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**I. Contorted Polycyclic Aromatic Hydrocarbons:
Attempted Synthesis Of [12]circulene Derivatives
ii. Synthesis And Characterization Of Novel
[1]benzothieno[3,2-B][1]benzothiophene Derivatives**

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I. CONTORTED POLYCYCLIC AROMATIC HYDROCARBONS: ATTEMPTED
SYNTHESIS OF [12]CIRCULENE DERIVATIVES

II. SYNTHESIS AND CHARACTERIZATION OF NOVEL
[1]BENZOTHIENO[3,2-b][1]BENZOTHIOPHENE DERIVATIVES

A Dissertation Presented

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ABSTRACT

There has been increasing interest in the development of organic materials due to their unique structural and electronic properties. Organic compounds have the advantage of being able to be deposited from solution, leading to low-cost, high-area electronics production. Contorted polycyclic aromatic hydrocarbons have been shown to have potential for use in organic field-effect transistors (OFETs) and organic photovoltaic devices (OPVs) due to their supramolecular properties and charge carrier mobilities. Thiophene-based materials have also shown great promise in OFETs due to their high charge carrier mobilities, stability during device operation, solubility in organic solvents, and structural versatility.

[n]Circulenes are a class of polycyclic aromatic compounds whose shape depends on the central n-membered ring. These range from bowl-shaped when $n < 6$, planar when $n = 6$, and saddle-shaped when $n > 6$. The shapes of these molecules, especially for the contorted circulenes, imparts interesting and useful properties such as a polarizable π -system and coordination to fullerenes. Using methods developed in our group, synthesis of [12]circulene derivatives was attempted. Synthetic difficulties, results, and a synthetic plan to overcome these problems are presented herein.

2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) is a thiophene-based p-type semiconducting material with one of the highest reported OFET mobility to date. Alterations to BTBT have been made to improve device processing and tune the electronic structure. However, structural alterations have generally been limited to functionalization with electron-donating groups and extension of the π -system. The lack of electron deficient derivatives has prevented further tuning of the electronic structure. Additionally, installation of strongly electron-withdrawing substituents could give BTBT n-type character as seen with perylene diimides. Several synthetic strategies to develop BTBTs with electron-withdrawing groups were explored. Limitations to developing electron deficient BTBTs as well as synthesis and characterization of novel imide-functionalized derivatives are described.

DEDICATION

I dedicate this work to my parents. Thank you for your constant love, understanding, and support.

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LIST OF ABBREVIATIONS

μ wave.....	Microwave heating
^{13}C NMR.....	Carbon nuclear magnetic resonance
^1H NMR	Proton nuclear magnetic resonance
BDT.....	Benzodithiophene
BHJ	Bulk heterojunction
BTBT	[1]Benzothieno[3,2-b][1]benzothiophene
C8-BTBT	2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene
<i>c</i> -HBC	Hexa- <i>cata</i> -hexabenzocoronene
Cl-BTBT	2,7-Dichloro[1]benzothieno[3,2-b][1]benzothiophene
Cp.....	Cyclopentadienyl
CV.....	Cyclic voltammetry
Cy.....	Cyclohexyl
dba.....	Dibenzylideneacetone
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DC12O-BTBT-I.....	2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-dicarboxylic imide

DC8O-BTBT-I.....	2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-dicarboxylic imide
DME.....	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DPE.....	Diphenylether
DPh-BTBT	2,7-Diphenyl[1]benzothieno[3,2-b][1]benzothiophene
EDG	Electron-donating group
EWG	Electron-withdrawing group
FET	Field-effect transistor
FVP	Flash vacuum pyrolysis
HB[12]C.....	Hexabenz[12]circulene
HBC	Hexabenzocoronene
HBC	Hexabenzocoronene
HOAc	Acetic acid
HOMA	Harmonic oscillator measure of aromaticity
HOMO	Highest occupied molecular orbital
HRMS	High-resolution mass spectrometry

LAH Lithium aluminum hydride

LUMO..... Lowest unoccupied molecular orbital

m/z..... Mass-to-charge ratio

MOSFET.....Metal-oxide-semiconducting field-effect transistor

NBO Natural bond orbital

NBS..... N-Bromosuccinimide

ⁿBuLi..... n-Butyl lithium

NICS Nucleus independent chemical shift

NMP N-methylpyrrolidone

NMR Nuclear magnetic resonance

OFET..... Organic field-effect transistor

OLED..... Organic light-emitting diode

OM-TB[8]C Octamethyltetrabenzo[8]circulene

OPV..... Organic photovoltaic device

P3HT..... Poly-3-hexylthiophene

PAH..... Polycyclic aromatic hydrocarbon

PCBM Phenyl-C₆₁-butyric acid methyl ester

PCC..... Pyridinium chlorochromate

PDI	Perylene diimide
<i>p</i> -HBC	Hexa- <i>peri</i> -hexabenzocoronene
PVP	Poly-4-vinylphenol
TB[7]C	Tetrabenzo[7]circulene
TB[8]C	Tetrabenzo[8]circulene
TBAF	Tetrabutylammonium fluoride
TBHP	Tert-butyl hydroperoxide
TBQ.....	Tetrabenzoquadrannulene
^t BuLi.....	tert-Butyl lithium
TFA	Trifluoroacetic acid
TFT	Thin-film transistor
TLC	Thin-layer chromatography
TMS	Trimethylsilyl
TMS ₄ -TBQ.....	Tetramethoxytetrabenzoquadrannulene
TsOH.....	<i>p</i> -Toluenesulfonic acid

CHAPTER 1: ORGANIC MATERIALS: BACKGROUND

1.1 Properties and Applications of Organic Semiconductors

Development of organic materials for use in electronic devices has become an increasingly prominent field of research for synthetic organic chemistry. Over the past several decades, advances in understanding of the structural and electronic properties of such materials has led to organic molecules being utilized in numerous electronics applications, including organic light emitting diodes (OLEDs), organic photovoltaic (OPV) cells, and organic field-effect transistors (OFETs). Device function has a direct effect on the design of the material, leading to a wide range of materials with unique functionality as seen in figure 1.1.

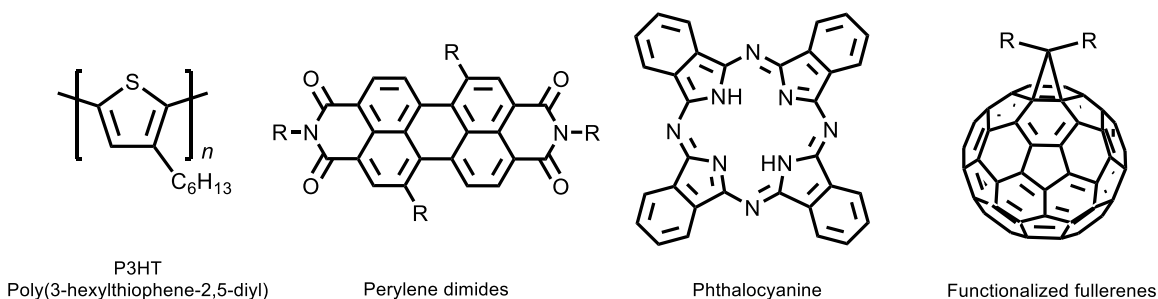


Figure 1.1 Example molecules utilized in organic electronics.

One objective of the research conducted in the Whalley group is the synthesis of functional organic materials that can be used as the semiconducting layer in field-effect transistors (FETs). After experiencing a lack of applications following a patent initially

granted in 1930 to Lilienfeld,¹ FETs, and more notably metal oxide semiconducting field-effect transistors (MOSFETs), have become ubiquitous in modern electronic devices. While numerous materials exist that exhibit semiconducting properties, silicon-based FETs are by far the most utilized in modern electronics. This is partially due to the abundance of silicon, which comprises over 25% by mass of the Earth's crust.² More importantly, crystalline silicon exhibits very high charge carrier mobility (μ), above $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, while amorphous silicon has a much lower mobility of $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Both materials also exhibit extremely rapid on/off switching, the other primary attribute of merit for materials used in FETs. While these properties allow silicon to be unrivaled in many electronics applications, organic semiconducting materials offer unique advantages in device design and fabrication.

Production of electronic grade silicon is a highly energetically demanding process.³ First, high purity quartz is heated with carbon in an electrode arc furnace to $1500\text{-}2000 \text{ }^\circ\text{C}$ to produce metallurgical grade silicon (MG-Si, 98% pure). Powdered MG-Si is then reacted with anhydrous HCl at $300 \text{ }^\circ\text{C}$ to produce SiHCl_3 along with other metallic chlorides such as FeCl_3 , AlCl_3 and BCl_3 . SiHCl_3 is then distilled and reacted with H_2 at $1100 \text{ }^\circ\text{C}$ for up to 12 days, resulting in deposition of polycrystalline silicon. Polycrystalline silicon is then heated to $1425 \text{ }^\circ\text{C}$ under an atmosphere of argon in a crucible and spun while a counter-rotating seed crystal of silicon is dipped in and withdrawn at approximately 1.5

¹ Lilienfeld, J. E. US Patent 1,745,175, **1930**.

² Tasa, D.; Tarbuck, E.; Lutgens, F. *Essentials of Geology*, 13th Ed.; Pearson: New York, 2017.

³ Barron, A. *Chemistry of Electronic Materials*, Rice University, Houston, **2010**.

mm/min, eventually resulting in a 1-2-meter-long single crystal weighing over 180 kg after several days.⁴

One of the main advantages of organic materials over use of silicon in FETs is the ability to tune electronic and optical properties through synthetic modifications which allows orbital energies to be tuned to the specific needs of a device. Also, due to the solubility of organic molecules in volatile solvents, device fabrication can be accomplished through less energetically demanding processes such as inkjet printing or spin coating.^{5,6} Improvements to processing has also led to organic materials outperforming benchmark amorphous silicon devices ($0.5\text{-}1.0\text{cm}^2\text{V}^{-1}\text{s}^{-1}$).⁷ These advantages have led to many novel electronics applications which can be observed from the increasing prevalence of OLED televisions and advances toward utilizing flexible organic materials in consumer electronics and bio-electronic devices.^{8,9}

There are several notable drawbacks to utilizing organic materials in devices. For example, the semiconducting organic layer often breaks down over short periods of OFET operation, as seen in attempts to utilize polyacenes in OFETs.¹⁰ There is a distinct lack of widely available n-type organic semiconductors due to the difficulty in adding an electron

⁴ Czochralski, J. Z. *Phys. Chem.* **1918**, 92, 219-221.

⁵ Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. *Nature* **2011**, 475, 364-367.

⁶ Yuan, Y.; Giri, G.; Ayzner, A. L.; Zoombelt, A. P.; Mannsfeld, S. C. B.; Chen, J.; Norlund, D.; Toney, M. F.; Huang, J.; Bao, Z. *Nat. Comm.* **2013**, 5, 3005.

⁷ Sirringhaus, H. *Adv. Mater.* **2005**, 17, 2411-2425.

⁸ Xu, R. P.; Li, Y. Q.; Tang, J. X. *J. Mater. Chem. C* **2016**, 4, 9116-9142.

⁹ Choi, S.; Lee, H.; Ghaffari, R.; Hyeon, T.; Kim, D. H. *Adv. Mater.* **2016**, 28, 4203-4218.

¹⁰ Anthony, J. E. *Chem. Rev.* **2006**, 106, 5028-5048.

to an already electron-rich π -system. N-type semiconductors are majority negative (electron) transport materials while p-type semiconductors are majority positive (hole) transport materials. Doping is used to make extrinsic (n-type or p-type) silicon-based semiconductors while tuning of the HOMO and LUMO energy levels is required for organic materials.

Organic devices also have an inherent energetic mismatch at the electrode/organic interface, significantly lowering field-effect mobilities.¹¹ Finally, design of an organic material does not guarantee favorable stacking in the solid-state. Despite these drawbacks, several small-molecule, polycyclic aromatic hydrocarbon (PAH), and polymer based organic semiconductors have been developed, many of which can be further broken down into several subclasses such as rylene-based diimides, oligothiophenes, fullerenes and fullerene fragments, circulenes, etc.^{12,13,14}

1.2 Organic Field-Effect Transistors

Field-effect transistors allow control of the flow of electric current between two terminals by application of an electric field. This is achieved by applying voltage between

¹¹ Parker, I. D. *J. Appl. Phys.* **1994**, 75, 1656-1666.

¹² Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y. *J. Mater. Chem. C* **2017**, 5, 8654-8681.

¹³ Sumy, D. P.; Dodge, N. J.; Harrison, C. M.; Finke, A. D.; Whalley, A. C. *Chem Eur. J.* **2016**, 22, 4709-4712.

¹⁴ Miller, R. W.; Duncan, A. K.; Schneebeli, S. T.; Gray, D. L.; Whalley, A. C. *Chem. Eur. J.* **2014**, 20, 3705-3711.

a source and gate terminal (see figure 1.2), which introduces charge carriers to the semiconducting material of a FET, allowing current to flow from the source to the drain terminal. This has allowed precise control of current and on/off switching in electronic devices, eventually leading to the development of MOSFETs and their use in integrated circuits.¹⁵

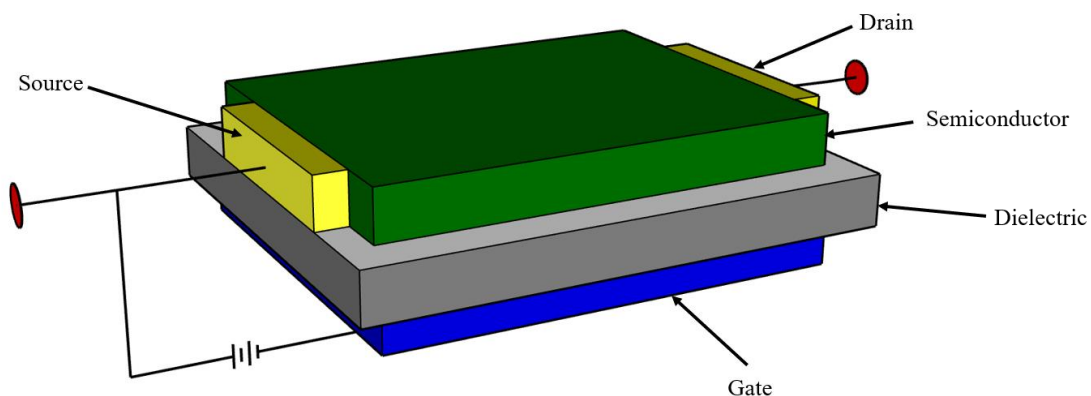


Figure 1.2 General schematic of a field-effect transistor.

There are some simple differences between inorganic and organic materials and their operation in FETs. Silicon charge transfer occurs through covalent bonds, leading to the high mobility in crystalline silicon. Organic compounds in the solid state are bound much more weakly by van der Waals forces, resulting in much larger distances required for charge transfer. As a result, charge transfer in OFET's undergoes a so-called hopping mechanism. This causes organic materials to have an inherent limitation to their conductivity and, therefore, mobility compared to crystalline inorganic materials. Despite

¹⁵ Horowitz, G. *Adv. Mater.* **1998**, *10*, 365-377.

this limitation, there are several large-area electronics applications where amorphous, rather than crystalline or polycrystalline, silicon is preferred in which organic materials can provide significant advantages to device processing and allow production of new types of electronic devices.

The first observations of the field effect in organic materials dates as far back as 1970.^{16,17,18} However, the first reported use of an organic material in an OFET was described in 1987 by Ando and coworkers.¹⁹ Utilizing polythiophenes as the semiconducting layer, mobilities of $1 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were reported. Following this report, mobilities of OFETs were greatly improved in polythiophenes over the next decade with dialkylated sexithiophene mobilities reported as high as $0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and C₆₀, which behaves as an n-type semiconductor, having mobility as high as $0.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^{20,21} Alterations to molecular structure and processing techniques therefore demonstrated organic materials approaching the performance of amorphous silicon devices.

Development of PAH-based semiconductors greatly improved organic semiconductor mobilities with the use of pentacene in OFETs. Lin and coworkers produced pentacene thin-film transistors (TFTs) with high on/off ratios with field-effect

¹⁶ Barbe, D. F.; Westgate, C. R. *J. Phys. Chem. Solids* **1970**, *31*, 2679-2687.

¹⁷ Petrova, M. L.; Rozenshtein, L. D. *Fiz. Tverd. Tela*. **1970**, *12*, 961-962.

¹⁸ Ebisawa, F.; Kurokawa, T.; Nara, S. *J. Appl. Phys.* **1983**, *54*, 3255-3259.

¹⁹ Koezuka, H.; Tsumura, A.; Ando, T. *Synth. Met.* **1987**, *18*, 699-704

²⁰ Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716-8721.

²¹ Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming R. M. *Appl. Phys. Lett.* **1995**, *67*, 121-123.

mobility up to $1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.²² In 2002, thermally evaporated pentacene devices with mobilities of $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were produced using spin-coated poly-4-vinylphenol (PVP) as the dielectric material.²³ This was a significant advancement as the highest previously reported mobility for an organic material using a polymer-based dielectric was $0.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Unfunctionalized pentacene, however, suffered from low solubility and instability in aerobic environments. Functionalization of pentacene greatly improves solubility, stability, and utility. For example, functionalization of pentacene with trialkyl-silyl-protected alkynes (figure 1.3) resulted in oxidatively stable and highly soluble pentacene derivatives.²⁴ TFTs made from these derivatives had lower mobility than unsubstituted pentacene.²⁵ Perfluoropentacene was synthesized as a possible n-type semiconductor for use in complimentary-metal-oxide-semiconductor (CMOS) logic gates. However, the mobility of perfluoropentacene was limited to $0.024 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.²⁶

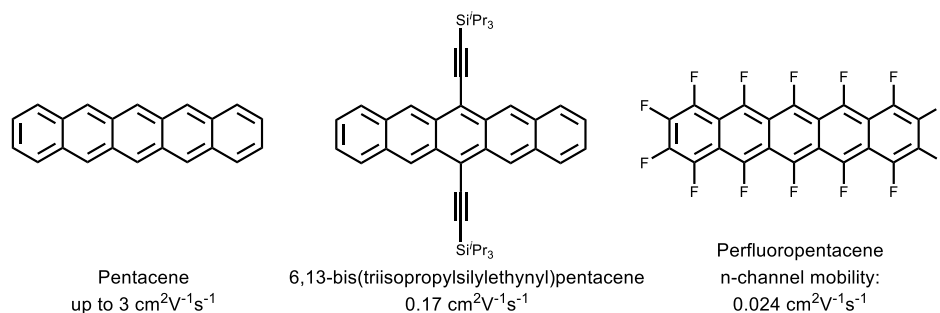


Figure 1.3 Selected pentacene derivatives and their reported mobility.

²² Lin, Y. Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electr. Device L.* **1997**, *18*, 606-608.

²³ Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W. *J. Appl. Phys.* **2002**, *92*, 5259.

²⁴ Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15-18.

²⁵ Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986-4987.

²⁶ Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138-8140.

The reduced mobility of the pentacene derivative was due to the decreased order in solid state structure. This represents the tradeoff in increasing solubility while attempting to maintain efficient orbital overlap. Increasing this overlap *via* extension of the π -system is one strategy to maintain increased mobility as seen with larger acenes. Hexacene and heptacene have been shown to have increased charge carrier mobility caused by the lower reorganization energy required for the expanded system.²⁷ Consequently, these materials become increasingly reactive with increasing size. Alternatively, increasing solubility while maintaining stability in larger PAHs by contorting these structures from planarity has been shown to be a possible solution to these issues.

1.2.1 Use of Contorted PAHs in Electronic Devices

There are several applications of nonplanar PAHs in electronic devices. The most notable example being the use of buckminsterfullerene derivatives in OPVs and OFETs. C₆₀ is a useful model compound for the examination of properties that arise from contorting a nominally planar structure. C₆₀, along with other contorted PAHs, has a polarizable π -system, making it a useful compound for use as a semiconductor as it allows increased charge transfer due to the increased ability to have charges displaced by an external electric field. This is caused by the alteration of bond lengths in the molecule compared to the

²⁷ Mondal, R.; Tönshoff, C.; Khon, D.; Neckers, D. C.; Bettinger, H. F. *J. Am. Chem. Soc.* **2009**, *131*, 14281-14289.

planar structure. Krygowski's update to the harmonic oscillator measure of aromaticity (HOMA) demonstrated this by comparing the atom-atom polarizability of benzene to that of butadiene.²⁸ The results showed that non-uniformity in a conjugated system results in increased mobility and reactivity, explaining both the ability of C₆₀ to behave as a semiconductor and the various reactions used to functionalize fullerenes.

As previously noted, fullerenes behave as n-type materials in semiconductor applications. This is highly desirable for organic materials as the lack of majority electron carrier compounds limits development of organic circuits analogous to CMOS logic gates. Buckminsterfullerene has a triply degenerate lowest unoccupied molecular orbital (LUMO), allowing up to six single-electron reductions.^{29,30} Along with the relatively low LUMO energy, this gives C₆₀ its n-type semiconducting properties. However, C₆₀ has yet to be used in any widely available industrial applications.

Though C₆₀ and larger fullerenes have many useful and desirable properties for OFET development, the low solubility of fullerenes presents a major limitation to their use in electronics applications. Fullerenes can be functionalized in numerous ways which is the main strategy for overcoming device processing issues. For example, Hummelen et al. reported the reaction of C₆₀ with diazo compounds to generate soluble derivatives such as phenyl-C₆₁-butyric acid methyl ester (PCBM).³¹ Unfortunately, functionalization also has

²⁸ Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70-78.

²⁹ Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593-601.

³⁰ Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978-3980.

³¹ Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, G.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532-538.

the effect of lowering electron mobility in FET applications, primarily due to the introduction of non-uniformity in the π -system of the molecule and the introduction of large functional groups that result in less efficient packing in the solid state. This has affected the field of PAHs by increasing research into alternatives to using C₆₀ in OFETs.

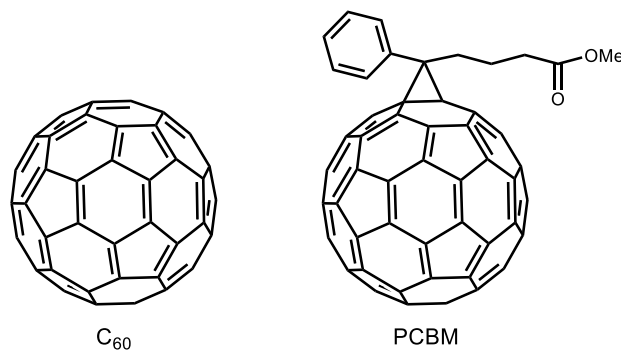


Figure 1.4: Structures of C₆₀ and PCBM – Functionalization increases solubility of C₆₀ at the cost of mobility due to the loss of symmetry and electron affinity.

Although fullerenes are used more widely in OPV applications due to their optoelectronic properties and their limitations in large-area semiconductor applications, several other PAHs have been targeted for study in OFETs. For example, polyacenes have been widely used in OFET and OPV applications with pentacene being largely used in TFTs as a benchmark material against which other organics are measured.³² Several functionalized derivatives have also been synthesized, often making them highly soluble and therefore improving the device fabrication process.³³ Pentacene transistor devices, however, often suffer from decreased performance over time due to a thermal photo degradation with oxygen.³⁴ Diphenyldibenzotetracene, a contorted derivative of tetracene

³² Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452-483.

³³ Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99-117.

³⁴ Kagan, C. R.; Afzali, A.; Graham T. O. *Appl. Phys. Lett.* **2005**, *86*, 193505.

has also been investigated for its stability, solubility and electronic properties.³⁵ OLED devices were produced from this derivative and functioned as both electron and hole carrier materials. Although the materials were stable under ambient conditions, the electron transport capability of was notably lower than common analogous organometallic materials.

Decacycene is a commercially available PAH with a propeller-shaped structure that forms helical crystals when grown in solution.³⁶ Interest in decacycene is due to its interesting shape as well as its ability to reversibly accept up to four electrons.³⁷ The contorted structure of decacycene is due to the steric interactions between hydrogens of the peripheral naphthalene groups. Functionalization with tert-butyl groups resulted in decacycene behaving as a single molecular rotor while installation of imides to decacycene has resulted in electron deficient derivatives which self-assemble into ordered crystalline structures and behave as n-type semiconductors.^{38,39} Interestingly, these derivatives, including the unsubstituted parent structure, are all highly soluble in organic solvents due to the lower propensity to aggregate in solution compared to planar species. These examples show the utility of generating nonplanar PAHs and the useful properties that arise from contorting aromatic molecules from planarity.

³⁵ Zhang, Q.; Divayana, Y.; Xiao, J.; Wang, Z.; Tiekink, E. R. T.; Dzung, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *Chem. Eur. J.* **2010**, *16*, 7422-7426.

³⁶ Ho, D. M.; Pascal, R. A. *Chem. Mater.* **1993**, *5*, 1358-1361.

³⁷ Saji, T.; Aoyagui, S. *J. Electroanal. Chem.* **1979**, *1*, 139-141.

³⁸ Gimzewski, J. K.; Schlittler, J. R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science*, **1998**, *281*, 531-533.

³⁹ Pho, T. V.; Tona, F. M.; Chabinyk, M. L.; Wudl, F. *Angew. Chem. Int. Ed.* **2013**, *52*, 1446-1451.

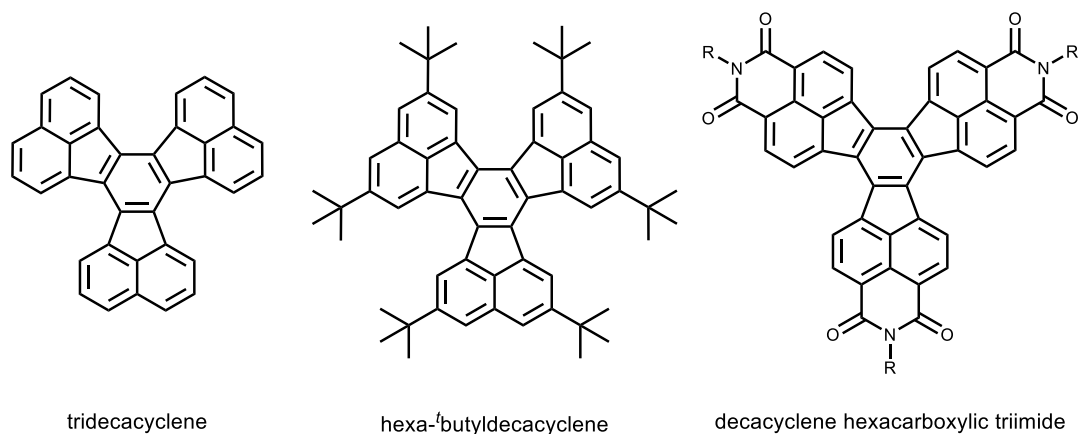


Figure 1.5 Selected examples of decacycene derivatives.

1.2.2 Use of Thiophene based Materials in Electronic Devices

As oligothiophenes were the first materials used in OFETs, thiophene containing compounds and polymers have been widely used in all types of organic materials. These materials are most widely utilized as the donor material in bulk heterojunction (BHJ) solar cells. For example, regioregular poly-3-hexylthiophene (P3HT) and PCBM have been shown to be stable and highly efficient in OPV devices over long periods of operation.^{40,41,42} Regioregular P3HT has also been utilized in TFTs with mobilities as high as $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁴³ Due to the success of these materials in device applications, thiophenes have also been incorporated into fused systems with the expectation of increased mobilities

⁴⁰ Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, 258, 1474-1476.

⁴¹ Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, 270, 1789-1791.

⁴² Hauch, J. A.; Schilinsky, P.; Choulis, S. A.; Childers, R.; Biele, M.; Brabec, C. J. *Sol. Energy Mater. Sol. Cells* **2008**, 727-731.

⁴³ Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, 280, 1741-1744.

due to increased π -stacking in the solid state and the ability to functionalize thiophenes in new ways. Benzodithiophene (BDT), thienothiophenes, thienoacenes, and benzothienobenzothiophene (BTBT) are just a few examples (Figure 1.6).

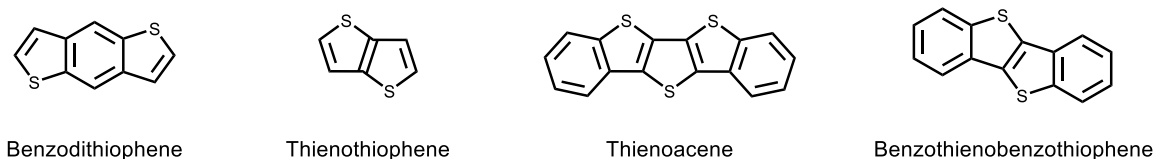


Figure 1.6 Representative examples of fused thiophene based materials.

In general, these fused thiophenes and their functionalized derivatives often behave as p-type semiconductors in OFETs. They have also been able to achieve the highest mobilities in organic semiconductors to date, with dialkyl-BTBT derivatives, specifically 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT), exhibiting field-effect mobility as high as $31.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with an average mobility of $16.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ over 54 transistors.³ This was achieved using a dual shot inkjet method in which the solution of dialkyl-BTBT was confined to a surface pattern on the substrate. Reliable processing methods have therefore shown that organic thiophene containing compounds can achieve mobilities much higher than amorphous silicon while being able to be processed from solution. Their technique is also expected to be applicable to numerous other soluble organic materials, potentially allowing greatly increased mobilities for wide range of compounds.

However, C8-BTBT behaves as a p-type semiconductor. Therefore, there is still a need to produce stable electron deficient organic materials that are also soluble and have high field-effect mobilities. The most common strategy used to synthesize n-type materials is the introduction of electron-withdrawing groups through functionalization. For example,

perylene diimides (PDIs) are a class of rylene-based organic materials which behave as n-type semiconductors due to the presence of highly electron-withdrawing imide groups. This is because addition of the imides lowers the LUMO due to their strongly electron withdrawing nature. The increased conjugation length also has the effect of raising the highest occupied molecular orbital (HOMO), and therefore the oxidation potential which has often been used in the design of air-stable ambipolar materials.⁴⁴

1.3 Conclusions and Introductory Remarks

Due to the unique electronic properties and structures exhibited by contorted aromatic hydrocarbons, this field of research has seen increasing growth over the past several decades. This has led to a desire for highly contorted PAHs that can be easily purified and functionalized to tune electronic properties and solubility. Additionally, materials that exhibit n-type character which are more easily processed than fullerenes are in high demand. Despite this demand, relatively few n-type organic materials have been synthesized that are stable under OFET operation, have high charge carrier mobility, and are easily synthesized. For these reasons, two materials were targeted for development in our lab. These two materials are a stable derivative of [12]circulene as well as electron deficient BTBT derivatives.

⁴⁴ Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876-3892.

Described in the following chapters is previous work involving the synthesis of [n]circulenes, a class of polycyclic aromatic hydrocarbons along with work performed in our lab involving studies toward the synthesis of [12]circulene derivatives. Additionally, previous work involving the synthesis and functionalization of BTBT derivatives will be described followed by current work in our lab involving the synthesis of imide-functionalized BTBT derivatives. This will include discussion of synthetic challenges, characterization, future directions, and outlooks.

**CHAPTER 2: CONTORTED POLYCYCLIC AROMATIC HYDROCARBONS:
ATTEMPTED SYNTHESIS OF [12]CIRCULENE DERIVATIVES**

2.1 The [n]Circulenes

[n]Circulenes are a class of PAHs defined by an n -membered central ring surrounded by n radially-fused aromatic rings. Most of the circulenes have interesting three-dimensional shapes which vary based on the size of the central ring as shown in Figure 2.1. These structurally unique molecules have generated interest in the synthesis and functionalization of larger circulenes due to the synthetic challenge of generating highly strained molecules and due to the useful properties exhibited by contorted aromatics outlined in chapter 1.

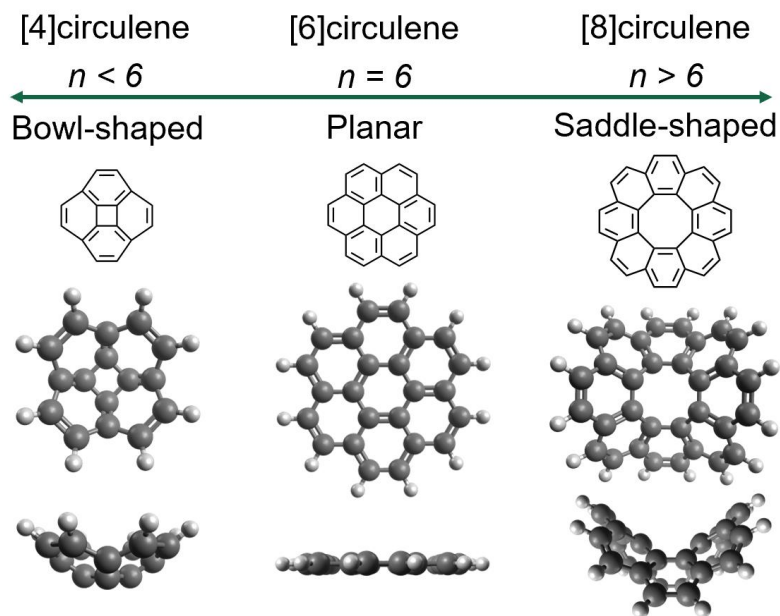
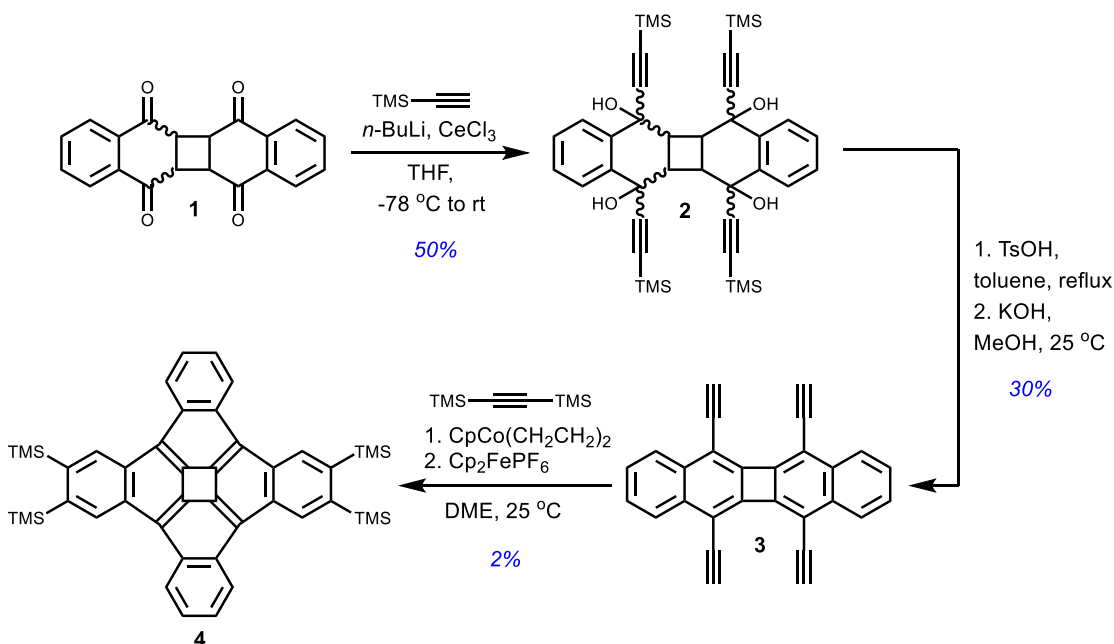


Figure 2.1 Models of [n]circulene molecules.

2.1.1 [4]Circulene

[4]Circulene, or quadrannulene is the smallest circulene analogue and one of the more recently synthesized derivatives. While there is one report of a previous attempted synthesis of quadrannulene, King and coworkers have reported the only successful synthesis of a substituted [4]circulene derivative, 1,8,9,16-tetrakis(trimethylsilyl)tetrabenzocata-tetra-*cata*-tetrabenzocquadrannulene (**4**, TMS₄-TBQ) Scheme 2.1).^{45,46}



Scheme 2.1 Reported synthesis of tetrakis(trimethylsilyl)tetrabenzocquadrannulene, the smallest successfully synthesized member of the [*n*]circulenes by King and coworkers; TsOH = *p*-toluenesulfonic acid, DME = 1,2-dimethoxyethane, Cp = cyclopentadienyl.

⁴⁵ Christoph, H.; Grunenberg, J.; Hopf, H.; Dix, I.; Jones, P. G.; Scholtissek, M.; Maier, G. *Chem. Eur. J.* **2008**, *14*, 5604-5616.

⁴⁶ Bharat, A.; Bhola, R.; Bally, T.; Balente, A.; Cyranski, M. K.; Dobrozycki, L.; Spain, S. M. Rempala, P.; Chin, M R.; King, B. *Angew. Chem. Int. Ed.* **2010**, *49*, 399-402.

The synthetic strategy for the formation of **4** was to introduce strain early in the molecule, accomplished by starting with naphthoquinone dimer (**1**). In the presence of CeCl_3 to suppress enolization, acetylated product **2** was generated in a 50% yield by treatment with *n*-butyl lithium and TMS-acetylene. Subsequent elimination and treatment with KOH resulted in removal of the hydroxyl and TMS groups to yield the deprotected alkyne product (**3**) in a 30% yield. The tetrabenzozquadannulene (TBQ) precursor, **3**, was subjected to cyclotrimerization conditions inspired by synthesis of previously reported strained systems.^{47,48} Use of Jonas' catalyst, $\text{CpCo}(\text{CH}_2\text{CH}_2)_2$, produced a previously uncharacterized intermediate that was found to be a $\text{CpCo-TMS}_4\text{-TBQ}$ complex. In the presence of Cp_2Fe^+ , TMS-TBQ was successfully isolated on the milligram scale.

This strategy precluded synthesis of the parent quadannulene structure, however, the authors note that addition of the peripheral benzene rings protects the highly reactive and strained bonds of the central structure. The distal TMS groups allowed removal of an order of symmetry in NMR analysis while providing further protection to the reactive olefins and increased solubility.

Structurally, TMS-TBQ takes on a bowl-shaped configuration which behaves as a radialene as opposed to a benzannulated cyclobutadiene. This determination was accomplished using single crystal x-ray diffractometry in conjunction with nucleus independent chemical shifts (NICS) calculations and natural bond orbital (NBO)

⁴⁷ Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860-8871.

⁴⁸ Wu, Y. T.; Hayama, T.; Baldrige, K. K.; Linden, A.; Siegel, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 6870-6844.

calculations. The calculations and structural data showed that the TBQ core contained a single-bonded cyclobutane with no antiaromatic character surrounded by radial alkenes. TMS-TBQ was found to be stable for short times in aerobic solvent and in visible light. However, the role played by the TMS and benzo groups in stabilizing the parent quadrannulene core were not explicitly evaluated.

2.1.2 [5]Circulene

[5]Circulene, better known as corannulene, has become one of the most widely studied polycyclic aromatic hydrocarbons due to its bowl-like structure and as a representative of the smallest repeating fragment of buckminsterfullerene. Synthesis of corannulene was first reported by Barth and Lawton as the result of an exhaustive 16-step synthesis, resulting in an overall yield of less than 1%.⁴⁹ Barth and Lawton also gave corannulene its trivial name due to the possibility of the strained structure behaving as a so-called “annulene-within-an-annulene” (AWA). A point of contention in the literature,^{50a-h} it was suggested that corannulene exists as an inner cyclopentadienyl anion fused to an outer cyclopentadecaptaneyl cation (Figure 2.2). However, due to the extreme difficulty in producing corannulene, investigation into this model was limited until Scott

⁴⁹ Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730-1745.

⁵⁰ (a) Sygula, A.; Rabideau, P. W. *J. Mol. Struct. (Theochem.)* **1995**, *333*, 215-226; (b) Zhou, Z. *J. Phys. Org. Chem.* **1995**, *8*, 103-107; (c) Bühl, M. *Chem. Eur. J.* **1998**, *4*, 734-739; (d) Steiner, E.; Fowler, P. W.; Jenneskens, L. W. *Angew. Chem. Int. Ed.* **2001**, *40*, 362-366; (e) Steiner, E.; Fowler, P. W. *J. Phys. Chem. A* **2001**, *105*, 9553-9562; (f) Monaco, G.; Scott, L. T.; Zanasi, R. *J. Phys. Chem. A* **2008**, *112*, 8136-8147; (g) Eisenberg, D.; Shenhar, R. *Wires Comput. Mol. Sci.* **2012**, *2*, 525-547; (h) Dickens, T. K.; Mallion, R. B. *Croat. Chem. Acta.* **2014**, *87*, 221-232.

et al. reported a significantly shorter and higher yielding synthesis in 1991 which allowed further investigation into corannulene's aromatic properties.⁵¹

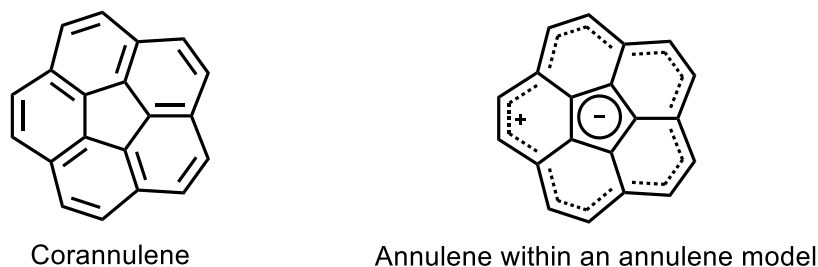


Figure 2.2 Corannulene structure and suggested annulene-within-an-annulene (AWA) model structure. The AWA model features an inner six-electron anion with a surrounding 14-electron cation.

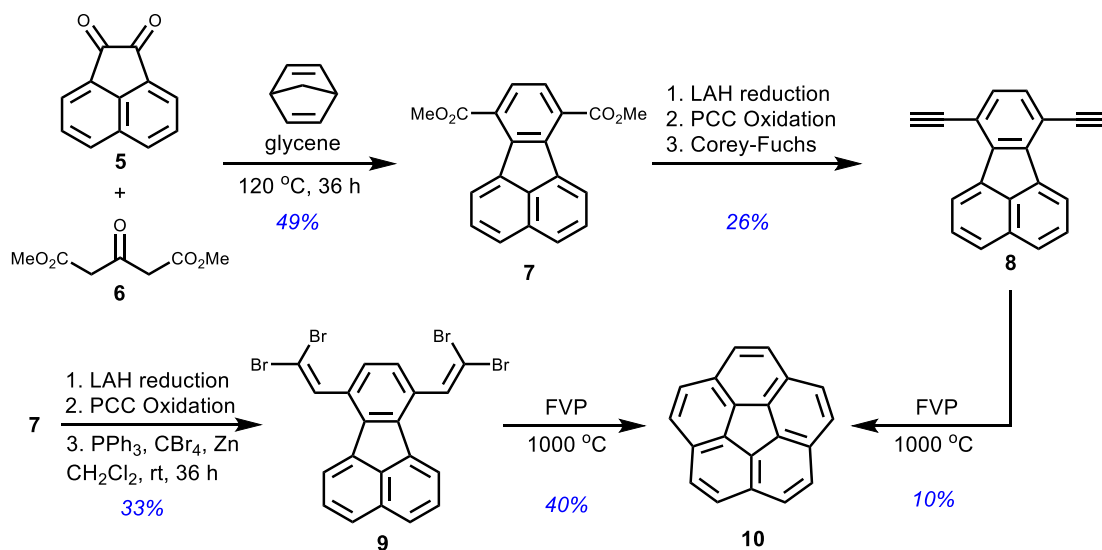
Many previously reported attempts to generate corannulene proved unsuccessful due to the difficulty in closing bonds across the bay region of corannulene precursors. Scott et al. overcame this problem by employing the high-temperature method of flash vacuum pyrolysis (FVP). FVP had been shown by Brown et al. to generate carbenes from rearranged terminal acetylenes.⁵² Scott's strategy thus required generation of an acetylated intermediate material that could be subjected to FVP.

This was accomplished by a four-step synthesis starting from acenaphthenequinone (**5**, scheme 2.2). In a one-pot procedure, **5** underwent a double Knoevenagel condensation with dimethyl-1,3-acetonedicarboxylate (**6**) to produce a cyclopentadienone intermediate which reacted with norbornadiene *via* an inverse-demand Diels-Alder cycloaddition. The highly unstable intermediate then loses both carbon monoxide and cyclopentadiene by

⁵¹ Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082-7084.

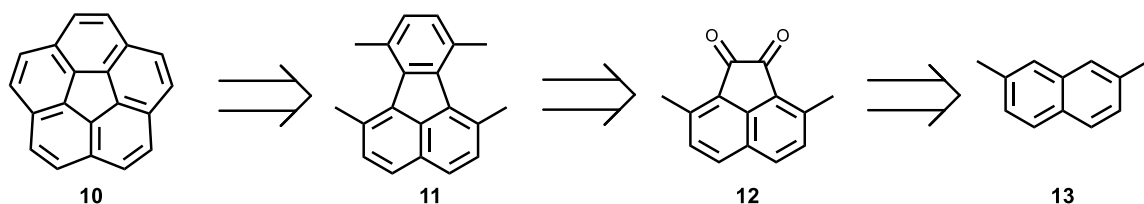
⁵² Brown, R. F. C.; Harrington, K. J.; McMullen, G. L. *J. Chem. Soc. Chem. Commun.* **1974**, 123-124.

subsequent retro-Diels-Alder reactions, resulting in diester fluoranthene, **7**, in a 49% yield. Diester **7** was reduced to the diol using LAH followed by oxidation to the dialdehyde using PCC and subjected to Corey-Fuchs reaction conditions to generate dialkyne **8**. Under FVP conditions, corannulene (**10**) was successfully generated. Unfortunately, most of the material was lost to polymerization in the sublimation chamber of the FVP apparatus. However, subjecting the tetrabromide intermediate (**9**) of the Corey-Fuchs reaction to FVP resulted in a substantially improved yield.



Scheme 2.2 Scott's successful synthesis of corannulene using FVP; LAH = lithium aluminum hydride, PCC = pyridinium chlorochromate.

The following year, Siegel et al. published a similar methodology to generate corannulene.⁵³ Over the following decade Scott,^{54,55} Siegel,⁵⁶ and Rabideau⁵⁷ published five additional synthetic strategies to produce corannulene culminating in a 10-step synthesis with an overall yield of 18%.⁵⁸ While similar to Scott's strategy, Siegel's optimized synthesis utilized only solution-based chemistry which allowed corannulene to be produced on the kilogram scale.⁵⁷



Scheme 2.3 Siegel's synthetic strategy to generate corannulene on the kilogram scale. As opposed to Scott's procedure, this plan avoided FVP, allowing large scale synthesis.

Corannulene has many useful properties beyond being synthetically interesting as a bowl-shaped molecule. The ability of PAHs to reversibly accept and delocalize electrons is well studied, as seen with studies on C₆₀, and corannulene has been shown to undergo one- and two-electron reductions.⁵⁹ Corannulene is also able to coordinate with C₆₀ as

⁵³ Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921-1923.

⁵⁴ Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcherm, M. S.; Meyer, D. T.; Warren, H. *J. Am. Chem. Soc.* **1997**, *119*, 10963-10968.

⁵⁵ Stefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868-4884.

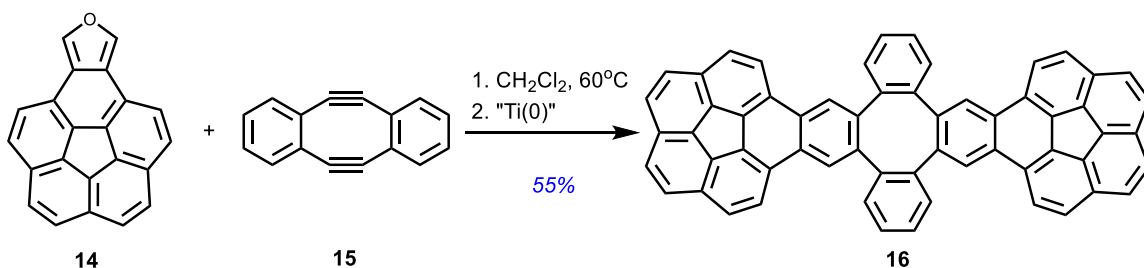
⁵⁶ Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843-4867.

⁵⁷ Aygula, A.; Tabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323-6324.

⁵⁸ Butterfield, A. M.; Gilomen, B.; Siegel, J. S. *Org. Process. Res. Dev.* **2012**, *16*, 664-676.

⁵⁹ Zabula, A. V.; Spisak, S. N.; Filatov, A. S.; Grigoryants, V. M.; Petrukhina, M. A. *Chem. Eur. J.* **2012**, *18*, 6476-6484.

shown with the report by Sygula et al. of a “buckycatcher.”⁶⁰ The buckycatcher (**16**, Scheme, 2.4) was synthesized *via* a Diels-Alder reaction between isocorannulene (**14**) and dibenzocyclooctadiyne (**15**). After removal of the oxo bridges using oxophilic low-valent titanium, the resulting compound had two concave faces that were able to bind C₆₀. This complex was crystallized and its structure confirmed by x-ray diffractometry.



Scheme 2.4 Synthesis of the buckycatcher *via* Diels-Alder cycloaddition and subsequent treatment with low-valent titanium.

Binding affinity for C₆₀ in combination with the reduction potential of corannulene gives strong potential for use in BHJ cells due to the potential for increased charge transfer and the potential to solubilize C₆₀. Corannulenes have been incorporated into electronic devices, with functionalized derivatives being used as acceptor materials in organic solar cells.⁶¹ Unsubstituted corannulene has also been used in OFETs as both n- and p-type materials, with reported electron mobility of 0.02 cm²V⁻¹s⁻¹ and hole mobility of 0.05 cm²V⁻¹s⁻¹.⁶² Corannulene therefore has great potential for use in many electronics applications.

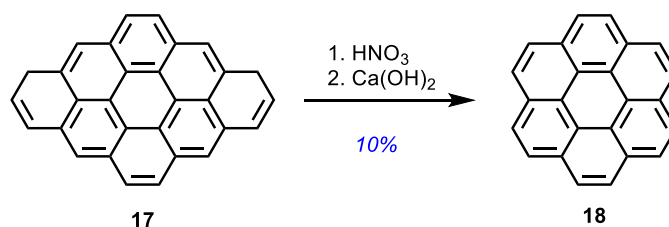
⁶⁰ Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **2007**, *129*, 3842-3843.

⁶¹ Lu, R.-Q.; Zheng, Y.-Q.; Zhou, Y.-N.; Lei, T.; Shi, K.; Zhou, Y.; Pei, J.; Zoppi, L.; Baldrige, K. K.; Siegel, J. S.; Cao, X.-Y. *J. Mat. Chem. A* **2014**, *2*, 20515-20519.

⁶² Shi, K.; Lei, T.; Wang, X.-Y.; Wang, J.-Y.; Pei, J. *Chem. Sci.* **2014**, *5*, 1041-1045.

2.1.3 [6]Circulene

[6]Circulene, or coronene, is another widely studied member of the circulene family. It is the only planar member of the circulene family and also a naturally occurring compound, found as the rare mineral carpathite.⁶³ Synthesis of coronene (**18**) was first reported by Scholl and Meyer by decomposing *anti-peri*-dibenzocoronene (**17**) in the presence of nitric acid followed by washing with a calcium hydroxide solution.⁶⁴ The naming of coronene follows that of corannulene, as Scholl and Meyer suggested it followed AWA model of aromaticity as well. Though it should be noted that ring currents in both molecules have been shown not to follow this model.⁶⁵



Scheme 2.5 Scholl and Meyer's synthesis of coronene.

Limited availability of coronene prevented significant use and modification beyond determination of crystal packing until Müllen and Rohr's reported synthesis of coronene diimides (CDIs).⁶⁶ Bromination of perylene-3,4,9,10-tetracarboxylic dianhydride (**19**), a

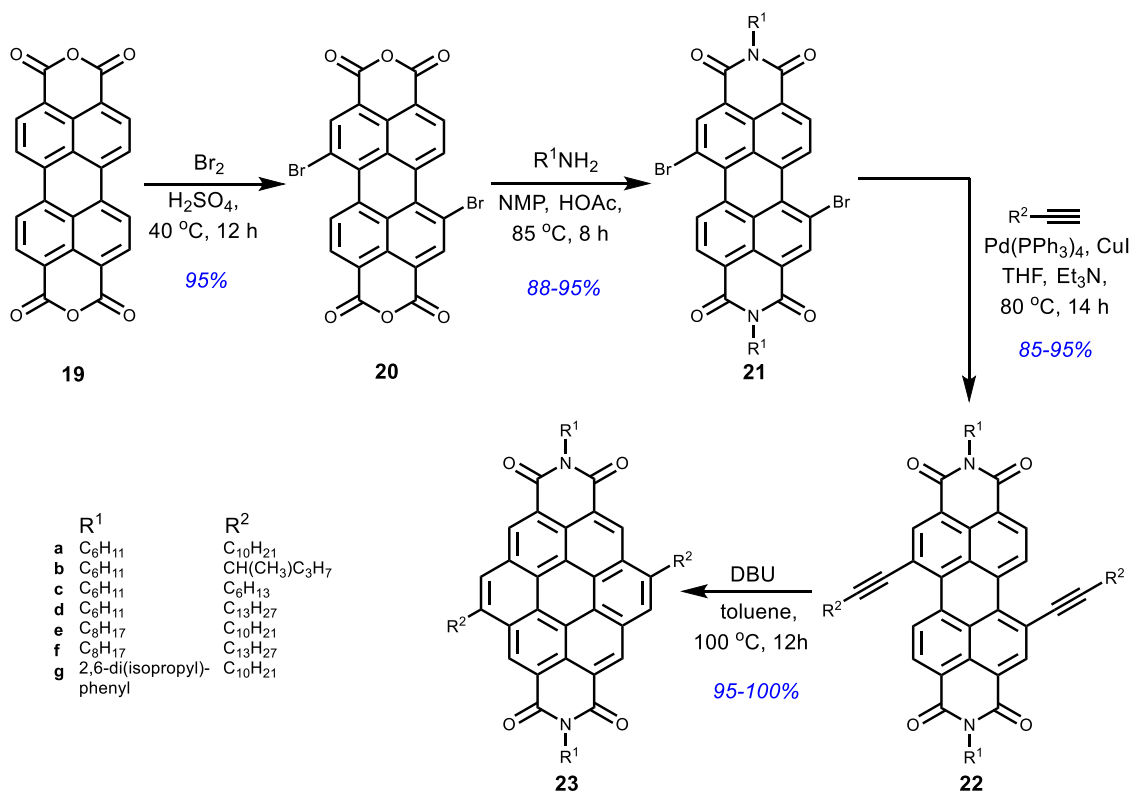
⁶³ Pietrovski, G. L. *Lvovskoe geol. Obshch., Mineral. Sbornik* **1955**, 9, 120-127.

⁶⁴ Scholl, R.; Meyer, K. *Ber. Dtsch. Chem. Ges. A* **1932**, 65, 902-915.

⁶⁵ Dickens, T. K.; Mallion, R. B. *Chem. Phys. Lett.* **2011**, 517, 98-102.

⁶⁶ Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C; Müllen, K. *Angew. Chem. Int. Ed.* **1998**, 37, 1434-1437.

common starting material for functionalized PDIs, with Br₂ gave 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (**20**). **20** can be easily converted to the corresponding diimide by treatment with a primary amine to generate dibromo-PDI derivatives (**21a-g**). Sonogashira coupling then afforded alkyne-functionalized PDIs (**22a-g**). The coronene structure could then be generated *via* DBU-mediated cyclization, resulting in the desired CDI derivatives (**23a-g**). Removal of the imide groups by treatment of KOH and subsequent decarboxylation using Cu/CuO was then completed, though no yield or characterization data was reported, resulting in dialkyl-functionalized coronene (**24**).



Scheme 2.6 Synthesis of coronene diimide derivatives by Rohr and Müllen; DBU = 1,8-diazabicyclo[0.4.2]undec-7-ene; NMP = N-methylpyrrolidone; HOAc = acetic acid.

This methodology has been expanded by further functionalization to generate CDIs that form discotic liquid crystals with high electron carrier mobilities. For example, Zeshang et al. generated several CDI derivatives with an N-perfluorooctyl derivative having the highest mobility of $6.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁶⁷ X-ray studies of the various thin films revealed increased order in the films with higher mobility. The authors note, however, that many challenges to device fabrication must be overcome for CDIs to be used as high mobility semiconductors in electronics applications.

Efforts to modify packing arrangements of functionalized coronene has led to a subclass of coronenes with extended π -systems. Addition of benzo groups to the periphery has led to two types of hexabenzocoronenes (HBCs), the *peri*- (**A**, figure 2.3) and *cata*- (**B**) derivatives. While similar structurally, the difference in location of the benzo substituents plays a large role in the properties of these two molecules.

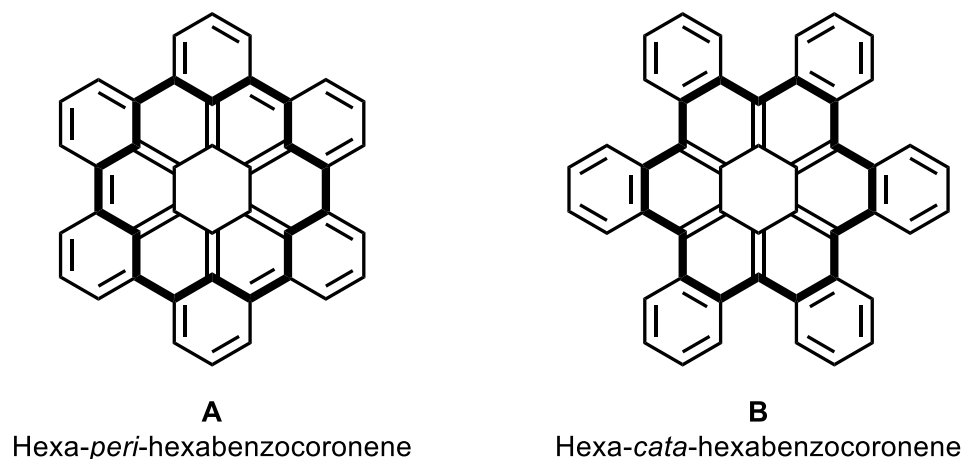
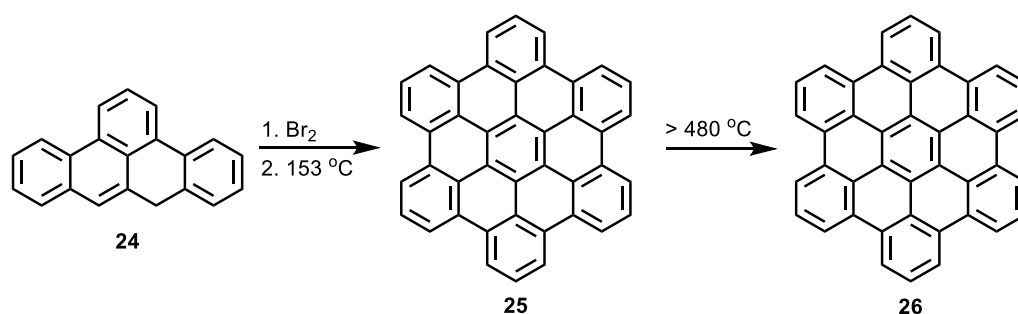


Figure 2.3 Structures of **A**) hexa-*peri*-hexabenzocoronene and **B**) Hexa-*cata*-hexabenzocoronene with highlighted coronene interior structure.

⁶⁷ Zeshang, A.; Yu, J.; Domercq, B.; Jones, S. C.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, 6688-6698.

Hexa-*peri*-hexabenzocoronene (*p*-HBC) was first synthesized by Clar et al. in 1959 by brominating 2:3-7:8-dibenzo-*peri*-naphthene (**24**) and heating the recovered solid either in refluxing trichlorobenzene or at 153 °C under vacuum to give tetrabenzoperopyrene (**25**).⁶⁸ Heating **25** above 480 °C produced *p*-HBC (**26**) which was recrystallized from boiling pyrene as pale yellow solid. A notably high melting point (>700 °C), low solubility, and long-lived fluorescence were noted. Utilizing *p*-HBC in electronics applications has become an area of great interest due to the potential for high mobility self-assembled materials.⁶⁹



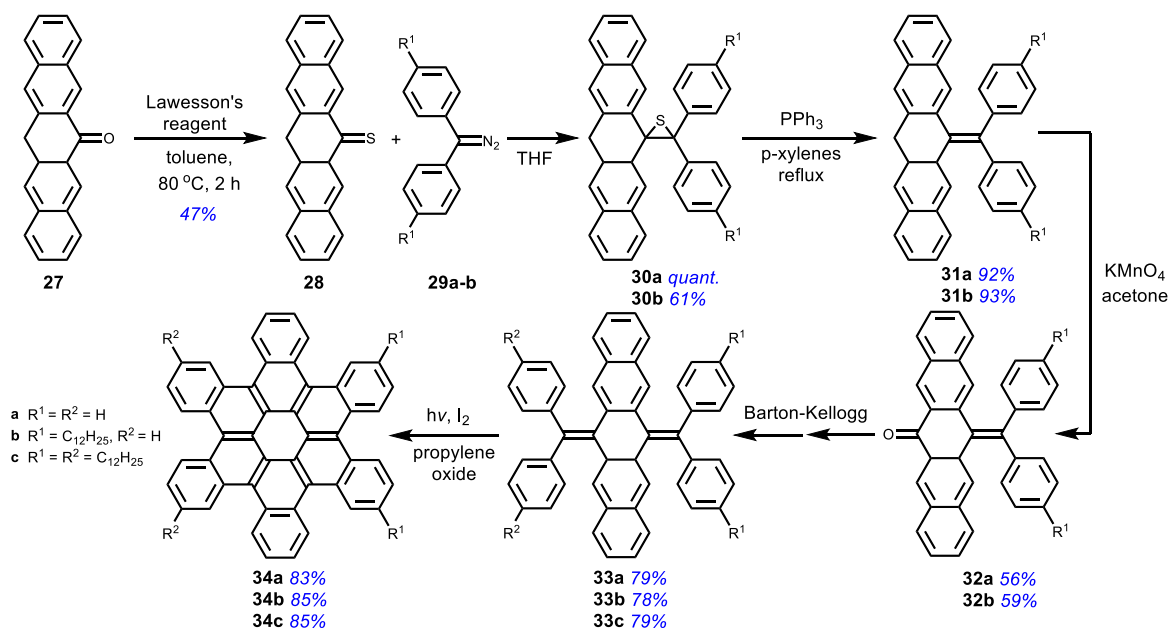
Scheme 2.7 Clar's initial synthesis of hexa-*peri*-hexabenzocoronene (**26**).

Clar was also the first to synthesize hexa-*cata*-hexabenzocoronene (*c*-HBC) in 1965 and compare the physical properties to those of *p*-HBC. It was noted that the *cata*-variant was much more soluble and had a melting point of 516 °C, making *c*-HBCs a much more viable material for use in electronics applications. Increased solubility and lower melting point is a result of steric congestion between hydrogens in the bay regions of *c*-HBCs.

⁶⁸ Clar, E.; Ironside, C. T.; Zander M. *J. Chem. Soc.* **1959**, 0, 142-147.

⁶⁹ Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, 304, 1481-1483.

The development of contorted HBCs in electronic devices did not occur until many decades later with the synthesis of functionalized *c*-HBCs by Nuckolls and coworkers in 2005.⁷⁰ Introduction of strained bonds in PAHs is the general cause of their synthetically-challenging nature. In the case of *c*-HBCs, this was overcome using sequential oxidations and Barton-Kellogg olefination followed by photolysis to close the final bonds (scheme 2.8).



Scheme 2.8 Synthesis of contorted HBCs by Nuckolls and coworkers.

OFET mobility data was then collected on both unsubstituted (**34a**) and alkylated (**34b**) *c*-HBCs. It was noted that **34c**, the tetraalkylated derivative, gave the best looking and most well-ordered films, resulting in a mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This was the highest mobility to date for a columnar discotic liquid crystalline material. Following this report,

⁷⁰ Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M. L.; Nuckolls, C. *Angew, Chem. Int. Ed.* **2005**, *44*, 7390-7394.

Whalley and Nuckolls reported on their use of palladium-catalyzed arylation and subsequent Scholl coupling to generate bowl-shaped *c*-HBCs.⁷¹ Bowl-shaped *c*-HBCs were found to have a high binding affinity for fullerene C₇₀. As with corranulene's coordination to C₆₀, this has implications for use in BHJ solar cells.

Coronene is the only planar member of the circulene family of molecules. The insoluble and unreactive nature of a large planar PAH has made incorporation of coronene into electronic materials difficult. However, it has been shown that functionalizing and contorting the nominally planar structure of coronene allows it to be used in many novel and interesting electronics applications. Incorporation of imides into the structure of coronene to generate CDIs has yielded n-type materials with promising mobilities. Generating contorted *c*-HBCs and bowl-shaped coronenes has allowed coronenes with extended π -systems to be utilized in devices due to increased solubility and more favorable stacking and coordination in the solid state. This provides further evidence that non-planar PAHs are useful materials for organic electronics applications.

2.1.4 [7]Circulene

[7]Circulene, or pleiadannulene is the largest successfully synthesized unfunctionalized circulene. It is also the smallest saddle-shaped circulene. Initial work

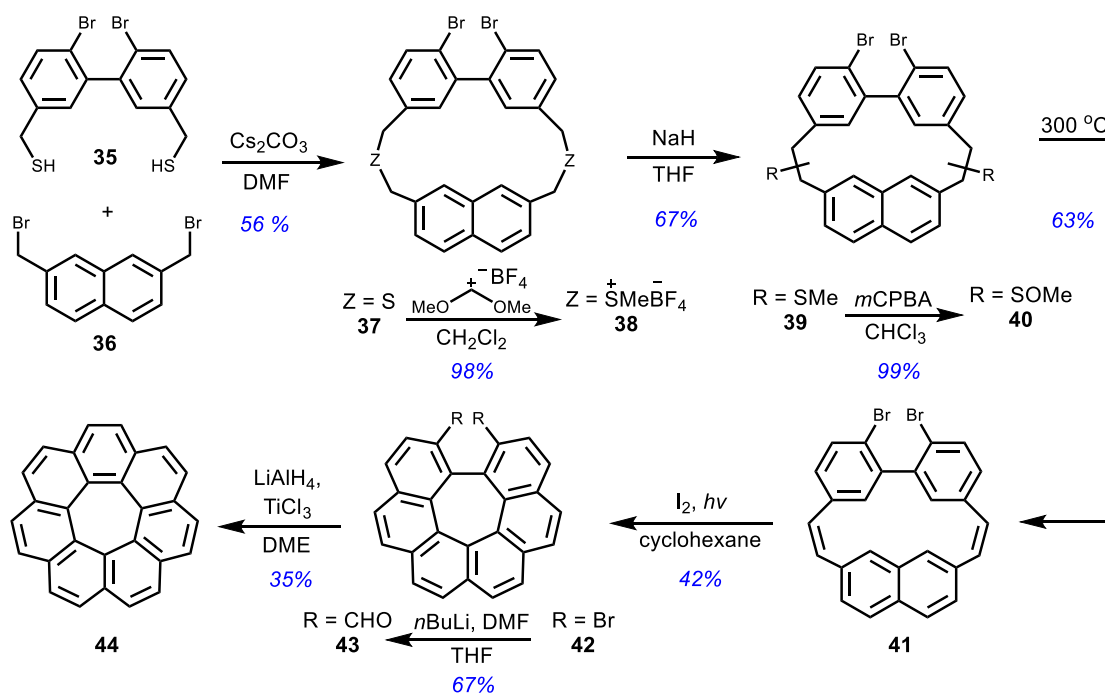
⁷¹ Whalley, A. C.; Plunkett, K. N.; Gorodetsky, A. A.; Schenck, C. L.; Chiu, C.-Y.; Steigerwald, M. L.; Nuckolls, C. *Chem. Sci.* **2011**, 2, 132-135.

synthesizing a [7]circulene analogue structure by Reiss and Jessup resulted in a synthetic strategy that would later be exploited to successfully generate the parent molecule.⁷² Utilizing this methodology with a brominated starting material (compound **35**, scheme 2.9), Yamamoto and coworkers were able to successfully produce [7]circulene.⁷³ Starting with a reaction between the dithiolate anion of 2,2'-dibromo-5,5'-bis(thiomethyl)biphenyl (**35**) and 2,7-bis(bromomethyl)naphthalene (**36**) produced dithiocyclophane, **37**. Treating **37** with dimethoxycarbonium tetrafluoroborate generated the disulfonium salt (**38**) which underwent Steven's rearrangement in the presence of NaH to generate sulfide **39**. Oxidation of **39** using *meta*-chloroperoxybenzoic acid (*m*CPBA) generated sulfoxide **40**. Pyrolysis at 300 °C, followed by UV-irradiation in the presence of iodine generated 1,16-dehydro-2,15-dibromohexahelicene (**42**). Lithium halogen exchange followed by addition of DMF gave the dialdehyde (**43**) which was treated with LAH and TiCl₃ resulting in [7]circulene (**44**). X-ray data of [7]circulene confirmed the predicted saddle-shape of the molecule. Yamamoto and coworkers improved upon their synthesis in 1996 utilizing FVP as a key step.⁷⁴ This improved synthesis allowed collection of CV data which revealed reversible one-electron oxidation and reductions as well as an irreversible second reduction, similar, though lower in energy, to those of coronene.

⁷² Jessup, P. J.; Reiss, J. A. *Tetrahedron Lett.* **1975**, *17*, 1453-1454.

⁷³ Yamamoto, K.; Harada, T.; Nakazaki, M. *J. Am. Chem. Soc.* **1983**, *105*, 7171-7172.

⁷⁴ Yamamoto, K.; Sonobe, H.; Matsubara, H.; Soto, M.; Okamoto, S.; Kitaura, K. *Angew. Chem. Int. Ed.* **1996**, *1*, 69-70.



Scheme 2.9 Yamamoto and coworkers' original synthesis of [7]circulene; DMF = dimethylformamide.

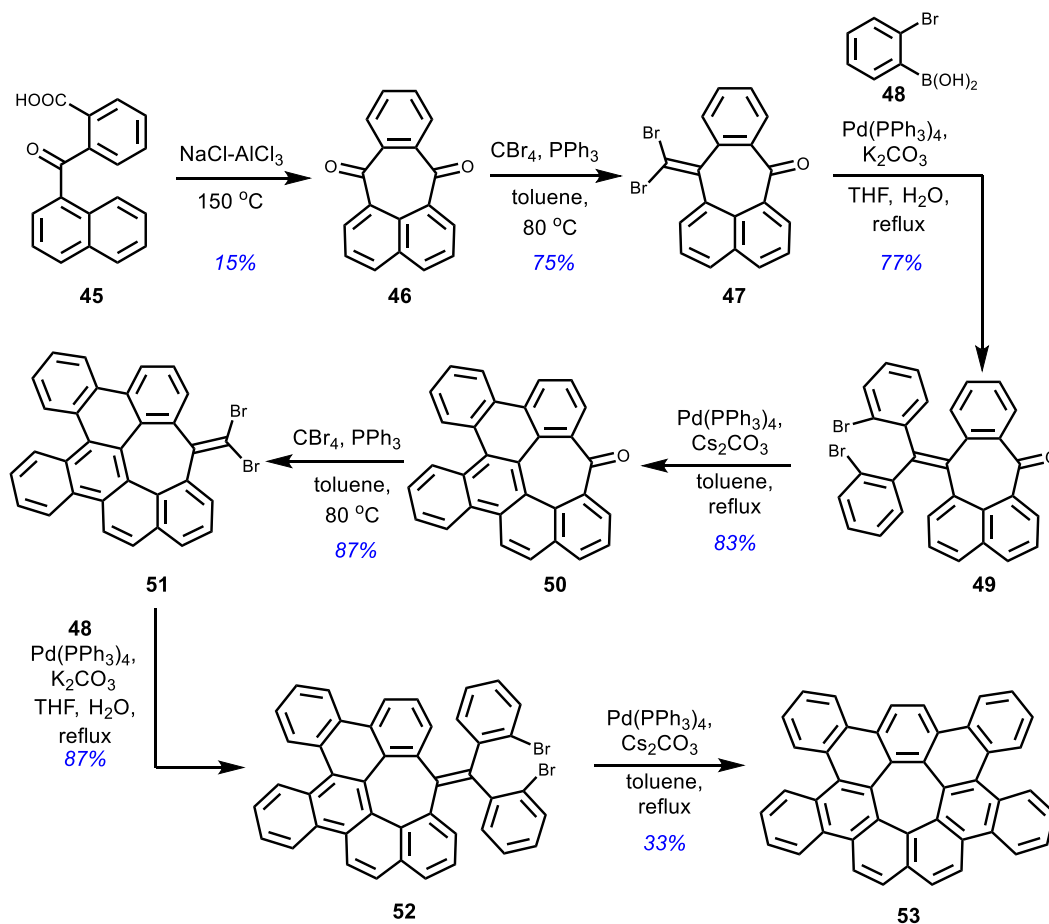
Recently, Miao's group reported two derivatives of [7]circulene. The first contained was an extended aromatic structure containing two seven-membered rings, thus the compound contained two [7]circulene subunits.⁷⁵ Structural data revealed π -stacking interactions between the exterior benzo groups and TFTs of these PAHs exhibited low mobility due to low long-range order.

Following this, Miao and coworkers reported synthesis of tetrabenzo[7]circulene (TB[7]C) where, unlike Yamamoto's synthesis, generation of the internal seven-membered ring was completed early in the synthetic procedure (scheme 2.10).⁷⁶ Starting with an intramolecular Friedel-Crafts acylation of 2-(1-naphthoyl)-benzoic acid (**45**), produced

⁷⁵ Cheung, K. Y.; Xu, X.; Miao, Q. *J. Am. Chem. Soc.* **2015**, *137*, 3910-3914.

⁷⁶ Gu, X.; Li, H.; Shan, B.; Liu, Z.; Miao, Q. *Org. Lett.* **2017**, *19*, 2246-2249.

5,12-pleiadenedione (**46**), isolated as a minor product in 15% yield. Dione **46** underwent Corey-Fuchs olefination to generate only the single dibromo olefin, **47**, with a 75% yield. **47** was subjected to Suzuki coupling with 2-bromophenylboronic acid (**48**) to generate arene **49** with a 77% yield. Palladium-catalyzed arylation conditions were employed to generate ketone **50** in an 83% yield. The second Corey-Fuchs and Suzuki coupling sequence also proceeded well resulting in a 75% yield over two steps to generate the second arylated product (**52**). Though the yield of the final palladium-catalyzed arylation step was relatively low (33%), the desired TB[7]C (**53**) was successfully isolated.



Scheme 2.10 Miao and coworkers' synthesis of TB[7]C.

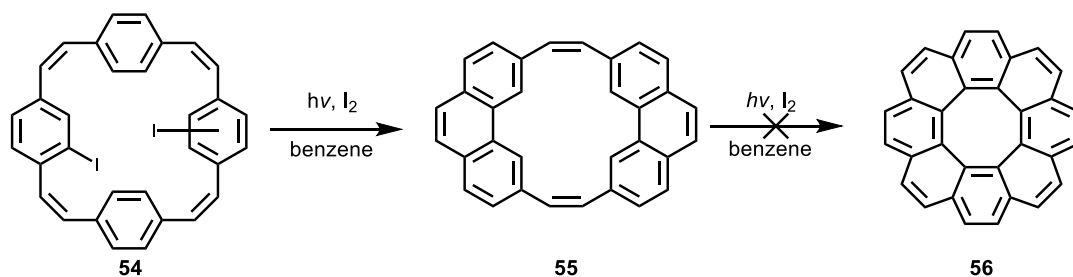
Using this methodology, Miao and coworkers were also able to generate thiophene-annulated derivatives of [7]circulene. Crystallization of TB[7]C as well as a cocrystal with C₆₀ was successful which allowed determination of the solid state structure. CV data showed a quasi-reversible oxidation and no reduction in the testing window. The combination of crystal structure data and oxidation potential shows that TB[7]C could potentially function as a p-type semiconductor. However, no mobility data was collected.

Successful synthesis of [7]circulene and TB[7]C has provided access to saddle-shaped molecules. [7]circulene is also the smallest saddle-shaped member of the circulene family and it is the largest successfully synthesized unsubstituted circulene. However, these methodologies still suffer from low overall yields which limits exploration of these materials and their use in electronic devices. Due to the interest in highly contorted or uniquely shaped PAHs, there remains a strong desire for synthesis of more saddle-shaped molecules.

2.1.5 [8]Circulene

[8]Circulene is the next largest in the series and is also a saddle-shaped molecule. Derivatives of [8]circulene are the largest successfully synthesized to date, while the parent structure remains unable to be isolated. The first reported attempt to synthesize [8]circulene (**56**, Scheme 2.11) was carried out by Thulin and Wennerström in 1976 but their attempts to close the final bonds by photo-induced cyclization only resulted in

isolation of the bis-phenanthrene intermediate (**55**). They postulate that this is due to the reversibility of the photoreaction being unable to close the final two highly strained bonds of [8]circulene.



Scheme 2.11 Thulin and Wennerström's attempted synthesis of [8]circulene.

Density functional theory (DFT) studies into the structure of [8]circulene and its stability would later show that the parent structure is inherently unstable due to its concentric aromatic ring currents.⁷⁷ The two-dimensional representation of the molecule suggests a fully conjugated aromatic system based on Kekulé's theory of aromaticity. In the broadest sense, this would mean the electrons in the π -system of the molecule are free to move throughout the entire system.⁷⁸ While this holds true for small aromatic compounds, PAHs, especially contorted aromatics, have been shown to deviate from Kekulé's model. Eric Clar first proposed the idea of the aromatic sextet as a more accurate description of the electronic structure of PAHs.

⁷⁷ Salcedo, R.; Sansores, L. E.; Picazo, A.; Sansón, L. *J. Mol. Struct. (Theochem.)* **2004**, *678*, 211-215.

⁷⁸ Pauling, L. *J. Chem. Phys.* **1936**, *4*, 673-677.

2.2 Clar's Theory of Aromaticity and its Application to Polycyclic Aromatic Hydrocarbons

Clar's model is a description of aromaticity in which π -electrons are localized into aromatic sextets, as opposed to being evenly distributed throughout the entirety of the π -system.⁷⁹ Put simply, Clar's theory states that the most important resonance structure for describing physical and electronic properties of a PAH is the one with the most aromatic sextets. Experimental bond lengths in the molecule kekulene (figure 2.4), which has over 200 possible resonance structures, is a great example to illustrate Clar's model of aromaticity. If every resonance structure of kekulene were an equal contribution to the overall description of the molecule, each bond length should be identical. However, the actual bond lengths of kekulene suggest significant bond localization.⁸⁰

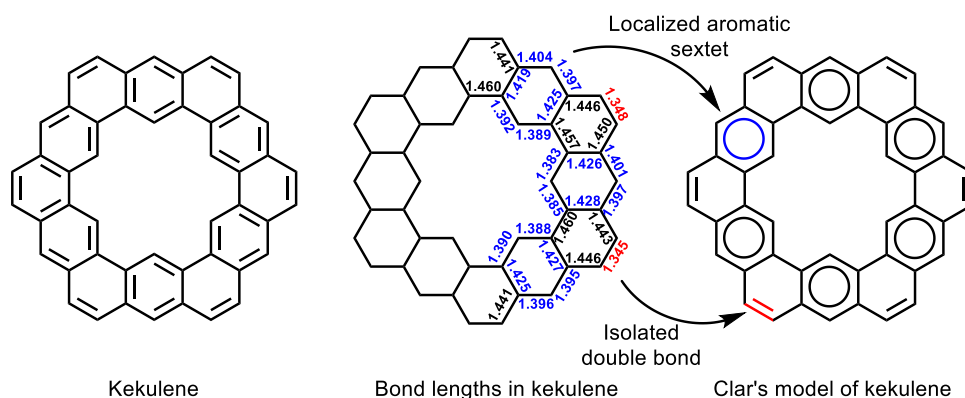


Figure 2.4 Bond lengths in kekulene; the unique bond lengths suggest the molecule has localized aromatic sextets and isolated double bonds, a source of reactivity in PAHs.

⁷⁹ Clar, E. *The Aromatic Sextet*, Wiley, New York, **1972**.

⁸⁰ Krieger, C.; Diederich, F.; Schweizer, D.; Staab, H. A. *Angew. Chem. Int. Ed.* **1979**, *18*, 699-701.

This localization of electron density into aromatic sextets helps stabilize larger aromatic systems. However, as seen in the kekulene example, localization can also leave isolated double bonds as a reactive site. Applying this idea to [8]circulene gives insight into the instability of unsubstituted parent structure (figure 2.5). Maximizing the number of aromatic sextets leaves four isolated double bonds. In the case of planar aromatic compounds, this would not result in significant instability as is the case with kekulene. Additional instability due to the strain of contorted aromatics leads to these isolated double bonds being highly reactive.

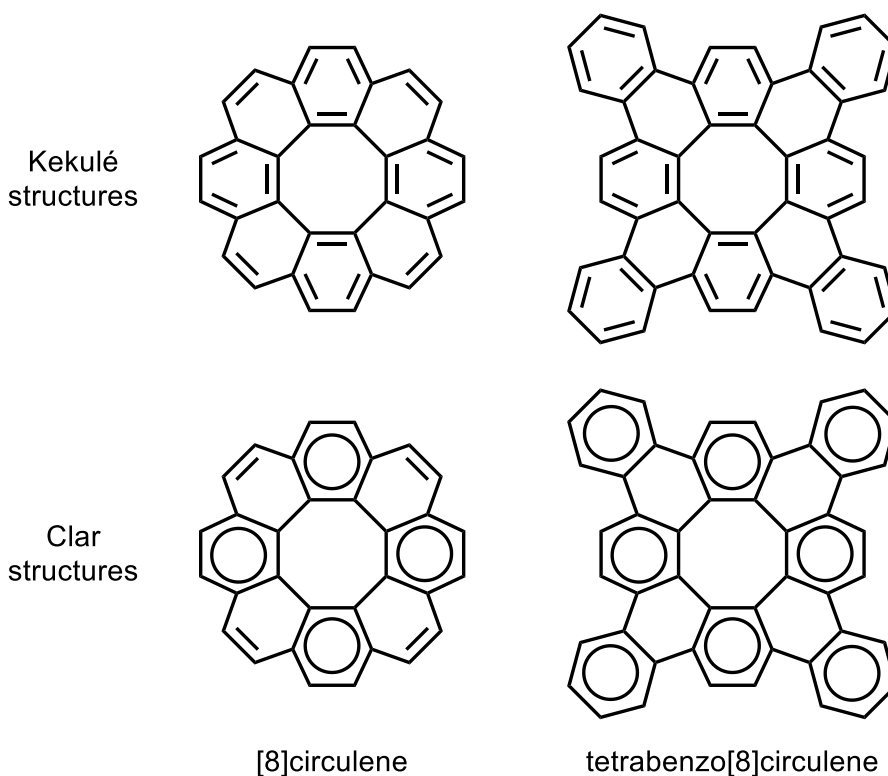
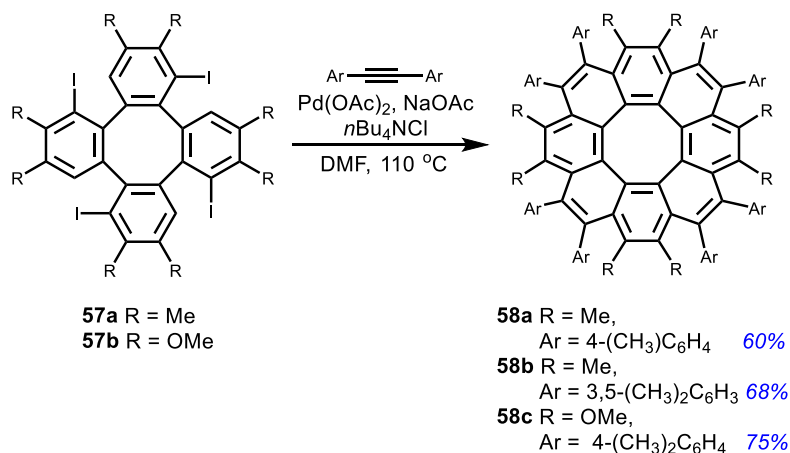


Figure 2.5 [8]Circulene and tetrabenzo[8]circulene in their Kekulé and Clar illustrations. Incorporation of the isolated double bonds into aromatic sextets by the expansion of benzo-substituents has allowed generation of stable derivatives of [8]circulene.

One strategy employed to successfully generate [8]circulene derivatives is to incorporate these isolated double bonds into stable functional groups. Indeed, this was accomplished in three separate reports detailing unique synthetic strategies.^{14,81,82} Wu and coworkers were the first to report successful synthesis of [8]circulene derivatives, though their highly substituted derivative lacked the stability imparted by incorporation of the peripheral double bonds into additional fused benzene rings. Their strategy involved starting with the central eight-membered ring intact by first generating a tetraiodinated tetraphenylene (**57**) which could undergo four palladium-catalyzed annulations in one step to produce highly substituted [8]circulene derivatives (**58a-c**).



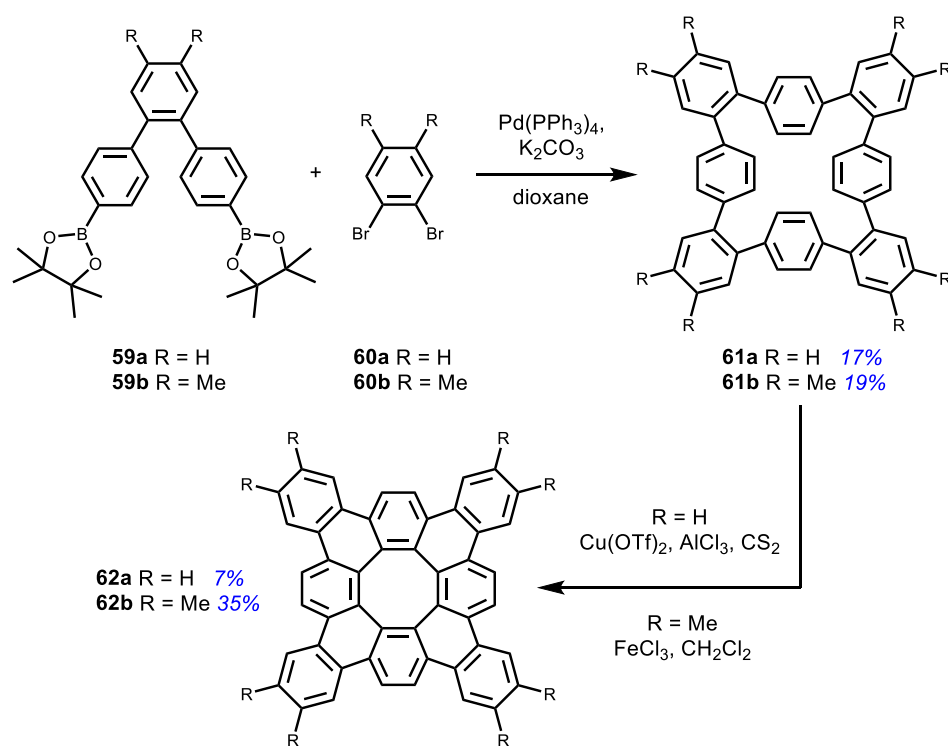
Scheme 2.12 Wu and coworkers' successful synthesis of [8]circulene derivatives.

Sakamoto and Suzuki subsequently published an alternative synthetic strategy in which the eight-membered core was generated in the final step of their synthesis in an “outside-in” approach. After synthesis of borylated terphenylene starting materials (**59a-**

⁸¹ Feng, C.-N.; Kuo, M. Y.; Wu, Y.-T. *Angew. Chem. Int. Ed.* **2013**, *52*, 7791-7794.

⁸² Sakamoto, Y.; Suzuki, T. *J. Am. Chem. Soc.* **2013**, *135*, 14074-14077.

b), Suzuki coupling conditions using either 1,2-dibromobenzene (**60a**) or 1,2-dibromo-4,5-dimethylbenzene (**60b**) gave the desired cyclooctaphenylenes (**61a-b**). Under oxidative dehydrogenation conditions, or Scholl coupling, using either $\text{Cu}(\text{OTf})_2$ and AlCl_3 in CS_2 or FeCl_3 in CH_2Cl_2 , the desired tetrabenzo[8]circulene (TB[8]C, **62a**) and octamethyltetrabenzo[8]circulene (OM-TB[8]C, **62b**) were formed. It was noted that Scholl coupling of the non-methylated cyclooctaphenylene derivative resulted in significant dimerization at the benzo positions, leading to the low yield of 7%. Blocking these positions with methyl groups allowed the increased yield of 35%.



Scheme 2.13 Sakamoto and Suzuki's synthesis of [8]circulene derivatives using an outside-in approach.

With successful synthesis of TB[8]C derivatives, x-ray structural data was collected, confirming the saddle-shaped molecular structure. OFETs were also produced

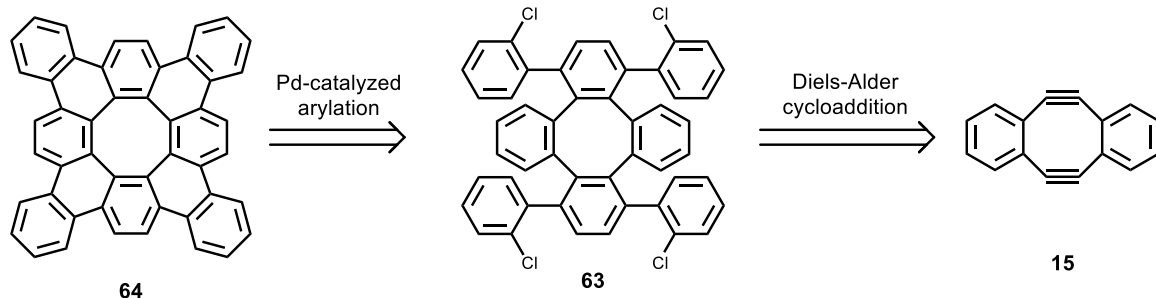
from OM-TB[8]C and it behaved as a p-type semiconductor, though the mobility was quite low at $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. However, little emphasis was placed on the remarkable stability of [8]circulene with the addition of the benzo groups considering the calculated instability of the parent structure and relatively rapid decomposition of [8]circulene derivatives produced by Wu and coworkers. Additionally, these advancements had not yet demonstrated the utility further functionalization of stable derivatives of [8]circulene will have on the electronic and structural properties.

2.3 Previous Work in the Whalley Group: Tetrabenzo[8]circulene

As opposed to the outside-in strategy used by Sakamoto and Suzuki, Dr. Robert Miller in our lab used an inside-out approach in which the formation of the eight-membered ring would be in place before formation of the final bonds. With this plan in mind, dibenzocyclooctadiyne (**15**, scheme 2.14), or the Sondheimer-Wong diyne,⁸³ was the ideal starting material as it contained the required eight-membered ring and was known to undergo Diels-Alder cyclization reactions with highly-reactive dienes. After reaction with an appropriate diene, palladium-catalyzed arylation conditions were envisioned as a method to form the final four bonds as they had been previously reported in the synthesis of several strained molecules.^{58,67,84}

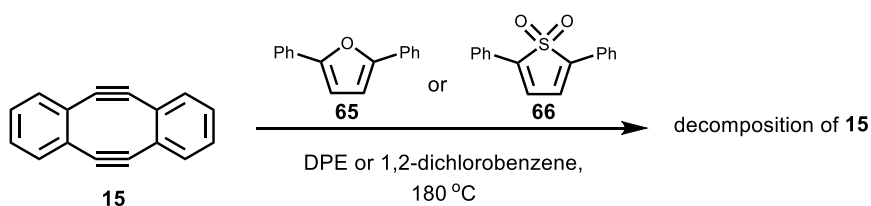
⁸³ Wong, H. N. C.; Garrett, P. J.; Sondheimer, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 5604-5605.

⁸⁴ Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427-1430.



Scheme 2.14 Retrosynthetic plan to generate tetrabenzocyclooctadiene using an inside-out approach.

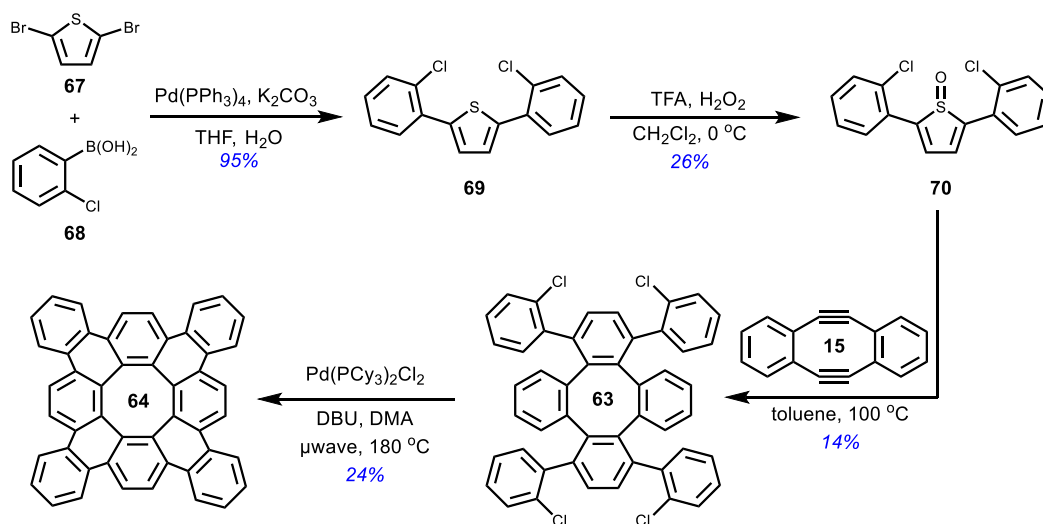
With a suitable dienophile, reactive dienes were screened. Though **15** had been shown to react with 3,4-disubstituted furans in Diels-Alder reactions, 2,5-diphenylfuran (**65**, scheme 2.15) was unreactive towards **15**. Higher temperatures led to the decomposition of **15**, with no Diels-Alder product detected. Utilizing another known highly reactive diene, 2,5-diphenylthiophene dioxide (**66**) also led to decomposed product at the high temperatures required for Diels-Alder reactions of thiophene dioxides.



Scheme 2.15 Screening of reactive dienes in Diels-Alder reactions with dibenzocyclooctadiene, the high temperatures resulted in decomposition of starting material; DPE = diphenylether.

Fortunately, as an intermediate in the synthesis of thiophene dioxides, thiophene oxides are also generated. Upon searching the literature, it was noted that synthesis of thiophene oxides and evidence of their dimerization through cycloaddition had been known

for over a decade.⁸⁵ However, there was surprisingly little precedent for their use in Diels-Alder reactions. The desired thiophene oxides were prepared by first reacting 2,5-dibromothiophene (**67**, scheme 2.16) *via* Suzuki coupling with 2-chlorophenylboronic acid (**68**) to generate 2,5-bis-(2-chlorophenyl)thiophene (**69**) in a 95% yield. Oxidation by dropwise addition of 30% H₂O₂ (aq.) into a TFA/CH₂Cl₂ solution at 0 °C could generate the desired thiophene oxide (**70**) in a 26% yield. Overoxidation was avoided by stopping the reaction as soon as thiophene dioxide was detected by TLC. It should be noted that the remaining starting material can be collected during purification in a nearly quantitative amount.



Scheme 2.16 Dr. Miller's synthesis of TB[8]C in our lab using the inside-out synthetic strategy; TFA = trifluoroacetic acid; μ wave = microwave heating.

The double Diels-Alder reaction between **70** and **62** was accomplished in toluene at 100 °C with a 14% yield. Palladium-catalyzed arylation of the Diels-Alder product (**63**)

⁸⁵ Pouzet, P; Erdelmeier, I.; Ginderow, D.; Mornon, J.-P.; Dansette, P.; Mansuy, D.; *J. Chem. Soc. Chem. Commun.* **1995**, 473-474.

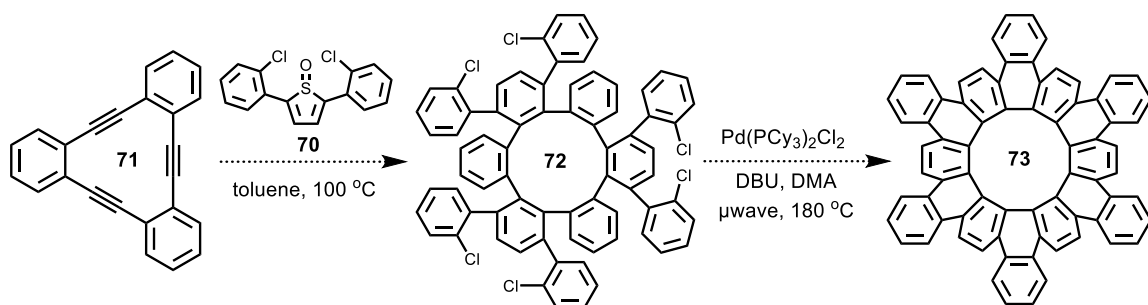
under microwave heating conditions produced TB[8]C in a 24% yield (70% per bond). Interestingly, the crystal structure of TB[8]C does not match the DFT minimized structure. TB[8]C takes on a pinwheel-like shape due to crystal packing forces and π -stacking interactions of the peripheral benzo groups. TB[8]C was also found to be stable under ambient conditions for several months, showing that incorporation of the isolated double bonds in [8]circulene into benzo substituents significantly stabilized the molecule. This synthetic methodology was also improved upon in order to generate TB[8]C functionalized with electron-donating and electron-withdrawing groups.^{86,87}

2.4 Initial Synthetic Strategy to Generate [12]Circulene Derivatives

Following the strategy employed by to generate TB[8]C by our group, it was initially envisioned that a 12-membered macrocycle could undergo a similar Diels-Alder cycloaddition and palladium-catalyzed arylation sequence leading to hexabenzoc[12]circulene (HB[12]C, **73**, Scheme 2.17). The hexabenzoc-derivative was targeted in order to incorporate the isolated double bonds of circulene into aromatic sextets. Beginning with the 12-membered ring intact would also make closure of the final bonds more likely as closure of interior bonds would need to overcome significant strain.

⁸⁶ Miller, R. W.; Dodge, N. J.; Dyer, A. M.; Fortner-Buczala, E. M.; Whalley, A. C. *Tetrahedron Lett.* **2016**, *57*, 1860-1862.

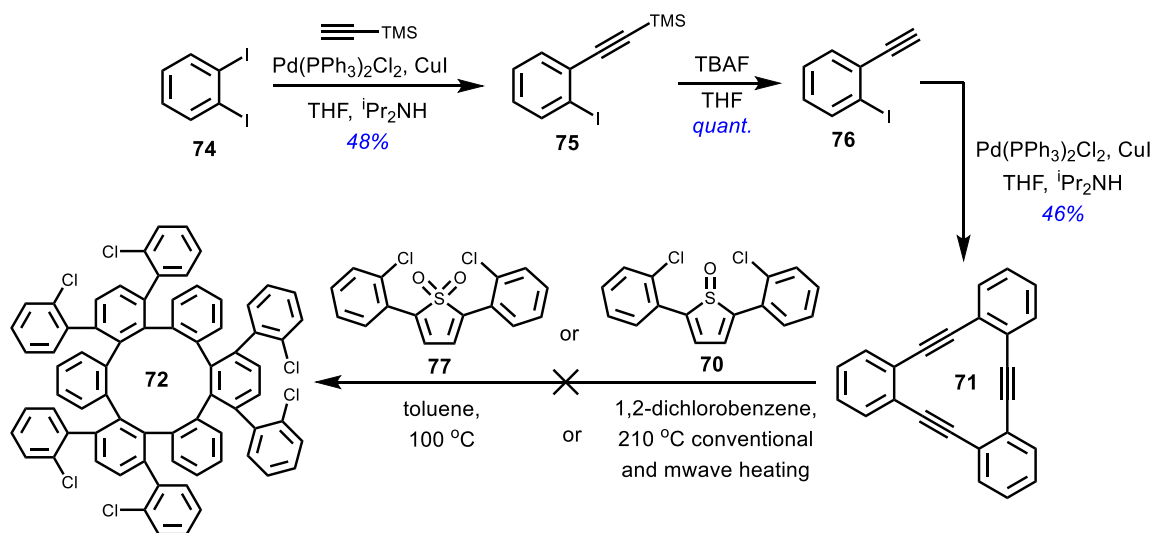
⁸⁷ Miller, R. W.; Averill, S. E.; Van Wyck, S. J.; Whalley, A. C. *J. Org. Chem.* **2016**, *81*, 12001-12005.



Scheme 2.17 Proposed synthesis of hexabenzocirculene based on the successful synthesis of tetrabenzocirculene.

Generation of the starting hexadehydro[12]annulene (**71**) was accomplished by modifying a previously reported procedure.⁸⁸ Starting with Sonogashira coupling of 1,2-diodobenzene (**74**, scheme 2.18) and trimethylsilylacetylene (TMSA) produced a 48% yield of the monocoupled product (**75**), with 25% recovery of starting material and 25% dicoupled product. Deprotection of the alkyne by dropwise addition of a 1.0 M solution of TBAF in THF produced the terminal alkyne, **76**, in quantitative yield. Using the palladium-free coupling methods outlined by Iyoda and coworkers failed to produce the desired [12]annulene (**71**) in reasonable yields. However, standard Sonogashira coupling conditions produced **71** in a 46% yield.

⁸⁸ Iyoda, M.; Sirinintasak, S.; Nishiyama, Y.; Vorasingha, A.; Saultana, F.; Nakau, K.; Kuwatani, Y.; Matsuyama, H.; Yoshida, M.; Miyake, Y. *Synthesis* **2004**, 9, 1527-1531.



Scheme 2.18 Synthesis of [12]annulene and attempted Diels-Alder with thiophene oxide and thiophene dioxide.

With [12]annulene in hand, the Diels-Alder reaction with diene **70** was attempted resulting in recovery of both starting materials even after extended reaction times. Increasing the temperature in 1,2-dichlorobenzene led to decomposition of **70** to the unoxidized thiophene (**69**). Thiophene dioxides have the advantage of being stable and, unlike with dibenzocyclooctadiyne, [12]annulene is stable at elevated temperatures. Therefore, attempts were made to react **71** with thiophene dioxide (**77**) using conventional and microwave heating up to 210 °C. Unfortunately, all attempts to react **71** resulted in recovery of starting material. The stability of the alkynes in **71** prevents reactivity towards these dienes in Diels-Alder reactions. As opposed to the strained alkynes in dibenzocyclooctadiyne, **71** has alkynes that are linear and planar. Being unable to activate **71** thermally, electronic modifications to the [12]annulene were attempted to increase reactivity of the alkynes toward Diels-Alder reactions.

2.4.1 Electronic Modifications to the Dienophile

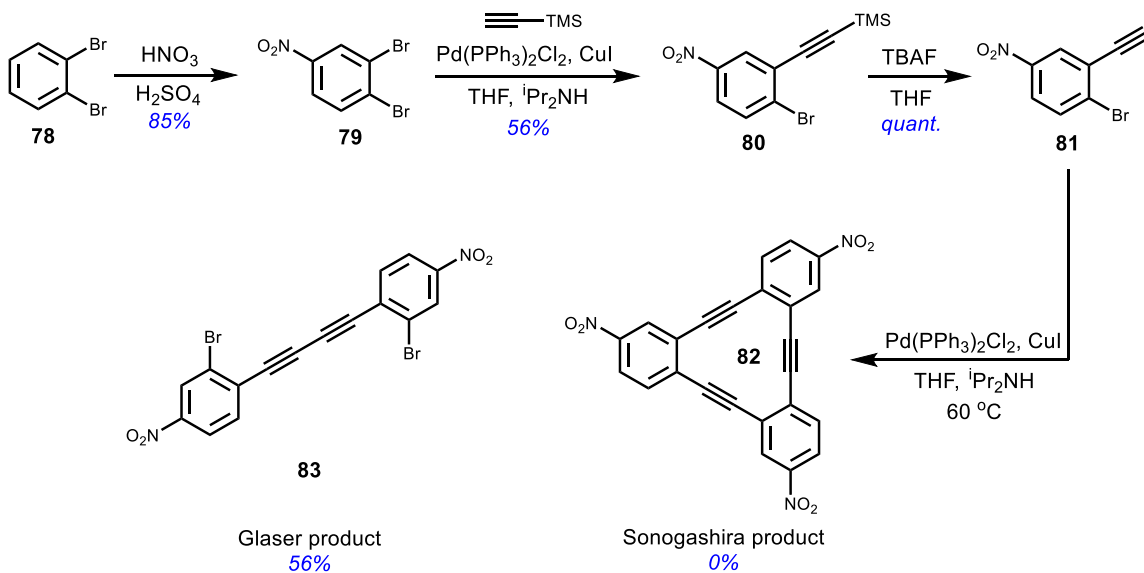
Initially, electron-withdrawing group (EWG) modifications were planned for [12]annulene as electron deficient dienophiles are known to increase reactivity in Diels-Alder reactions. Additionally, a functional group that could be removed or used as a reactive site for further functionalization was desired. Any additional functional group would also have to be relatively small as to not sterically impede approach of the diene. Therefore, we envisioned generating a nitrated derivative of [12]annulene.

Beginning with nitration of 1,2-dibromobenzene (**78**) resulted in an 85% yield of 1,2-dibromo-4-nitrobenzene (**79**). Sonogashira coupling of **79** with TMSA generated the monocoupled product (**80**) in 54% yield, again with recovery of starting material and approximately 20% dicoupled product. Deprotection with TBAF generated the terminal alkyne (**81**) in quantitative yield. Sonogashira coupling to form trinitro[12]annulene (**82**) appeared to go well based on carbon and proton NMR data. Mass spectrometry (MS) data revealed the exclusive generation of the Glaser (homocoupled) product (**83**) instead of the desired cross-coupled product *via* Sonogashira coupling under even the most stringent oxygen-free conditions. Attempts were made to generate **82** *via* reported copper-free Sonogashira coupling, Negishi coupling, and Iyoda and coworkers' palladium-free method.^{89,90} However, all cases generated none of the desired product and the use of elevated temperatures often resulted in decomposition of the starting material.

⁸⁹ Méry, D.; Heuzé, K.; Astruc, D. *Chem. Commun.* **2003**, 1934-1935.

⁹⁰ Anastasia, L.; Negishi, E.-I; *Org. Lett.* **2001**, 3, 3111-3113.

Additionally, 1,2-diiodo-4-nitrobenzene was synthesized but difficulty separating the products of the subsequent Sonogashira coupling and deprotection reactions prevented attempts to utilize the more reactive iodine substituent using these conditions.

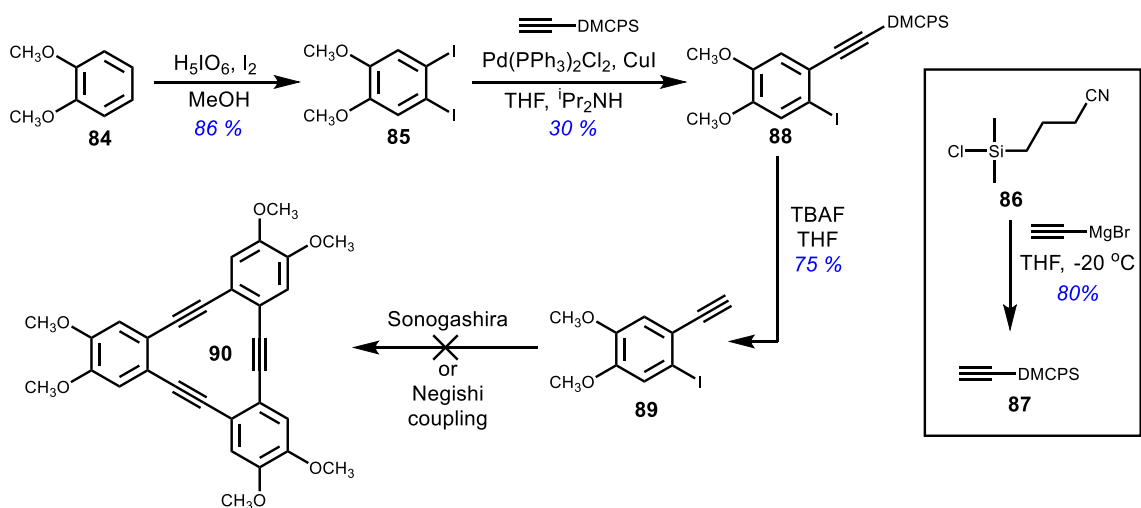


Scheme 2.19 Attempted synthesis of trinitro[12]annulene derivative led to exclusively the Glaser, or homocoupled, product.

With the inability to generate an electron deficient [12]annulene derivative, and after evidence that the Diels-Alder to generate TB[8]C is inverse-demand, our focus shifted to generate a [12]annulene derivative with electron-donating groups (EDGs). Using a previously reported procedure, veratrole (**84**) was iodinated to give 1,2-diiodo-3,4-dimethoxybenzene (**85**).⁹¹ Using identical Sonogashira coupling conditions with TMSA, the starting material, mono, and dicoupled products could not be separated. Therefore, synthesis of a terminal alkyne with a polar protecting group was required. This was accomplished *via* a Grignard reaction between ethynyl magnesium bromide (**86**) and

⁹¹ Fisher, T. J.; Dussault, P. H. *Eur. J. Org. Chem.* **2012**, *14*, 2831-2836.

cyanopropyldimethylsilyl chloride (**87**).⁹² Sonogashira coupling of **85** to **87** produced the same ratio of products as previously seen but only approx. 30% of monocoupled product (**88**) could be isolated. Deprotection of the alkyne using TBAF resulted in surprisingly low yields of 75% for terminal alkyne (**89**). Nevertheless, this was carried forward and subjected to Sonogashira or Negishi coupling conditions. However, both reactions resulted in no recovery of starting material or the desired cyclic trimer (**90**).



Scheme 2.20 Attempted synthesis of hexamethoxy[12]annulene; Inset: Synthesis of a polar analogue of TMSA; DMCPs = dimethylcyanopropylsilyl.

The reason for the inability to generate **90** is likely due to the instability of the terminal alkyne. During and after purification of **89** it was noted that it would quickly turn dark brown in solution and, therefore, the elevated temperatures required for both Sonogashira and Negishi conditions prevented formation of the desired product. Interestingly, only Iyoda and coworkers have reported generation and use of **89** in their reported synthesis of **90**. Being unable to easily modify the electronics of the Diels-Alder

⁹² Höger, S.; Bonrad, K. *J. Org. Chem.* **2000**, *65*, 2243-2245.

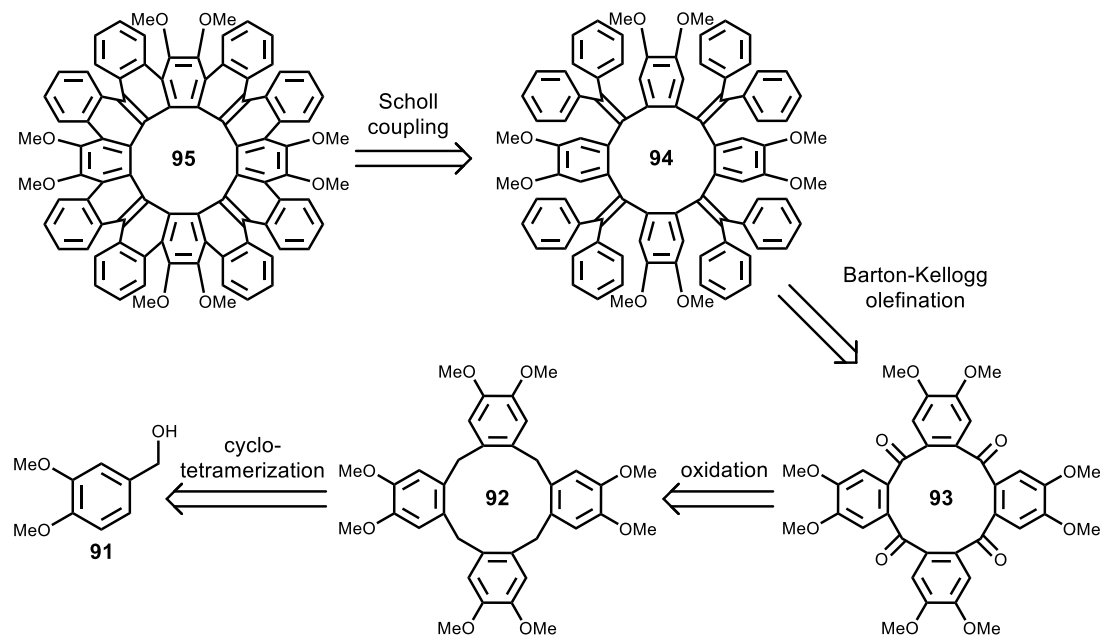
reaction by functionalization of the dienophile, alternative methods for generating [12]circulene were explored.

2.4.2 Barton-Kellogg Olefination

As seen in the synthesis of functionalized contorted HBCs, the Barton-Kellogg reaction is a powerful method of generating strained molecules.⁹³ Therefore, a plan to generate [12]circulene using these methods was developed (scheme 2.21). This new strategy also had the central 12-membered ring generated early in the synthetic strategy as the exterior of the molecule is much more accessible. Cyclotetramerization of veratryl alcohol (**91**) followed by oxidation of the benzylic positions of the cyclotetramer product (**92**) would generate tetraketone, **93**. **93** could then be subjected to the Barton-Kellogg olefination sequence to generate the octaphenyl tetraene (**94**). If successful, **94** would be subjected to Scholl coupling conditions to generate octamethoxyoctaphenyl[12]circulene (**95**). While this Scholl coupling reaction would need to form eight bonds in one reaction, the electron-donating methoxy groups improve oxidative coupling and are ortho-para directing.⁹⁴ Additionally, Scholl couplings can be repeated to close additional bonds.

⁹³ Plunkett, K. N.; Godula, K.; Nuckolls, C.; Tremblay, N.; Whalley, A. C.; Xiao, S *Org. Lett.* **2009**, *9*, 2225-2228.

⁹⁴ Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem. Int. Ed.* **2013**, *52*, 9900-9930.



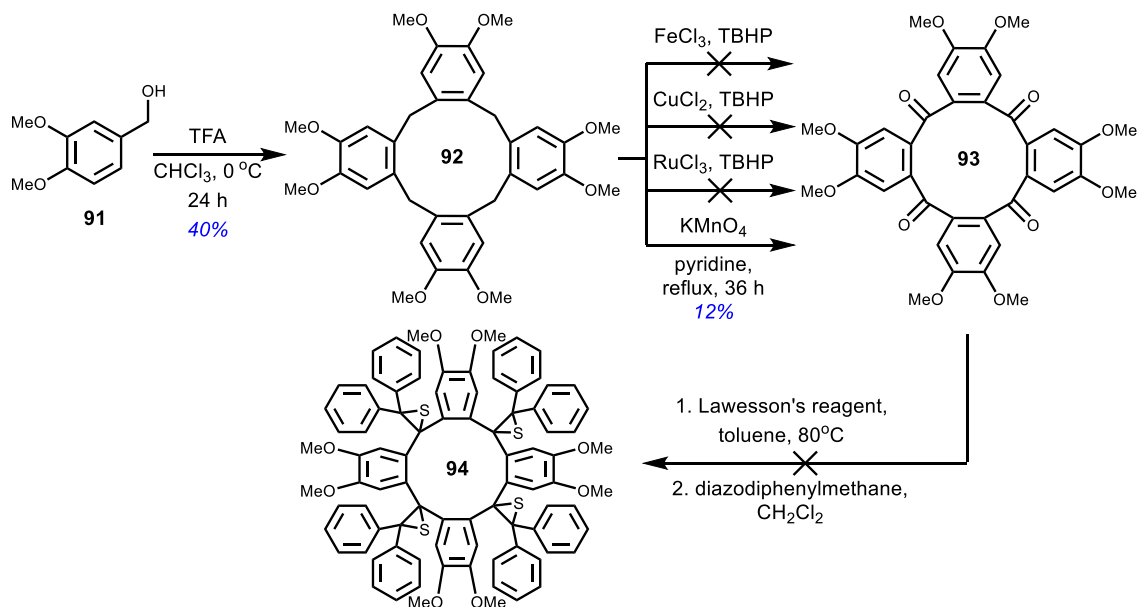
Scheme 2.21 Retrosynthetic plan to generate a new [12]circulene derivative using Barton-Kellogg olefination.

Cyclotetramerization of veratryl alcohol by slow addition to trifluoroacetic acid in chloroform is a previously reported procedure, generating **92** in a 40% yield along with the trimer, pentamer, and hexamer.⁹⁵ Oxidation of **92** to the tetraketone, also a previously reported procedure, was completed using 100 equivalents of KMnO_4 in refluxing pyridine in a 12% yield along with the mono-, di-, and triketone.⁹⁶ **93** was treated with Lawesson's reagent resulting in several new products seen by TLC analysis. These various products were collected by filtering the crude reaction mixture through a plug of silica before dissolving in chloroform and addition of a freshly made solution of diazodiphenylmethane. However, after purification, no product or starting material was detected by ^1H NMR.

⁹⁵ Al-Farhan, E.; Keehn, P. M.; Stevenson, R. *Tetrahedron Lett.* **1992**, *33*, 3591-3594.

⁹⁶ Lutz, M. R.; Zeller, M.; Sarsah, S. R. S.; Filipowicz, A.; Wouters, H.; Becker, D. P. *Supramol. Chem.* **2012**, *24*, 803-809.

While the various materials collected had reasonable aromatic signals, no peaks that corresponded to the methoxy groups could be found.



Scheme 2.22 Synthesis of tetraketone **93** and benzylic oxidation conditions attempted to increase yield; TBHP = tert-butyl hydroperoxide.

The ability to troubleshoot the Barton-Kellogg step required larger amounts of tetraketone **93**. In attempts to increase the yield of **93**, conditions known to oxidize benzylic positions using aqueous solutions of tert-butyl hydroperoxide (TBHP, 70%) and several Lewis acids were applied to **92**.^{97,98,99} Each set of conditions resulted in either recovery of the starting material or oxidation to the diketone. Difficulty increasing the yield of tetraketone **93** has prevented analysis of the results of the Barton-Kellogg

⁹⁷ Nakanishi, M.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 861-864.

⁹⁸ Rothenberg, G.; Feldberg, L; Wiener, H.; Sasson, Y. *J. Chem. Perkin. Trans.* **1998**, *2*, 2429-2434.

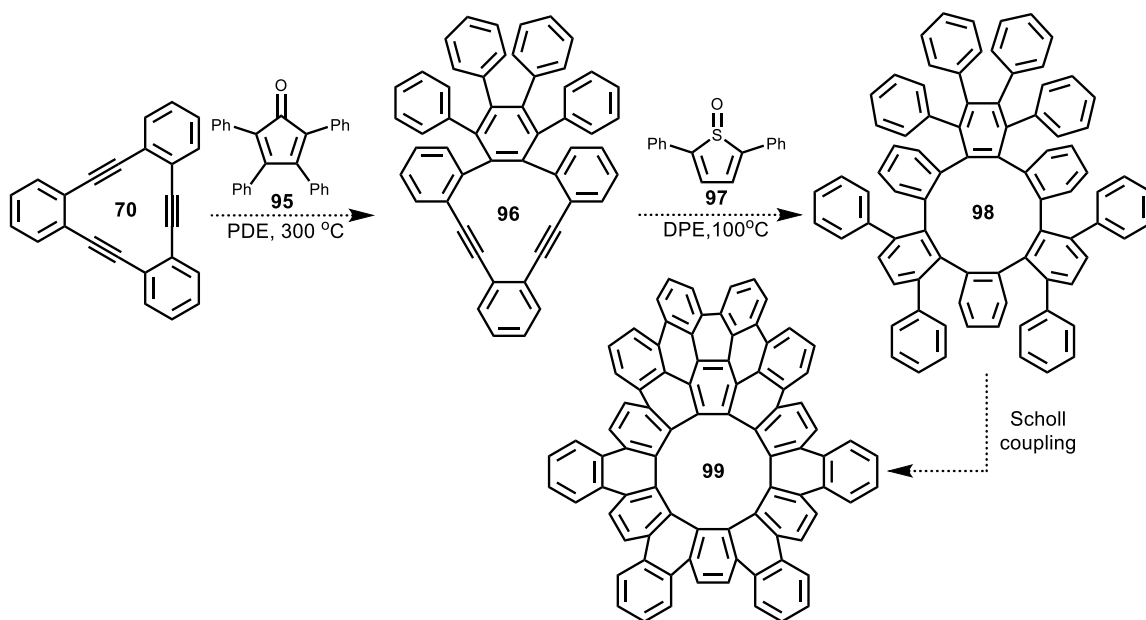
⁹⁹ Amaya, T.; Hifumi, M.; Okada, M.; Shimizu, Y.; Moriuchi, T.; Segawa, K.; Ando, Y.; Hirao, T. *J. Org. Chem.* **2011**, *76*, 8049-8052.

olefination. However, other projects in our group have made progress optimizing reaction conditions and their results may help improve this strategy to generate [12]circulene.

2.5 Outlook and Future Work

While several difficulties have been encountered attempting to generate [12]circulene derivatives, we believe our strategy of generating the [12]membered ring early is the best method to generate larger circulenes due to the difficulty in forming interior bonds as the size of the central ring increases. Methods developed in our lab also offer methods to functionalize circulenes after formation of the central ring. Future work on developing the Barton-Kellogg reaction shows promise in producing highly substituted derivatives of these and other strained molecules. Additionally, there is literature precedent in reacting [12]annulene in Diels-Alder cycloaddition reactions using cyclopentadieneones.¹⁰⁰ Using tetraphenylcyclopentadieneone (**95**, Scheme 2.23), a step-wise Diels-Alder sequence could be performed. Forcing the first Diels-Alder reaction to occur at 300 °C in a sealed tube could increase reactivity of the remaining alkynes and, upon cooling, allow the resulting intermediate to react with 2,5-diphenylthiophene oxide. Subsequent Scholl coupling could then be used to form an asymmetric [12]circulene derivative (**99**).

¹⁰⁰ Song, Q.; Lebeis, C. W.; Shen, X.; Ho, D. M.; Pascal, Jr., R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13732-13727.



Scheme 2.23 Proposed synthesis of an asymmetric [12]circulene derivative using step-wise Diels-Alder cycloadditions with two different dienes followed by Scholl coupling.

Chapter 3: SYNTHESIS AND CHARACTERIZATION OF NOVEL [1]BENZOTHIENO[3,2-b][1]BENZOTHIOPHENE DERIVATIVES

Thiophene-based materials have been of particular interest for use in OFETs as a result of their high charge carrier mobility, stability in OFET applications, solubility in organic solvents, and structural versatility.^{101,102} For example, liquid crystalline and electron transport properties of BTBT derivatives have been extensively studied. Initially, investigation into the liquid crystalline properties of polycyclic aromatic systems containing thiophene groups with alkane spacers led to synthesis of 2-alkyl and 2,7-dialkyl substituted BTBT derivatives. These alkylated BTBTs were obtained *via* Friedel-Crafts acylation followed by Wolff-Kishner reduction with the resulting products exhibiting liquid crystalline phase transitions.¹⁰³ This report showed the potential in using alkylated BTBT derivatives in electronic devices by highlighting their ability to form highly-ordered films. Though Kořata and coworkers were able to show that alkylated BTBTs self-organized, they did not report on any electronic data of their BTBT derivatives. Further investigation into BTBT to determine its utility in electronics applications is therefore a potentially beneficial avenue of research. This chapter focuses on the synthesis of novel BTBT derivatives containing electron-withdrawing groups and the difficulty in purification and processing of electronic devices using these materials.

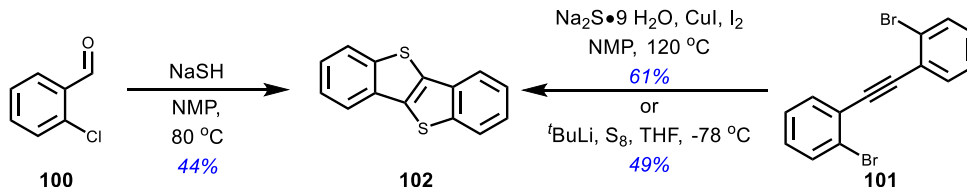
¹⁰¹ Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Adv. Phys. Lett.* **1996**, *69*, 4108.

¹⁰² Zhang, C.; Zhu, X. *Acc. Chem. Res.* **2017**, *50*, 1342-1350.

¹⁰³ Kořata, B.; Kosmík, V; Svoboda, J. *Liq. Cryst.* **2003**, *30*, 603-610.

3.1 Synthesis of [1]Benzothieno[3,2-b][1]benzothiophene

Synthesis of BTBT (**102**) can be accomplished in one step by heating 2-chlorobenzaldehyde (**100**) with sodium hydrosulfide in NMP.¹⁰⁴ This is typically the method used to generate the core structure when preparing functionalized BTBTs. Additionally, BTBT can be synthesized from bis-2-bromophenylacetylene (**101**) by treatment with sodium sulfide nonahydrate, copper (I) iodide, and iodine in NMP or tert-butyl lithium and sulfur in THF.^{105,106} Though higher yielding, these methods require synthesis of **101** via Sonogashira couplings.



Scheme 3.1 Synthetic processes to generate BTBT; ^tBuLi = tert-butyl lithium.

The first report of synthesizing functionalized BTBT was reported in 1980 and generated the desired 2,7-halogenated BTBTs (**108**) in eight steps starting from a nitrated stilbene disulfonate salt (**103**).¹⁰⁷ This report was problematic, however, as yields for individual derivatives were not reported and the methodology used for the conversion of sulfonate salt, **105**, to the corresponding sulfonyl chloride (**106**) was not described. This

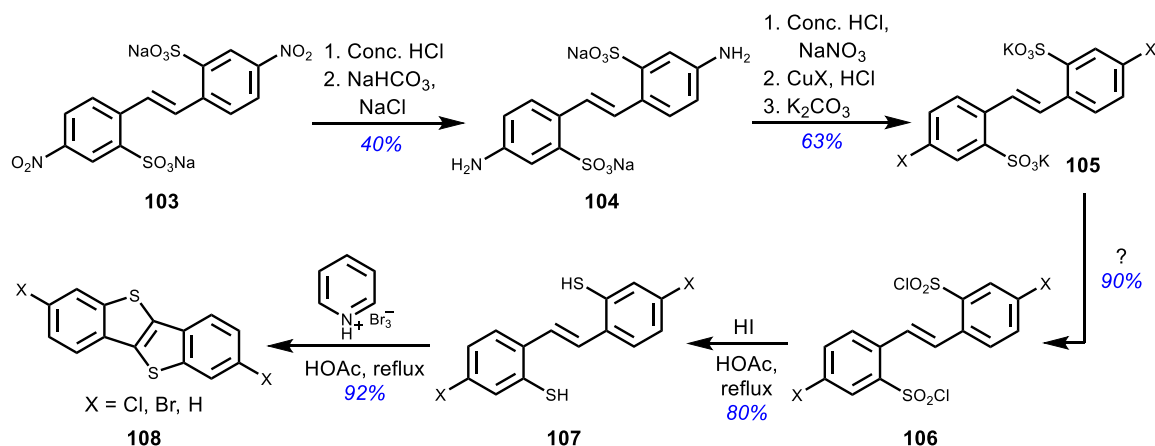
¹⁰⁴ Saito, M.; Yamamoto, T.; Osaka, I.; Miyazaki, E.; Takiyama, K.; Kuwabara, H.; Ikeda, M. *Tetrahedron Lett.* **2011**, *51*, 5277-5280.

¹⁰⁵ Li, Y.; Nie, C.; Wang, H.; Li, X.; Verpoort, F.; Duan, C. *Eur. J. Org. Chem.* **2011**, *36*, 7331-7338.

¹⁰⁶ Sashida, H.; Yasuike, S. *J. Heterocyclic Chem.* **1998**, *35*, 725-726.

¹⁰⁷ Zherdeva, S. Y.; Barudi, A. Y.; Stepanov, B. I. *Zh. Org. Khim.* **1980**, *16*, 430-438.

reference is, however, cited as the method to obtain 2,7-diiodo BTBT which was synthesized as the starting material in the production of 2,7-diphenyl BTBT (DPh-BTBT) by Takimiya and coworkers in 2006.¹⁰⁸ This was the first report to utilize BTBT derivatives in OFET devices, resulting in DPh-BTBT exhibiting mobilities as high as $2.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.



Scheme 3.2 First reported synthesis of halogen-functionalized BTBT derivatives. Though this gave access to functionalized BTBTs, the synthetic strategy proved difficult to execute effectively.

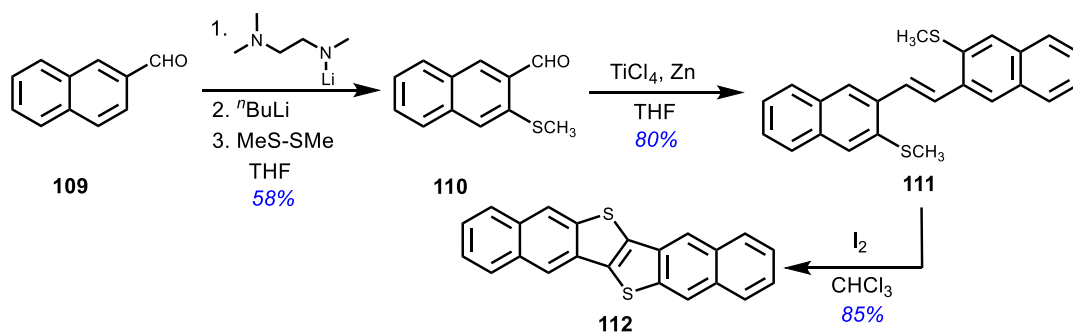
Overall, these methods are reasonable pathways to functionalized BTBTs and are generally cited as the methods used in the synthesis of functionalized derivatives. Despite being seemingly readily available and exhibiting very favorable electronic properties, commercially available functionalized BTBTs are still prohibitively expensive. At time of writing, 2,7-dialkyl, and DPh-BTBT derivatives cost approx. \$2500/gram and \$1400/gram,

¹⁰⁸ Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604-12605.

respectively. This indirectly illustrates the difficulty in synthesis and purification of BTBT derivatives.

3.1.1 Expanded π -System Derivatives

Following the initial report of DPh-BTBT's utility in OFET devices, Yamamoto and Takimiya synthesized the first extended π -system BTBT derivatives.¹⁰⁹ Generating the thiophene core of these systems required a modified strategy. Starting from commercially available 2-naphthaldehyde (**109**, scheme 3.3), an ortho-directed metallation procedure was followed using N,N,N'-trimethylethylenediamide and excess *n*-butyl lithium to generate the methylthiolated product (**110**) selectively at the 3-position in 58% yield. McMurry coupling of **110** using low-valent titanium produced the olefin intermediate (**111**) in good yields. Finally, **111** was treated with excess iodine in chloroform to generate dinaphthothienothiophene (**112**) with an 85% yield.



Scheme 3.3 Synthesis of dinaphthothienothiophene; *n*-BuLi = *n*-butyl lithium.

¹⁰⁹ Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224-2225.

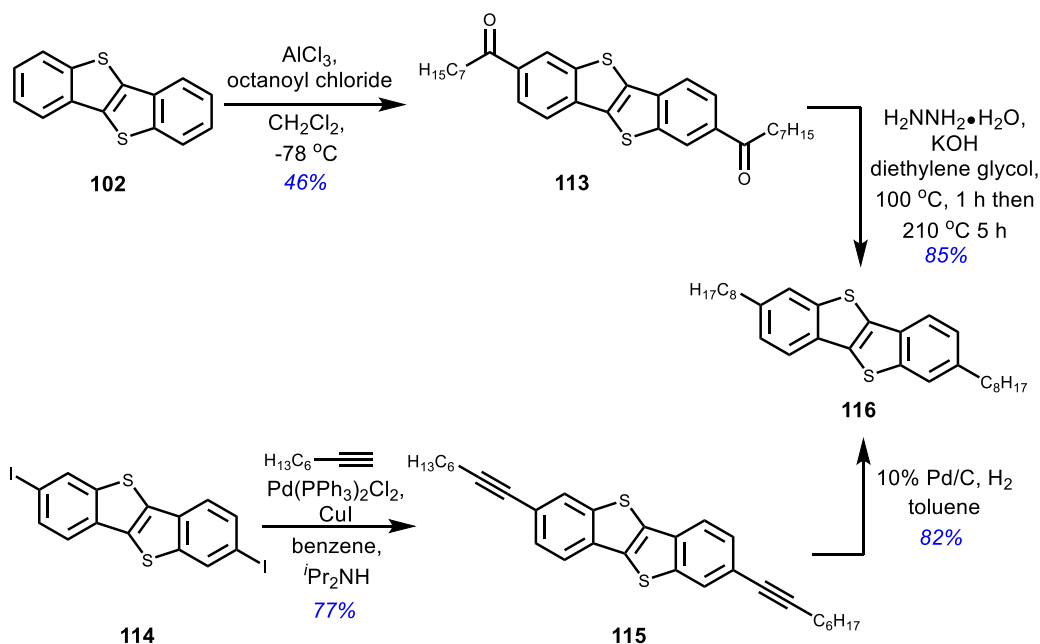
Purification of **112** was accomplished by vacuum sublimation or recrystallization to produce thermally stable yellow crystals. OFETs fabricated from **112** operated as p-type devices with average mobilities above $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The stability of these BTBT derivatives was due to the low-lying HOMO and large HOMO-LUMO gap relative to other extended arenes. However, reported in the same journal issue, 2,7-dialkyl-substituted BTBT derivatives were found to have superior field-effect mobilities.

3.1.2 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene

Košata and coworkers were the first to synthesize C8-BTBT by first reacting **102** with octanoyl chloride *via* Friedel-Crafts acylation to generate bis-(2,7-octan-1-one)[1]benzothienopheno[3,2-b]benzothienophene (**113**, scheme 3.4) in a 67% yield.⁸⁹ Subsequent Wolff-Kishner reduction produced C8-BTBT (**116**) in good yields. Liquid crystalline phase transitions of C8-BTBT were observed, indicating the possibility of highly ordered solid-state structure. Ebata and coworkers eventually used this methodology, as well as a Sonogashira/hydrogenation strategy starting from 2,7-diiodo BTBT (**114**) to generate analytically pure C8-BTBT as part of a series of alkylated BTBTs with chain lengths of C5-C14.¹¹⁰ The authors noted that only the octyl, decyl, and dodecyl derivatives were synthesized *via* the Friedel-Crafts method on larger scales, while all other

¹¹⁰ Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc.* **2007**, *129*, 15732-15733.

derivatives were more readily available *via* the Sonogashira method due to the commercial availability of the alkynes. Though these products are analytically pure after column chromatography, further purification is required for use in electronic devices. Generating sufficiently pure samples can be completed by successive recrystallizations or sublimation. The various alkylated BTBTs had electronic and optical properties which were nearly identical.

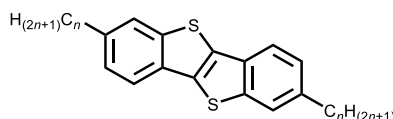


Scheme 3.4 Synthesis of C8-BTBT in two steps starting from either unsubstituted BTBT or 2,7-diiodo BTBT.

Spin coated films of C_n -BTBTs were found to be highly ordered by x-ray diffraction, with longer-chain derivatives having larger interlayer distances. Field-effect mobilities with a range of $0.16\text{-}2.75\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was found, with the C8 and C13 derivatives having the highest average mobility. Most derivatives were also found to be highly soluble in chloroform at room temperature with the solubility dropping as chain lengths increased

above C10. All alkylated derivatives were found to be stable during OFET operation under ambient conditions and in a solution of chloroform over 72 hours, conditions in which other organic semiconductors such as pentacene quickly decompose. A summary of Ebata and coworkers' results are shown in table 1.

Table 3.1 Summary of alkylated BTBT properties by Ebata et al.



<i>n</i>	Solubility (gL ⁻¹)	μ_{FET} (cm ² V ⁻¹ s ⁻¹)
5	>60	0.16-0.43
6	70	0.36-0.45
7	70	0.52-0.84
8	80	0.46-1.80
9	90	0.23-0.61
10	24	0.28-0.86
11	13	0.73-1.76
12	8.6	0.44-1.71
13	5.0	1.20-2.75
14	2.3	0.19-0.72

From these results C13-BTBT is the ideal candidate for use in OFETs. However, being able to generate BTBT from 2-chlorobenzaldehyde in one step allowed C8-BTBT to be generated in higher yields in only three steps due to the commercial availability of octanoyl chloride. In the years following this initial report, improvements to device processing has led to ever higher field-effect mobilities for C8-BTBT. Minemawari and coworkers' inkjet method, for example, produced single-crystal transistors with average mobilities of 16.4 cm²V⁻¹s⁻¹.⁵ Using an off-center spin-coating method, Yuan and

coworkers were able to generate transparent TFTs with the highest organic mobilities to date, up to $43 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with an average mobility of $25 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.¹¹¹

3.1.3 Limitations to Functionalization

While the improvements to fabrication of BTBT-based devices have allowed extremely high mobility for C8-BTBT, these devices have been limited to operating as p-type semiconductors. The lack of electron deficient derivatives are due to the inherent reactivity of the BTBT core. BTBT can be metallated at position 1 (figure 3.1) in the presence of butyllithium or undergo electrophilic aromatic substitution at positions 2, 4, and 7.¹¹²

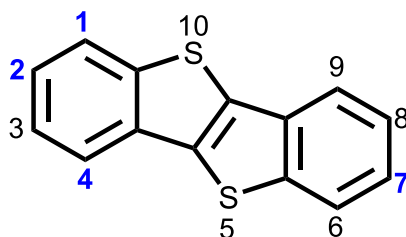


Figure 3.1 BTBT with positions 1-10 numbered; functionalization of the core structure has generally been limited to positions 1, 2, 4, and 7.

These limitations offered us an opportunity to expand the utility of BTBT derivatives by introduction of novel electron-withdrawing functionality. As seen in

¹¹¹ Yuan, Y.; Giri, G.; Ayzner, A. L.; Zoombelt A. P.; Mannsfield, S. C. B.; Chen, J.; Nordlud, D.; Toney, M. F.; Huang, J.; Bao, Z. *Nat. Commun.* **2014**, 5, 3005.

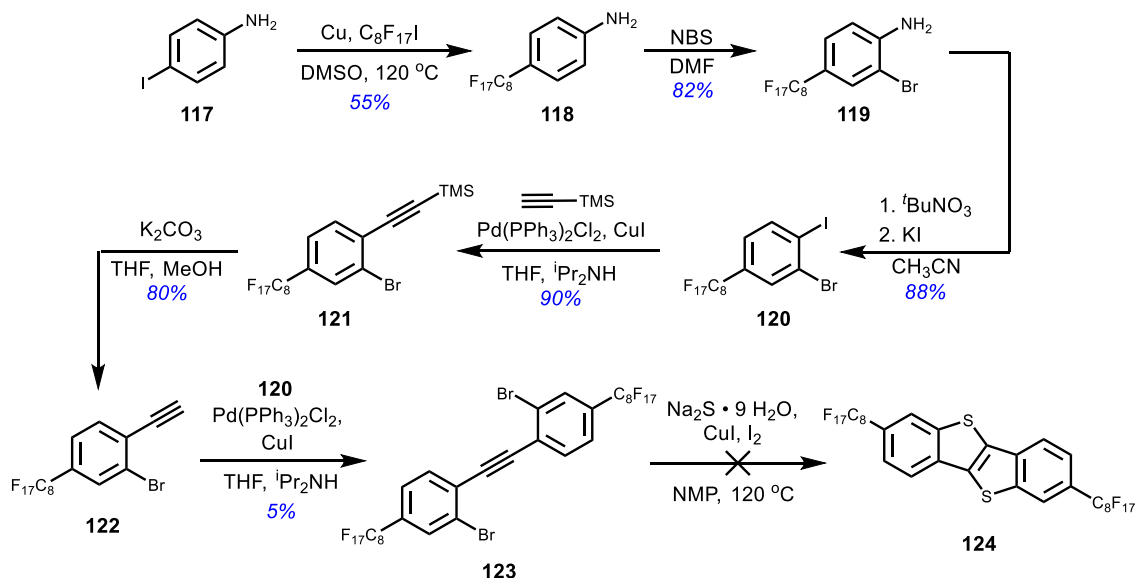
¹¹² Kořata, B.; Kosmík, V.; Svoboda, J. *Collect. Czech. Chem. Commun.* **2002**, 67, 645-664.

previous examples and because of BTBT's reactivity, functionalization is typically introduced after formation of the core structure. Therefore, our strategy was to introduce electron-withdrawing groups at an early stage and form the core thiophenes using known methods.^{91,92} Beyond tuning the electronic properties, alteration of the structure of BTBT would also likely have a large impact on the solid-state packing in device applications. Therefore, the main concern of introducing new functionality was preservation of solubility and favorable π - π interactions in the solid state.

3.2 2,7-Bis(perfluorooctyl)[1]benzothieno[3,2-b][1]benzothiophene

One of the most common strategies for generating electron deficient materials is by functionalization with perfluorinated alkyl chains. Therefore, our initial strategy for generating n-type BTBT derivatives was to introduce perfluorooctyl chains at an early stage in the synthesis and form the thiophene core using either Sashida and Yasuie or Li and coworkers' methods, the so-called thienannulations. Starting with 4-iodoaniline (**117**), copper-catalyzed cross coupling with perfluorooctyl iodide can be accomplished in moderate yields by heating in DMSO to generate 4-perfluorooctylaniline (**118**). Bromination with NBS produced 2-bromo-4-perfluorooctylaniline (**119**) in good yields. **119** underwent a Sandmeyer reaction to convert the aniline to the corresponding aryl iodide (**120**) in high yields. Sonogashira coupling with TMSA gave the cross coupled product (**121**) in 90% yield. Base-catalyzed deprotection using K_2CO_2 in a mixture of THF and

methanol gave the deprotected alkyne (**122**) in 80% yield. It was noted at this point that solubility dramatically decreased after removal of the TMS group. Nevertheless, Sonogashira coupling of **122** to aryl iodide **120** was attempted, with the cross-coupled product (**123**) only isolated in a 5% yield. The result of the Sonogashira coupling was a complex mixture of mostly insoluble products. A small amount of **123** was able to be isolated by trituration with dichloromethane and hot chloroform. **123** was treated with sodium sulfide nonahydrate, copper (I) iodide, and iodine in NMP, however, no perfluorooctyl-BTBT product was able to be detected.

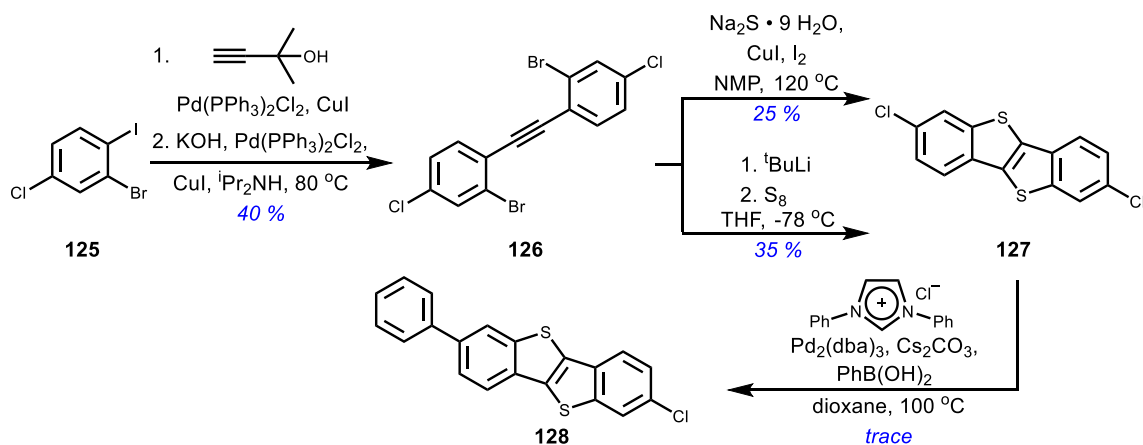


Scheme 3.5 Attempted synthesis of 2,7-perfluorooctyl-BTBT; low solubility of the alkyne precursor and, likely, the BTBT product prevented isolation; DMSO = dimethylsulfoxide; NBS = N-bromosuccinimide.

Isolation of **123** and **124** proved highly problematic due to the extremely low solubility of both materials in all conventional solvents. With no avenue to improve these conditions, other functionalization pathways were explored.

3.3 2,7-Dichloro[1]benzothieno[3,2-b][1]benzothiophene

Though DPh-BTBT is commercially available, there is a lack of other aryl-functionalized derivatives due to the difficulty in synthesizing the diiodo- and dibromo-BTBTs. Therefore, we devised an efficient synthetic strategy for generating diaryl-BTBTs. 2-Bromo-4-chloriodobenzene (**125**) was converted to 2,2'-dibromo-4,4'-dichlorophenylacetylene (**126**) in a one-pot Sonogashira coupling procedure using 2-methylbutyn-2-ol. Both sets of thienannulation conditions successfully generated 2,7-dichloro-BTBT (Cl-BTBT, **127**). Using Suzuki coupling conditions for aryl chlorides¹¹³, only one occasion resulted in evidence (MS and TLC) for the successful generation of the monocoupled product (**128**). However, low solubility and yield prevented isolation of **128**.



Scheme 3.6 Attempted synthesis of DPh-BTBT via Suzuki coupling resulted in successful synthesis of 2,7-dichloro-BTBT; dba = dibenzylideneacetone

¹¹³ Zhang, C.; Trudell, M. L. *Tetrahedron Lett.* **2000**, *41*, 595-598.

Unfortunately, this methodology was unable to generate DPh-BTBT. Though the thienannulation conditions worked reasonably well, and Cl-BTBT was pure by NMR spectroscopy; significant difficulty was encountered while trying to remove sulfur byproducts even after successive recrystallizations. This, however, does not completely explain the partial reaction under Suzuki coupling conditions as additional reagents were added after partial conversion of the starting material which did not improve the yield. Due to the inability to use this methodology to efficiently generate diaryl-substituted BTBTs, our focus returned to generating electron deficient derivatives.

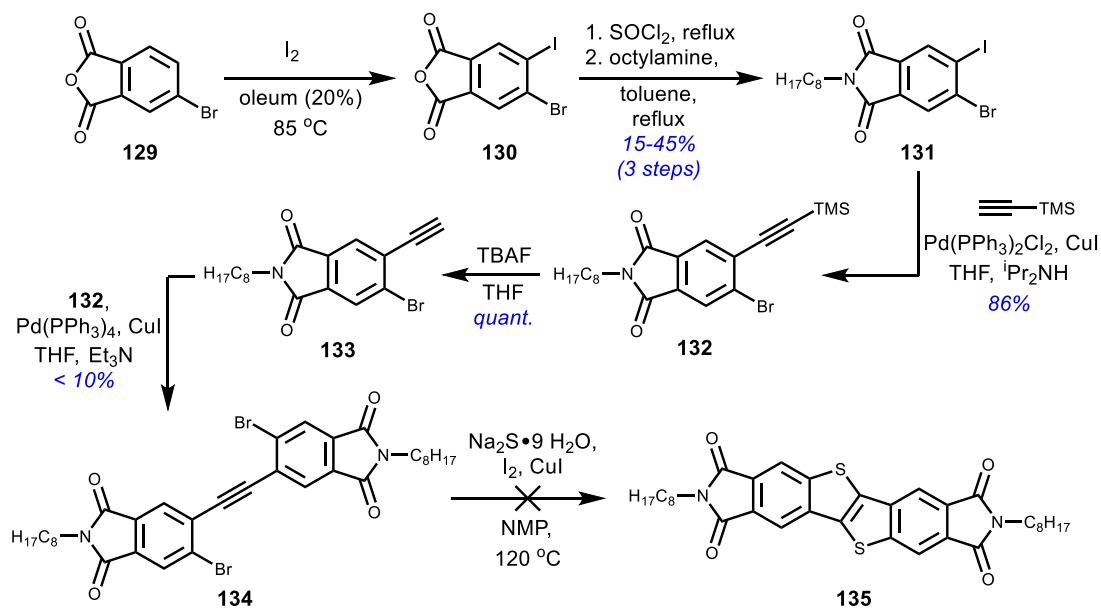
3.4 Diimide-Functionalized [1]Benzothieno[3,2-b][1]benzothiophene

Interest in imide-functionalized compounds such as PDIs, decacyclene triimides, and triphenylene triimides and their electronic properties, particularly their n-type semiconducting ability, led to our decision to incorporate imide functional groups into BTBT as a strategy to develop high mobility n-type organic materials. As shown with the synthesis of CDIs, a simple procedure to generate imides is the conversion from corresponding anhydrides by treatment with primary amines.⁵² Using this strategy to install imides was therefore incorporated into the synthesis of BTBT.

Commercially available 4-bromophthalic anhydride (**129**) was used as the starting anhydride as there is a previously reported method for iodination at the 5-position.¹¹⁴ **129**

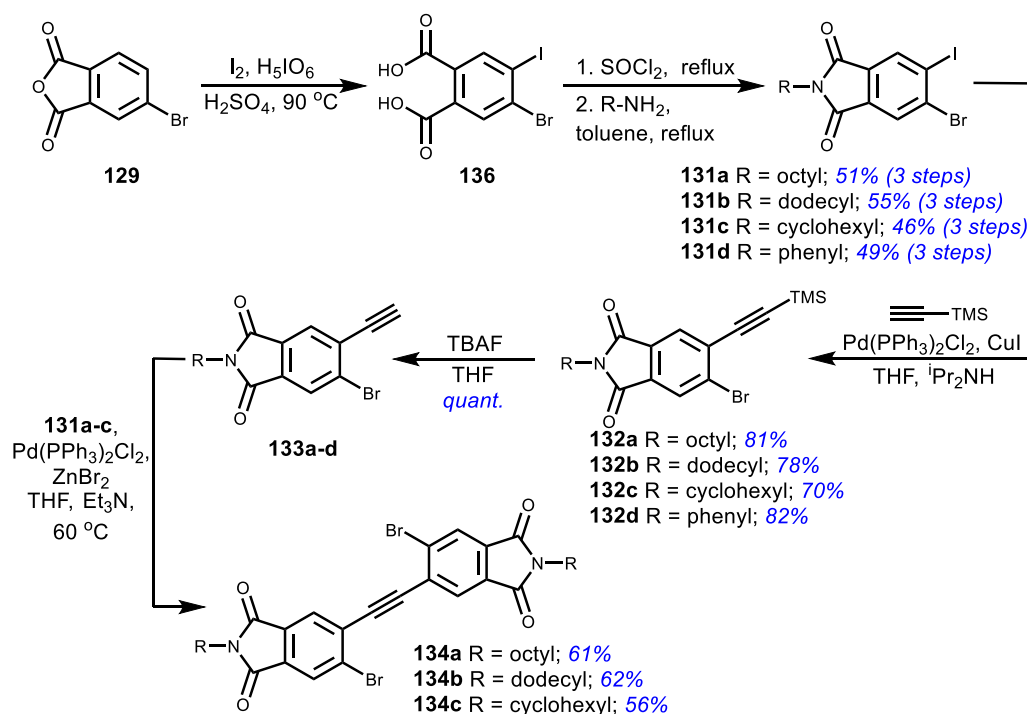
¹¹⁴ Leu, W. C. W.; Hartley, S. *Org. Lett.* **2013**, *15*, 3762-3765.

was iodinated by heating in a solution of fuming sulfuric acid in the presence of iodine. After purification, treatment of the crude product with refluxing thionyl chloride followed by addition of octylamine and refluxing in toluene produced the N-octylimide (**131**). Several issues would often be encountered during workup of the iodination step leading to the inconsistent 15-45% yields observed over three steps. Sonogashira coupling of **131** proceeded well with the monocoupled alkyne (**132**) isolated in 86% yield. Deprotection of the alkyne using TBAF generated terminal alkyne, **133**, in quantitative yield. Unfortunately, Sonogashira coupling conditions to generate alkyne **134** resulted in difficulties noted in earlier procedures utilizing electron deficient alkynes resulting in yields below 10%. Though yields were very low, initial attempts to generate BTBT using sodium sulfide nonahydrate were attempted, resulting in no product being isolated.



Scheme 3.7 Initial strategy to generate diimide-substituted BTBT derivatives; low yields required alternate methods for iodination and Sonogashira coupling.

The very low overall yield to obtain **134** required changes to the iodination and second coupling steps. The iodination step was vastly improved using a method for the periodination of phthalic anhydride.¹¹⁵ A stoichiometric iodate solution was generated by the addition of iodine to periodic acid in sulfuric acid and heating at 90 °C. This reaction varied and was generally allowed to continue until the brown iodate solution gave way to a yellow solution, typically in 12-16 hours. Quenching and filtration of this reaction resulted a yellow precipitate which was dissolved in saturated K₂CO₃ and reacidified with HCl which produced 4-bromo-5-iodophthalic acid (**136**). These changes resulted in generation of the iodinated imide in yields averaging around 50%.

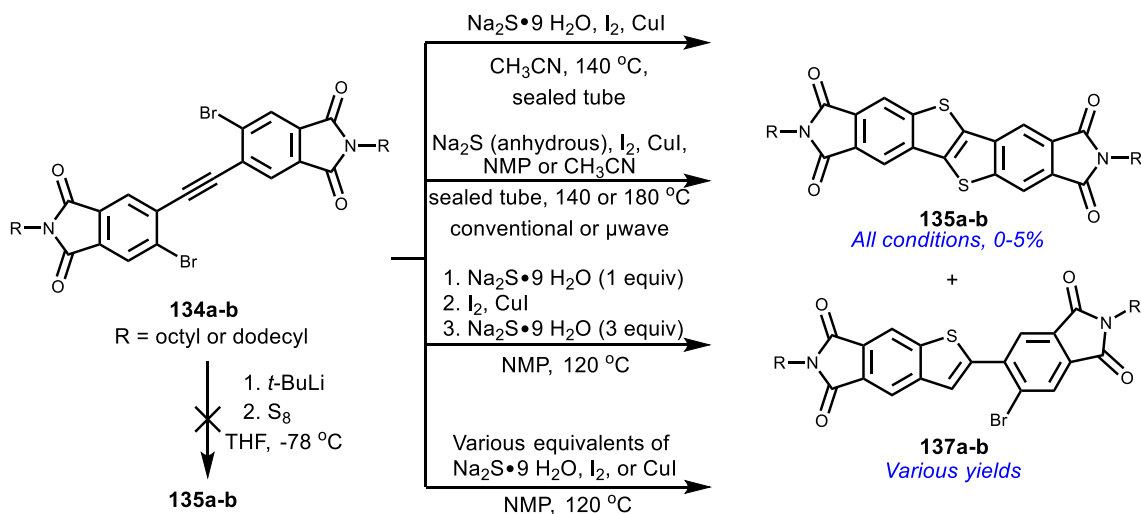


Scheme 3.8 Revised synthesis of BTBT diimide precursors, the increased yields allowed synthesis of **136a-d** in large enough quantities to attempt thienannulation reactions.

¹¹⁵ Mattern, D. L. *J. Org. Chem.* **1984**, *49*, 3051-3053.

All Sonogashira conditions utilized in the second coupling step resulted low yields or no product formation. Switching to Negishi coupling conditions resulted in successful cross coupling to generate diimides **134a-c**. These diimides precipitated out of solution and were collected *via* vacuum filtration and washed with methanol, leaving bright yellow precipitates in much improved 50-60% yields. Additionally, Negishi coupling conditions resulted in no detectable homocoupled product as seen under Sonogashira conditions.

With access to **134a-b**, generation of the thiophene core was attempted using the sodium sulfide nonahydrate thienannulation conditions. Unfortunately, these conditions resulted in formation of a highly insoluble precipitate which, after filtration and washing with acetone and dichloromethane, could not be characterized. Mass spectrometry data of the crude reaction mixture indicated the presence of the desired product, however. Therefore, thienannulation conditions using the octyl- and dodecyl-derivatives were adjusted to increase yield of the desired product.

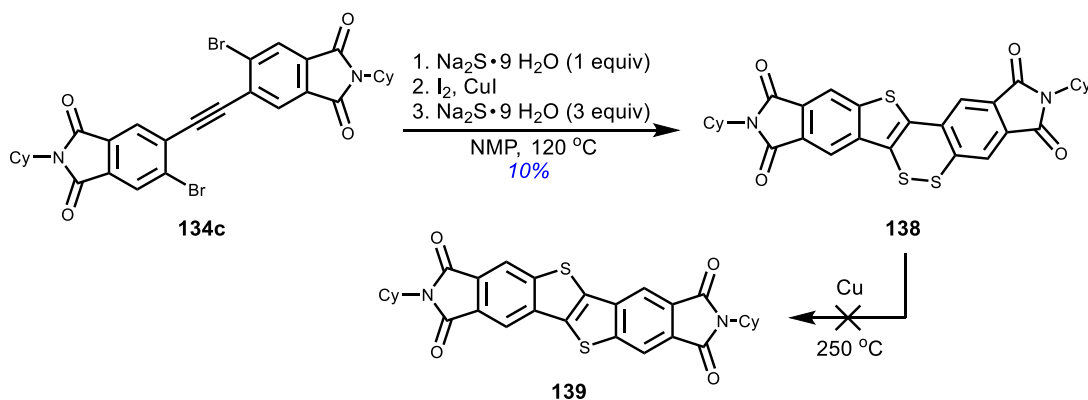


Scheme 3.9 Various conditions attempted to generate BTBT diimides.

Unfortunately, under all conditions only small quantities of the desired product was ever detected. Insolubility of the products prevented purification by column chromatography and recrystallization from toluene or chloroform was ineffective in removing unknown contaminants. Small (less than 5 mg) amounts of **135a-b** were isolated in some cases *via* column chromatography after washing the column with boiling chloroform. These yields were far too low and of poor purity to be thoroughly characterized and, after finding the products of these thienannulation reactions highly insoluble, the cyclohexyl (**134c**) and asymmetric phenyl (**140**) alkyne derivatives were synthesized and subjected to thienannulation conditions (schemes 3.10 and 3.11, respectively). The cyclohexyl derivative was expected to have increased solubility, potentially eliminating purification difficulties. Synthesis of **140** was completed to determine if a lower molecular weight imide-substituted BTBT derivative could be isolated *via* vacuum sublimation.

There was a noticeable increase in the solubility of **134c** before treatment with thienannulation conditions. Analysis by TLC and increased solubility upon workup suggested the product could be purified by column chromatography. This resulted in isolation of a bright orange solid without the need to wash the column with boiling chloroform. ¹H NMR and ¹³C NMR analysis of this material revealed signals which suggested an asymmetric product. It should be noted all derivatives of BTBT are not asymmetric after generation of the thiophene core. Mass spectrometry of this product revealed a 575.3 m/z peak, 32 m/z higher than the expected protonated molecular ion peak (MH⁺) of 543 m/z. This data indicated that the disulfide derivative (**138**) was generated

instead of the desired second fused thiophene. Similar disulfide compounds were encountered by Hagashino and coworkers in their synthesis of hydroxy-substituted BTBT derivatives.¹¹⁶ While dechalcogenation conditions with copper mesh at 250 °C proved successful in their case, no N-cyclohexyl-BTBT-diimide product was able to be isolated in our case.

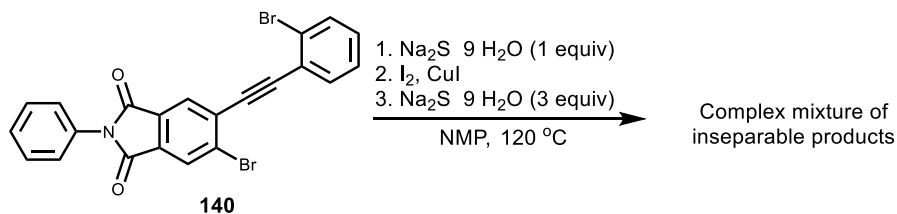


Scheme 3.10 Attempted thienannulation to N-cyclohexyl-BTBT-diimide resulted in the disulfide derivative (**138**) which could not successfully be converted to the desired BTBT derivative (**139**).

Subjecting the asymmetric phenyl derivative to the same thienannulation conditions once again resulted in a highly insoluble mixture of products. The crude material was therefore filtered and washed with acetone and dichloromethane before attempting to purify by sublimation under vacuum. This resulted in apparent decomposition of most of the crude material. An insoluble colorless solid was collected which was unable to be characterized by NMR or mass spectrometry. However, this

¹¹⁶ Higashino, T.; Ueda, A.; Yoshida, J.; Mori, H. *Chem. Commun.* **2017**, 53, 3426-3429.

material appeared to be an allotrope or compound of sulfur as reheating caused it to melt and, upon cooling, to form a bright yellow solid that smelled of hydrogen sulfide.



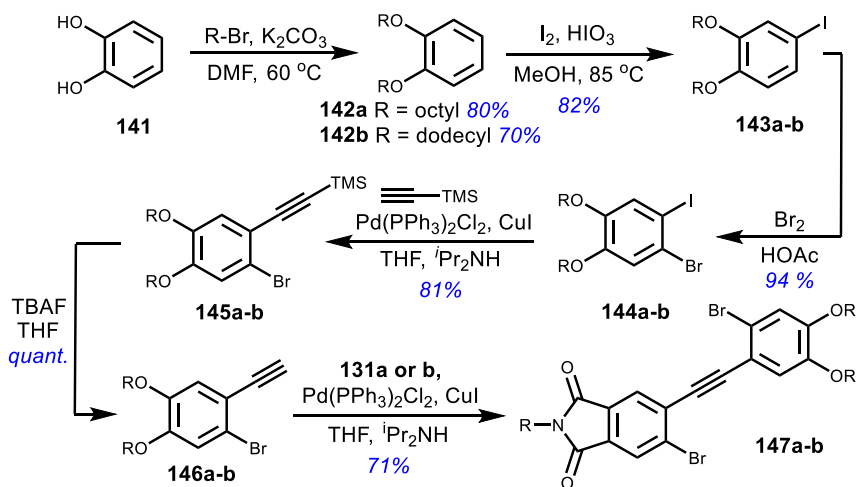
Scheme 3.11 Subjecting **140** to thienannulation conditions produced an insoluble crude material that could not be purified.

The inability to isolate the desired BTBT derivatives from either of these reactions led us to believe these conditions are inherently problematic for substrates containing strongly electron-withdrawing groups. Therefore, an alternative strategy for synthesis of novel BTBT derivatives was devised in an attempt to overcome these problems.

3.5 Push-Pull-Functionalized [1]Benzothieno[3,2-b][1]benzothiophene

Following the significant difficulties encountered during synthesis of BTBT-diimides, our focus switched to synthesis of so-called push-pull compounds. There were two reasons behind this strategy. First, additional alkyl chains could be installed to increase solubility and the presence of electron-donating groups would alleviate some of the difficulty in generation of the second thiophene in the BTBT core. We envisioned using a similar synthetic strategy to couple the electron rich and electron deficient substituents followed by thienannulation.

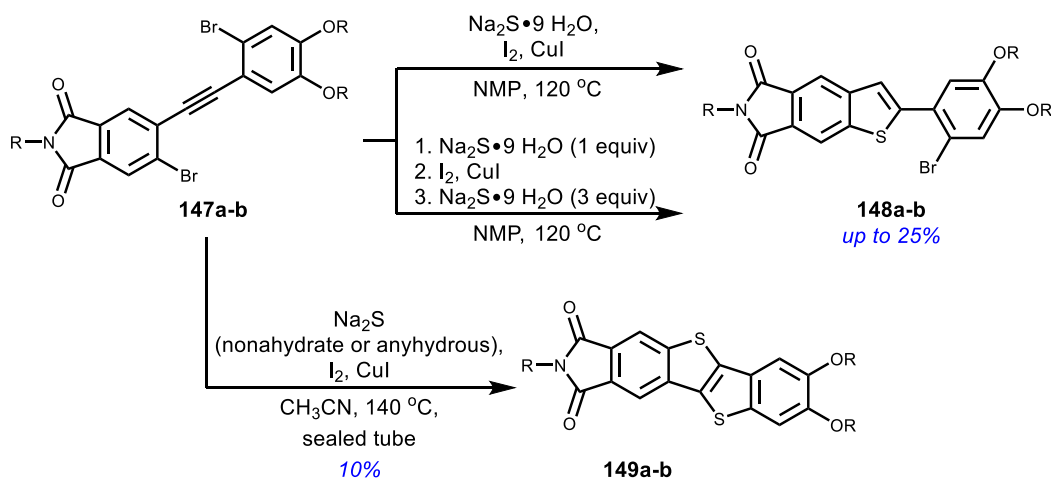
Williamson ether synthesis with catechol (**141**, scheme 3.12) using 1-bromooctane or 1-bromododecane proceeded well. Isolation of the dodecyl-derivative was lower yielding due to the difficulty in removing excess alkyl halide. However, there was no notable difference in yields between the two derivatives following this step. Iodination of both 1,2-dialkoxybenzene derivatives (**142a-b**) was completed in good yields by generating a stoichiometric iodate solution using iodine and iodic acid in methanol.¹¹⁷ This was followed by bromination in acetic acid to generate 1-bromo-2-iodo-4,5-dialkoxybenzene derivatives (**144a-b**) in high yields. Standard Sonogashira coupling conditions with TMSA generated the monocoupled products (**145a-b**) in good yields which was followed by treatment with TBAF to generate the terminal alkynes (**146a-b**) in quantitative yields. Sonogashira coupling with the corresponding imides (**131a-b**) generated the desired cross coupled products (**147a-b**) in good yields. Unfortunately, solubility of these alkynes did not appear to be significantly improved.



Scheme 3.12 Synthesis of alkynes **147a-b** proceeded well and in overall good yields.

¹¹⁷ Mujahidin, D.; Doye, S. *Eur. J. Org. Chem.* **2005**, 13, 2689-2693.

Subjecting alkynes **147a-b** to thienannulation conditions again resulted in insoluble crude mixtures and, most often, resulted in the formation of only one thiophene (**148a-b**, scheme 3.13). Both standard conditions and stepwise addition resulted in generation of **148a-b**. After finding thiophenes could be generated using anhydrous potassium sulfide in acetonitrile in a sealed reaction vessel, **147a-b** were subjected to these conditions using anhydrous sodium sulfide.¹¹⁸ This copper-catalyzed C-S coupling required no addition of a ligand, contrary to typical Ullmann coupling conditions. Isolation of the single thiophene product in many of the reaction conditions also gave the impression that removal of water from the system would prevent quenching by protonation of the charged intermediate (scheme 3.14). Under these conditions, the products, **149a-b**, were obtained in low yields.



Scheme 3.13 Thienannulation conditions leading to successful synthesis of push-pull BTBT derivatives.

There was a notable increase in the solubility of compounds **149a-b** as they were able to be isolated by column chromatography using a mixture of hexanes and chloroform

¹¹⁸ You, W.; Yan, X.; Liao, Q.; Xi, C. *Org. Lett.* **2010**, *12*, 3930-3933.

as the eluent. The purified products, 2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-dicarboxylic imide (DC8O-BTBT-I) and 2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-dicarboxylic imide (DC12O-BTBT-I), are fluorescent bright yellow solids. The structure of the products was confirmed by ^1H NMR and HRMS. Though these materials are more soluble than their diimide counterparts, characterization by ^{13}C NMR proved unsuccessful.

We were unable to obtain reliable electrochemical data or mobility data (*via* spin coating) due to the low solubility of the products. However, the products were able to be investigated by UV/Vis spectroscopy (figure 3.2) and compared to C8-BTBT, the octyl and dodecyl derivatives had no discernable difference in their absorption spectra. The optical HOMO-LUMO gap was calculated to be 2.863 eV, significantly reduced relative to the calculated optical HOMO-LUMO gap of 3.605 eV for C8-BTBT. This result was expected due to the incorporation of EDGs and EWGs raising the HOMO and lowering the LUMO, respectively. Without reliable electrochemical or mobility data we chose to ask our collaborators to generate predicted spectra for comparison. TDDFT calculations were performed on truncated compound **149** using the BLYP functional and TZVP basis set. The calculated spectrum gave a reasonably accurate prediction compared to the experimental data with a theoretical lowest energy transition value of 2.537 eV.^{119,120,121}

¹¹⁹ Beck, A. D.; *Phys. Rev. A* **1988**, *38*, 3098-3100.

¹²⁰ Lee, C.; Yang, W.; Parr, R. *Condens. Matter Mater. Phys.* **1988**, *37*, 785-789.

¹²¹ Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571-2577.

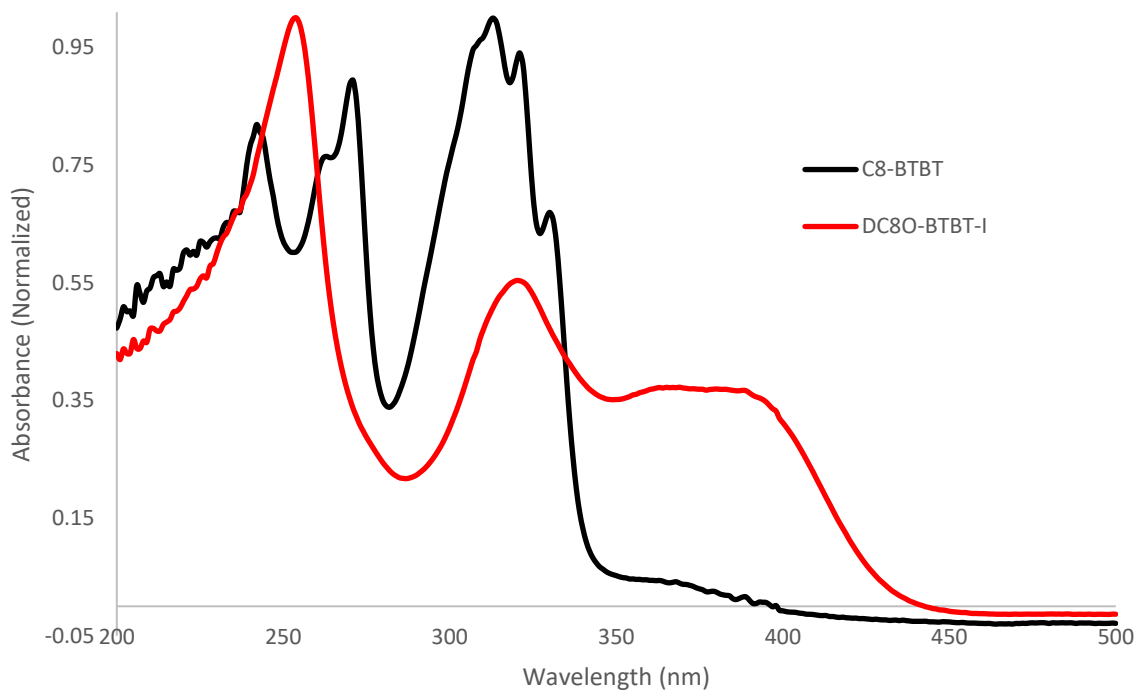


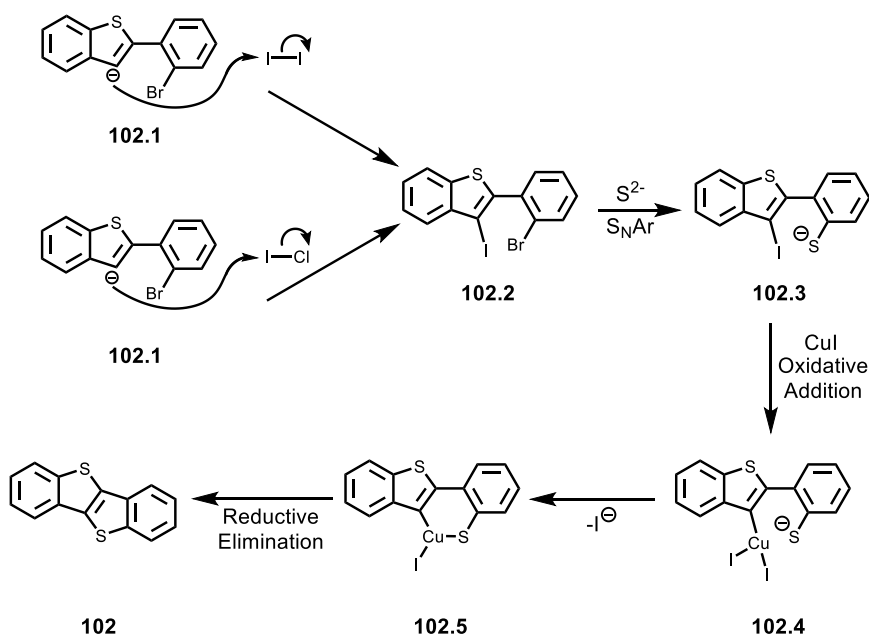
Figure 3.2 UV/Vis absorbance spectra of C8-BTBT and DC8O-BTBT-I in CH₂Cl₂ (~50 μM).

Due to the low solubility of these compounds full electronic characterization was unable to be completed. However, the methods attempted to obtain this data was by no means exhaustive, leaving open the possibility of further investigation into the electronic properties of these materials.

3.6 Outlook and Future Work

The significant difficulty in generating the BTBT core using thienannulation conditions was the major limitation to producing diimide-functionalized derivatives. All attempts to alter these conditions failed to improve the results of these reactions. Though

these alterations were extensive, the possibility of improving the yield remains. For example, based on Li and coworkers' optimization of the reaction conditions, generation of intermediate **102.2** (Scheme 3.14) is due to the nucleophilic attack on elemental iodine. The presence of EWGs during this step would likely significantly hinder this attack. Therefore, use of a more electrophilic iodine source, such as iodine monochloride in the stepwise procedure could improve product yield.



Scheme 3.14 Possible mechanism of thienannulation to generate BTBT; a more electrophilic iodine source may improve reaction yield.

Continued work processing devices from the push-pull BTBT derivatives (**149a-b**) should be completed as the mobility data of these materials is crucial in evaluating their utility in electronic devices. Additionally, investigation of the fluorescence and electrochemical properties of these compounds are required for a thorough understanding of the optical and electronic properties of these novel compounds.

Chapter 4: EXPERIMENTAL PROCEDURES

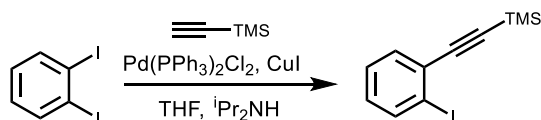
4.1 Methods and Materials

All commercially available starting materials were purchased from Sigma-Aldrich, Fisher Scientific, Matrix Chemical, or Oakwood Chemical and used without further purification unless stated otherwise. Anhydrous and anaerobic solvents were obtained from purification columns (Pure Process Technology, Nashua, NH). All reactions were run under a nitrogen atmosphere and those monitored by TLC were done so using silica gel 60 F₂₅₄ precoated plates (Silicycle, Quebec City, Québec). Column chromatography was performed on a CombiFlash R_f200 system using RediSep normal phase silica columns (ISCO, Inc., Lincoln, NE) unless stated otherwise. ¹H NMR spectra were collected on either a Bruker Ascend 500 MHz (Bruker, Billerica, MA) or Varian 500 MHz spectrometer (Varian Medical Systems, Palo Alto, CA). ¹³C NMR spectra were collected on a Bruker Ascend 500 MHz spectrometer at 125 MHz. All spectra were calibrated to an internal tetramethylsilane (TMS) standard. High-resolution mass spectra were recorded on a Waters Xevo G2-XS LCMS-QTOF spectrometer (Waters Corp., Milford, MA). Low-resolution mass spectra were recorded on a Bruker Daltonics UltrafleXtreme MALDI-TOF-MS. UV-Vis spectra were obtained on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan).

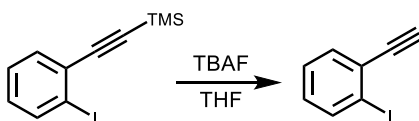
General procedure for the Sonogashira cross coupling of aryl halides and TMSA: A 5:1 mixture of THF and $i\text{-Pr}_2\text{NH}$ was added to a flame-dried round bottom flask equipped with a stir bar and degassed by bubbling N_2 through the solution for 20 minutes. Aryl halide (1.0 equiv.), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.02 equiv.), CuI (0.02 equiv.), and trimethylsilyl acetylene (1.05 equiv.) were then added and the reaction was stirred until determined complete by TLC. The reaction was then quenched with saturated NH_4Cl and extracted with EtOAc . The combined organic layers were dried with MgSO_4 , filtered, and the solvent removed under reduced pressure.

General procedure for the deprotection of silane-protected alkynes: THF was added to a flame-dried round bottom flask equipped with a stir bar and degassed by bubbling N_2 through the solution for 20 minutes. Silane-protected alkyne (1.0 equiv.) was then added before cooling the solution in an ice-water bath. A 1.0 M solution of TBAF in THF (1.05 equiv.) was then added dropwise. After addition, the cold bath was removed and the reaction mixture was analyzed by TLC. Upon completion, the reaction was quenched with saturated NH_4Cl and extracted with EtOAc . The combined organic layers were dried with MgSO_4 , filtered, and the solvent was removed under reduced pressure.

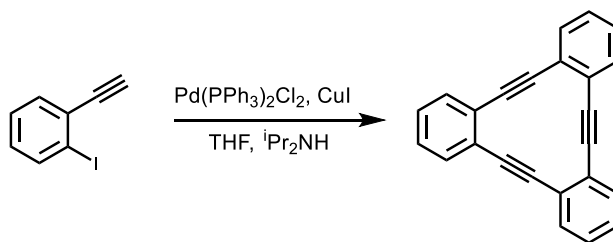
**4.2 Experimental Procedures for CONTORTED POLYCYCLIC AROMATIC
HYDROCARBONS: ATTEMPTED SYNTHESIS OF [12]CIRCULENE
DERIVATIVES**



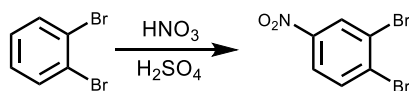
Synthesis of (2-iodophenylethynyl)trimethylsilane (75): The general Sonogashira cross coupling procedure was followed. **77** was purified by column chromatography (SiO₂, hexanes) as an orange oil. TLC (hexanes) $R_f = 0.35$. Spectral characterization matched literature values.⁷⁴



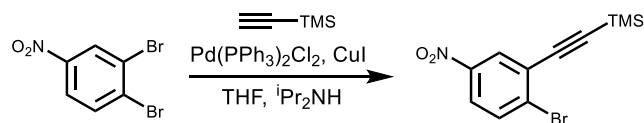
Synthesis of 1-iodo-2-ethynylbenzene (76): The general deprotection method was followed. **78** was purified by column chromatography (SiO₂, hexanes) as a pale-yellow oil. TLC (hexanes) $R_f = 0.4$. Spectral characterization matched literature values.⁷⁴



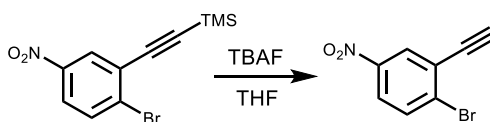
Synthesis of tribenzohexadehydro[12]annulene (70): The general Sonogashira coupling procedure leaving out TMSA was followed. The product was purified according to the previously reported method and produced the product as a bright yellow crystalline material in 46% yield. Spectral characterization matched literature values.⁷⁴



Synthesis of 3,4-dibromonitrobenzene (79): 30 mL of concentrated sulfuric acid was added to 30 mL nitric acid were combined in a round bottom flask equipped with a stir bar at 0 °C and stirred for 30 min. before dropwise addition of 5 mL of 1,2-dibromobenzene (**80**, 41.4 mmol) and the reaction mixture was warmed to RT. The reaction was then heated at 50 °C for 18 h then poured over crushed ice, filtered through a fritted funnel, and washed with and cold water. The crude material was then dissolved in DCM and washed with saturated sodium bicarbonate was purified by column chromatography (SiO₂, 10% EtOAc/hexanes) to give 9.88 g (85% yield) of product as a yellow solid. TLC (10% EtOAc/hexanes) $R_f = 0.5$ ¹H NMR (500 MHz, CDCl₃): $\delta = 8.681$ (s, $J = 2$ Hz, 1H), 8.146 (dd, $J = 4$ Hz, 1H), 7.573 ppm (d, $J = 7$ Hz, 1H).

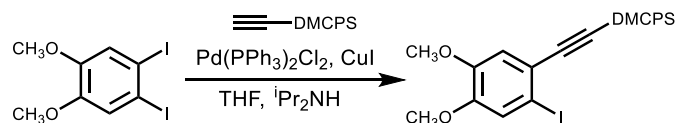


Synthesis of (2-bromo-5-nitrophenylethynyl)trimethylsilane (80): The general Sonogashira cross coupling procedure was followed. The crude material was purified by column chromatography (SiO₂, 20% DCM/hexanes). Spectral characterization matched literature values.¹²²

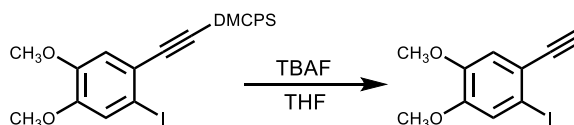


Synthesis of 1-bromo-2-ethynyl-4-nitrobenzene (82): The general TMS deprotection method was followed resulting in collection. The crude material was purified by passing through a plug of silica and washing with a 1:1 mixture of DCM/hexanes. ¹H NMR (500 MHz, CDCl₃): δ = 8.697 (d, J = 2 Hz, 1H), 8.171, (dd, J = 7.5, 2 Hz, 1H), 7.635 (d, J = 8.5 Hz, 1H), 3.687 ppm (s, 1H).

¹²² Blaszczyk, A.; Chadim, M.; Von Haenisch, C.; Mayor, M.; *Eur. J. Org. Chem.* **2006**, *17*, 3809-3825.

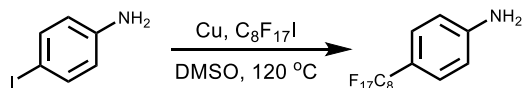


Synthesis of 2-iodo-4,5-dimethoxyphenylethynylcyanopropyltrimethylsilyl ether (88): The general Sonogashira cross coupling procedure was followed using the polar protected alkyne (**87**) instead of TMSA. The product was purified by column chromatography (SiO_2 , 25% EtOAc/hexanes) to produce a pale-yellow oil in 30% yield. TLC $R_f = 0.5$. $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.210$ (s, 1H), 6.956 (s, 1H), 3.870 (s, 3H), 3.861 (s, 3H), 2.449 (t, $J = 7$ Hz, 2H), 1.932-1.870 (m, 2H), 1.259 (t, $J = 7$, 2H), 0.285 ppm (s, 6H).

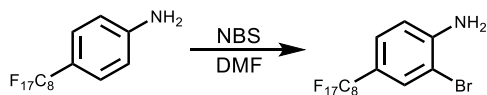


Synthesis of 1-ethynyl-2-iodo-4,5-dimethoxybenzene (89): The standard deprotection procedure was followed. The product was purified by passing through a silica plug and washing with a 100% DCM to produce a colorless liquid in 73% yield that decomposed to a black liquid. Spectral characterization matched literature values.⁷⁴

4.3 Experimental Procedures for SYNTHESIS AND CHARACTERIZATION OF NOVEL [1]BENZOTHIENO[3,2-b][1]BENZOTHIOPHENE DERIVATIVES



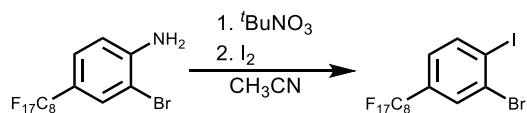
Synthesis of 4-perfluorooctylaniline (118): DMSO (25 mL) was added to a round bottom flask equipped with a stir bar and degassed by bubbling N₂ for 15 minutes. 4-iodoaniline (1.50 g, 6.75 mmol), Cu powder (1.89 g, 29.7 mmol), and perfluorooctyl iodide (1.90 mL, 7.20 mmol) were then added and the reaction heated at 120 °C for 24 h. Workup procedure followed a previously reported.¹²³ **118** was obtained as a colorless solid in 55% yield. Spectral characterization matched literature values.¹⁰⁹



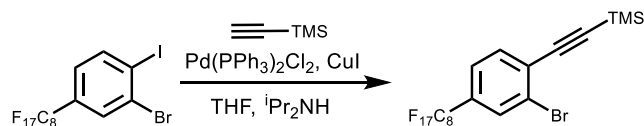
Synthesis of 2-bromo-4-perfluorooctylaniline (119): Anhydrous DMF was added to a flame-dried round bottom flask followed by 4-perfluorooctylaniline (1.05 g, 2.05 mmol) and NBS (375 mg, 2.10 mmol). The reaction was allowed to stir for 18 h before addition of 100 mL of water. **119** was extracted with chloroform and the combined organic layers were washed brine and 3 x 100 mL water. The combined organic layers were then dried with MgSO₄, filtered, and the solvent removed under reduced pressure. Recrystallization

¹²³ Crich, D.; Hao, X.; Lucas, M. A. *Org. Lett.* **1999**, *1*, 269-271.

of the crude material from hexanes/chloroform gave a bright orange solid that was taken forward without further purification due to the low solubility of the material.

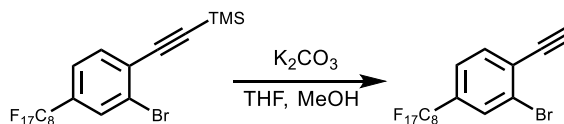


Synthesis of 2-bromo-1-iodo-4-perfluorooctylbenzene (120): Acetonitrile was added to a round bottom flask equipped with a stir bar and degassed by bubbling N₂ through the solution for 15 minutes. **119** (1.0 g, 1.7 mmol), tert-butyl nitrite (0.212 mL, 1.1 equiv.), and iodine (1.3 g, 3.0 equiv.) were then added and the reaction stirred for 1h before quenching with NH₄Cl and extracting with EtOAc. The combined organic layers were washed with dilute sodium thiosulfate and water, dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. Purification by column chromatography (SiO₂, 50% DCM/hexanes) allowed isolation of the product as an orange solid (88% yield). ¹H NMR (500 MHz, CDCl₃): δ = 8.018 (d, *J* = 4 Hz, 1H), 7.810 (d, *J* = 2 Hz, 1H), 7.201 (dd, *J* = 8.5 Hz, 2 Hz, 1H) ppm.

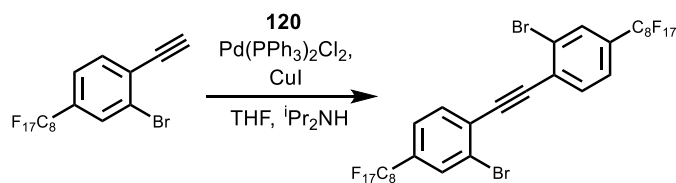


Synthesis of (2-bromo-4-perfluorooctylphenylethynyl)trimethylsilane (121): The standard Sonogashira cross coupling procedure was followed. The product was purified by column chromatography (SiO₂, 50% DCM/hexanes) to give the product as an orange

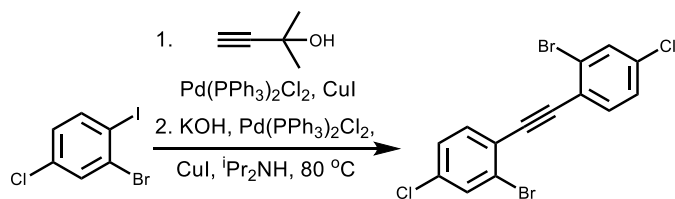
solid in 90% yield. ^1H NMR (500 MHz, CDCl_3): δ = 7.798 (d, J = 1 Hz, 1H), 7.590 (d, J = 8 Hz, 1H), 7.457 (dd, J = 8, 1 Hz, 1H), 0.291 (s, 9H) ppm.



Synthesis of 2-bromo-4-perfluorooctylethynylbenzene (122): A 4:1 mixture of $\text{THF}:\text{MeOH}$ was added to a round bottom flask equipped with a stir bar and degassed by bubbling N_2 through the solution for 15 minutes. **121** (350 mg, 0.5 mmol) was added followed by K_2CO_3 (15 mg, 0.1 equiv.) and the reaction allowed to stir for 30 minutes. The reaction was then quenched with ammonium chloride and extracted with EtOAc . The combined organic layers were dried with MgSO_4 , filtered, and the solvent removed under reduced pressure. The crude material was purified by recrystallization from hexanes/chloroform to yield 80% of a pale orange solid. ^1H NMR (500 MHz, CDCl_3): 7.822 (d, J = 1 Hz, 1H) 7.646 (d, J = 8 Hz, 1H), 7.497 (dd, J = 8 Hz, 1 Hz, 1H), 3.525 (s, 1H) ppm.

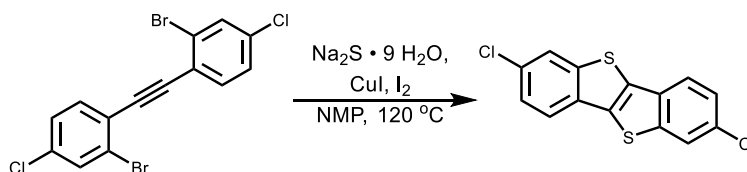


Synthesis of 2,2'-dibromo-4,4'-diperfluorooctyldiphenylacetylene (123): The standard Sonogashira cross coupling procedure was used with alkyne **120** replacing TMSA. The reaction resulted in precipitation of an insoluble yellow solid that could not be purified by column chromatography or recrystallization. A small amount of product (~5% yield) was purified by trituration with dichloromethane and chloroform. Dilute NMR samples were able to be prepared, however, the concentration was too low to obtain ^{13}C NMR data. ^1H (500 MHz, CDCl_3): 7.846 (d, $J = 1$ Hz, 1H), 7.708 (d, $J = 8$ Hz, 1H), 7.537 (dd, $J = 8$ Hz, 1 Hz, 1H) ppm.

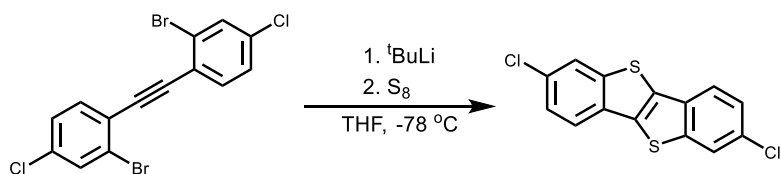


One-pot synthesis of 2,2'-dibromo-4,4'-dichlorophenylacetylene (126): Diisopropylamine (40 mL) was added to a round bottom flask equipped with a stir bar and reflux condenser. The solvent was degassed for 15 minutes by bubbling N_2 through the solution for 15 minutes. 2-bromo-4-chloriodobenzene (2.0 g, 6.45 mmol), 2-ethynepropan-2-ol (0.65 ml, 1.05 equiv.), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (226 mg, 0.05 equiv.), and CuI (61 mg, 0.05 equiv.) were then added and the reaction allowed to proceed for 6 h. KOH (3.0

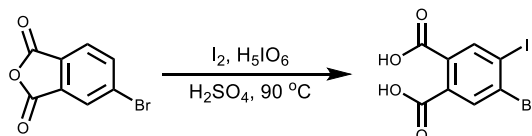
g, 8.0 equiv.), additional Pd(PPh₃)₂Cl₂ (226 mg, 0.05 equiv.), and CuI (61 mg, 0.05 equiv.) were then added and the reaction heated to 80 °C for 12 h. After cooling to RT, the reaction was diluted with 50 mL of water and the product was extracted with chloroform. The combined organic layers were washed with saturated NH₄Cl and water, dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. The product exhibited very low solubility and was purified by sonication in a solution of dichloromethane followed by vacuum filtration and washing with MeOH and chloroform to yield a colorless solid in 40% yield. The low solubility of the product prevented spectroscopic analysis and it was subjected to thienannulation conditions without further purification.



Copper-catalyzed thienannulation of 2,7-dichloro[1]benzothieno[3,2-b][1]benzothiophene (127): Alkyne **126** was subjected to Li and coworkers' thienannulation conditions⁹¹ and purified *via* vacuum filtration. The crude solid was washed with dichloromethane and recrystallized from toluene. **127** was isolated as a colorless solid (~25% yield) with small amounts of a yellow-orange sulfur impurity that could not be detected by NMR.

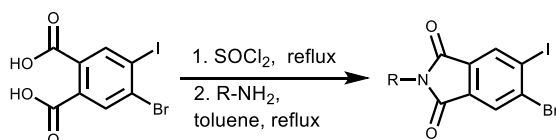


Lithium halogen exchange mediated thienannulation of 2,7-dichloro[1]benzothieno[3,2-b][1]benzothiophene (127): Subjecting **126** to Sashida and coworkers' thienannulation conditions with identical workup conditions as **127** via sodium sulfide nonahydrate conditions resulted in moderately higher yields (~35%). However, this material also had notable contamination of sulfur byproducts. The spectral data for **127** was identical for both methods. Low solubility of the product prevented detection by ^{13}C NMR. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.902$ (d, $J = 1.5$ Hz, 2H), 7.788 (d, $J = 7$ Hz, 2H), 7.438 (dd, $J = 7, 1.5$ Hz, 2H) ppm.

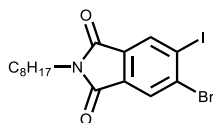


Synthesis of 4-bromo-5-iodophthalic acid (136): 4-Bromophthalic anhydride (**136**) (5.00 g, 22.025 mmol) was added to a 250 mL round-bottom flask equipped with a stir bar and reflux condenser followed by freshly sublimated iodine (2.237 g, 8.813 mmol, 0.35 equiv.), sulfuric acid (60 mL), and periodic acid (1.005 g, 4.409 mmol, 0.3 equiv.). The reaction mixture was then heated at 90 °C under an atmosphere of N_2 for 16 h. After cooling to RT, the reaction mixture was poured over crushed ice forming a yellow-white precipitate. This

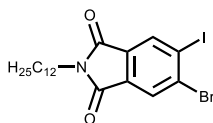
was filtered through a fritted funnel and washed with minimal amounts of H₂O. The solid was then dissolved in a saturated NaHCO₃ solution. Adjusting the pH using HCl produced a colorless precipitate which was filtered and dried under vacuum affording a mixture of 4-bromo-5-iodophthalic acid and 4-bromo-5-iodophthalic anhydride which was taken forward without further purification.



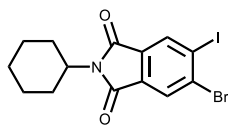
General procedure for the synthesis of 4-bromo-5-iodophthalimides (131a-d): The crude 4-bromo-5-iodophthalic acid and 4-bromo-5-iodophthalic anhydride mixture was added to a flame-dried 200 mL round-bottom flask equipped with a stir bar and reflux condenser followed by thionyl chloride (10-20 equiv.). The reaction mixture was heated at reflux for 12 h and allowed to cool overnight for a total of 16 h reaction time. Thionyl chloride was then distilled off followed by addition of anhydrous toluene and primary amine (1.05 equiv.). The reaction was heated to reflux for 6 h. Upon completion of the reaction, solvent was removed under reduced pressure leaving the crude material as a brown solid. The product was purified by column chromatography (SiO₂, 25% DCM/hexanes).



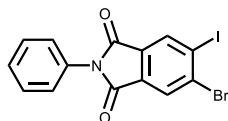
4-bromo-5-iodo-N-octylphthalimide (131a): Colorless solid (51% yield from 4-bromophthalic anhydride), $R_f = 0.3$ ^1H NMR (500 MHz, CDCl_3): $\delta = 8.318$ (s, 1H), 8.056 (s, 1H), 3.653 (t, $J=7.5$ Hz, 2H), 1.645 (m, 2H), 1.280 (m, 10H), 0.869 ppm (t, $J=7$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 166.705, 166.374, 136.370, 134.822, 132.946, 131.380, 127.015, 108.042, 38.489, 31.745, 29.132, 29.097, 28.440, 26.821, 22.612, 14.069$ ppm.



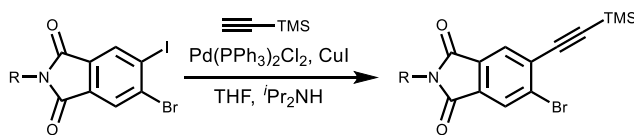
4-bromo-5-iodo-N-dodecylphthalimide (131b): Colorless solid (55% yield from 4-bromophthalic anhydride), $R_f = 0.3$ ^1H NMR (500 MHz, CDCl_3): $\delta = 8.316$ (s, 1H), 8.054 (s, 1H), 3.653 (t, $J = 7$ Hz, 2H), 1.644 (m, 2H), 1.279 (m, 18H), 0.876 ppm (t, $J = 7$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 166.707, 166.375, 136.171, 134.824, 132.949, 131.384, 127.016, 108.035, 38.924, 31.914, 29.609, 29.537, 29.466, 29.338, 29.134, 22.688, 14.122$ ppm.



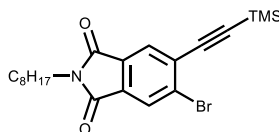
4-bromo-5-iodo-N-dodecylphthalimide (131c): Colorless solid (46% yield from 4-bromophthalic anhydride), $R_f = 0.4$ $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 8.289$ (s, 1H), 8.028 (s, 1H), 4.109-4.044 (m, 1H), 2.202-2.120 (m, 2H), 1.879-1.852 (m, 2H), 1.722-1.692 (m, 3H), 1.396-1.248 (m, 3H) ppm.



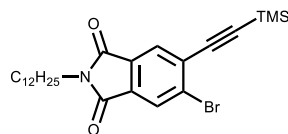
4-bromo-5-iodo-N-dodecylphthalimide (131d): Colorless solid (49% yield from 4-bromophthalic anhydride), $R_f = 0.35$ $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 8.441$ (s, 1H), 8.176 (s, 1H), 7.401-7.529 (m, 5H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3): $\delta = 165.603$, 165.252, 136.843, 135.402, 132.471, 131.396, 131.197, 130.849, 129.246, 128.476, 127.529, 126.420 ppm.



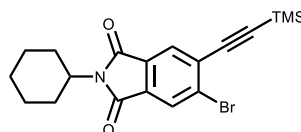
General procedure for the Sonogashira coupling of phthalimides 132a-d: A 5:1 mixture of THF and *i*Pr₂NH were added to a flame-dried round bottom flask equipped with a stir bar and degassed by bubbling N₂ through the solution for 20 minutes. Phthalimide (1.0 equiv.), Pd(PPh₃)₂Cl₂ (0.02 equiv.), CuI (0.02 equiv.), and trimethylsilyl acetylene (1.05 equiv.) were then added and the reaction was stirred for 14 h. The reaction was then quenched with saturated NH₄Cl and extracted with EtOAc. The combined organic layers were dried with MgSO₄, filtered, and the solvent removed under reduced pressure. The products were purified by column chromatography (SiO₂, 25% DCM/hexanes)



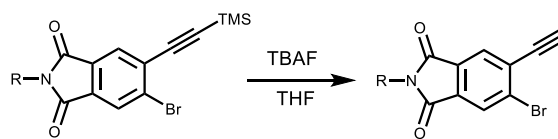
4-bromo-5-(2-trimethylsilylethynyl)-N-octylphthalimide (132a): Pale yellow solid (81% yield). *R*_f = 0.25 ¹H NMR (500 MHz, CDCl₃): δ = 8.033 (s, 1H), 7.896 (s, 1H), 3.562 (t, *J* = 7.5 Hz, 2H), 1.650 (m, 2H), 1.301 (m, 10H), 0.868 (t, *J* = 7 Hz, 3H), 0.299 (s, 9H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 167.071, 166.654, 131.849, 130.773, 127.750, 127.254, 105.490, 101.622, 38.450, 31.748, 29.134, 29.105, 28.476, 26.842, 22.612, 14.065, 0.393 ppm.



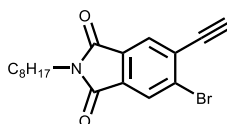
4-bromo-5-(2-trimethylsilylethynyl)-N-dodecylphthalimide (132b): Pale yellow solid (78% yield). $R_f = 0.25$ $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 8.034$ (s, 1H), 7.896 (s, 1H), 3.652 (t, $J = 7.5$ Hz, 2H), 1.661-1.634 (m, 2H), 1.304-1.203 (m, 18H), 0.877 (t, $J = 7$ Hz, 3H), 0.299 (s, 9H).



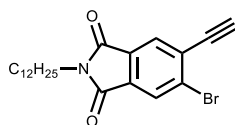
4-bromo-5-(2-trimethylsilylethynyl)-N-cyclohexylphthalimide (132c): Colorless solid (70% yield) $R_f = 0.4$ $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 8.006$ (s, 1H), 7.869 (s, 1H), 4.106-4.056 (m, 1H), 2.210-2.128 (m, 2H), 1.877-1.850 (m, 2H), 1.725-1.679 (m, 3H), 1.395-1.248 (m, 3H), 0.298 (s, 9H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3): $\delta = 167.064$, 166.646, 131.794, 131.745, 130.668, 130.527, 127.634, 127.114, 105.298, 101.660, 51.339, 29.776, 25.957, 25.043, 0.385 ppm.



General procedure for deprotection of alkynes 133a-c: The general deprotection method for silane-protected alkynes was followed.

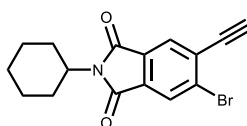


4-bromo-5-ethynyl-N-octylphthalimide (133a): Pale yellow solid (quantitative yield). ^1H NMR (500 MHz, CDCl_3) δ = 8.060 (s, 1H), 7.939 (s, 1H), 3.679-3.644(m, 3H), 1.668-1.639 (m, 2H), 1.310-1.254 (m, 10H), 0.869 (t, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 166.929, 166.508, 132.477, 131.901, 130.717, 129.809, 128.244, 127.377, 86.341, 80.778, 38.497, 31.748, 29.131, 29.101, 28.459, 26.832, 22.612, 14.065 ppm.



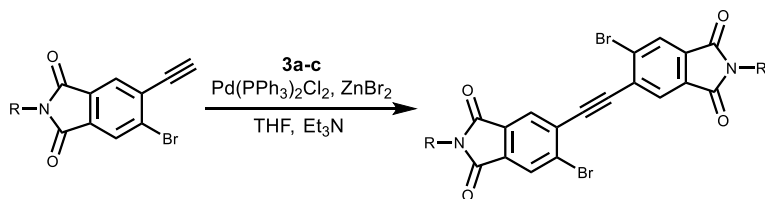
4-bromo-5-ethynyl-N-dodecylphthalimide (133b): Pale yellow solid (quantitative yield).

^1H NMR (500 MHz, CDCl_3) δ = 8.055 (s, 1H), 7.933 (s, 1H), 3.679-3.638 (m, 3H), 1.690-1.612 (m, 2H), 1.308-1.243 (m, 18H), 0.889-0.861 (t, J = 7 Hz) ppm.



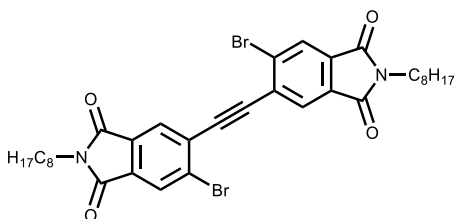
4-bromo-5-ethynyl-N-cyclohexylphthalimide (133c): Pale yellow solid (quantitative

yield). ^1H NMR (500 MHz, CDCl_3) δ = 8.033 (s, 1H), 7.914 (s, 1H), 4.123-4.058 (m, 1H), 3.631 (s, 1H), 2.213-2.131 (m, 2H), 1.882-1.855 (m, 2H), 1.732 (m, 3H), 1.401-1.252 (m, 3H) ppm.



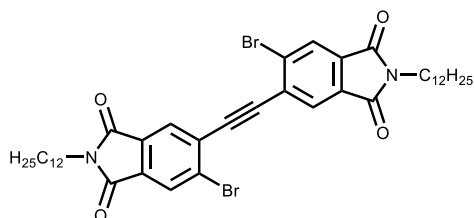
General procedure for Negishi coupling of alkynes (133a-c) with imides (134a-c):

THF and Et₃N (3.5 equiv.) were added to a round bottom flask equipped with a stir bar and reflux condenser. The solution was degassed with bubbling N₂ for 15 minutes before addition of ZnBr₂ (1.2 equiv.). After an additional 10 minutes, alkyne (1.0 equiv.), aryl iodide (1.0 equiv), and Pd(PPh₃)₂Cl₂ (0.05 equiv.) were added and the solution heated at 60°C for 16 h. The reaction mixture was then diluted with EtOAc resulting in precipitation of the product. The precipitate was filtered through a fritted funnel and washed with hexanes and MeOH.



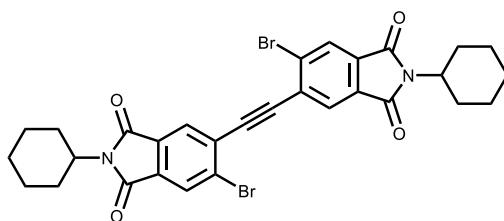
2,2'-dibromophenylacetylene-N,N'-dioctyl-4,4',5,5'-tetracarboxylic diimide (134a):

Bright yellow solid (61% yield). ¹H NMR (500 MHz, CDCl₃): δ = 8.121 (s, 1H), 8.053 (s, 1H), 3.689 (t, *J* = 7.5 Hz, 2H), 1.700-1.643 (m, 2H), 1.32-1.261 (m, 10H), 0.874 (t, *J* = 7 Hz, 3H).



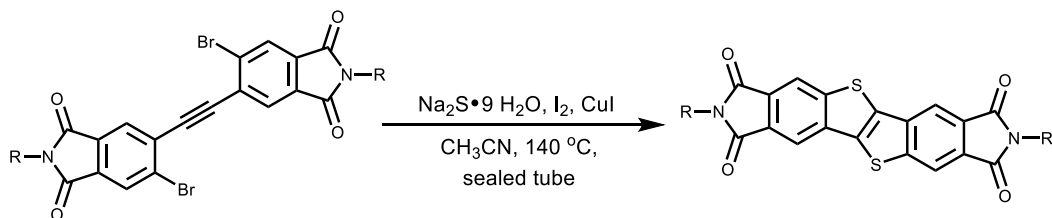
2,2'-dibromophenylacetylene-N,N'-didodecyl-4,4',5,5'-tetracarboxylic diimide

(134b): Bright yellow solid (62% yield). ^1H NMR (500 MHz, CDCl_3): δ = 8.118 (s, 1H), 8.050 (s, 1H), 3.688 (t, J = 7 Hz, 2H), 1705-1640 (m, 2H), 1.320-1.249 (m, 18H), 0.877 (t, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 166.843, 166.403, 132.798, 131.948, 130.891, 129.660, 127.947, 127.601, 94.882, 38.581, 31.915, 29.618, 29.612, 29.546, 29.476, 29.314, 29.146, 22.688, 14.120 ppm.

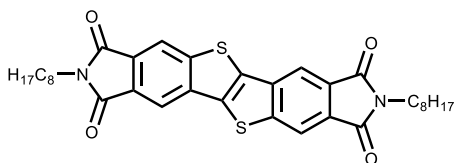


2,2'-dibromophenylacetylene-N,N'-dicyclohexyl-4,4',5,5'-tetracarboxylic diimide

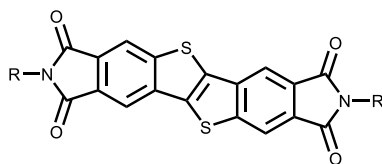
(134c): Bright yellow solid (56% yield). ^1H NMR (500 MHz, CDCl_3): δ = 8.087 (s, 1H), 8.022 (s, 1H), 4.145-4.080 (m, 1H), 2.229-2.148 (m, 2H), 1.894-1.876 (m, 2H), 1.746-1.694 (m, 3H), 1.419-1.257 (m, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 166.842, 166.411, 132.712, 131.842, 130.782, 129.591, 127.851, 127.463, 94.823, 51.491, 29.776, 25.952, 25.031 ppm.



Thienannulation of alkynes 134a-b: Acetonitrile (5 mL) was added to a pressure vessel and degassed by bubbling N₂ through the solution for 15 minutes. Alkyne (0.35 mmol), sodium sulfide nonahydrate (4.0 equiv.), CuI (0.2 equiv.), and iodine (2.0 equiv.) were added all at once and the reaction vessel was sealed and heated at 140 °C for 24 h. The crude material was diluted with dichloromethane, filtered, and washed with additional dichloromethane and acetone. The collected precipitate was dissolved in boiling chloroform and loaded onto silica. The column was run in 100% chloroform but the product did not elute until washing with boiling chloroform. Removal of solvent left a colorless amorphous solid (<5% yield). Additionally, the alternative previously reported thienannulation conditions had similar results.

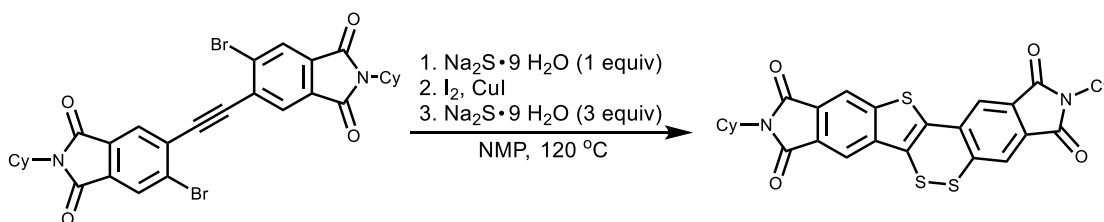


N,N'-dioctyl[1]benzothieno[3,2-b][1]benzothiophene-2,3,6,7-tetracarboxylic diimide (134a): ¹H NMR (500 MHz, CDCl₃): δ = 8.436 (s, 1H), 8.396 (s, 1H), 3.751 (t, *J* = 7.5 Hz, 2H), 1.753-1.696 (m, 2H), 1.352-1.218 (m, 10H), 0.873 (t, *J* = 7 Hz, 3H) ppm.



N,N'-didodecyl[1]benzothieno[3,2-b][1]benzothiophene-2,3,6,7-tetracarboxylic

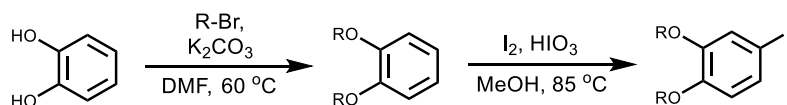
diimide (134b): ^1H NMR (500 MHz, CDCl_3): δ = 8.431 (s, 1H), 8.391 (s, 1H), 3.750 (t, J = 7 Hz, 2H), 1.761-1.681 (m, 2H), 1.394-1.193 (m, 18H), 0.870 (t, J = 7 Hz, 3H) ppm.



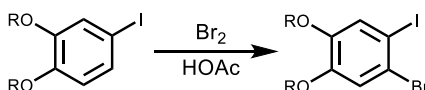
Attempted synthesis of N,N'-cyclohexyl[1]benzothieno[3,2-b][1]benzothiophene-

2,3,6,7-tetracarboxylic diimide: Subjecting **134c** to thienannulation conditions in a stepwise addition resulted in disulfide **138**. Product was purified by column chromatography (SiO_2 , 75% DCM/hexanes) to give an orange solid in 10% yield. ^1H NMR (500 MHz, CDCl_3): δ = 8.306 (s, 1H), 8.228 (s, 1H), 7.964 (s, 1H), 7.945 (s, 1H), 4.199-4.107 (m, 2H), 2.273-2.197 (m, 4H), 1.903-1.881 (m, 4H), 1.762-1.732 (m, 6H), 1.431-1.263 (m, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 167.620, 167.540, 167.035,

166.859, 143.712, 142.314, 140.674, 139.331, 137.221, 132.401, 132.369, 129.224, 129.179, 128.972, 123.718, 121.898, 118.492, 118.428, 51.471, 51.383, 29.847, 29.820, 26.013, 25.972, 25.101, 25.047 ppm.



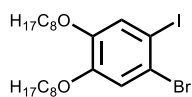
Synthesis of 1,2-bis(octyloxy)-4-iodobenzene and 1,2-bis(dodecyl)-4-iodobenzene (143a-b): Starting from catechol, **143a** and **143b** were synthesized and purified following a literature procedure. Spectral characterization of both compounds matched literature values.¹²⁴



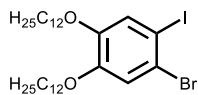
General procedure for the bromination of 1,2-bis(alkoxy)-4-iodobenzenes: Acetic acid (50 mL) was added to a round bottom flask equipped with a stir bar and degassed by bubbling N₂ through the solution for 15 minutes. 1,2-bis(alkoxy)-4-iodobenzene (10 mmol) was added followed by Br₂ (1.0 equiv.) and the reaction was stirred for 24 h. The reaction mixture was then diluted with 100 mL of water and extracted with hexanes. The

¹²⁴ Prabhu, D. D.; Sivadas, A. P.; Das, S. *J. Mater. Chem. C* **2014**, *34*, 7039-7046.

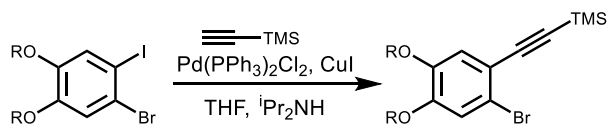
combined organic layers were washed with saturated NaHCO₃, sodium thiosulfate, and water. The organic layers were then dried with MgSO₄, filtered, and the solvent removed under reduced pressure. The products were purified by column chromatography (SiO₂, hexanes). Products were isolated as colorless solids (94% yield).



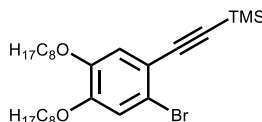
1,2-bis(octyloxy)-4-iodobenzene (144a): ¹H NMR (500 MHz, CDCl₃): δ = 7.232 (s, 1H), 7.072 (s, 1H), 3.948-3.913 (m, 4H), 1.822-1.760 (m, 4H), 1.444-1.283 (m, 20H), 0.899-0.871 (m, 6H) ppm.



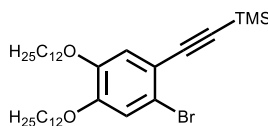
1,2-bis(dodecyloxy)-4-iodobenzene (144b): ¹H NMR (500 MHz, CDCl₃): δ = 7.231 (s, 1H), 7.071 (s, 1H), 3.947-3.912 (m, 4H), 1.820-1.758 (m, 4H), 1.441-1.758 (m, 36H), 0.881 (t, *J* = 7 Hz, 6H) ppm.



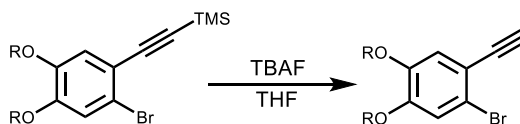
Synthesis of (4,5-bis(alkoxy)-2-bromophenylethynyltrimethyl)silanes (145a-b): The general Sonogashira cross coupling method was followed. Products were isolated by column chromatography (SiO₂, hexanes) as colorless solids.



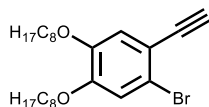
(4,5-bis(octyloxy)-2-bromophenylethynyltrimethyl)silane (145a): ¹H NMR (500 MHz, CDCl₃): δ = 6.995 (s, 1H), 6.958 (s, 1H), 3.970-3.930 (m, 4H), 1.831-1.763 (m, 4H), 1.318-1.281 (m, 20H), 0.884 (t, J = 7 Hz, 6H) ppm.



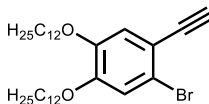
(4,5-bis(dodecyloxy)-2-bromophenylethynyltrimethyl)silane (145b): ¹H NMR (500 MHz, CDCl₃): δ = 6.995 (s, 1H), 6.957 (s, 1H), 3.969-3.928 (m, 4H), 1.829-1.761 (m, 4H), 1.442-1.261 (m, 36H), 0.881 (t, J = 7 Hz, 6H) ppm.



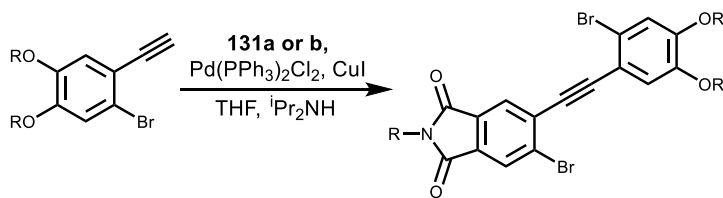
Synthesis of bis-1,2-(alkoxy)-4-bromo-5-ethynylbenzenes (146a-b): The standard deprotection of silane-protected alkynes procedure was followed. Products were purified by passing through a plug of silica and washing with hexanes.



Bis-1,2-(octyloxy)-4-bromo-5-ethynylbenzenes (146a): Colorless solid that slowly turned brown at elevated temperatures (quantitative yield). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.007$ (s, 1H), 6.989 (s, 1H), 3.984-3.935 (m, 4H), 1.840-1.767 (m, 4H), 1.322-1.274 (m, 20H), 0.885 (t, $J = 7$ Hz, 6H) ppm.

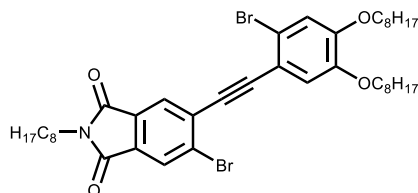


Bis-1,2-(dodecyloxy)-4-bromo-5-ethynylbenzenes (146b): Colorless solid that slowly turned brown at elevated temperatures (quantitative yield). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.007$ (s, 1H), 6.989 (s, 1H), 3.983-3.934 (m, 4H), 1.824-1.779 (m, 4H), 1.342-1.262 (m, 36 H), 0.881 (t, $J = 7$ Hz, 6H) ppm.

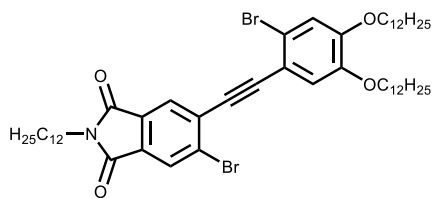


Synthesis of bis(alkoxy)-imide-functionalized dibromophenyl acetylenes (**147a-b**):

The standard Sonogashira coupling conditions were followed using aryl iodides **131 a or b** with terminal alkynes **146 a or b**. The reaction mixture was diluted with hexanes and the resulting precipitate was filtered through a fritted glass funnel and washed with methanol and hexanes.

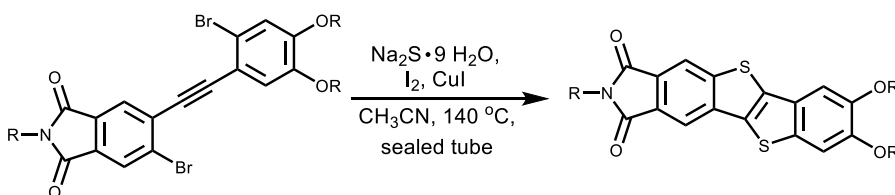


Bis(octyloxy)-N-octylimide-functionalized dibromophenyl acetylene (147a**):** Bright yellow solid (71% yield). ^1H NMR (500 MHz, CDCl_3): $\delta =$ ^{13}C NMR (125 MHz, CDCl_3): $\delta = 8.069$ (s, 1H), 7.995 (s, 1H), 7.071 (s, 1H), 7.066 (s, 1H), 4.022-3.986 (m, 4H), 3.669 (t, $J = 7.5$ Hz, 2H), 1.863-1.797 (m, 4H), 1.682-1.640 (m, 2H), 1.498-1.441 (m, 4H), 1.375-1.249 (m, 26H), 0.891-0.864 (m, 9H) ppm.



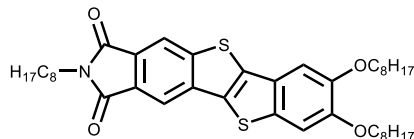
Bis(dodecyloxy)-N-dodecylimide-functionalized dibromophenyl acetylene (147b):

Bright yellow solid (71% yield). ^1H NMR (500 MHz, CDCl_3): δ = 8.071 (s, 1H), 7.997 (s, 1H), 7.072 (s, 1H), 7.067 (s, 1H), 4.022-3.987 (m, 4H), 3.684-3.655 (t, J = 7.5 Hz, 2H), 1.851-1.811 (m, 4H), 1.688-1.634 (m, 2H), 1.498-1.442 (m, 4H), 1.377-1.249 (m, 50H), 0.892-0.865 (m, 9H) ppm.



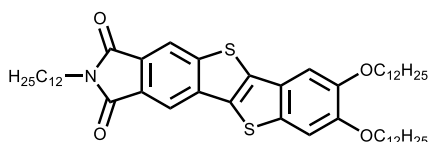
Synthesis of 2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-

dicarboxylic imide (149a-b): Acetonitrile was added to a pressure vessel equipped with a stir bar and degassed for 15 minutes before addition of alkyne (**147**) (1.0 equiv.), sodium sulfide nonahydrate (3.0 equiv.), I_2 (2.0 equiv.), and CuI (0.2 equiv.). The reaction vessel was sealed and heated at 140 °C for 24 h. After cooling to RT, the crude material was filtered and washed with H_2O and dichloromethane. The product was purified by column chromatography (eluent gradient from 30% CHCl_3 /hexanes to 100% CHCl_3).



2,3-dioctyloxy-N-octyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-dicarboxylic

imide (149a): Bright yellow solid (10% yield). ^1H NMR (500 MHz, CDCl_3): δ = 8.193 (s, 1H), 8.097 (s, 1H), 7.035 (s, 1H), 6.878 (s, 1H), 3.953 (t, J = 6.5 Hz, 2H), 3.801 (t, J = 6.5 Hz, 2H), 3.715 (t, J = 7.5 Hz, 2H), 1.833-1.803 (m, 2H), 1.726-1.711 (m, 4H), 1.453-1.483 (m, 4H), 1.310-1.280 (m, 26H), 0.896-0.862 (m, 9H) ppm.



2,3-didodecyloxy-N-dodecyl[1]benzothieno[3,2-b][1]benzothiophene-6,7-

dicarboxylic imide (149b): Bright yellow solid (10% yield). ^1H NMR (500 MHz, CDCl_3): δ = 8.191 (s, 1H), 8.095 (s, 1H), 7.031 (s, 1H), 6.876 (s, 1H), 3.950 (t, J = 6 Hz, 2H), 3.799 (t, J = 6 Hz, 2H), 3.713 (t, J = 7.5 Hz, 2H), 1.831-1.802 (m, 2H), 1.739-1.696 (m, 4H), 1.451-1.436 (m, 4H), 1.342-1.252 (m, 50H), 0.887-0.861 (m, 9H) ppm.

DFT calculations: The electronic ground state model of compound **151** with truncated alkyl chains was prepared in ArgusLab (Planaria Software). TDDFT calculations were performed in ORCA 3.0.0 software package on the 380 node IBM Bluemoon cluster at the

Vermont Advanced Computing Core (VACC). All TDDFT calculations employed the BLYP density functional, the TZVP basis set, and tight SCF convergence criteria. TDDFT was used to calculate the excitation energies and transition intensity from the electronic ground state to the first 14 electronic excited states. The UV/Vis absorption spectrum was simulated based on the TDDFT data by convoluting Gaussian-shaped bands with full width at half maximum bandwidths of 5000 cm^{-1} .

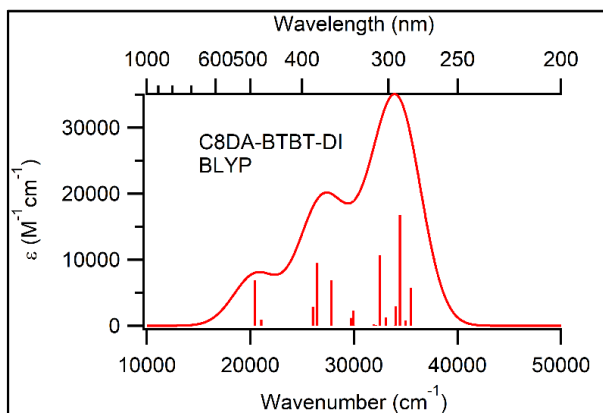


Figure S1 BLYP TDDFT-predicted Abs spectra of truncated compound **149**. The vertical sticks represent the TDDFT predicted transition energies and intensities and the spectral curves arise from convolution of Gaussian-shaped bands with full width at half maximum band-widths of 5000 cm^{-1} .

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