SYNTHESIS OF ASYMMETRIC HETEROCYCLE-FUSED INDACENES FOR ORGANIC ELECTRONIC APPLICATION

by

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A THESIS

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This thesis describes the development of a synthetic route to create the asymmetric indenofluorene derivative indacenobenzofuranbenzothiophene (IBFBT). Synthesis and characterization of indenofluorenes and indenofluorene derivatives are active areas of research within the Haley Lab due to inherent properties of indenofluorenes that can be tuned to fit various organic electronic applications. Indenofluorenes themselves already display high levels of pi-conjugation and electron delocalization, making them suitable for conducting an electric current. Additionally, the antiaromatic character caused by the *s*-indacene core within the structure of indenofluorenes further improves the capability for electron mobility through the structure. Indenofluorene derivatives have demonstrated even greater potential for organic electronic application as the incorporation of various functional groups and heterocycles allows for further fine tuning of electronic properties. Continued synthesis and characterization of new indenofluorene derivatives will help us to better understand how we can continue to fine tune the electronic capabilities of these compounds for application in organic electronics.

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Introduction

Electronic devices have become a core part humanity. At the heart of most electronic devices today is the element silicon, whose inherent chemical properties make it incredibly useful in electronic applications. However, the harnessing of raw materials and the manufacturing of those materials to yield pure silicon is a highly energy intensive process that leaves detrimental effects on the environment (1,6,7). With the demand and production of electronic devices only growing, it is important that we find alternatives to silicon moving forward in the electronics industry. The field of organic electronics aims to prepare such alternatives that have potential to be manufactured through much greener means than silicon production (2,12). Furthermore, organic electronic devices hold the potential to be applied in ways that are restricted with silicon-based devices (2,11). Before getting deeper into the nuances between silicon-based and organic electronic materials though, it is important to understand the principles of electricity that define the parameters by which we examine these materials.

Electricity and Classes of Electronic Materials

The most basic definition of electricity is the flow of an electric charge, and electric charges are inherent characteristics of subatomic particles. An atom is composed of a nucleus, containing positively charged protons and neutron which display no charge, at the core of the atom. Occupying spaces around the nucleus at distinct energy levels are negatively charged electrons. The spaces that electrons occupy are known as orbitals and different orbitals display different levels of energy. For an electric charge to flow, electrons occupying orbitals of the highest energy, also known as valence electrons, must delocalize from their parent atom and flow freely between atoms within a substance. For these electrons to delocalize, they must be excited with energy. The energy levels of localized and delocalized electrons can be depicted through band structures shown in Figure 1. The latent energy that valence electrons reside at is represented as the valence band, and the energy level necessary for electrons to conduct electricity is represented as the conductance band. Based on the amount of energy necessary to promote valence electrons from the valence band to the conductance band, materials can be classified as one of three types of electronic materials: conductors, semiconductors, and insulators.

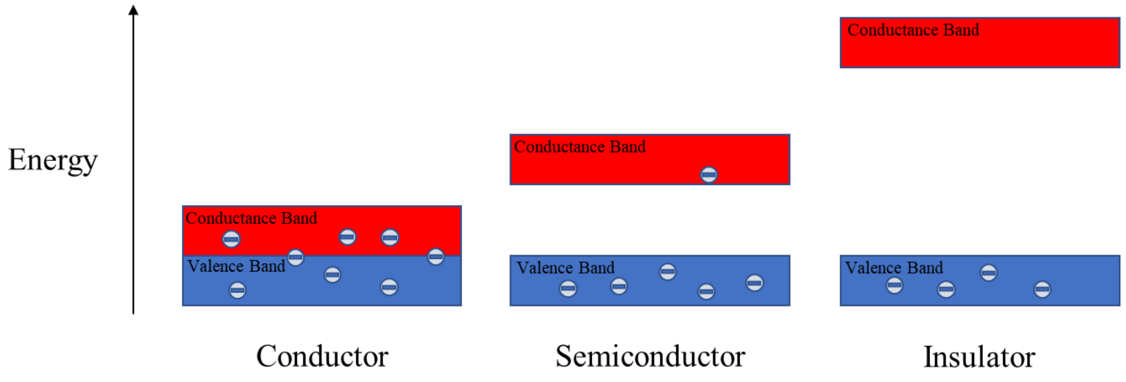


Figure 1: Depiction of energy gaps between the conductance and valence band within different types of conductive materials

Within conductors, the valence band and the conduction band overlap, and thus there is no energy gap at all, and electrons freely flow through the substance to conduct electricity. For semiconductors and insulators though, there is an energy gap that an electron must overcome, but this gap is much smaller in semiconductors and thus minimal conductivity is exhibited within them. The energy gap between the conduction and valence band within substances is analogous to what is known as the HOMO-LUMO energy gap within individual molecules (or atoms). The HOMO is the highest occupied molecular orbital, or highest energy orbital that contains electrons. The

LUMO represents the lowest unoccupied molecular orbital or the orbital of lowest energy that does not contain any electron. When an electron in the HOMO gets excited with energy, it can jump into the LUMO, giving the electron enough energy to delocalize from its parent atom and allowing it to conduct electricity.

Silicon-Based Electronic Materials

Silicon is an important aspect of modern electronics as it is the primary semiconductor used in electronic devices today (3). The demand for silicon comes from its use in devices known as transistors. Transistors are considered the fundamental building blocks of electronic devices, as they are used to control the flow of an electric current (4). This ability to control the flow of an electric current is the basis on which practically all electronic devices are built on, as control of electric currents enables the capability for electronic devices to perform complicated functions. Since the invention of transistors, numerous types of transistors have been developed for use within different kinds of electronic devices. The world of transistors could yield an entire paper of its own, but the important fact to note here is that most transistors employed today are primarily made up of highly pure silicon (5).

Silicon is an extremely abundant element on our planet making it a favorable resource to utilize in the growing electronics industry. However, how it is harvested, and the steps necessary to manufacture it for electronic devices have proven to be less favorable for the environment. The environmental impact stems from the intense demand for energy to manufacture silicon, which leads to detrimental long term environmental issues that will be compounded through the growing demand for silicon (5). Silicon primarily comes from the mining of silica, and this mining process causes numerous environmental drawbacks including land deterioration and the pollution of local environments that negatively impact the health of residents and the land around them (1). Furthermore, purification of silica to silicon requires extreme heating through the burning of fossil fuels, releasing lots of carbon monoxide into the atmosphere (6). Additionally, silicon on its own actually behaves more like a insulator rather than a semiconductor. Trace amount of impurities in the forms of other atoms are doped into the highly pure silicon crystal in order to make it function as a semiconductor. This chemical doping process utilizes trade-secret chemical reagents specific to different silicon manufacturers, and these reagents often come without safety and environmental protocols (7). These issues associated with silicon production prompt a demand for an alternative semiconductor material.

Organic Electronic Materials

The field of organic electronics aims to provide such an alternative through the synthesis of new organic electronic materials. Organic electronic materials are primarily composed of carbon and hydrogen-based molecules as opposed to inorganic electronic materials which are primarily composed of metals and metalloids such as silicon. These carbon-based structures come in various shapes and forms ranging from small molecules (8) to large polymers (9) or even hybrid organic-inorganic structures (10). These different variations in structure give them different electronic properties. It is important to note that the field of organic electronics is not a new industry; rather, it is a very broad industry with different applications at various stages of development.

A potential organic electronic material would have numerous advantages over its silicon counterpart. The properties of organic compounds lend them to be far more flexible, literally and figuratively in their application (2,11). As the purification of silicon requires intense heating, the silicon wafers produced are extremely rigid (2,6). Thus, silicon-based electronic devices must remain rather rigid as well to maintain the structural integrity of the silicon incorporated into these devices. Organic substances on the other hand, can display flexibility depending on their synthetic structure. The flexible character of organic compounds brings about potential for an entirely new field of electronics developed based on this property. Furthermore, organic compounds are far more compatible with biological systems as synthesis of organic electronic materials can be geared toward specific biological environments (11,12). Development of organic bioelectronic materials geared toward specific biological pathways can improve the biocompatibility of current bioelectronic devices, such as pacemakers, which can lead to improved functionality (11). The fine tuning of organic bioelectronic devices can also extend beyond humans to be applied in all living organisms to help build research on other biological systems that cannot be studied with current bioelectronic devices (11).

Finally, there is optimism that synthesis of organic electric compounds will be more eco-friendly through both the energy efficiency of the organic electronic devices as well as resource consumption in their synthesis (2,12). Currently, synthesis of organic electronic materials is on such small scales that production of organic electronic materials is not eco-friendly. However, sustainability is certainly a major goal for the of organic electronics (2,12). Thus, organic electronics offer numerous realms of electronic development that have only been accessed in very limited forms thus far. Additionally, they possess the potential to help move us towards a more sustainable electronic industry. These factors demonstrate the potential for how organic electronics could revolutionize the electronics industry.

Basis for Indenofluorene as an Organic Electronic Material

Indenofluorenes fall within a class of compounds known as polycyclic hydrocarbons. Polycyclic hydrocarbons have been targets for organic electronic application because they display high levels of pi-conjugation. Pi-conjugation refers to a characteristic where the p-orbitals of atoms within a compound overlap. This characteristic is favorable for electronic application as it allows for valence electrons within a compound to move between atoms more easily. Extensive research on polycyclic hydrocarbons as organic electronic materials has been focused on a compound known as an acenes. Acenes are defined as linearly linked benzene ring structures of various lengths as shown in Figure 2.

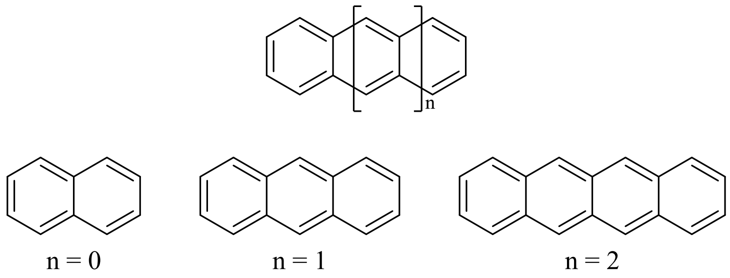


Figure 2: Different sizes and structures of acenes

Acenes were targeted as organic electronic compounds because of the decreasing HOMO-LUMO energy gaps that they displayed as their size increased (13). This decrease in energy gap is favorable as it can help improve the conductance of a compound. However, these compounds also displayed decreased stability with increased size, and further examination of acene electronic properties demonstrated extreme purity and high structural order are necessary to induce favorable electronic properties (14). Furthermore, it has been demonstrated that increases in the temperature of acenes also mitigate their electronic properties (14). These factors, along with the fact that acenes are susceptible to oxidative degradation (15), make acenes unsuitable for use as an organic electronic material that can be applied in the electronics industry.

Thus, research has shifted to indenofluorenes and their derivatives (16). Indenofluorenes are similar to acenes in their cyclic structure and conjugation but differ in that they incorporate five membered rings. Indenofluorenes can be thought of as fusion of an indene to a fluorene, though actual synthesis of indenofluorene is not done through this fusion. The combination of the two yields five different isomers that differ in the connectivity of the two compounds as shown in Figure 3.

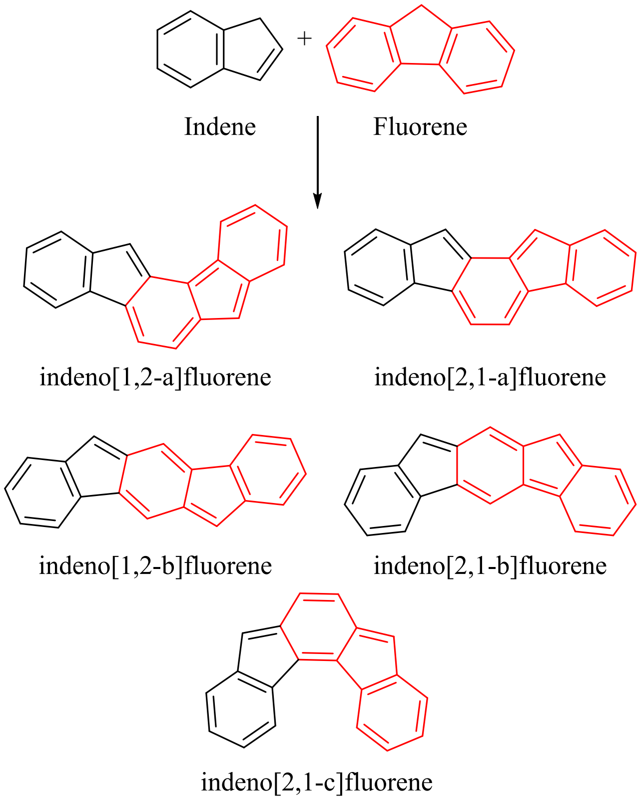


Figure 3: Isomers of indenofluorene

Indenofluorenes are interesting compounds for organic electronic application because they contain an *s*-indacene core within their structures. The *s*-indacene core refers the central benzene ring fused to the two five membered rings on either side as displayed in Figure 4.

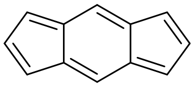


Figure 4: Structure of *s*-indacene

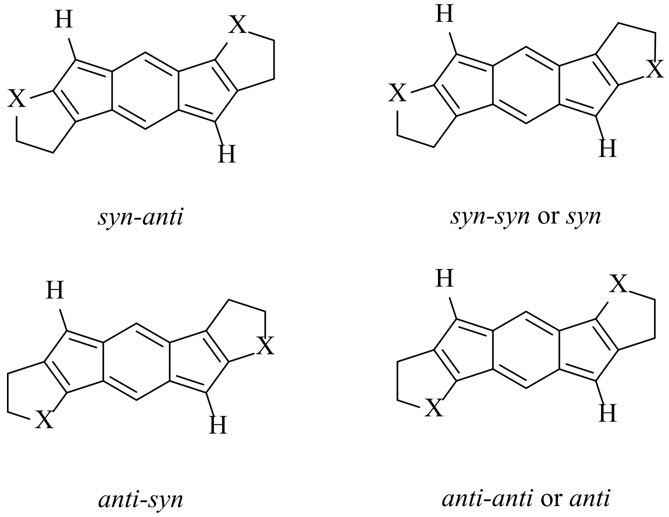
The *s*-indacene core contains 12 pi-electrons, making it an antiaromatic compound. Conjugated polycyclic hydrocarbons can be split into two separate categories, aromatic and antiaromatic. For a structure to be considered aromatic, it must be cyclic, planar, contain full pi-conjugation and follow Hückel's rule. This rule states that a structure is aromatic if it contains 4n+2 pi electrons. Aromaticity helps to contribute to the overall stability of a compound (17). Antiaromatic structures, on the other hand, display the same characteristics as aromatic structures, except they only contain 4n pi electrons. Antiaromaticity contributes to destabilization of a compound (17). Exposure of aromatic and antiaromatic structures to an external magnetic field induces a flow of pi electrons within these compounds, and this flow of charged particles generates a magnetic field within these cyclic structures known as a ring current (18). Aromatic structures display diatropic ring currents where the magnetic field within the ring opposes the direction of the external magnetic field. Antiaromatic structures display paratropic ring currents where magnetic field within the ring matches the direction of the external magnetic field.

The highly antiaromatic character of *s*-indacene makes it favorable for organic electronic application, as the antiaromatic character lowers the HOMO-LUMO energy gap within compounds, improving their conductance (19). However, *s*-indacene is so antiaromatic and unstable that it is impossible to synthesize and isolate it on its own. The fusion of benzene rings to the outside of the *s*-indacene core stabilizes the molecule enough to be isolated as indenofluorene. The benzene rings, however, display aromatic character which interferes with and reduces the antiaromatic character that the *s*-indacene core can displays within indenofluorene. To attempt to fine tune the antiaromatic character of the *s*-indacene core, the Haley Lab has been focused on the synthesis of indenofluorene derivatives.

Heterocycle-Fused *s*-Indacene Indenofluorene Derivatives

Reliable synthetic routes to yield indenofluorenes have already been established by the Haley Lab (16), allowing pursuit of further modifications to their structure. These modifications have created different families of indenofluorene derivatives which display modulated electronic properties that are beneficial toward potential organic electronic application. Understanding the relationship between the modifications made to the structure and the observed changes in electronic properties is necessary to create structures that exhibit properties fit for application in the electronics industry. My research focuses specifically on heterocycle-fused *s*-indacene indenofluorene derivatives. These derivatives replace the outer benzene rings of indenofluorene with heterocycles, which are cyclic structures that contain at least one non-carbon atom.

The presence of non-carbon atoms within heterocycles makes the heterocycle an asymmetric compound. The incorporation of asymmetric compounds onto *s*-indacene can be done in multiple orientations, and these different orientations are referred to as different structural isomers. Different structural isomers of a compound can display different chemical properties, even though their chemical formulas remain the same. Thus, it is important to denote the orientation in which these heterocycles are incorporated onto the *s*-indacene core. The terms *syn* and *anti* are used to denote the orientation of the incorporated heterocycle. Figure 5 illustrates the use of *syn* and *anti* nomenclature in their referral to heterocycle-fused *s*-indacenes.



syn-anti

syn-syn or *syn*

anti-syn

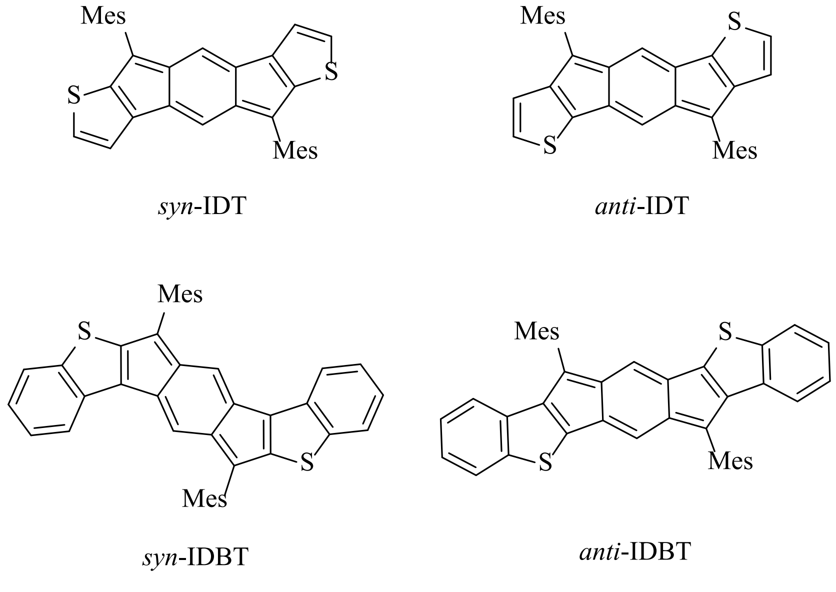
anti-anti or *anti*

Figure 5: Nomenclature of heterocycle-fused *s*-indacene structural isomers

When a heterocycle is fused to one of the five membered rings of *s*-indacene, only one carbon within *s*-indacenes five membered ring displays a bond to a group or atom outside of the cyclic structure. This is represented with a hydrogen atom in Figure 5. When a heteroatom and the outer group of the adjacent rings are on the same side of a compound, it is considered *syn*. When a heteroatom and the outside group of the adjacent rings are on opposite sides of a compound it is considered *anti*. The following section details specific heterocycle-fused *s*-indacenes that display such isomerism. These specific indenofluorene derivatives also serve as the foundation for my project.

Indacenodibenzothiophenes (IDBTs)

Indacenodibenzothiophene is an indenofluorene derivative that fuses benzothiophene heterocycles to *s*-indacene rather than benzene rings. Prior to synthesis of IDBT, synthesis of a thiophene fused pentacene (5 ringed acene) derivative, known as anthradithiophene, illustrated that incorporation of heterocycles into pentacene allowed for tuning of its physical and electronic properties (20). Later literature would also indicate that incorporation of thiophenes specifically is favorable for organic electronic materials due to their favorable electron transport properties (21). Inspired by the synthesis of anthradithiophene, the Haley Lab aimed to incorporate thiophene into indenofluorene, resulting in the synthesis *syn* and *anti* isomers of both indacenodithiophene (IDT) and IDBT (22, 23) displayed in Figure 6.



syn-IDT

anti-IDT

syn-IDBT

anti-IDBT

Figure 6: Structures of *syn* and *anti* indacenodithiophene and indacenodibenzothiophene

Characterization of both IDTs and IDBTs was done through several means to yield information about the antiaromatic character of *s*-indacene within these compounds as well as the energies of their HOMO and LUMO. Characterization of antiaromatic character was done through Nuclear Independent Chemical Shift (NICS) calculations, which is a theoretical method used to quantify aromaticity and antiaromaticity (24). UV-Vis spectroscopy was then used to measure the absorbance of the compound at different energies, or wavelengths, of light. This data was then used to calculate the optical and energy band gaps within the compounds (25). Finally, a process known as cyclic voltammetry was employed, in which thermodynamic evaluation of the redox process within these compounds is analyzed to reveal the energy levels of the HOMO and the LUMO (26).

These analytical processes revealed that the *s*-indacene core displays more antiaromatic character within IDT and IDBT than in their analogous indenofluorene isomers (22). Additionally, both IDT and IDBT also displayed smaller HOMO-LUMO energy gaps than their indenofluorene analogues. Comparison of IDT to IDBT shows that *s*-indacene is more antiaromatic within IDBT, and that HOMO-LUMO energy gaps are smaller in IDBT as well. This smaller HOMO-LUMO energy gap is a result of the extended pi-conjugation within IDBT which serves to lower the energy level of the LUMO (22). As IDBT displayed more favorable properties for organic electronic application, research started to focus on IDBTs over IDTs.

Later studies show the electronic properties of the IDBTs could be further modified through the late-stage modification of the compound (27). This late-stage modification was a simple one step oxidation of the sulfur atoms contained in the benzothiophene rings to their sulfone derivatives shown in Figure 7.

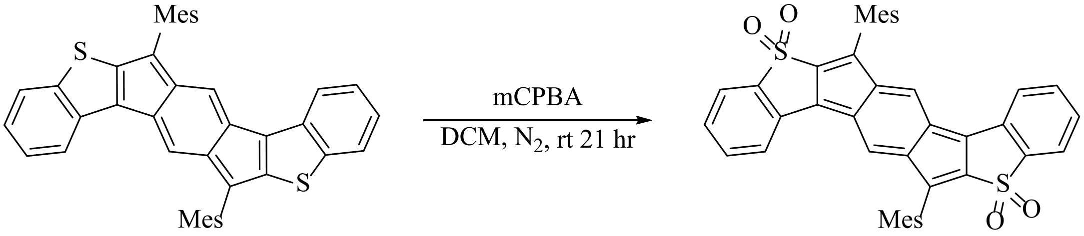
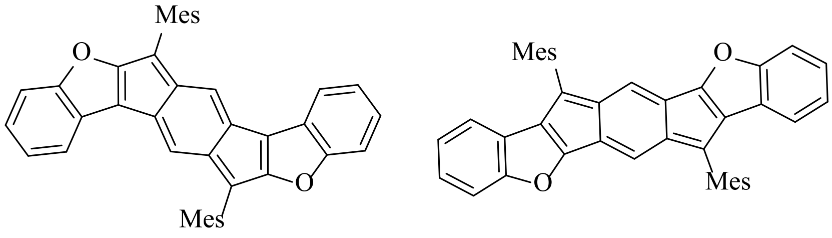


Figure 7: Late-stage modification of *syn* indacenodibenzothiophene to its sulfonated derivative

This simple transformation incorporates the electron withdrawing sulfonyl group which detracts from the electron density within the compound. This significantly altered the energy levels of the HOMO and the LUMO. The overall energies of the HOMO and the LUMO were lowered, but the gap between the two was increased to a slight degree. Additionally, the sulfone derivative displayed a change in the bond alternation pattern within the *s*-indacene core. This is explained through NICS calculations that show the flipped bond pattern alleviates antiaromatic character of the *s*-indacene, helping to stabilize the sulfonated derivative. Though the reduced antiaromatic character is not favorable for organic electronic application of IDBTs, the effect of incorporating electron withdrawing groups on the electronic properties of the compound is an interesting way of tuning the electronic properties of a compound. Typically, such modification of the electronic properties of a structure would entail an entirely new synthetic route, taking time and resources to develop. However, this study indicates there is potential for late-stage modifications and fine tuning of electronic properties.

Indacenodibenzofurans (IDBFs)

Another family of indenofluorene derivatives that have been synthesized by the Haley Lab are indacenodibenzofurans (28) displayed in Figure 8. In this work, benzofurans were fused to the *s*-indacene core rather than benzothiophenes to examine the effects of incorporating a more electronegative heteroatom. NICS calculations provided further inspiration for synthesis of IDBFS. These calculations indicated the *s*-indacene within the *syn* isomer of the IDBF should display more antiaromatic character than the *s*-indacene itself, while the *anti* isomer should display increased antiaromaticity compared to its IDBT counterpart.

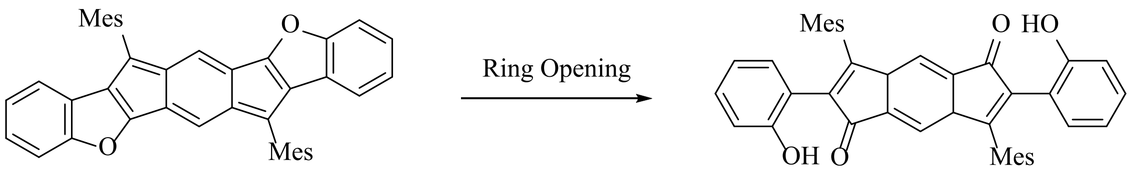


syn-IDBF

anti-IDBF

Figure 8: Structure of *syn* and *anti* indacenodibenzofuran

Synthesis of IDBF yielded a result that illustrated major differences between the *syn* and *anti* isomers of the product. The *syn* isomer of IDBF displayed only a slight decrease in the HOMO-LUMO energy gap but also highly increased antiaromatic character. Incorporation of the more electronegative oxygen heteroatom perturbed the charge distribution within the *s*-indacene, explaining the increased antiaromatic character found through NICS calculations. In the case of IDBF's *anti* isomer, this product was only synthesized in trace amounts as the five membered ring of the fused heterocycle would undergo a spontaneous ring opening displayed in Figure 9. This research illustrated the ability to fine tune electronic properties of organic compounds through variation of incorporated heteroatoms, which opens the door or future analysis of other potential heteroatoms.

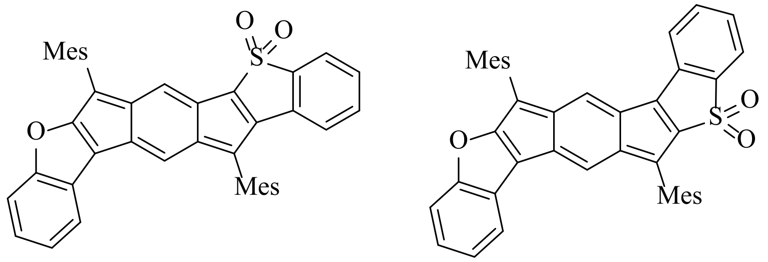


anti-IDBF

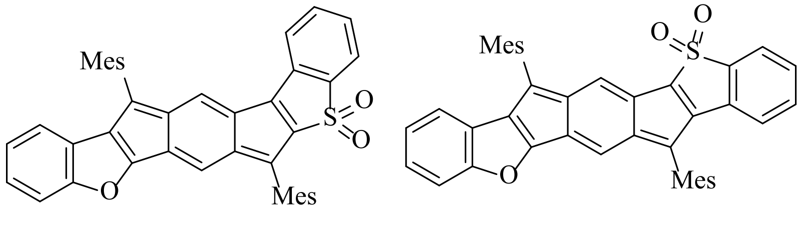
Figure 9: Spontaneous ring opening of *anti* indacenodibenzofuran

Proposed Study

In an attempt to further modulate the properties of indenofluorene derivatives, I aimed to synthesize indacenobenzofuranbenzothiophene (IBFBT) which combines the findings of the previous studies into an asymmetric heterocycle-fused *s*-indacene. The structure of IBFBT is shown in Figure 10.



syn-anti IBFBT *syn-syn* IBFBT



anti-syn IBFBT *anti-anti* IBFBT

Figure 10: Structure of all isomers of indacenobenzofuranbenzothiophene

This asymmetric structure fuses both a benzofuran and a benzothiophene onto the *s*-indacene core and utilizes a late-stage modification from the literature to create the sulfone derivative. We are interested in how the electronic properties of this asymmetric structure compare to those of the previously synthesized indenofluorene derivatives as the structure of IBFBT contains both an electron donating group in the oxygen heteroatom and electron withdrawing group in the sulfonyl group.

It is important to note that prior work had already been conducted towards the synthesis of IBFBT before I had joined the project. The foundation of this prior work was based off another asymmetric indenofluorene derivative that had been synthesized in the Haley Lab in the past (29) known as benzo-indaceno-thiophene (BIT). This asymmetric indenofluorene derivative replaced one of the outer benzene rings of indenofluorene with a thiophene heterocycle. Synthesis of BIT utilized a compound known as diethyl 2-bromo-5-chloroterephthalate, in which the bromine atom was first replaced by a benzene before the chlorine atom was replaced by a thiophene. This was accomplished through successive Suzuki cross-coupling reactions that are described in greater detail in the following section.

Initial efforts to synthesize IBFBT aimed to follow a similar model, in which benzofuran and benzothiophene would be incorporated onto diethyl 2-bromo-5-chloroterephthalate as well through successive Suzuki cross-coupling reactions. However, the use diethyl 2-bromo-5-chloroterephthalate proved to be unfeasible in the synthesis of IBFBT as upon initial Suzuki cross-coupling, both the bromine and the chlorine atoms would be replaced by a single heterocycle, making synthesis of IBFBT impossible with this compound. It was at this point where I joined the project with the focus on developing a new core material that would prove to be more selective in the initial Suzuki cross-coupling.

Methods

In this study we aimed to develop a reliable synthetic route to our target IBFBT by building upon the synthetic routes of other indenofluorene derivatives. The established synthetic pathway entails synthesis of a core coupling partner that is functionalized with leaving groups and carbonyl groups. It also entails the synthesis of outer coupling partners that are appended to the core through a Suzuki cross-coupling reaction. Following incorporation of the outer coupling partners to the core coupling partner, a saponification generates the dicarboxylic acids for a Friedel-Crafts acylation. The Friedel-Crafts acylations cyclizes the coupled product to yield the general structure of the desired final product. This cyclized product will undergo a mesityl lithiation addition to incorporate bulky mesityl groups that stabilize the compound. Finally, a tin reduction and oxidation of the sulfur heteroatom will yield IBFBT. The following section details the mechanism of these important synthetic reactions.

Important Synthetic Reactions

Suzuki Cross-Coupling

The Suzuki cross-coupling reaction is a fundamental reaction in organic synthesis as it enables the formation of carbon-carbon bonds within structures (30). This reaction has been essential to the preparation of many organic compounds including prior indenofluorene derivatives. This reaction links together coupling partners functionalized with either a nucleophile or a boronated structure using a palladium (II) catalyst. Generally, a Suzuki cross-coupling works through the following reaction scheme shown in Figure 11. The palladium undergoes an oxidative addition with the coupling partner containing a strong nucleophile. For our purposes, this nucleophile is a triflate group (-OTf), which is bound to the core benzene of our final product. The oxidative addition yields an organopalladium complex in which palladium bonds to both the triflate and the organic material while breaking the bond between. The triflate group is then removed from the organopalladium complex through the addition of a base, which replaces the triflate to form an intermediate. This intermediate species is highly reactive and will react with the boronated coupling partner through a process known as transmetalation. For our synthesis there are two separate boronated coupling partners, the benzofuran and the benzothiophene, to yield an asymmetric product. The boronate ester, which has been turned into boronic acid through the addition of water, removes the base on the intermediate and replaces it with the heterocycle going into the product. This then forms a complex in which both organic materials from each coupling partner are attached to the palladium center, to eventually bond together the carbons within their structures. This bond is created through a reductive elimination that frees the palladium catalyst and forms a carbon-carbon bond between the core coupling partner and the outer coupling partner, forming a precursor for our target molecule.

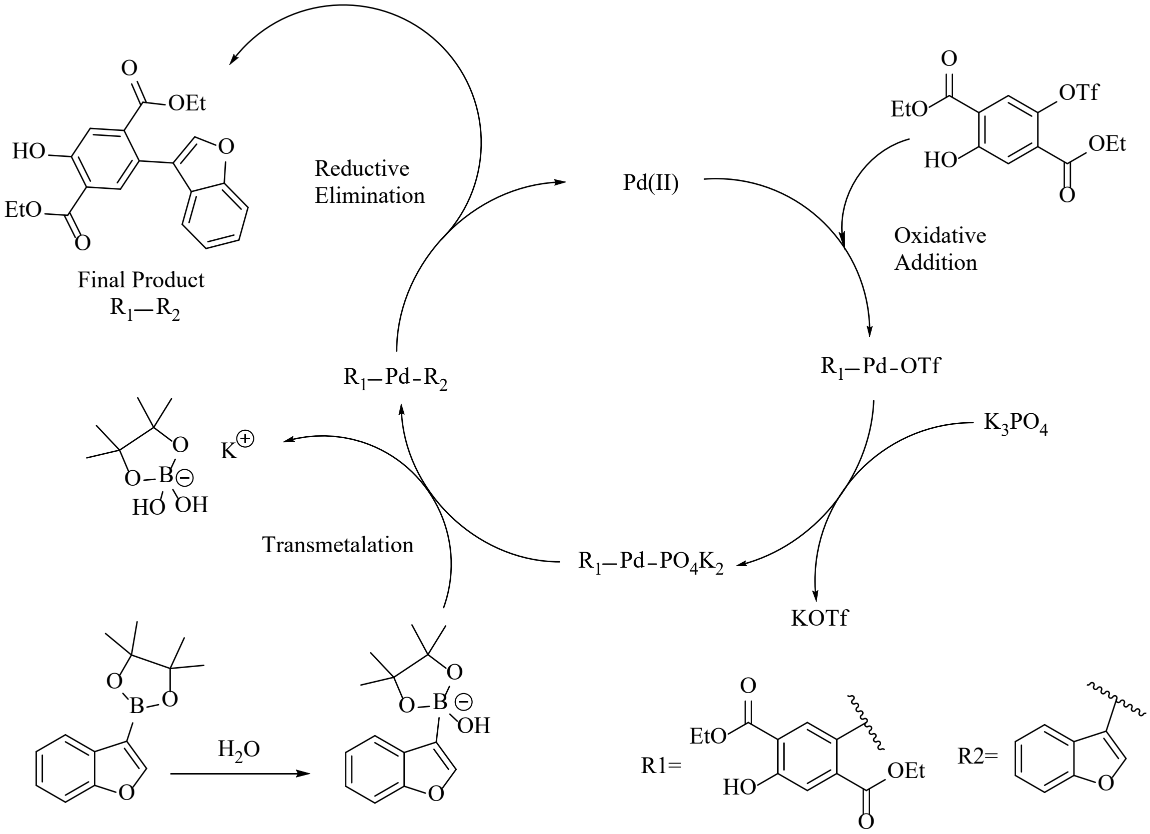


Figure 11: Reaction mechanism of Suzuki cross-coupling reaction

Friedel-Crafts Acylation

Friedel-Crafts acylation is another fundamental organic chemistry reaction in which an arene reacts with an acyl chloride using an aluminum chloride catalyst (31). Acyl chlorides refer to a functional group in which a carbonyl is bonded to a chlorine atom. For our synthesis, the core coupling partner from the Suzuki reaction already contains carbonyl groups in the form of esters. These esters can then be easily saponified into carboxylic acids. Exposure of the carboxylic acids to phosgene ($COCl_2$) will replace the hydroxyl with a chlorine, preparing it for the acylation reaction. The Friedel-Crafts acylation mechanism starts with the addition of the aluminum chloride catalyst. The aluminum chloride will bond to the chlorine to form a negatively charged structure. The remaining acylium ion is positively charged and unstable. To compensate for the instability of the ion, the positive charge is shared between the oxygen and carbon. The fused heterocycle then utilizes one of its double bonds, as they are electron dense, to bind to the carbon exhibiting an electron deficiency to create a carbon-carbon bond. Finally, the negatively charged aluminum chloride intermediate removes a hydrogen from the heterocycle's ring to form hydrochloric acid restoring both the aluminum chloride as well as the conjugation of the heterocycle. This process is illustrated in Figure 12.

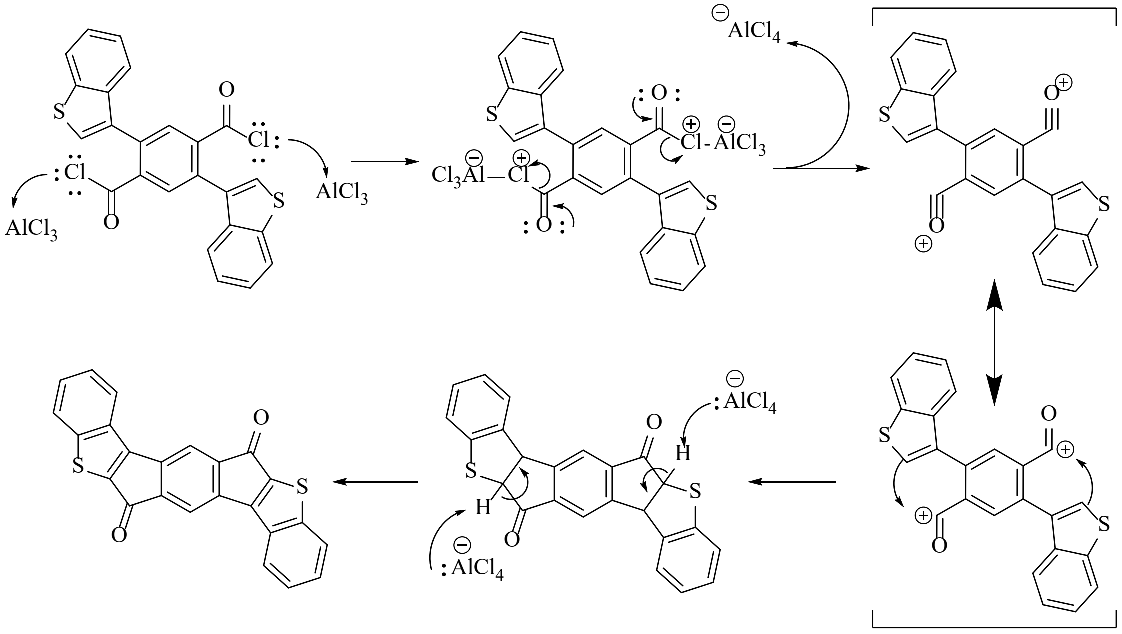


Figure 12: Reaction mechanism of Friedel-Crafts acylation

Lithiation Reactions

Lithiation addition reactions are yet another way for us to form carbon-carbon bonds and incorporate different carbon-based groups into an organic structure. Lithiation additions start with the use of an organolithium reagent such as *n*-butyllithium. Organolithium reagents are highly reactive due to the nature of carbon-lithium bonds. The difference in electronegativity of the two atoms makes the bond display practically ionic character (32). This ionic character makes the carbon-lithium bond highly reactive, and this quality can be used in different ways to help combine organic materials. The most widely employed use of organolithium reagents is in a carbolithiation reaction. In this reaction, structures containing double or triple carbon-carbon bonds can incorporate the organolithium reagent, adding the lithium to one end of the bond and the organic material on the other end. Carbolithiation reactions are useful in synthesizing new organolithium reagents for specific needs within reactions.

Another way that organolithium reagents combine organic structures is through an SN2 reaction. In an SN2 reaction, the organic material that the organolithium reagent reacts with contains a good leaving group. Carbon bound to lithium attacks the other carbon connected to the leaving group. This results in the lithium being taken away by the leaving group and the formation of carbon-carbon bond. Organolithium reagents will also attack carbonyls to create a carbon-carbon bond and an alcohol group. Such reactions have been utilized in synthesis of prior indenofluorene derivatives to incorporate the mesityl groups necessary to stabilize the structure (23) followed by a tin reduction with an unknown mechanism to yield the final product. This specific reaction was performed in the presence of THF, which is a solvent that can bind to the free lithium ion produced by the reaction. This reaction scheme is illustrated in Figure 13.

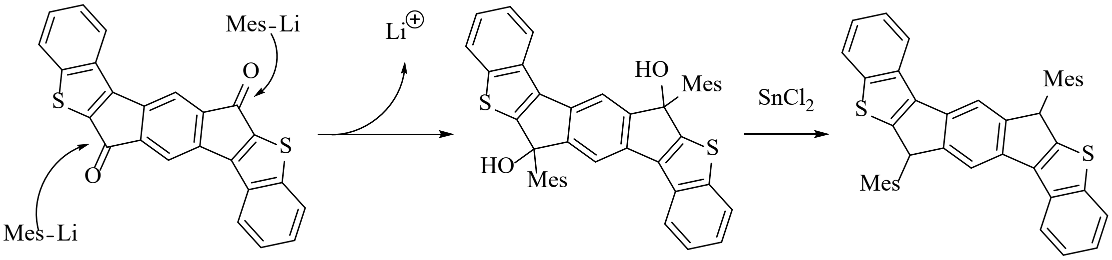


Figure 13: Reaction mechanism of mesityl lithiation addition followed by tin reduction

Purification and Characterization

The preparation of the desired compound cannot be accomplished through successive synthetic reactions alone. After each reaction it is necessary to isolate the product from the reaction, to remove impurities, and to verify that the desired product was indeed synthesized. Different purification processes are utilized based off the chemical properties of each synthetic reaction and sometimes multiple methods must be used together to best purify the product. The following section outlines the processes used to purify and characterize the desired product after each synthetic step.

Chromatography

Chromatography is a means of separating compounds that are in a mixture (33). The process works based off the difference in polarity of the compounds within the mixture. General separation of products is typically done through column chromatography where silica is loaded in a column, followed by a thin layer of sand and the crude reaction product on top. These compounds are then eluted down the column through the silica using a predetermined solvent mixture. Normal column chromatography simply allows the solvent to flow down the column with gravity while flash chromatography introduces air pressure to help increase the rate at which solvent flows through the column. The solvent mixture used is determined through thin layer chromatography (TLC). During TLC, a small amount of the crude reaction product is placed at one end of a silica plate, and a chamber is prepared containing a thin layer of the solvent mixture. The end of the silica plate containing the product is placed directly into the thin layer of solvent, and the plate is stood vertically against the wall of the chamber. As the solvent runs up the plate, the compounds will move up along with it. Silica is a highly polar substance, and products will move up the silica plate at different rates based on how polar they are. Ideally, a solvent mixture would move products at rates different enough to yield separation. Separation of products observed on a TLC plate would translate to separation of products within a column. As the solvent mixture flows through the column, fractions of the solvent are collected. Collection of the solvent in fractions will isolate products from one another, and once all products are separated, fractions containing the desired product can be combined. The solvent is then removed under reduced pressure yielding the pure product.

Recrystallization

Another means by which organic compounds can be purified is through recrystallization of the product (34). Recrystallization is best done when it is known that the amount of impurities in the product is small and when product solubility can be increased with temperature. Recrystallization starts with heating the crude reaction mixture in a solvent until the products is completely dissolved. As the solution cools, the desired product will become less soluble and begin to form crystal lattices that precipitate out of solution. Formation of crystals only occurs through the proper selection of solvent based off the solubility properties of the product and the impurities with the chosen solvent. Ideal solvent-product interactions in a recrystallization process would have the product display high levels of solubility when the solvent is at high temperatures, and low solubility at lower temperatures, while the solubility of the impurities remain high at both temperatures. Screening of the solubility of the product in different solvents may be necessary, and mixtures of multiple solvents can also be used to create ideal solubility conditions for recrystallization. Once crystals have been formed, they are filtered, dried and examined for purity. If the crystals are not pure then the process can be repeated either with the same or modified solvent conditions to further purify the product.

^{1}H NMR Spectroscopy

Characterization of products is done through ^{1}H nuclear magnetic resonance (NMR) spectroscopy, which provides valuable insight into the structure and purity of the compound (35). Nuclei of atoms can be thought to be spinning and display a magnetic moment that causes a magnetic field. In NMR spectroscopy, compounds are dissolved in a deuterated solvent and exposed to a high intensity external magnetic field. Different nuclei will be affected by this external field at specific nuclear magnetic frequencies inherent to the nuclei, yielding different types of NMR spectroscopy. In this study we focus on hydrogen nuclei as they are abundant throughout the structure of our product molecules. The intrinsic magnetic field of the hydrogen nuclei can either align with this external field or oppose it, creating two separate spin states of higher or lower energy level. This difference in energy between the spin states is affected by the electronic environment of the nuclei which is related to the structure of the compound. The difference in energy of the two spin states can be measured and then spectropically depicted yielding information about the compound’s structure and purity.

Results and Discussion

Synthesis

Synthesis begins with functionalization of the outer coupling partners, benzofuran and benzothiophene. Both compounds are commercially available and thus I started with synthesis of the benzofuran coupling partner. To incorporate the boronic ester, it is first necessary to install a bromine at the desired position on the benzofuran. Instillation at the 2-position creates an *anti* coupling partner while instillation at the 3-position yields a *syn* coupling partner. Benzofuran underwent a bromination reaction where two bromines were added across the carbon-carbon double bond within the five membered ring. I desired to first create the *syn* coupling partner thus the bromine at the 2-position was removed so that the boronic ester will only be installed at the 3-position. The bromine was removed through a dehalogenation reaction to yield the desired product of 3-bromobenzofuran (Figure 14).

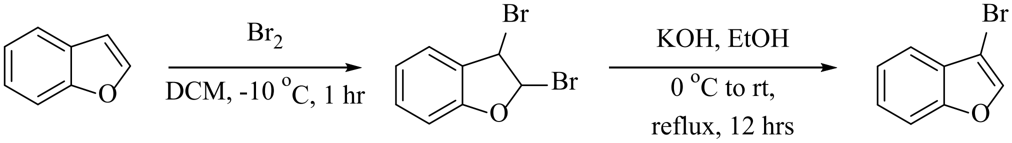


Figure 14: Synthesis of 3-bromobenzofuran

At this point, the bromine can be replaced with the boronic ester we desire to use within the later Suzuki cross-coupling reaction. Incorporation of the boronic ester was done through a borylation reaction using *n*-butyllithium (*n*-BuLi) and the boronic ester isopropoxy pinacol borate in diethyl ether. The *n*-BuLi in this reaction helps to catalyze the addition of the boronic pinacol ester onto the bromobenzofuran, replacing the bromine that we attached as it is a good leaving group (Figure 15).

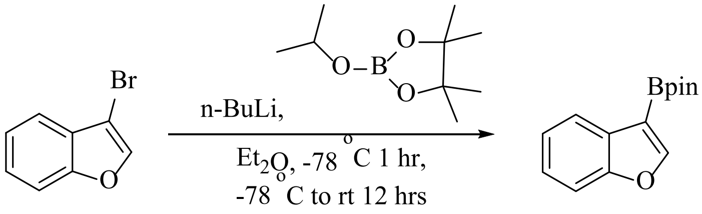


Figure 15: Synthesis of benzofuran coupling partner

Preparation of a new core coupling partner was the next target in our synthetic route. As the previous core displayed low selectivity, we initially aimed to synthesize a core that contained an alcohol and a triflate group rather than a chlorine and a bromine. In Suzuki reactions, triflate groups serve as extremely good leaving groups due to their ability to stabilize their charge when they are removed as an anion. Triflates would be specifically targeted in a Suzuki cross-coupling as alcohols do not function as leaving groups. Synthesis began with 1,4-dibromo-2,5-dimethoxybenzene which was chosen due to the belief that incorporation of the necessary functional groups for more selective Suzuki could be accomplished relatively easily. To begin, the first step was to incorporate carbonyl groups onto the structure, in the form of aldehyde groups, to be used later in Friedel-Crafts acylations. Incorporation of aldehydes was done through a common reaction to form aldehydes using the *n*-BuLi and DMF. After incorporation of the carbonyl, boron tribromide was used to change the methoxy groups on the compound (-OMe) into hydroxy groups (-OH). These hydroxy groups are targeted in a monotriflation reaction in which a single alcohol is exchanged for a triflate group, yielding our desired core. This synthetic scheme is depicted in Figure 16. Unfortunately, this synthetic route led to unforeseen difficulties, as the aldehyde groups proved to be very unstable and caused decomposition of the diol product before the monotriflation could be performed.

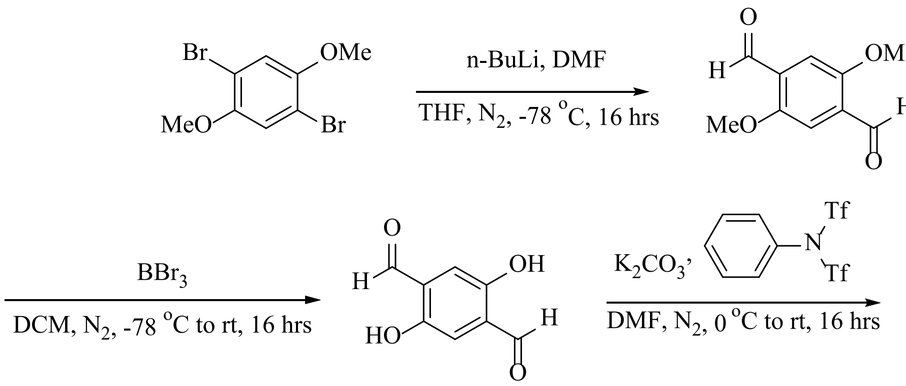


Figure 16: Synthetic route of redesigned core coupling partner

New starting material dimethyl-2,5-dihydroxy-1,4-cyclohexanedicarboxylate was chosen as the next starting material to form the core coupling partner. This starting material incorporated carbonyls in the form of esters rather than aldehydes to create more stable products during the synthesis. The first synthetic steps for this material were done by my mentor. The starting material was aromatized using N-chlorosuccinimide (NCS) to yield the benzene core for our final product, and the material was trans-esterified to give the diethyl ester. The synthetic route for this core depicted within Figure 17.

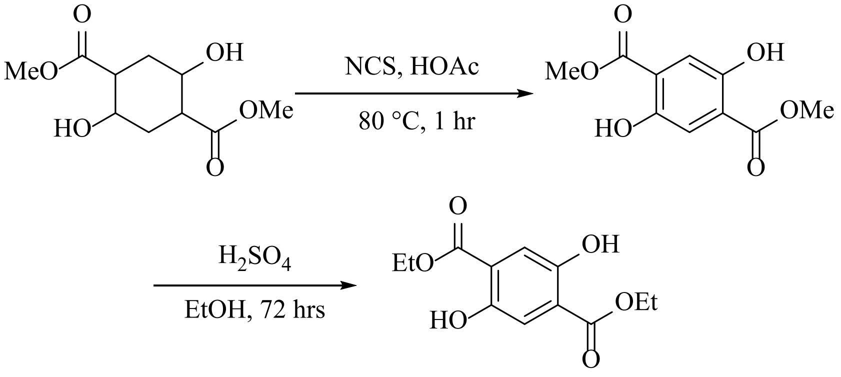


Figure 17: Synthesis of diethyl ester diol core

From here, I attempted to run the mono-triflation reaction (Figure 18) that we failed to perform on the prior core coupling partner. This reaction is commonly done within the Haley lab in other projects conducted by member Efrain Vidal. The reaction utilizes K_2CO_3 along with N-phenylbis(trifluoromethanesufonimide), which is a milder triflation reagent than other triflation reagents used for reactions that need greater selectivity.

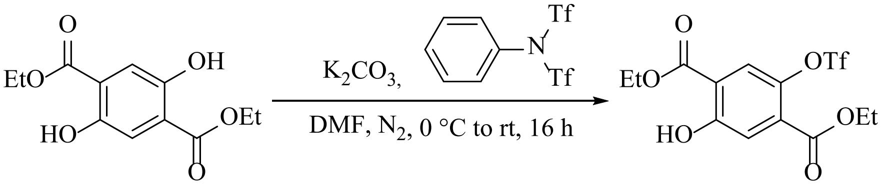


Figure 18: Mono-triflation reaction

This reaction, however, yielded the triflated product in too small of a yield to be considered viable this early in the synthetic route. Another core had to be designed for the synthesis of our desired product.

It was during this time where we decided to revisit the original core coupling partner utilized in the synthesis of BIT. We reasoned that exchanging the bromine atom for an iodine atom would make this core much more selective during the Suzuki reaction. Iodine serves as a better leaving group than other halides due to its size. As iodine is a bigger atom than other halides, the charge density of the ion is stabilized due to greater charge distribution through its structure. This makes iodine a better leaving group than bromine, which should make it more selective during the initial Suzuki cross-coupling. Synthesis of the redesigned core coupling partner began as it did in the synthesis of BIT. Starting with 1-bromo-4-chloro-2,5-dimethylbenzene, this compound underwent an oxidation reaction to change the methyl groups into carboxylic acids, incorporating the carbonyl group. This then underwent an esterification reaction to replace the hydroxyl groups with esters. Finally, the bromine atom was exchanged for an iodine using a Finkelstein halide exchange reaction. Synthesis of the redesigned original core coupling partner is shown in Figure 19.

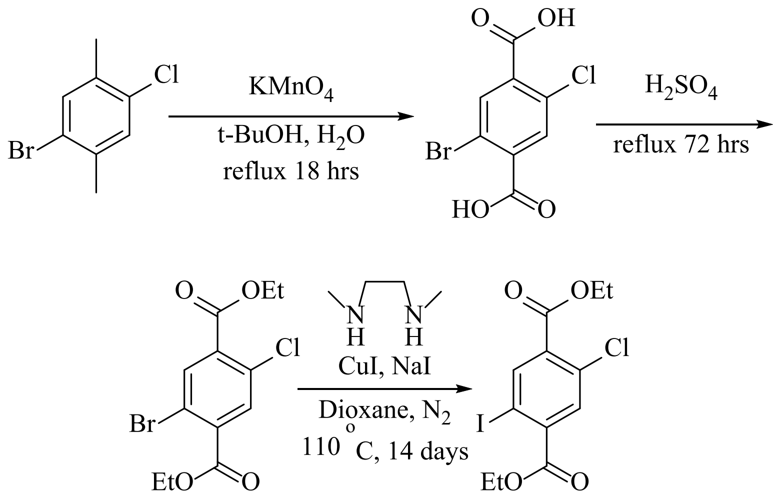


Figure 19: Synthetic route for final core design

Discussion

Unfortunately, this was as far as I was able to manage in the synthesis of indacenobenzofuranbenzothiophene. The synthetic route proved to be trickier than expected as certain reactions along our synthetic path did not yield as much product as expected and past methods of synthesizing indenofluorene derivatives had to be altered to suit the synthesis of the asymmetric product. Furthermore, the rerunning of reactions to build up suitable amounts of coupling partners proved to be quite time consuming and further detracted from my ability to reach the final product. Nonetheless, the work done has provided insight into how to synthesize the target IBFBT. An optimal core coupling partner, that is selective enough in initial Suzuki cross-coupling has been identified for the synthesis of IBFBT. Additionally, the selectivity of this newly synthesized core coupling partner could be utilized in the synthesis of additional indenofluorene derivatives.

Future Work

In the immediate future, work will focus on the full synthesis of all four IBFBT isomers. Upon synthesis of these products, characterization will be performed through several means to understand both the fundamental chemical properties as well as electronic properties and capabilities of IBFBT. Firstly, analysis through ^{1}H NMR spectroscopy will be done to roughly characterize their structures. Next ^{13}C NMR spectroscopy will be used to corroborate the findings of ^{1}H NMR spectroscopy. Once it has been determined through spectroscopy that the desired product has been synthesized and is pure, crystals of the product will be isolated and submitted for X-ray crystallography. In this process, a single crystal of the product is subjected to light rays that diffract off the atoms within the crystal. This diffraction is measured and used to compute a 3-D image of the structure of the compound, revealing structural information such as bond length and how the structure packs in the crystal.

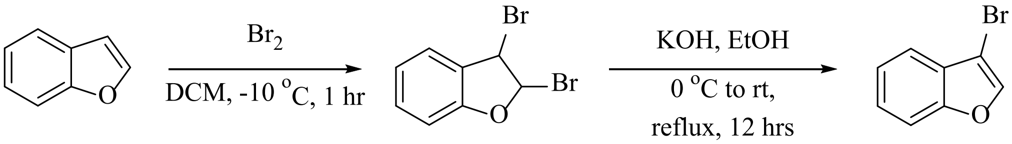
Knowing these structural properties will help elucidate the electronic properties. As far as electronic analysis goes, the final product will be subject to analysis done on other indenofluorene derivatives. Cyclic voltammetry will be utilized to determine the energies of the HOMO and LUMO, UV-Vis spectroscopy will be used as another means to calculate the energy gap, and NICS calculations will be performed to determine the aromatic and antiaromatic character of the different rings within IBFBT with particular focus on the antiaromatic character of the *s*-indacene core.

Following characterization of the IBFBT isomers, the chemical and electronic properties of IBFBT can be compared to indenofluorene derivatives synthesized in the past. Characterization data will reveal if the asymmetric structure is favorable for organic semiconductor applications, and analysis of the effects of the incorporated electron donating and electron withdrawing groups may shed light on what other modification to the structure would be beneficial to the electronic properties. Potential modifications include changing the structure of the incorporated heterocycle, as well as changing of the incorporated heteroatom. Comparison of the newly synthesized IBFBT to past indenofluorene derivatives will help to decide what specific changes should be incorporated in future indenofluorene derivatives.

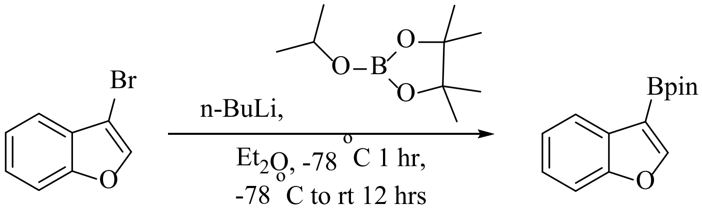
Long term, the goal remains to synthesize an organic compound capable of mimicking the electronic properties of silicon for application as a semiconductor within electronic devices. The synthesis of such a compound and the development of a reliable synthetic route that can be scaled for manufacturing purposes could spur an evolution within the electronics industry. New classes of electronic devices, based off the flexibility and biocompatibility of organic electronic materials, can revolutionize how we utilize electronic devices in all industries. Accessing such potential for organic electronic application will rely on the continued synthesis and improvement of organic electronic materials today.

Experimental Details

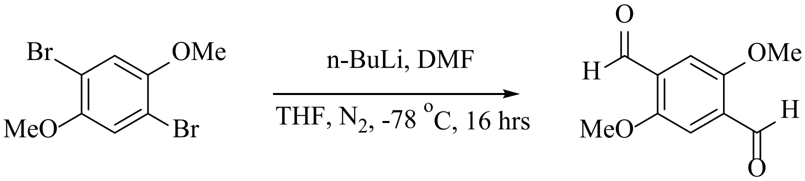
The following section details the experimental procedures and ^1H NMR spectroscopy characterization of the products obtained.



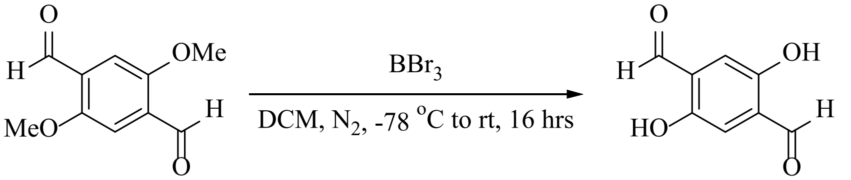
3-Bromobenzofuran: Benzofuran (4.6 mL, 42.3 mmol, 1 equiv.) was dissolved in 100 mL DCM and cooled to -10 ºC. Bromine (3 mL, 46.6 mmol, 1.1 equiv.) was dissolved in 15 mL DCM and added dropwise. After 1 h, saturated NaOH (5 mL) solution was added and dissolved before saturated $Na_2S_2O_3$ (100 mL) solution was added. The brominated product was extracted with DCM before being dissolved in EtOH (100 mL). Saturated KOH (100 mL) was placed in a 0 ºC ice bath, and the solution of the crude dibromide was added dropwise. The reaction refluxed for 12 h before EtOH was removed through reduced pressure. The crude product was then extracted using EtOAc and washed 3x with water and once with brine. Solvent was again removed through reduced pressure to yield a brown-orange oil. (1.97 g, 24 %) This reaction was conducted multiple times to build a stockpile of the product. ^1H NMR (500 MHz, Chloroform-d_3) δ 7.66 ppm (s, 1H), 7.56 ppm (dd, J = 7.5, 1.6 Hz, 1H), 7.50 ppm (dd, J = 7.8, 1.2 Hz, 1H), 7.43 – 7.30 ppm (m, 2H).



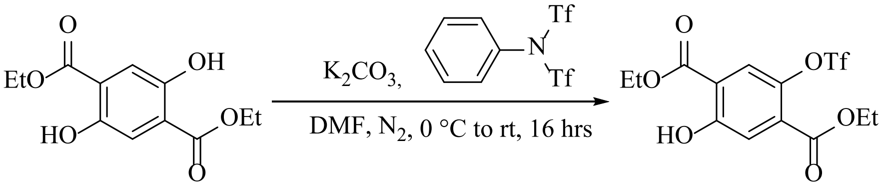
Borylation of 3-Bromobenzofuran: 3-Bromobenzofuran (4.88 g, 24.8 mmol, 1 equiv.) was dissolved in ether and cooled to -78 °C and stirred for 20 min. *n*-Butyllithium (10.9 mL, 27.2 mmol, 1.1 equiv.) was added dropwise and the reaction stirred an additional 1 h. Isopropoxy pinacol borate (7 mL, 34.7 mmol, 1.4 equiv.) was added dropwise, and the reaction stirred and warmed to rt over 12 h. The reaction was quenched with water, extracted with DCM, and the organic layer was washed 3x with water and once with brine. Solvent was removed through reduced pressure to yield colorless crystals. Yield undetermined as repeated process of recrystallizations yielded increments of product that were used. ^{1}H NMR (500 MHz, Chloroform-d$_3$) δ 7.95 ppm (s, 1H), 7.92 ppm (dd, J = 6.8, 2.3 Hz, 1H), 7.50 ppm (dd, J = 6.9, 1.7 Hz, 1H), 7.32 – 7.25 ppm (m, 2H), 1.37 ppm (s, 12H).



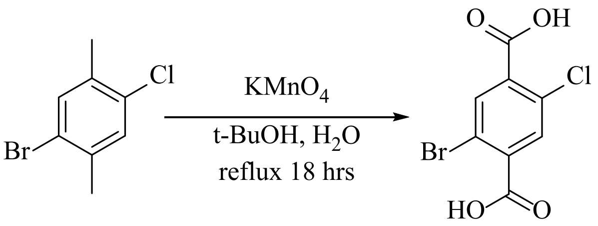
2,5-Dimethoxy-1,4-benzenedicarboxaldehyde: 1,4-Dibromo-2,5-dimethoxybenzene (2 g, 6.76 mmol, 1 equiv.) was dissolved in 34 mL THF and cooled to -78 °C. *n*-Butyllithium (9.2 mL, 14.72 mmol, 2.17 equiv.) was added dropwise and stirred for 3 h. DMF was then added (2.4 mL, 30.9 mmol, 4.5 equiv.) and stirred 1 h at -78 °C and then 1 h at rt. The product was extracted with DCM, and washed 3x with water. Solvent was removed with reduced pressure to yield a solid. (0.68 g, 52%). ^{1}H NMR (500 MHz, Chloroform-d_3) δ 10.51 ppm (s, 2H), 7.46 ppm (s, 2H), 3.95 ppm (s, 6H).



2,5-Dihydroxy-1,4-benzenedicarboxaldehyde: 2,5-Dimethoxy-1,4-benzenedicarboxaldehyde (0.68 g, 3.53 mmol, 1 equiv.) was dissolved in 15.3 mL sparged DCM and cooled to -78 °C. BBr_3 (1.45 mL, 15.3 mmol, 4.32 equiv.) was added dropwise and the reaction was warmed to rt over 12 h. The reaction was quenched with water and the product was extracted with DCM and washed 3x with water. Solvent was removed through reduced pressure yielding a solid. (0.58 g, 98%). ^{1}H NMR (500 MHz, Chloroform-d_3) δ 10.22 ppm (s, 2H), 9.96 ppm (s, 2H), 7.24 ppm (s, 2H).



Diester Diol Mono Triflation: 2,5-Dihydroxyterephthalic acid diethyl ester (130 mg, 0.51 mmol, 1 equiv.) and K_2CO_3 (141 mg, 1.02 mmol, 2 equiv.) was dissolved in 15 mL sparged DMF and cooled in a 0 °C. N-phenylbis(trifluoromethanesufonimide) (182 mg, 0.51 mmol, 1 equiv.) was dissolved in 10 mL sparged DMF, and added dropwise. The reaction was allowed to rise to rt over 16 h. The reaction was quenched with 3M HCl, diluted with distilled water, and stirred 10 min to yield a solid. Characterization and yield undetermined as majority of product was starting material.



2-Bromo-5-chloro-1,4-benzenedicarboxylic acid: 1-Bromo-4-chloro-2,5-dimethylbenzene (10 g, 45.56 mmol, 1 equiv.) was dissolved in 80 mL *t*-BuOH and 80 mL of water. $KMnO_4$ (21.59 g, 136.67 mmol, 3 equiv.) was added and the reaction was refluxed for 1 h. Additional $KMnO_4$ (21.59 g, 136.67 mmol, 3 equiv.) was then added to the reaction and the reaction refluxed an additional 24 h. After cooling the reaction was filtered and then was quenched with HCl to retrieve a white powder. This white powder was stirred at reflux with H_2SO_4 and EtOH for 18 h. Once cool, the reaction was neutralized with $NaHCO_3$ and small amounts of KOH. The resultant precipitate was filtered and dissolved in CH_2Cl_2. Solvent was removed under reduced pressure yielding white crystals. (7.31 g, 57%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.93 ppm (s, 2H), 8.06 ppm (s, 1H), 7.87 ppm (s, 1H).

Glossary

Aromatic: Carbon ring structure that is planar, contains full pi-conjugation, follows the rule of 4n+2 pi electrons, and displays diatropic ring currents

Antiaromatic: Carbon ring structure that is planar, fully conjugated, follows the rule of 4n pi electrons, and displays paratropic ring current

Conductor: A material that freely conducts electricity through the movement of electrons

Conjugated: A molecule is conjugated when the p-orbitals of the atom within the structure overlap.

Cyclic Voltammetry: Electrochemical technique to measuring the current response of a redox active solution to a sweep of potentials

Heteroatom: Within chemistry this means any atom not carbon or hydrogen

Heterocycle: Any cyclic structure that contain at least one heteroatom within the ring itself

HOMO: The Highest Occupied Molecular Orbital, lower in energy than the LUMO

Indenofluorene: A carbon structure with 5 fused rings, the center and outer rings contain six carbon atoms and the rings in between only contain 5 atoms. The entire structure contains 20 fully conjugated carbon atoms.

Insulator: A material that resists the flow of electrons and is not conductive

LUMO: The Lowest Unoccupied Molecular Orbital, higher energy than the HOMO

Moiety: A molecule that is given a name because it is found in multiple different molecules

NICS: Nuclear Independent Chemical Shift, NICS values are the negative of the absolute shielding. Typically positive NICS values are associated with paratropic ring current and negative NICS values are associated with diatropic ring currents

NMR Spectroscopy: An technique which applies a magnetic field to an atomic nucleus, mainly hydrogen for my purposes, and radio frequency pulses to characterize the resonant frequency of that atomic nucleus according to its chemical or environmental surroundings.

Polymer: A substance comprised of building blocks that are identical or very similar

Ring Current: Electric current caused by charged particles flowing in a circle, such as electrons within a cyclic structure

Semiconductor: A material that has a conductivity somewhere between and insulator and a conductor commonly used in electronic devices. Ex: Silicon

Structural Isomer: Each of two or more compounds with the same formula but different arrangement of atoms

UV-Vis Spectroscopy: Ultraviolet visual spectroscopy is used to measure how much light a substance absorbs. This is done by measuring the intensity of the light that goes through the sample with respect to the intensity of a light going through a reference or blank

Valence Electrons: The electrons that occupy the highest energy orbital of an atom or the HOMO

Bibliography

(1) Mishra, Ashutosh. “Impact of silica mining on environment”. *Journal of Geography and Regional Planning* 8, no. 6 (2015): 150-156

(2) Zhang, Xi., Peter Bäuerle, Takuzo Aida, Peter Skabara, and Cherie Kagan. 2012. “Organic Electronics for a Better Tomorrow: Innovation, Accessibility, Sustainability” Paper presented at Chemical Sciences and Society Summit (CS3), San Francisco, CA, September. https://www.rsc.org/globalassets/04-campaigning-outreach/policy/research-policy/global-challenges/organic-electronics-for-a-better-tomorrow.pdf

(3) Rhaman, Atikur., “A Review on Semiconductors Including Applications and Temperature Effects in Semiconductors”. *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)* 7, no. 1 (2014): 50-70

(4) J. E. Lilienfeld. “Method and apparatus for controlling electric currents”, U. S. Patent No. 1,745,175. (1930)

(5) World Semiconductor Trade Statistics. “WSTS News Release March 2022” *WSTS Inc* (2022) https://www.wsts.org/esraCMS/extension/media/f/WST/5401/WSTS_nr-2022_03.pdf

(6) Yolkin, K. ,S., D. K. Yolkin, A D Kolosov, N A Ivanov, and M G Shtayger. 2018. “Technologies, which allow to reduce an impact of metal silicon production on the environment”. Paper presented at International Scientific and Research Conference "Metallurgy: Technologies, Innovation, Quality. Metallurgy, Novokuznetsk, Russia, November 15-16. https://iopscience.iop.org/article/10.1088/1757-899X/411/1/012028

(7) Kim, Sunju, Chungsik Yoon, Seunghon Ham, Jihoon Park, Ohun Kwon, Donguk Park, Sangjun Choi, Seungwon Kim, Kwonchul Ha, and Won Kim. “Chemical Use in the Semiconductor Manufacturing Industry”. *International Journal of Occupational and Environmental Health* 24, no. 3–4 (2018): 109–118.

(8) Zani, Lorenzo., Alessio Dessì, Daniele Franchia, Massimo Calamante, Gianna Reginato, and Alessandro Mordini. “Transition metal-catalyzed cross-coupling methodologies for the engineering of small molecules with applications in organic electronics and photovoltaics”. *Coordination Chemistry Reviews* 392, (2019): 177-236.

(9) Maust, Ruth L., Penghao Li, Baihao Shao, Sarah M. Zeitler, Peiguan B. Sun, Harrison W. Reid, Lev N. Zakharov, Matthew R. Golder, and Ramesh Jasti. "Controlled Polymerization of Norbornene Cycloparaphenylenes Expands Carbon Nanomaterials Design Space". *ACS Central Science* 7, no. 6 (2021): 1056–1065.

(10)Gomez-Romero, Pedro., "Hybrid Organic-Inorganic Materials-In Search of Synergic Activity". *Adv. Mater.* 13, no. 3 (2001): 163-174.

(11)Simon, Daniel T., Erik O. Gabrielsson, Klas Tybrandt, and Magnus Berggren. "Organic Bioelectronics: Bridging the Signaling Gap Between Biology and Technology". *Chemical Reviews* 116, no. 21 (2016): 13009–13041.

(12)Zvezdin, Alexandra., Eduardo Di Mauro, Denis Rho, Clara Santato, and Mohamed Khalil. "En route toward sustainable organic electronics". *MRS Energy and Sustainability* 7, no. 16 (2020): 1-8.

(13)Anthony, John E.. "The Larger Acenes: Versatile Organic Semiconductors". *Angewandte Chemie International Edition* 47, no. 3 (2008): 452–483.

(14)Karl, Norbert. "Charge carrier transport in organic semiconductors". *Synthetic Metals* 133, (2003): 649-657

(15)Fudickar, Werner, and Torsten Linker. "Why Triple Bonds Protect Acenes from Oxidation and Decomposition". *Journal of the American Chemical Society* 134, no. 36 (2012): 15071–15082.

(16)Fix, Aaron G., Daniel T. Chase, and Michael M. Haley. "Indenofluorenes and Derivatives: Syntheses and Emerging Materials Applications". *Topics in Current Chemistry* 347,(2014), 159–195.

(17)Spitler, Eric L., Charles A. Johnson, and Michael M. Haley. "Renaissance of Annulene Chemistry". *Chemical Reviews* 106, no. 12 (2006): 5344–5386.

(18)Merino, Gabriel, Thomas Heine, and Gotthard Seifert. "The Induced Magnetic Field in Cyclic Molecules". *Chemistry – A European Journal* 10, no. 17 (2004): 4367–4371.

(19)Schmidt, Maximilian, Daniel Wassy, Mathias Hermann, M. Teresa González, Nicolás Agräit, Linda A. Zotti, Birgit Esser, and Edmund Leary. "Single-molecule Conductance of Dibenzopentalenes: Antiaromaticity and Quantum Interference". *Chemical Communications* 57, no. 6 (2021): 745–748.

(20)Laquindanum, Joyce G., Howard E. Katz, and Andrew J. Lovinger. “Synthesis, Morphology, and Field-effect Mobility of Anthradithiophenes”. *Journal of the American Chemical Society* 120, no. 4 (1998): 664–72.

(21)Turkoglu, Gulse., M. Emin Cinar, and Turan Ozturk. “Thiophene-Based Organic Semiconductors”. *Sulfur Chemistry. Topics in Current Chemistry* 375, no. 6 (2017): 79-123

(22)Young, Brian S., Daniel T. Chase, Jonathan L. Marshall, Chris L. Vonnegut, Lev N. Zakharov, and Michael M. Haley. “Synthesis and Properties of Fully-conjugated Indacenedithiophenes”. *Chemical Science* 5, no. 3 (2014): 1008–1014.

(23)Marshall, Jonathan L., Kazuyuki Uchida, Conerd K. Frederickson, Christian Schütt, Andrew M. Zeidell, Katelyn P. Goetz, Tristan W. Finn, et al.. “Indacenodibenzothiophenes: Synthesis, Optoelectronic Properties and Materials Applications of Molecules with Strong Antiaromatic Character”. *Chemical Science* 7, no. 8 (2016): 5547–5558.

(24)Chen, Zhongfang., Chaitanya S. Wannere, Clémence Corminboeuf, Ralph Puchta, and Paul von Ragué Schleyer. “Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion”. *Chemical Reviews* 105, no. 10 (2005): 3842–3888

(25)Makuła, Patrycja, Michał Pacia, and Wojciech Macyk. “How to Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–vis Spectra”. *The Journal of Physical Chemistry Letters* 9, no. 23 (2018): 6814–6817.

(26)Elgrishi, Noémie, Kelley J. Rountree, Brian D. Mccarthy, Eric S. Rountree, Thomas T. Eisenhart, and Jillian L. Dempsey. “A Practical Beginner’s Guide to Cyclic Voltammetry”. *Journal of Chemical Education* 95, no. 2 (2018): 197–206.

(27)Dressler, Justin J., Joshua E. Barker, Lucas J. Karas, Hannah E. Hashimoto, Ryohei Kishi, Lev N. Zakharov, Samantha N. Macmillan, et al.. “Late-stage Modification of Electronic Properties of Antiaromatic and Diradicaloid Indeno[1,2-b]fluorene Analogues via Sulfur Oxidation”. *The Journal of Organic Chemistry* 85, no. 16 (2020): 10846–10857.

(28)Barker, Joshua E., Tavis W. Price, Lucas J. Karas, Ryohei Kishi, Samantha N. Macmillan, Lev N. Zakharov, Carlos J. Gómez-García, Judy I. Wu, Masayoshi Nakano, and Michael M. Haley. “A Tale of Two Isomers: Enhanced Antiaromaticity/diradical Character Versus Deleterious Ring-opening of Benzofuran-fused S -indacenes and Dicyclopenta[B , G]naphthalenes”. *Angewandte Chemie International Edition* 60, no. 41 (2021): 22385–92.

(29)Marshall, Jonathan L., Nathaniel J. O'Neal, Lev N. Zakharov, and Michael M. Haley. "Synthesis and Characterization of Two Unsymmetrical Indenofluorene Analogues: Benzo[5,6]-s-indaceno[1,2-b]thiophene and Benzo[5,6]-s-indaceno[2,1-b]thiophene". *The Journal of Organic Chemistry* 81, no. 9 (2016): 3674–3680.

(30)Gujral, Sarbjeet S., Smriti Khatri, Poornima Riyal, "Suzuki Cross Coupling Reaction- A Review". *Indo Global Journal of Pharmaceutical Sciences* 2, no. 4 (2012): 351-367.

(31)Ashforth, Rebecca., and John Roger Desmurs. "Friedel-Crafts Acylation: Interactions Between Lewis Acids/Acyl Chlorides and Lewis Acids/Aryl Ketones." *Industrial Chemistry Library* 8, (1996): 3-14.

(32)García, Graciela V., and Norma Sbarbati Nudelman. "Tandem Reactions Involving Organolithium Reagents. A Review". *Organic Preparations and Procedures International* 35, no. 5 (2003): 445–500.

(33)Coskun, Ozlem. "Separation Techniques: Chromatography". *Northern Clinics of Istanbul* 3, no. 2 (2016):156–160.

(34)Tan, Helming, Maggie Reed, Kyung H. Gahm, Tony King, Mina Dilmeghani Seran, Tracy Bostick, Van Luu, et al.. "An Integrated High-throughput Screening Approach for Purification of Solid Organic Compounds by Trituration and Crystallization in Solvents". *Organic Process Research & Development* 12, no. 1 (2008): 58–65.

(35)Gerothanassis, Ioannis P., Anastassios Troganis, Vassiliki Exarchou, and Klimentini Barbarossou. "Nuclear Magnetic Resonance (NMR) Spectroscopy: Basic Principles and Phenomena: and Their Applications to Chemistry, Biology and Medicine". *Chemistry Education Research and Practice* 3, no. 2 (2002): 229–252.