



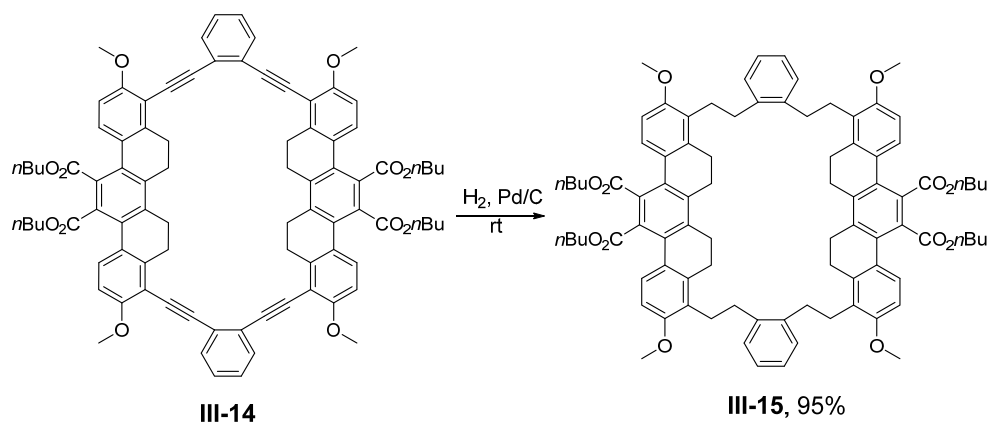
Treatment of **III-12** with  $\text{Me}_3\text{SnNMe}_2$  again produced, in situ, the stannylated product **III-13**. The palladium-mediated Stille-coupling reactions between **III-8** and the in situ generated **III-13** gave macrocycle **III-14** in 49% yield (Scheme 3.9). The success of the palladium-catalyzed macrocyclization reaction, as one of the key steps, is essential in the construction of the final carbon nanobelt. Molecular modeling indicates that the precursor leading to **III-14** is relatively rigid and has limited rotational freedom of, which may contribute to the relatively high efficiency of the macrocyclic step.

### Scheme 3.9. Construction of Macrocycle III-14



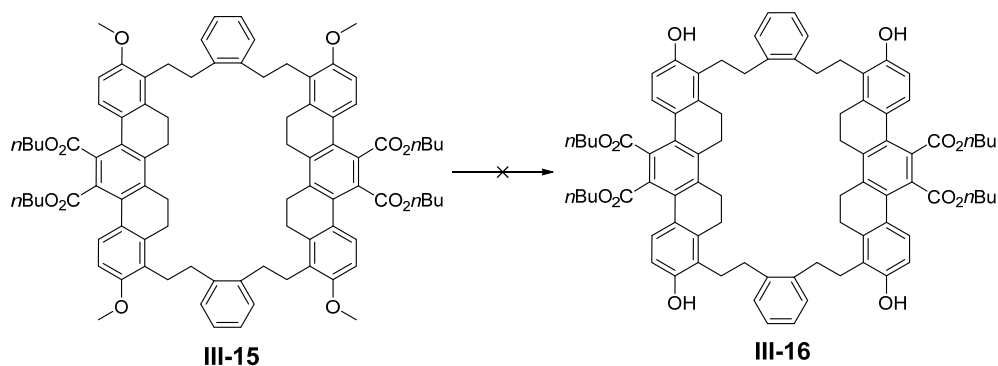
Catalytic hydrogenation of **III-14** with Pd/C at room temperature afforded macrocycle **III-15** in nearly quantitative yield (Scheme 3.10).

### Scheme 3.10. Hydrogenation of Macrocycle III-14 to form III-15



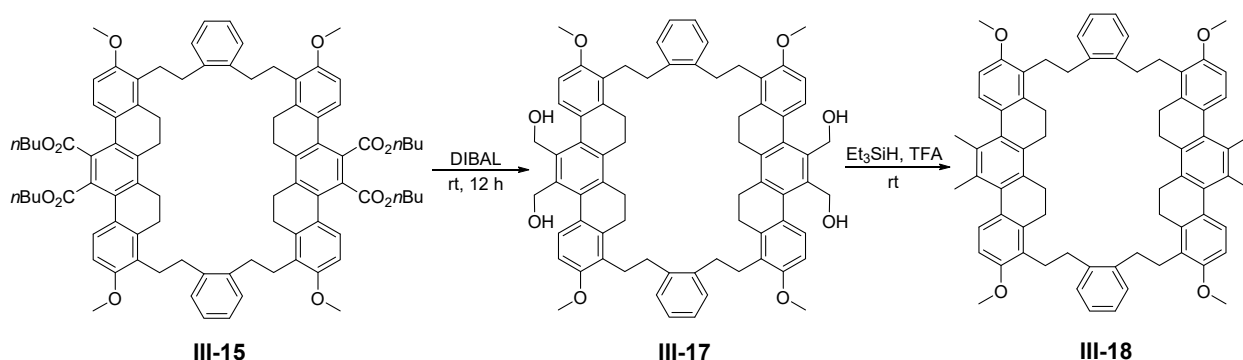
However, direct demethylation of compound **III-15** to form **III-16** with  $\text{BBr}_3$  or other demethylation reagents, such as  $\text{BCl}_3$ ,  $\text{BF}_3\text{SMe}_2$ , was not successful (Scheme 3.11). Many traditional acid-promoted demethylation methods were investigated, only  $\text{BBr}_3$  was found to be able to partially deprotect the methyl groups.<sup>15</sup> In addition, a competing reaction to form the corresponding anhydride derivatives from the two neighboring ester groups was also observed.

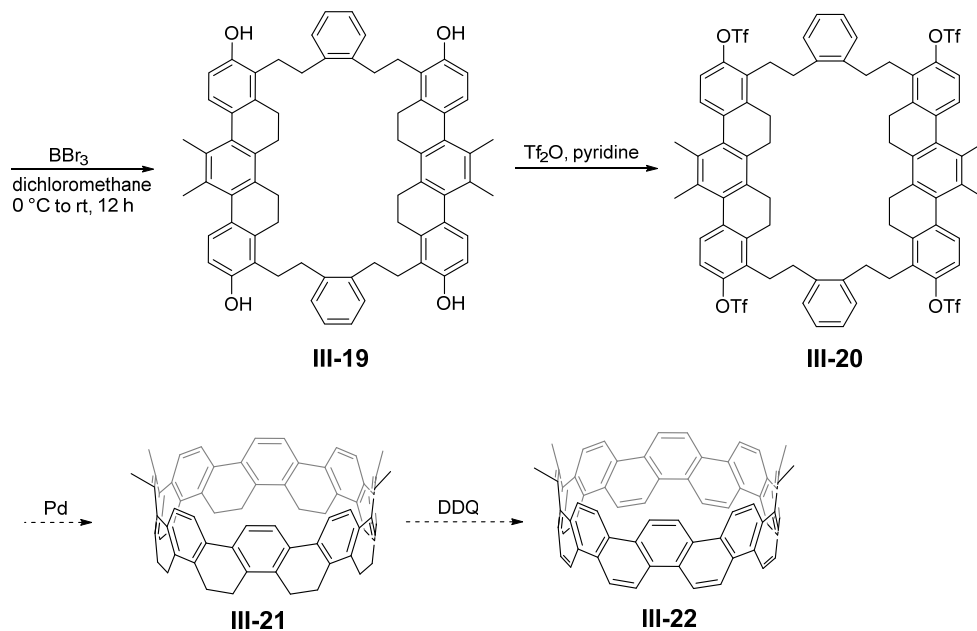
### Scheme 3.11. Attempts to form III-16 via Direct Demethylation



One strategy to resolve this problem is to remove all of the ester groups before the demethylation reaction (Scheme 3.12). Treatment of **III-15** with DIBAL at room temperature produced the corresponding tetraol **III-17**, which was used without purification because of its low solubility. The crude **III-17** was treated with triethylsilane and trifluoroacetic acid to give **III-18**.<sup>16</sup> Without the presence of ester groups in **III-18**, it was readily demethylated with  $\text{BBr}_3$  to give **III-19**. Then tetratriflate **III-20** was prepared by treating **III-19** with trifluoromethanesulfonic anhydride and pyridine.<sup>17</sup> We intend to use **III-20** as a precursor of **III-21**, which can be regarded as a tetramethylated and partially hydrogenated [16]cyclophenacene derivative. The triflate groups in the **III-20** could be used for the subsequent Pd-catalyzed intramolecular arylation reactions<sup>19</sup> to form **III-21**. Oxidative aromatization of **III-21** with DDQ could then give **III-22** as tetramethylated [16]cyclophenacene.

### Scheme 3.12. Preparation of [16]Cyclophenacene Precursor III-20

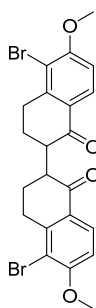




In this project, a synthetic pathway to the construction of an armchair-edged carbon nanobelt ([16]cyclophenacene) **III-22** has been designed. At this stage, the corresponding belt precursor **III-20** has been successfully synthesized. We are developing reaction conditions for the transformation to the target carbon nanobelt **III-22** from **III-20**.

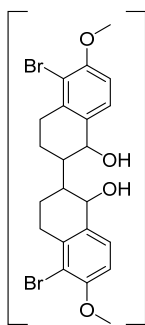
### 3.3 Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under an argon atmosphere. 5-Bromo-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-one **III-3**,<sup>8</sup> di-*n*-butyl acetylenedicarboxylate<sup>18</sup> and 2-ethynyl-1-[(triisopropylsilyl)ethynyl]benzene<sup>11</sup> were prepared according to the reported procedures. All other reagents were purchased from chemical suppliers and were used as received.



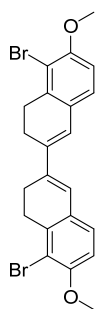
**III-4**

**Experimental Procedure for Dibromide III-4.** To a solution of freshly prepared LDA (14.9 mmol) in THF (20 mL) at  $-78$  °C under an argon atmosphere was added **III-3** (3.61g, 14.2 mmol) in THF (20 mL) dropwise. After 30 min at  $-78$  °C,  $[\text{Fe}(\text{DMF})_3\text{Cl}_2][\text{FeCl}_4]$  (3.86 g, 7.09 mmol) in 20 mL of DMF under argon was added slowly. The reaction mixture was then allowed to warm to room temperature. After 12 h, the reaction mixture was quenched with 100 mL of a 1 M aqueous HCl solution. After 30 minutes of stirring, the reaction mixture was filtered and then washed with water, ethanol, and hexanes subsequently to give **III-4** (2.50 g, 4.92 mmol, 69% yield) as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 and 8.07 (2 H, two doublets from two isomers,  $J = 9.0$  Hz), 6.90 (2 H, two doublets from the two overlapping diastereomers,  $J = 9.0$  Hz), 3.98 (6 H, s), 3.53-2.88 (8 H, m), 2.16-1.93 (2 H, m).



**III-5**

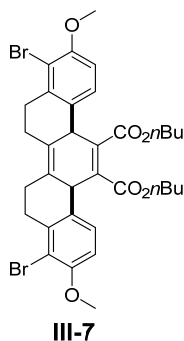
**Experimental Procedure for III-5.** To a 200-mL flask were added 2.50 g of **III-3** (4.92 mmol) and 1.70 g of sodium borohydride (44.9 mmol). The flask was flushed with argon before 100 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 1 h before 6 mL of methanol was added dropwise. Then, the reaction mixture was heated at reflux for an additional 12 h before it was cooled to room temperature. Then the reaction mixture was quenched with 50 mL of a 3.0 M sodium hydroxide solution. After 10 minutes of stirring, the reaction mixture was filtered and then washed with 20 mL of a 3.0 M sodium hydroxide solution and water. After the product was dried, crude **III-5** (2.4 g) was obtained as a white solid which was used without further purification. (The  $^1\text{H}$  NMR spectrum indicates the formation of several diastereomers).



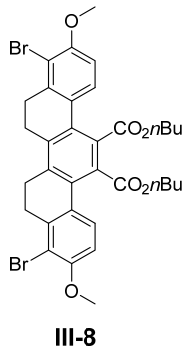
**III-6**

**Experimental Procedure for III-6.** To a 20-mL vial were added 0.300 g of compound **III-5**. The flask was capped with a rubber septum and flushed with argon, and then 10 mL of dichloromethane was introduced by a syringe. The reaction mixture was stirred at 0 °C for 5 min

before phosphorus tribromide (0.18 mL) was added, and the mixture was warmed to room temperature. After 2 h of stirring, the reaction mixture was filtered, and then washed with dichloromethane, a sodium hydroxide solution, water, and acetone to give **III-6** (0.158 g, 0.33 mmol, 54% yield from **III-4**) was obtained as a white solid: mp 142–143 °C; IR 1721, 1259  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.02 (2 H, d,  $J = 8.2$  Hz), 6.74 (2 H, d,  $J = 8.2$  Hz), 6.61 (2 H, s), 3.90 (6 H, s), 3.07 (4 H, t,  $J = 8.2$  Hz), 2.66 (4 H, t,  $J = 8.2$  Hz).

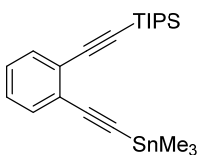


**Experimental Procedure for III-7.** To a mixture of diene **III-6** (0.206 g, 0.433 mmol) and an excess of di-*n*-butyl acetylenedicarboxylate (0.500 g, 2.21 mmol) in a sealed tube was added 2 mL of dry chlorobenzene under argon. The reaction mixture was stirred at 150 °C for 20 h before it was cooled to room temperature. The reaction mixture including insoluble impurities was filtered and washed with 5 mL of dichloromethane. Solvents were evaporated in vacuo, and the crude residue **III-7** was used without further purification.:



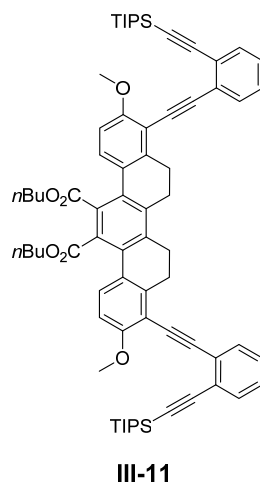


**Experimental Procedure for III-8.** To a 20-mL flask containing crude **III-7** prepared from 0.206 g (0.433 mmol) of diene **III-6** was added 0.150 g (0.661 mmol) of DDQ. The flask was flushed with argon and then 6 mL of chlorobenzene was introduced by a syringe. The reaction mixture was heated at 70 °C for 1 h before it was cooled to room temperature. Dichloromethane (10 mL) was added, and the solution was passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 100 mL of dichloromethane and ethyl acetate (1:1). Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica gel/methylene chloride: hexanes = 85:15) to produce **III-8** (0.163 g, 0.234 mmol, 54% yield from **III-6**) as a white solid. IR 1736, 1221  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.40 (2 H, d,  $J = 8.6$  Hz), 6.79 (2 H, d,  $J = 8.6$  Hz), 4.20 (4 H, t,  $J = 6.6$  Hz), 3.93 (6 H, s), 3.03 (4 H, t,  $J = 6.2$  Hz), 2.78 (4 H, t,  $J = 7.0$  Hz), 1.58 (4 H, quintet,  $J = 7.0$  Hz); 1.25 (4 H, sextet,  $J = 7.4$  Hz), 0.86 (6 H, t,  $J = 7.4$  Hz)

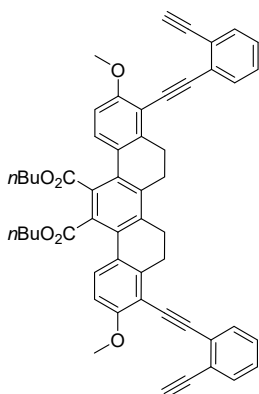


**III-10**

**Experimental Procedure for III-10.** Compound **III-9** (0.389 g, 1.37 mmol) was dissolved in THF (3 mL), and (dimethylamino)trimethylstannane (0.56 mL, 3.30 mmol) was added. The solution was heated to 60 °C for 16 h, and all volatile components were then removed in vacuo. The crude **III-10** was used without further purification.

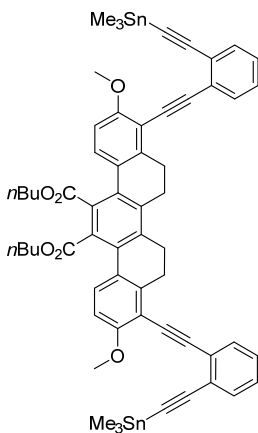


**Experimental Procedure for III-11.** To a mixture of **III-8** (0.410 g, 0.574 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.030 g, 0.033 mmol) and Sphos ligand (0.060 g, 0.146 mmol) in a sealed tube was added 20 mL of dry dioxane under argon. After stirring 10 min, the in situ prepared **III-10**, derived from 0.389 g of **III-9** (1.37 mmol), in 10 mL of dioxane was transferred to the sealed tube via cannula. The reaction mixture was stirred at 120 °C for 12 h before it was cooled to room temperature. Dioxane was evaporated in vacuo, and the crude residue was purified by flash column chromatography (silica gel/dichloromethane:hexanes = 90:10) to produce **III-11** (0.601 g, 0.544 mmol, 95% yield) as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (2 H, d,  $J = 7.4$  Hz), 7.53 (2 H, d,  $J = 7.4$  Hz), 7.43 (2 H, d,  $J = 8.6$  Hz), 7.31-7.24 (4 H, m), 6.76 (2 H, d,  $J = 8.6$  Hz), 4.22 (4 H, t,  $J = 6.7$  Hz), 3.90 (6 H, s), 3.10 (4 H, t,  $J = 6.2$  Hz), 2.76 (4 H, t,  $J = 6.7$  Hz), 1.59 (4 H, quintet,  $J = 7.2$  Hz), 1.28 (4 H, sextet,  $J = 7.4$  Hz), 1.06 (42 H, s), 0.88 (6 H, t,  $J = 7.0$  Hz);



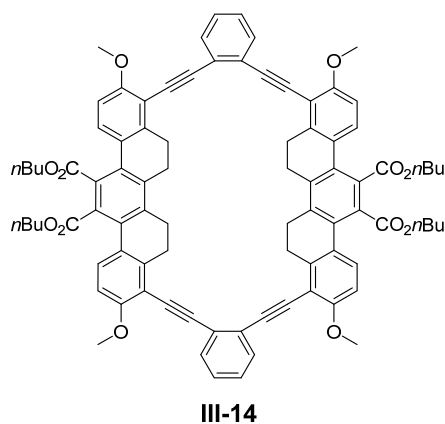
**III-12**

**Experimental Procedure for III-12.** To a solution of **III-11** (0.601 g, 0.544 mmol) in THF (5 mL) cooled to 0 °C, was added a solution of TBAF (1.0 M in THF, 1.36 mL, 1.36 mmol). The reaction mixture was then warmed to rt and stirred for 14 h. A saturated aqueous NaHCO<sub>3</sub> solution (5.0 mL) was added, and the mixture was poured into water (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over sodium sulfate. Solvents were evaporated in vacuo, and the crude residue was purified by flash column chromatography (silica gel/dichloromethane:hexanes = 90:10) to produce **III-12** (0.391 g, 0.495 mmol, 91% yield) as a white solid: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (2 H, d, *J* = 7.4 Hz), 7.55 (2 H, d, *J* = 7.4 Hz), 7.44 (2 H, d, *J* = 8.6 Hz), 7.35 (2 H, t, *J* = 7.4 Hz), 7.29 (2 H, t, *J* = 7.4 Hz), 6.79 (2 H, d, *J* = 9.0 Hz), 4.22 (4 H, t, *J* = 6.7 Hz), 3.95 (6 H, s), 3.35 (2 H, s), 3.21 (4 H, t, *J* = 6.7 Hz), 2.82 (4 H, t, *J* = 6.6 Hz), 1.59 (4 H, quintet, *J* = 7.2 Hz), 1.27 (4 H, sextet, *J* = 7.4 Hz), 0.88 (6 H, t, *J* = 7.4 Hz).



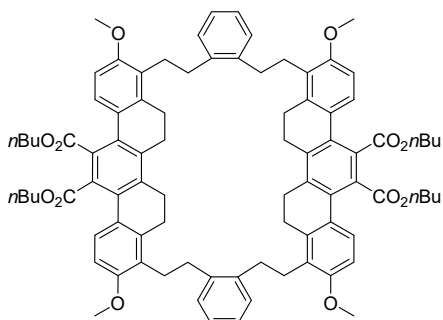
**III-13**

**Experimental Procedure for III-13.** Compound **III-12** (0.380 g, 0.480 mmol) was dissolved in THF (3 mL), and then (dimethylamino)trimethylstannane (0.40 mL, 2.36 mmol) was added. The solution was heated to 60 °C for 16 h. All volatile components were removed in vacuo. The crude **III-13** was used without further purification:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.59 (2 H, d,  $J$  = 7.0 Hz), 7.52 (2 H, d,  $J$  = 7.4 Hz), 7.44 (2 H, d,  $J$  = 9.0 Hz), 7.29–7.22 (4 H, m), 6.79 (2 H, t,  $J$  = 8.6 Hz), 4.22 (4 H, t,  $J$  = 6.2 Hz), 3.94 (6 H, s), 3.19 (4 H, t,  $J$  = 5.8 Hz), 2.80 (4 H, t,  $J$  = 6.7 Hz), 1.59 (4 H, quintet,  $J$  = 5.8 Hz), 1.28–1.23 (4 H, m), 0.87 (6 H, t,  $J$  = 7.4 Hz), 0.32 (18 H, s).



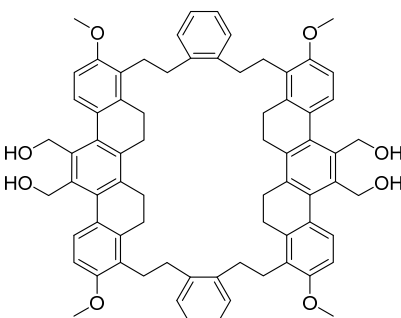
**Experimental Procedure for III-14.** To a mixture of **III-8** (0.335 g, 0.478 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.034 g, 0.037 mmol), and Sphos ligand (0.068 g, 0.165 mmol) in a sealed tube was added 30 mL of dry dioxane under argon. After 10 min of stirring, in situ prepared **III-13**, derived from 0.380 g of **III-12** (0.480 mmol), in 10 mL of dioxane was transferred to the sealed tube via cannula. The reaction mixture was stirred at 120 °C for 12 h before it was cooled to room temperature. Dioxane was evaporated in vacuo, and the crude residue was purified by flash column chromatography (silica gel/dichloromethane:ethyl acetate = 98:2) to produce **III-13** (0.336 g, 0.253 mmol, 53% yield) as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (4 H, dd,  $J$  = 5.8, 3.5 Hz), 7.32 (8 H, one doublet and one overlapping doublet of doublet,  $J$  = 8.6, 5.8, and 3.5 Hz), 4.18 (8 H, t,  $J$  = 6.6 Hz), 3.87 (12 H, s), 3.05 (8 H, broad triplet), 2.77 (8

H, broad triplet), 1.57 (8 H, quintet,  $J = 7.0$  Hz), 1.27 (8 H, sextet,  $J = 7.4$  Hz), 0.87 (12 H, t,  $J = 7.0$  Hz).



**III-15**

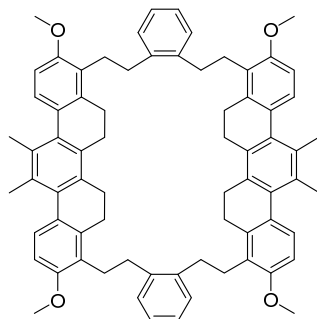
**Experimental Procedure for III-15.** A mixture of **III-14** (0.100 g, 0.075 mmol), a Pd/C catalyst (0.050 g, 10% Pd on carbon), 1.0 mL of acetic acid, 1.0 mL of methanol and 10 mL of ethyl acetate was stirred under an H<sub>2</sub> atmosphere (25 psi) at room temperature. After 6 h, the mixture was filtered, and the filtrate was concentrated in vacuo to give **III-15** (0.096 g, 0.071 mmol, 95% yield) as a white solid: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (4 H, dd,  $J = 5.5, 3.5$  Hz), 7.32 (4 H, d,  $J = 8.6$  Hz), 7.22 (4 H, dd,  $J = 5.5, 3.1$  Hz), 7.76 (4 H, d,  $J = 8.6$  Hz), 4.17 (8 H, t,  $J = 6.7$  Hz), 3.87 (12 H, s), 3.02 (8 H, broad triplet), 2.84 (16 H, two sets of broad triplet overlap), 2.76 (8 H, broad triplet), 1.54 (8 H, quintet,  $J = 7.0$  Hz), 1.19 (8 H, sextet,  $J = 7.8$  Hz), 0.83 (12 H, t,  $J = 7.4$  Hz).



**III-17**

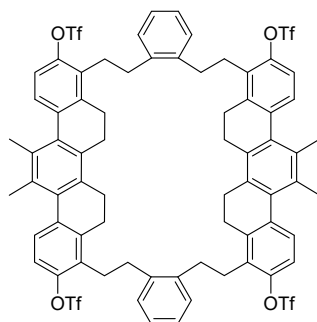
**Experimental Procedure for III-17.** Compound **III-15** (0.096 g, 0.071 mmol) was dissolved in 5 mL of dichloromethane under an argon atmosphere at 0 °C. To the mixture was added 0.7 mL

of DIBAL solution (1.2 M in toluene, 8.4 mmol). The reaction mixture was warmed to room temperature. After 10 h, the mixture was cooled to 0 °C and quenched with 3 mL of a sodium hydroxide solution (1 M). The mixture was extracted with dichloromethane (10 mL × 3) and pass through a short sodium sulfate column. The filtrate was concentrated in vacuo to give the corresponding crude **III-17** as a white solid, which was used without further purification.



**III-18**

**Experimental Procedure for III-18.** To a 20-mL flask containing the crude **III-17**, prepared from 0.096 g of **III-15** (0.071 mmol), were subsequently added 5.0 mL of dichloromethane, 1.0 mL of trifluoroacetic acid, and 1.0 mL of triethylsilane under an argon atmosphere by syringes. The reaction mixture was stirred at room temperature for 12 h. Solvents were removed in vacuo, and the residue was purified by preparative TLC (methylene chloride:hexanes = 1:1) to produce **III-18** (0.035 g, 0.035 mmol, 49% yield from **III-15**) as a white solid.



**III-20**

**Experimental Procedure for III-20.** To a 20-mL vial containing **III-18** (0.035 g, 0.035 mmol) was added 5.0 mL of dichloromethane at 0 °C under an argon atmosphere. Then 0.25 mL of a boron tribromide solution (1.0 M in heptane) was added by a syringe before the reaction mixture was allowed to warm to room temperature. After 4 h of stirring, the reaction mixture was cooled to 0 °C and quenched with a mixture of aqueous sodium bicarbonate and methanol solution. Water (5 mL) was added, and the reaction mixture was extracted with dichloromethane (10 mL  $\times$  3). The combined organic layers were dried over sodium sulfate. Solvents were removed in vacuo, and the residue was dissolved in 10 mL of anhydrous dichloromethane at 0 °C under an argon atmosphere. To the solution were added 1 mL of pyridine and 0.2 mL of trifluoromethanesulfonic anhydride. The reaction mixture was allowed to warm to room temperature. After 10 h of stirring, the reaction mixture was cooled to 0 °C and quenched with 20 mL of saturated sodium bicarbonate solution. The reaction mixture was extracted with dichloromethane (10 mL  $\times$  3). The combined organic layers were dried over sodium sulfate. Solvents were removed in vacuo, and the residue was purified by preparative TLC (methylene chloride:hexanes = 1:1) to produce **III-20** (0.022 g, 0.015 mmol, 42% yield from **III-18**) as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (8 H, one doublet and one overlapping doublet of doublet), 7.26 (4 H, dd, overlap with  $\text{CDCl}_3$ ), 7.18 (4 H, d,  $J = 8.6$  Hz), 3.08 (8 H, t,  $J = 7.1$  Hz), 2.81 (8 H, t,  $J = 8.2$  Hz), 2.74 (8 H, broad triplet), 2.54 (8 H, broad triplet), 2.38 (12 H, s).

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