

DESIGN & SYNTHESIS OF RHODANINE FLANKED BENZODITHIOPHENE
AND BENZOTHIADIAZOLE CONTAINING SMALL MOLECULE NON-
FULLERENE ACCEPTORS FOR ORGANIC SOLAR CELLS

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SMALL MOLECULE NON-FULLERENE ACCEPTORS FOR ORGANIC
SOLAR CELLS**

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ABSTRACT

DESIGN & SYNTHESIS OF RHODANINE FLANKED BENZODITHIOPHENE AND BENZOTHIADIAZOLE CONTAINING SMALL MOLECULE NON-FULLERENE ACCEPTORS FOR ORGANIC SOLAR CELLS

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Solar energy became the leading renewable energy source due to its zero-emission profile, economic advantages and abundance of its main energy source, the sun. For conversion of solar energy to electrical energy, photovoltaics is the main approach in both academia and industry while concentrated solar thermal methods gaining significant traction in the recent years. In the field of photovoltaics, organic photovoltaics have been showing significant progress over the last two decades. Although fullerene-based molecules such as PCBM as an electron acceptor entity give satisfactory outcomes for organic solar cells, significant issues, mainly the extreme cost, prevented additional developments in the area. At this point, non-fullerene acceptors came to the scene to circumvent the issues related to fullerene-based acceptors. There are a number of novel non-fullerene acceptors in the literature and rhodanine flanked molecules grabbed attention thanks to high power conversion efficiencies attained with the devices implement these acceptors. Currently, 19.50% PCE is reported and certified by the National Institute of Metrology for the small molecule NFA containing tandem solar cells. To push the

limits even further, this study aims to synthesize logically designed novel rhodanine flanked small molecules. Target small molecules contain three main parts namely, central, bridge and terminal units. For the central unit, indacenodithiophene (IDT) core and its alkylated and stannylated derivatives were synthesized successfully. Additionally, commercial benzodithiophene (BDT) and fluorene cores were utilized for practical and comparison purposes. Aldehyde modified benzothiadiazole and difluorinated benzothiadiazole were synthesized as the bridging units. A novel synthetic approach for the fluorinated derivative was demonstrated for the first time in the literature. To combine bridge units and core units, Stille and Suzuki Cross-Coupling reactions were applied. For the synthesis of the terminal unit, rhodanine was ethylated successfully. The synthesis of a rhodanine with pendant amine groups were envisioned however the attempts for their synthesis were not fruitful. The synthesis of the target final products was attempted via Knoevenagel Condensation however the expected products could not be isolated. Studies towards purification of the final products and utilization of these in organic solar cells are still ongoing.

Keywords: Organic Solar Cell, Non-Fullerene Acceptor, Benzothiadiazole, Indacenodithiophene, Benzodithiophene

ÖZ

RODANİN UÇLU BENZODİTİYOFEN VE BENZOTİYADİAZOL İÇEREN FULLEREN OLMAYAN KABUL EDİCİ KÜÇÜK MOLEKÜLLERİN ORGANİK GÜNEŞ PİLLERİ İÇİN TASARIMI VE SENTEZİ

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Güneş enerjisi temiz, ekonomik ve bol olduğu için diğer yenilenebilir enerji kaynakları arasında geniş bir paya sahiptir. Güneş enerjisinin elektrik enerjisine çevrilebilmesi için fotovoltaiikler muhteşem yöntemlerden biridir. Fotovoltaiik alanında, organik fotovoltaiikler günden güne iyi bir gelişim göstermektedirler. Fulleren-tabanlı moleküller tıpkı PCBM gibi organik güneş pilleri için yeterli sonuçlar vermesine rağmen, bazı eksiklikleri alandaki daha ileri gelişmeleri engellemektedir. Bu nedenle, özellikle rodanin uçlu moleküller yüksek güç dönüştürme verimleriyle dikkat çekerler. Bugünlerde, tandem güneş pilleri içeren küçük molekülü NFA'lar için %19,50 PCE bildirilmiş ve Ulusal Metroloji Enstitüsü tarafından onaylanmıştır. Bu hedefle, bu çalışma rodanin sonlu küçük moleküllerin sentezlenmesini ve organik güneş pillerine uygulanmasını amaçlar. Hedef küçük moleküller, merkez, köprü ve uç birimler olmak üzere üç kısımdan oluşur. Merkez birim için Indasenoditiyofen (IDT) çekirdeği sentezlendi ve başarıyla alkilenip, tinlendi. Ayrıca, benzoditiyofen (BDT) ve floren ticari çekirdek birimler olarak süreyi kısaltmak ve pratik amaçlar için kullanıldı. Florlanmamış ve florlanmış benzotiyadiazol kullanışlı sentez yöntemleri sayesinde köprü birim olarak

kullanılmak üzere oluşturuldu. Köprü ve çekirdek birimleri birleřtirmek amacıyla, Stille ve Suzuki Kenetlenme reaksiyonları uygulandı ve çeřitli denemeler yapıldı. Sonuç olarak, BDT & çift florlanmış benzotiyadiazol Stille reaksiyon ürünü düzgünce elde edildi. Uç birimi oluşturmak için, rodanın sorunsuz bir biçimde etillendi. Bu çalışma sonucunda hedef Knoevenagel Kondenzasyon ürünlerinin saflařtırılması ve organik güneş pillerine uygulanma çalışmaları devam etmektedir.

Anahtar Kelimeler: Organik Güneş Pilleri, Fulleren Olmayan Alıcılar, Benzotiyadiazol, Indasenoditiyofen, Benzoditiyofen

To everything that makes me “Deniz” ...

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ADA	Acceptor Donor Acceptor
BDT	Benzodithiophene
DCM	Dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EtOAc	Ethyl Acetate
FA	Fullerene Acceptor
FREA	Fused Ring Electron Acceptor
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectroscopy
IDT	Indacenodithiophene
ITO	Indium Tin Oxide
NDI	Naphthalene Diimide
NFA	Non-Fullerene Acceptor
NMR	Nuclear Magnetic Resonance
OSC	Organic Solar Cell
PCE	Power Conversion Efficiency
PCBM	Phenyl C ₆₁ Butyric Acid Methyl Ester
PDI	Perylene Diimide
Pd	Palladium
RDI	Rylene Diimide
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl

CHAPTER 1

INTRODUCTION

1.1 Organic Solar Cells (OSCs)

Nowadays, there is an increasing trend in utilization of renewable and sustainable energy resources towards supplying world's energy demand. The energy that can be generated from natural sources that can be replenished is called renewable energy. These natural resources can vary from wind to geothermal. Undoubtedly, solar energy is the shining star when compared to other alternatives to provide renewable energy since it's virtually inexhaustible and environmentally friendly. ¹

One of the leading solar energy conversion technologies is photovoltaics (PV). PV constitutes the major portion of all academic research and industry. Even though some drawbacks such as high initial cost, large area installation requirements, they offer clean energy in a reliable, stable and noiseless way. ² PV technologies are generally categorized into three generations as seen in table 1.1. ³

Table 1.1. Generation of photovoltaic technologies

Generation	Description
First	Simple Crystalline form (Sc-Si) & Multicrystalline form (mc-Si)
Second	(i) Amorphous silicon (<i>a</i> -Si) & micro amorphous silicon (a-Si) (ii) Cadmium Telluride (CdTe) (iii) Copper indium selenide (CIS) & Copper, indium gallium dieseline (CIGS)
★ Third	Organic Solar Cells Perovskite Solar Cells

In the last decades, organic solar cells have attracted great demand as a result of lower production costs, ease of applicability, being extremely light weight and flexible and probably most importantly, ability to fabricate semi-transparent cells.⁴ Generally, organic solar cells involve conductive organic molecules such as conjugated polymers or small molecules whereas inorganic counterparts contain silicon or other inorganic light absorbers such as CdTE and CIGS. Although technologies are quite different, they can complement each other in certain ways. One of the particular examples is hybrid tandem solar cells which is utilized by containing both organic and silicon solar cells. A study showed that complementary organic and silicon layers reached to PCE up to 7.5% whereas they showed 4.15% and 5.89% individually and respectively, in 2014.⁵ Moreover, one of the strengths of organic solar cell is semi-transparency/ transparency. Transparent organic solar cells or smart windows can be integrated into windows of buildings without any harm to aesthetics of the construction.⁶

Another important concern about this technology is that organic solar cells show some stability problems. However, stability issues started to be addressed with novel encapsulation strategies and certain devices started to provide good air stability.⁷

1.1.1 Device Construction of OSCs

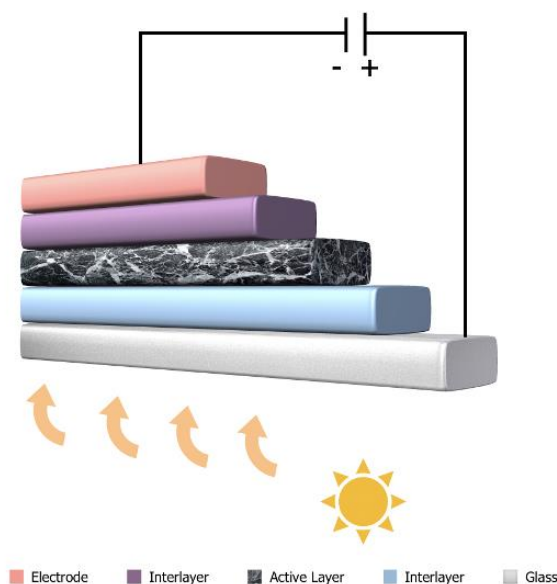


Figure 1.1. Device architecture of traditional organic solar cell

Organic solar cells have a planer-layer structure. A photoactive layer is inserted in between positive and negative electrodes. The negative electrode can be aluminum, calcium, gold, or magnesium. Other is chosen as a transparent to allow sunshine to pass into the inner layers and indium tin oxide (ITO) can be mostly preferred. In the organic solar cells, photoactive layer consists of two main elements which are electron donor and acceptor materials. Typically, electron donor part is a p-type molecule and electron acceptor part is a n-type molecule. In traditional organic solar cells, fullerene-based molecules are utilized as an electron acceptor material. Rather than fullerene, other molecules have started to be used in the devices and non-fullerene acceptor concept came out in the literature. Since replacing of non-fullerene acceptors with fullerene acceptors has so much potential, non-fullerene acceptors draw significant attention in the solar world.

1.1.2 How OSCs work?

To convert the solar power into electrical energy, there are five main stages which are light absorption and exciton formation(i), exciton dissociation(ii), charge separation(iii), charge transport(iv), and charge collection(v). In light absorption and exciton formation(i), the photoactive layer assembles photons from sunlight and electrons will be excited from the valence band into the conduction band which is a higher energy level. Due to light absorption, exciton generation is observed in the molecule and exciton means an electron-hole pair. In exciton diffusion(ii), to produce current, exciton must deal with large binding energy. Therefore, it must dissociate into free-charged electrons and holes. To dissociate, the exciton has to reach the interface in between two components which are electron donor and electron acceptor. In charge separation(iii), by using energy coming from the absorbed photons, an electron is transferred from an electron donor material to an electron acceptor material. In charge transportation(iv), charges start to move toward electrodes according to their mobilities. The efficiency of charge transport is controlled by the electrical conductivity and impedance of the organic materials. Charge collection(v) is achieved by the corresponding electrodes, indium tin oxide (ITO) and the metal layer. In the cathode, electrons transferred from acceptor side are collected and in anode, holes are collected. Therefore, external circuit electricity can be generated in the cell.

By using the logic behind the working principle, several device architectures were advanced, namely single, bilayer and bulk heterojunction. Most notable one between these architectures is bulk heterojunction solar cells because short lived exciton must be separated around 10 nm before the energy loss processes start. ⁸

1.2 Fullerene Acceptors (FAs)

OPVs utilizing fullerene-based molecules as the electron acceptor unit make up the major portion of all reported organic solar cells in the literature. As is known to all, fullerenes are allotropes of carbon which contains single and double bonds in a closed mesh. Particularly, PCBM was an essential part of the device engineering due to some of its outstanding properties such as extremely fast electron transfer capabilities and high electron affinity. Most known derivatives of fullerenes are organic soluble PCBM60 and PCBM70. These acceptors can be mixed with electron donors, generally conjugated polymers, very well and this provides aggregate domains in nanoscale dimension which is essential for required charge transport. C₇₀ provides enhanced optical absorption in the visible region compared to C₆₀ and provides better light-harvesting ability.

Unfortunately, these remarkable features of fullerenes are still insufficient to get PCEs in organic photovoltaics to the desired level. There are some drawbacks of fullerene-based acceptors. Firstly, chemical structure of fullerenes does not allow ease of modification other than adduction reaction. The challenges in the chemical modification restricted the structural flexibility and π conjugation cannot be modified which directly effects optoelectronic properties. Purification of the product is highly challenging and having impurity affects the device performance significantly. These combined with initial difficulties to synthesize and purify fullerenes results in extremely high costs. Fabrication cost has great importance when considering the commercialization and additionally polymers blend with fullerene derivatives was shown to exhibit thermal and photochemical instability.⁹

1.3 Non-Fullerene Acceptors (NFAs)

As their name refer, non-fullerene acceptors are the molecules which do not contain the fullerene-based molecules in their framework (Examples, Figure 1.2). Even

though, initial performance was quite behind fullerenes, tremendous success has been achieved in the last decade and their performance surpassed fullerenes in the recent years. NFAs vary significantly depending on their chemical structures many different derivatives have been realized. Most of these structures allowed ease of modification for tuning optical and electrical properties.¹⁰ Generally, their absorptions are better in visible and NIR region compared fullerene-based acceptors. Depending on the structure synthesis can be short and economically viable. Moreover, for some NFAs enhanced stability is observed which is one of major issues circumventing commercialization of this technology. Certainly, NFAs have their own drawbacks compared to fullerenes. Namely, strong recombination loss can be observed utilizing NFAs and extremely variable results are obtained with different donor polymers meaning that they cannot be utilized as universal acceptors.

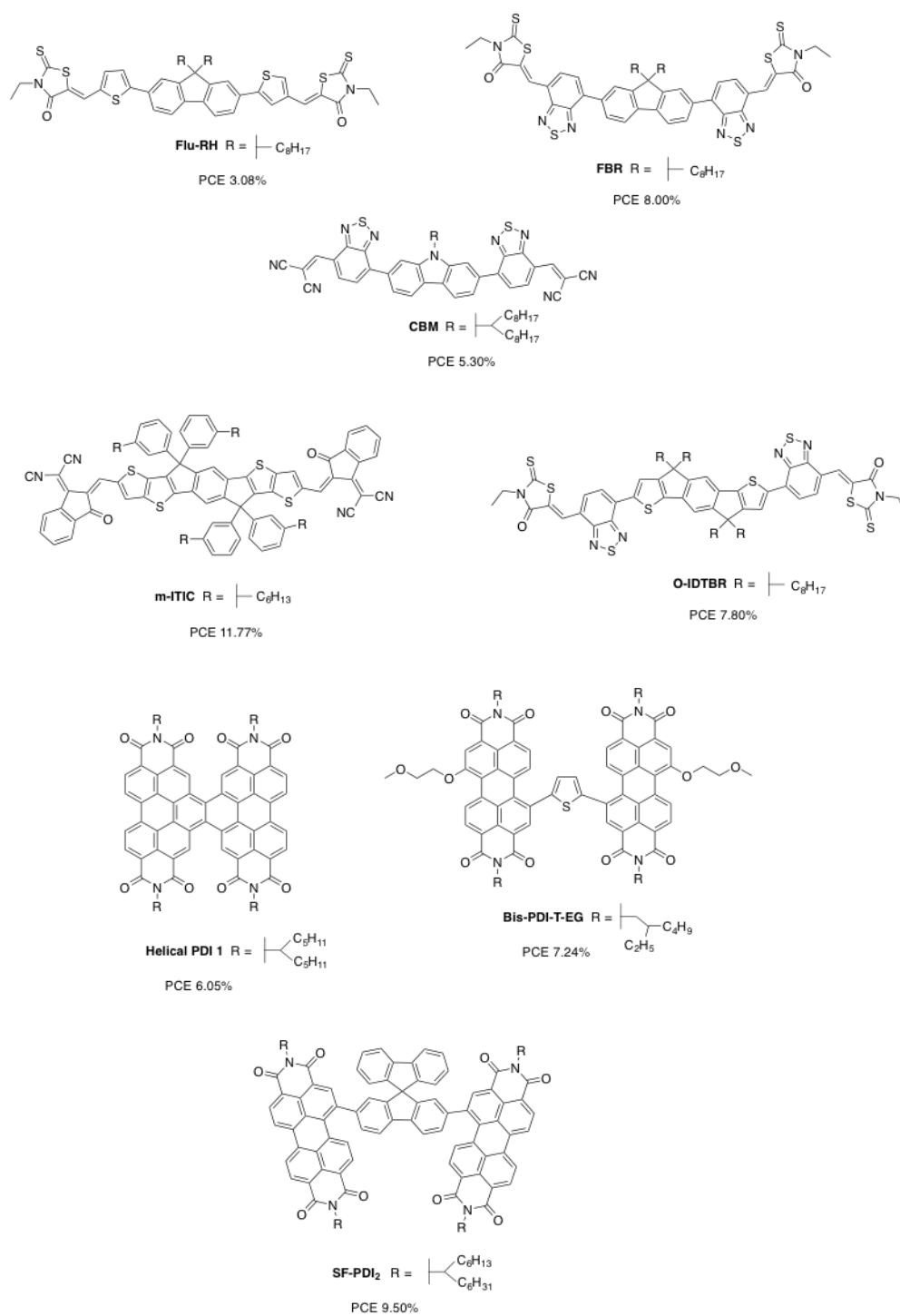


Figure 1.2. Fluorene, Carbazole, IDT, IDTT and PDI based small molecule acceptors with their PCEs

1.3.1 Classification of NFAs

Non-Fullerene acceptors can be classified as molecular structure and number of molecules. According to molecular structure, they can be rylene diimides or fused ring electron acceptors (FREAs).

Rylene diimides are excellent n-type semiconductors and have a planar structure. By raising conjugated cores, various properties like absorption spectra, energy levels can be arranged. They show excellent thermal and oxidative stability and high electron affinities.¹¹ Rylene diimides contain many sub-classes according to their “n” number. Naphthalene Diimides (NDIs) and Perylene Diimides (PDIs) are major two subclasses which n is equal to 0 and 1, respectively. NDI is the smallest homologue of rylene diimides (RDI). NDIs have been used in different areas from medicinal chemistry to supramolecular chemistry. PDIs discovered in 1913 by Kardos and used as a dye for textile. PDI can be enlarged by longitudinal and lateral expansions methods.¹² Photophysical and redox properties can be easily tuned by chemical reactions.

Fused ring electron acceptors (FREAs) are different from rylene diimides. They have a modular structure which is very suitable for molecular tailoring. Also, their synthesis is facile. Even they are quite promising for organic solar cells, moreover, they can be used in other field like transistors. They have rigid and planar framework. Good solvent processibility can be gained by introduction of alkyl chain into the structure. They tend to show good stability for devices incorporating them.¹³

1.3.2 Chronology of NFAs

In fact, Non-Fullerene acceptors are not a fresh idea, they have an extended and progressive history. As Ardalan Armin was proposed, the development of small

molecule NFAs can be examined in three periods which are 1986-2012, 2013-2016 and 2017-2020. ¹⁴

In the early stages between 1986 and 2012 years, there was no massive development in the power conversion efficiency, however this time frame had a major importance to motivate the development in the small molecule NFAs by supplying molecule diversity. In 1986, Tang was reach 1.0% PCE by using PDI derivative and this efficiency was increased around 0.5% by Forrest et al. ¹⁵ After that, Nunzi had reached 2.0% PCE. ¹⁶ Also, in this stage, solution-processed bulk heterojunction solar cell gain attention around worldwide. In the light of this advance, researchers tried to look out to make solution-processable molecules.

In the second period (2013-2016), research groups front to synthesize 3D-like molecules but based on 2D structure. To achieve this, they used two strategies namely “twist” and “bulky out-of-plane side chains”. Generally, these two tactics brought the success in the field and PCE values were increased to around 11.0%. ¹⁷

The last stage (2017-2020) was more current one and called “boom times”. In this period, PCE values were raised to 18.0% by focusing ADA-type molecular engineering. ¹⁸

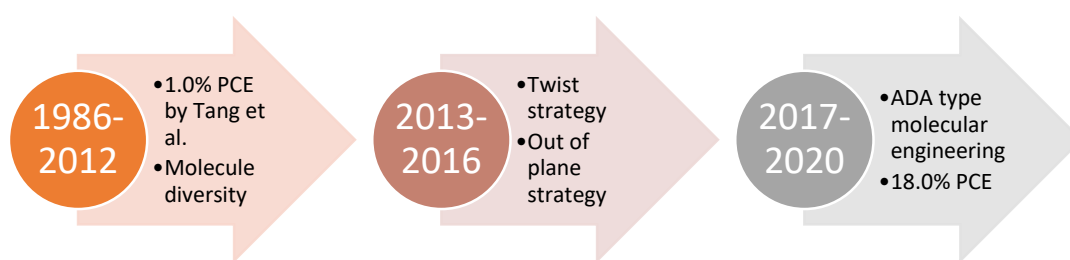


Figure 1.3. Key stages in history of SM-NFAs

1.4 Molecular Design

Undoubtedly, pattern of the molecule is an extremely key point to realize its purpose. For instance, if it is planned for Stille polymerization, it must contain two bromo- and two stannic- unit in itself. In this study, targets are designed to make small molecules for non-fullerene acceptors. Each ingredients of small molecule have an object with nice properties. Moreover, unites get together by using different pathways and these chosen methods will be explained.

1.4.1 Construction of the Molecule from Building Blocks

A small part of a large organic molecule is called as moiety or building block. In this study, main molecule constructed from three parts which are central, bridge and terminal units. Indacenodithiophene, fluorene and benzodithiophene are the conceivable central units. They are used as an essential conjugated system in the middle of the molecular design. Di-fluorinated benzothiadiazole, benzoselenadiazole and benzotriazole are chosen as the bridge unit in between central and terminal ones. Alkylated and aminated rhodanines stand as terminal unit in the outside of the molecule. All of them are selected with the purpose of being a building block during this study owing to some special qualities. These characteristics are clarified in the below respectively.

1.4.1.1 Possible Central Units

Indacenodithiophene (IDT) is one of the promising central units with five fused aromatic rings by including two thiophene rings. This aromaticity makes electron-rich itself. Therefore, it shows electron donor property. Moreover, conformational energetic disorder is reduced due to maximum π orbital overlap.¹⁹ Generally, IDT contains various alkyl chains to be soluble process and molecule ended with two stannylated methyl in favor of being suitable to Stille Coupling Reaction. Since IDT

based NFAs were showed PCE over 14% in OSCs, they are very suitable for this position.²⁰

Fluorene contains three fused rings. One of them is five-membered ring, whereas other two rings are six-membered. In the five-membered ring, two octyl chains are bonded to molecule to be used in soluble form and provides improved solubility.²¹ At both side ends, boronic acid esters are bonded to the molecule in order to being convenient to give Suzuki Coupling Reaction.

Benzodithiophene (BDT) is another central unit in this study. It contains three fused aromatic rings ended with thiophene rings in the main structure. Therefore, it demonstrates electron-rich property, and it is an electron donor unit. It has different derivatives but, in this study, BDT makes bond with two thiophenes from below and above sides. Also, ethyl and butyl alkyl chains are fixed on the molecule to increase solubility. It is widely used as a building block and emerging with good performance in the area since structural symmetry and fused aromatic system provide advanced electron delocalization and charge transport in the devices.²² BDT ended with two stannylated methyl to give Stille Coupling Reaction.

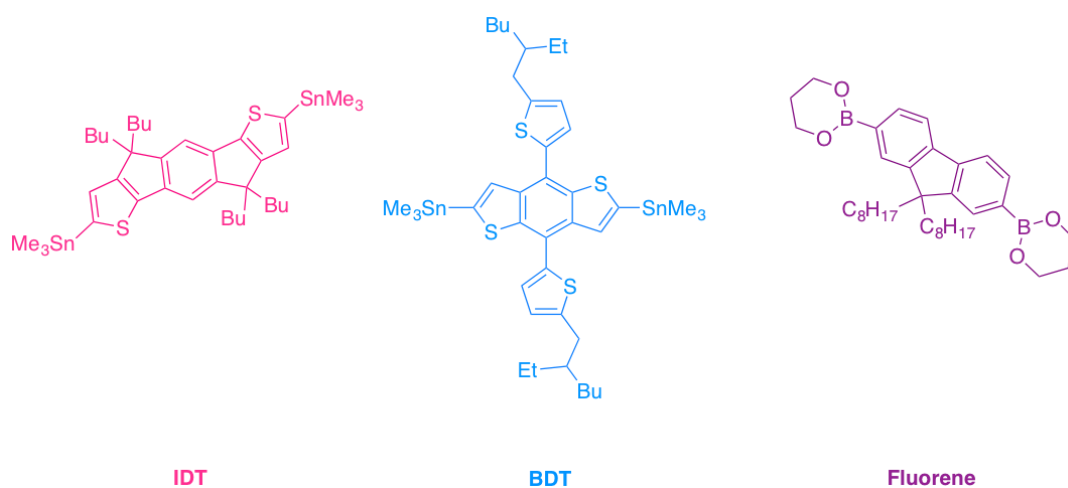


Figure 1.4. Structures of possible central units (pink: IDT, blue: BDT and purple: Fluorene)

1.4.1.2 Bridge Units

Benzothiadiazole act as a bridge in between central and terminal units. It is deficient in terms of electrons. When benzothiadiazole and rhodanine are kept together, they demonstrate outstanding long-term performance and thermal stability according the literature.²³ If benzothiadiazole is supported with fluorine atoms, thanks to the strong electronegativity of fluorine atoms, intramolecular & intermolecular interactions will be developed.²³ Also, charge-carrier transportation is affected in a positive way. For this reason, they are superior to the non-fluorinated counterparts. By using SeO₂ and NaNO₂, derivatives which are benzoselenadiazole and benzotriazole can be prepared.^{24,25}

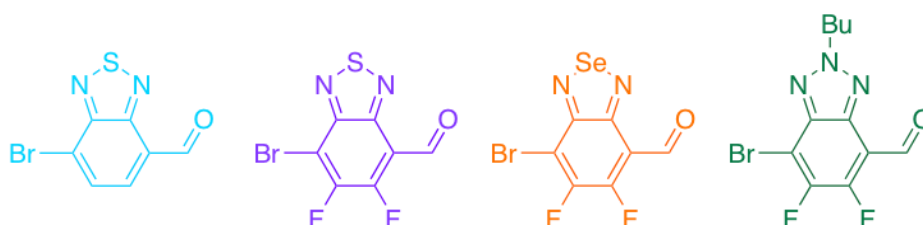


Figure 1.5. Structures of bridge units (pale blue: Benzothiadiazole, purple: Di-fluorinated benzothiadiazole, orange: Di-fluorinated benzoselenadiazole and green: Butylated-benzotriazole)

1.4.1.3 Terminal Units

Rhodanine is selected as the terminal unit. In the literature, several studies show that it is used in peripheral position which is flanked to the molecules. One of the prominent properties of rhodanine is electron-accepting thanks to thioketone and ketone groups in the molecular framework.²⁶ It provides strong push-pull. The second prominent property is provided by alkylation of nitrogen. This building block can go into the alkylation reaction from the nitrogen side and this property contribute to the solubility which makes it solvent-processing device. When short alkyl chain is preferred like ethyl group, hydrogen bonding is restricted.²⁷ Another rhodanine derivative was planned to synthesize is aminated version. If somehow, they are

converted to ammonium salt, then their solubility in polar solvents will increase and it can be soluble in solvents like ethanol or water.

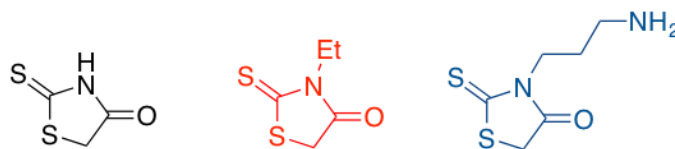


Figure 1.6. Structures of terminal units (black: Rhodanine, red: Ethylated-rhodanine and blue: Aminated-rhodanine)

1.4.2 Essential Reactions for Making Small Molecule NFAs

In this thesis, many reactions were performed to synthesize small molecules successfully. However, there is a fact that two major reactions, which are Cross-Couplings and Knoevenagel Condensation, constitute milestone for making them. Whereas, to bind stannanes and halides, Stille Coupling were carried out and, to bind boronic acids and halides, Suzuki Coupling were performed in the presence of Pd-based catalysts. Also, Knoevenagel Condensation was planned to get final product.

1.4.2.1 Stille Cross-Coupling Reaction

Stille Cross-Coupling reaction is one of the important coupling reactions used in synthesis of organic solar cell materials between organostannanes and halides or pseudohalides which was developed by Eaborn for the first time.²⁸ After that, it took the current name in 1978 thanks to Stille and co-workers.²⁹ Mechanism of Stille coupling is based on three main steps. First one is oxidative addition, second step is transmetallation, and final one is reductive elimination. Generally, Palladium catalyst such as $\text{Pd}(\text{PPh}_3)_4$ are used in these reactions. Anhydrous THF, toluene, DMF and DMSO can be preferred as reaction solvent. One negative side of this reaction is toxicity of tin compounds. They have low polarity so they cannot be dissolved in water. In this term, Suzuki coupling can be more preferable.³⁰

1.4.2.2 Suzuki Cross-Coupling Reaction

Suzuki Cross-Coupling reaction is one another significant reaction between organoboron species and organohalides. It was named after Akira Suzuki who takes the Nobel Prize in Chemistry in 2010. This reaction is different in terms of group involved and usage of an appropriate base solution. It contains same stages in the mechanism just as Stille Coupling. It has less toxic nature since boronic acids are safer than organotin compounds.³¹ When solvents are investigated, it provides more variations that organic-water, water-only or no solvent case. THF, toluene can be used as an organic solvent choice. Base solution preferred to break the bonds between boronic acid groups and core unit and mainly K_2CO_3 and $NaHCO_3$ are selected.

1.4.2.3 Knoevenagel Condensation Reaction

This reaction is named after Emil Knoevenagel in 1890s. When a water molecule is eliminated it is called as condensation reaction. Carbon-carbon bond is formed. An active hydrogen compound is added nucleophilically to a carbonyl group. Carbonyl group can be aldehyde or ketone. Also, weakly basic amine is used as catalyst. The application of primary and secondary amines and their salts in this type reaction cause the study of aminocatalysts.³² This reaction contains two main steps. In step one, enol intermediate is formed. In second step, enol react with aldehyde or ketone in the medium and the resulting aldol undergoes induced elimination. Product is unsaturated.

1.5 Motivation

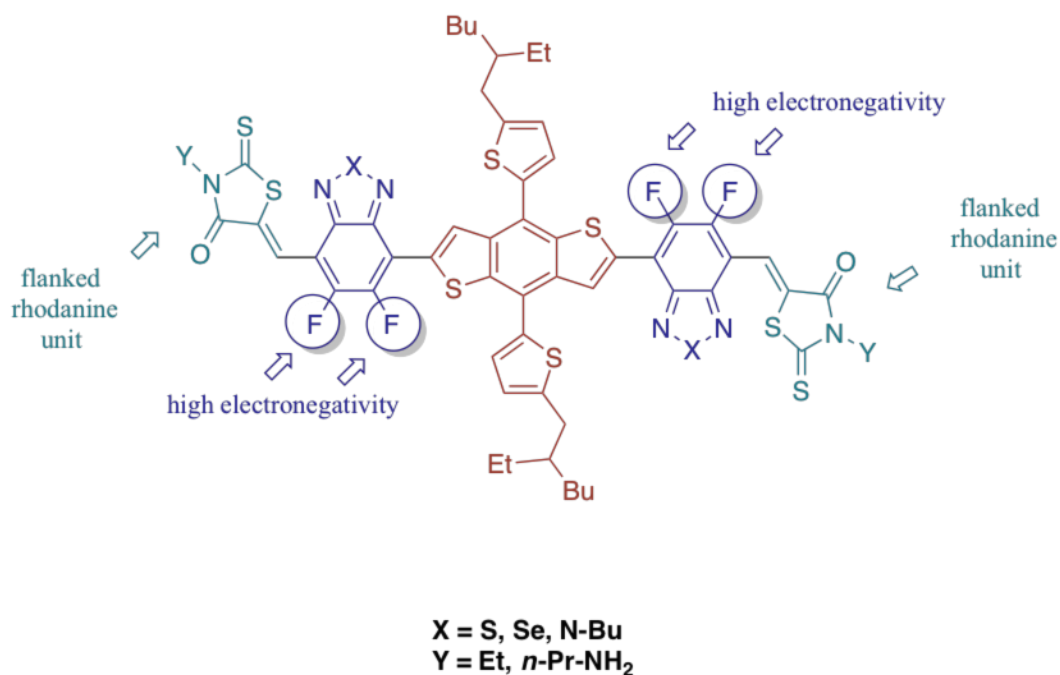


Figure 1.7. Structures of target molecules

In this study, several small molecules were aimed to be synthesized for application on organic solar cells as non-fullerene acceptors. Until now, synthesis of (5*Z*,5'*Z*)-5,5'-(((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one), (X = S Y = Ethyl) in figure 1.7., was attempted and it is proved that other derivatives can be synthesized by using related synthetic route.

Molecular designs were inspired of analogue molecules in the literature. NFAs with similar fragments were shown to have good performance in the literature. However, amine flanked materials are unique and never been studied in the literature. Having a terminal amine unit could interact with the transport layers for increasing surface passivation in solar cells, thus increased performance. Therefore, our aim was to realize these molecules and compare them in terms of properties such efficiency and stability. One additional motivation of the study was to realize novel synthetic

approach for the challenging synthesis of the bridging units using C-H activation combined with ozonolysis, to circumvent tedious radical bromination reactions that are commonly used in the literature.

CHAPTER 2

EXPERIMENTAL

In this chapter, there will be given information about chemicals, methods and equipments. Also, experimental procedures will be described step by step with ^1H -NMR, ^{13}C -NMR and HRMS characterization data.

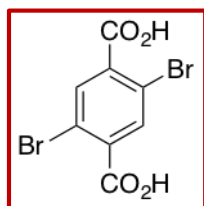
2.1 Materials, Methods and Equipment

1,4-Dibromo-2,5-dimethylbenzene and 2,3-di-amino-toluene were purchased from Tokyo Chemical Industry (TCI). 4,5-Difluoro-2-nitroaniline and 9,9-dioctylfluorene-2,7-diboronicacidbis(1,2-propandiol) ester were purchased from Sigma Aldrich. Rhodanine were bought from Alfa Aesar. Most of the reactions were performed under argon atmosphere by using Schlenk tube. Solvents like THF, DMF were used in dry form by providing the MBraun MB-SPS-5 solvent purification system directly. For the ozonolysis process, Sander Labor-Ozonisator was preferred by setting 50 mA, schalter 1, range 2 in 1 bar. CDCl_3 and DMSO-d_6 were suitable solvents for the ^1H and ^{13}C -NMR characterizations. Bruker Spectrospin Avance DPX-400 Spectrometer was used for the Nuclear Magnetic Resonance (NMR) characterization and tetramethyl silane (TMS) was used as the internal reference in METU Chemistry Department. Waters SYNAPT G1 MS system was used for High Resolution Mass Spectroscopy (HRMS) characterization in METU Central Laboratory.

2.2 Synthesis of Central Unit

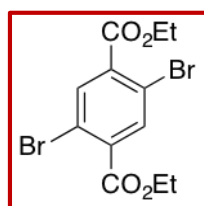
2.2.1 Synthesis of Indaceno[1,2-*b*:5,6-*b'*]dithiophene Containing Core

2.2.1.1 Synthesis of 2,5-Dibromoterephthalic Acid



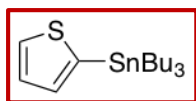
1,4-Dibromo-2,5-dimethylbenzene (5.00 g, 0.02 mol), celite (7.5 g) and water/tert-butyl alcohol (50 mL/50 mL) were added to three-necked reaction flask.³³ After that, KMnO₄ (15.00 g, 0.095 mol) was added to the reaction mixture in equal portions for 30 minutes. This purple mixture was mixed at 100 °C for 36 hours. At the end of this time, mixture was cooled to 70 °C and ethanol (20 mL) was slowly added. Resulting mixture was filtered and filtrate was concentrated. The product was precipitated by adding concentrated HCl (5 mL) and filtered. The residue was washed with cold ethanol. Product was obtained as a white bright solid (4.9 g, 80%). ¹H NMR (400 MHz, DMSO): δ 13.99 (s, 2H), 7.99 (s, 2H); ¹³C NMR (100 MHz, DMSO): δ 165.6, 137.1, 134.8, 118.7.

2.2.1.2 Synthesis of Diethyl 2,5-dibromoterephthalate



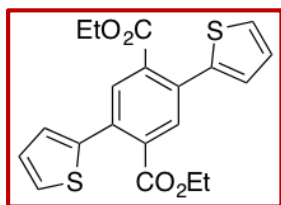
2,5-Dibromoterephthalic acid (2.50 g, 0.01 mol) was dissolved in absolute ethanol (12 mL) at 50 °C.³³ After that, concentrated H₂SO₄ (4 mL) was added to this mixture and it stirred overnight at 78 °C. It cooled to the room temperature and precipitate was filtered and recrystallized with ethanol. Product obtained as white solid (2.7 g, 90%). ¹H NMR (400 MHz, DMSO): δ 8.08 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, DMSO): δ 163.9, 136.2, 135.1, 118.9, 62.2, 13.9.

2.2.1.3 Synthesis of Tributyl(thiophen-2-yl)stannane



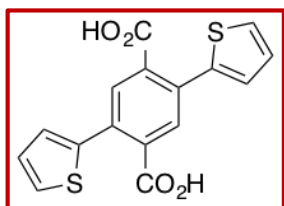
Thiophene (3.00 g, 35.7 mmol) was dissolved in anhydrous THF (35 mL).³⁴ Reaction was cooled to -78 °C by using dry ice/acetone mixture. After that, *n*-butyl lithium (4.00 mL, 42.8 mmol) was added to reaction mixture dropwise. After 1 hour stirring, tributyltin chloride (10.64 mL, 39.22 mmol) was added slowly. Resulting mixture was stirred overnight at room temperature. Finally, anhydrous THF was removed by using rotary evaporator and residue was extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Product obtained as yellow liquid (12 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, *J* = 4.7 Hz, 1H), 7.27 - 7.23 (m, 1H), 7.18 (d, *J* = 3.1 Hz, 1H), 1.58 - 1.51 (m, 6H), 1.39 - 1.31 (m, 6H), 1.12 - 1.06 (m, 6H), 0.89 - 0.87 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 135.2, 130.6, 127.8, 29.0, 27.3, 13.7, 10.8.

2.2.1.4 Synthesis of Diethyl 2,5-di(thiophen-2-yl)terephthalate



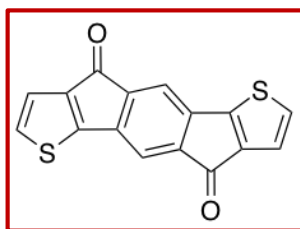
Diethyl 2,5-dibromoterephthalate (2.50 g, 6.58 mmol) and bis(triphenylphosphine)palladium(II) chloride (461.74 mg, 656.79 μmol) was dissolved in anhydrous THF (66 mL) and tributyl(thiophen-2-yl)stannane (7.36 g, 19.7 mmol) was added under argon atmosphere.³³ Mixture was stirred at 75 °C for 5 hours. After that, anhydrous THF was removed and saturated KF solution (100 mL) was added and stirred for 1 hour. Resulting mixture was extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and ethyl acetate (1:1) system with silica. Product obtained as light-yellow solid (1.6 g, 63%). ¹H NMR (400 MHz, CDCl₃): δ 7.82 (s, 2H), 7.39 (d, *J* = 4.8 Hz, 2H), 7.11 - 7.05 (m, 4H), 4.22 (q, *J* = 7.9 Hz, 4H), 1.15 (t, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 167.7, 140.5, 134.1, 133.4, 131.9, 127.4, 127.0, 126.5, 61.7, 13.8.

2.2.1.5 Synthesis of 2,5-Di(thiophen-2-yl)terephthalic Acid



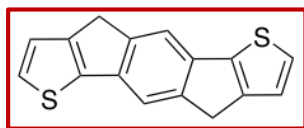
Diethyl 2,5-di(thiophen-2-yl)terephthalate (1.50 g, 3.88 mmol) was dissolved in absolute ethanol (38 mL).³⁵ KOH (1.52 g, 27.17 mmol) was dissolved in distilled water (6 mL) and added to reaction mixture. Resulting mixture was heated to 78 °C and refluxed for 15 hours. After that, ethanol was removed from the reaction medium, precipitate observed by adding concentrated H₂SO₄ (5 mL). Residue washed with cold distilled water. Product obtained as light-yellow solid (1.2 g, 95%).¹H NMR (400 MHz, DMSO): δ 13.45 (br, 2H), 7.72 - 7.63 (m, 2H), 7.28 - 7.21 (m, 2H), 7.18 - 7.10 (m, 4H); ¹³C NMR (100 MHz, DMSO): δ 168.9, 139.8, 134.6, 131.5, 130.2, 128.0, 127.6, 127.2.

2.2.1.6 Synthesis of *s*-Indaceno[1,2-*b*:5,6-*b'*]dithiophene-4,9-dione



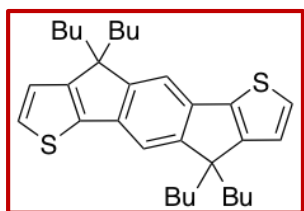
2,5-Di(thiophene-2-yl)terephthalic acid (1.20 g, 3.63 mmol) was dissolved in anhydrous DCM (30 mL) and oxalyl chloride (1.89 g, 19.1 mmol) was added.³⁵ After that, anhydrous DMF (0.50 mL) was added to reaction mixture dropwise. Resulting mixture was stirred at room temperature for 19 hours. At the end of this time, anhydrous DCM was removed from the reaction medium. Intermediate product dissolved in anhydrous DCM (16 mL) and AlCl₃ (2.27 g, 17.0 mmol) was dissolved in anhydrous DCM (25 mL) in separate argon-filled flasks and intermediate product-DCM mixture was added to other dropwise at 0 °C. After mixing for 15 minutes at 0 °C, reaction mixture was stirred for 4 hours at room temperature. Product obtained as blue solid (0.99 g) and it was used directly for next step without further purification.

2.2.1.7 Synthesis of 4,9-Dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene



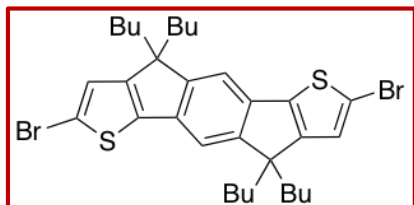
s-Indaceno[1,2-*b*:5,6-*b'*]dithiophene-4,9-dione (1.00 g, 3.40 mmol), KOH (3.81 g, 67.9 mmol) and hydrazine monohydrate (3.398 g, 67.88 mmol) were dissolved in diethylene glycol (38 mL).³⁵ Mixture was heated to 180 °C and stirred for 24 hours. After that, it was cooled to room temperature and poured to concentrated HCl (10 mL)/ice mixture. Precipitate was filtered and washed with distilled water. Product obtained as brown solid (0.6 g, 66%). ¹H NMR (400 MHz, DMSO): δ 7.71 (s, 2H), 7.55 (d, *J* = 4.4 Hz, 2H), 7.22 (d, *J* = 3.7 Hz, 2H), 3.77 (s, 4H); ¹³C NMR (100 MHz, DMSO): δ 147.3, 145.3, 142.3, 135.4, 127.5, 123.2, 115.9, 62.8.

2.2.1.8 Synthesis of 4,4,9,9-Tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene



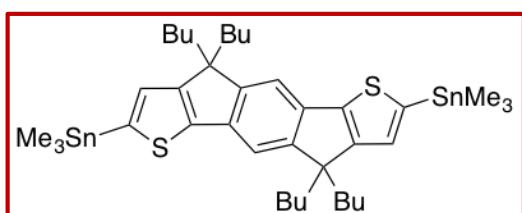
4,9-Dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (0.83 g, 3.10 mmol) was suspended with anhydrous DMSO (20 mL).³⁶ After that, KOH (2.30 g, 41.0 mmol) and KI (0.18 g, 1.08 mmol) were added. After stirring for 1 hour at room temperature, 1-bromobutane (2.55 g, 18.6 mmol) was added dropwise to reaction medium and heated to 80 °C. After 24 hours, reaction was cooled to room temperature and poured into ice/water mixture. Resulting mixture was extracted with CHCl₃ and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in petroleum benzene with silica. Product obtained as light-yellow color solid (0.3 g, 18%). ¹H NMR (400 MHz, CDCl₃): δ 7.26 (s, 2H), 7.23 (d, *J* = 4.9 Hz, 2H), 6.94 (d, *J* = 4.8 Hz, 2H), 2.00 - 1.78 (m, 8H), 1.10 (h, *J* = 7.3 Hz, 8H), 0.85 - 0.74 (m, 8H), 0.69 (t, *J* = 7.3 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 152.1, 140.5, 134.4, 125.0, 120.6, 112.1, 52.5, 37.9, 25.3, 22.0, 12.8.

2.2.1.9 Synthesis of 2,7-Dibromo-4,4,9,9-tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene



4,9-Dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (0.20 g, 0.75 mmol) was suspended with anhydrous DMSO (8 mL).³⁷ After that, *t*-BuOK (1.0 g, 8.9 mmol) was added to mixture. After stirring for 1 hour at 80 °C, 1-bromobutane (1.20 g, 7.27 mmol) was added dropwise and temperature was raised to 90 °C. After 24 hours, reaction was cooled to room temperature and poured into ice/water mixture. Resulting mixture was extracted with CHCl₃ and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and dichloromethane (5:1) system with silica. Product obtained as light-yellow color solid (0.1 g, 23%). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (s, 2H), 6.98 (s, 2H), 1.98 - 1.90 (m, 4H), 1.85 - 1.78 (m, 4H), 1.16 - 1.11 (m, 8H), 0.88 - 0.79 (m, 8H), 0.79 - 0.71 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 149.7, 139.4, 133.0, 122.4, 110.6, 110.0, 52.2, 36.4, 23.9, 20.6, 11.5. MS: 648.0911 [M+H] (calculated 648.0918)

2.2.1.10 Synthesis of (4,4,9,9-Tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane)



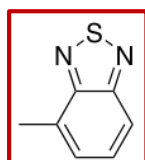
4,4,9,9-Tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (0.10 g, 0.20 mmol) was dissolved in anhydrous THF (7 mL).³⁶ Reaction medium was cooled to -78 °C and *n*-butyl lithium (0.48 mL) was added dropwise. After stirring for 1 hour, trimethyltin chloride (0.12 g) was added and stirred overnight at room temperature. Resulting mixture poured to distilled water and extracted with diethyl ether twice. Collected organic phase dried by MgSO₄ and

condensed. Product obtain as brown liquid (0.13 g) and it was used directly for next step without further purification. ^1H NMR (400 MHz, CDCl_3): δ 7.54 (s, 2H), 7.26 (s, 2H), 2.52 - 1.86 (m, 20H), 1.48 - 1.04 (m, 40H), 0.68 (t, $J = 7.3$ Hz, 30H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 151.6, 145.8, 137.5, 133.4, 127.5, 111.6, 51.1, 37.2, 37.1, 24.6, 24.6, 21.3, 21.3, 12.1.

2.3 Synthesis of Bridge Units

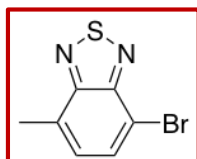
2.3.1 Synthesis of Benzo[*c*][1,2,5]thiadiazole Containing Unit

2.3.1.1 Synthesis of 4-Methylbenzo[*c*][1,2,5]thiadiazole



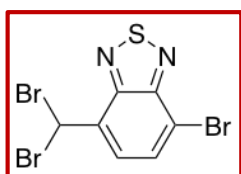
3-Methylbenzene-1,2-diamine (0.50 g, 4.09 mmol) was dissolved in anhydrous DCM (27 mL).³⁸ After, cooled to 0 °C and stirred for 15 minutes, triethylamine (2.30 mL, 16.4 mmol) was added slowly. Thionyl chloride (0.60 mL, 8.20 mmol) was dissolved in anhydrous DCM (7 mL) and added to reaction medium dropwise at 0 °C. Resulting mixture was stirred for 1 hour at this temperature and heated to 40 °C. After mixing 15 hours under argon atmosphere, it was cooled to room temperature and 2N HCl (7 mL) was added slowly. Mixture extracted with DCM, brine and water twice. Collected organic phase dried by Na_2SO_4 and condensed. Column chromatography was performed to purify product in hexane and ethyl acetate (7:1) system with silica. Product obtained as brown liquid (0.4 g, 59%). ^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.45 (t, $J = 8.6$ Hz, 1H), 7.31 (d, $J = 6.8$ Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 154.9, 131.6, 129.5, 127.9, 118.9, 17.9.

2.3.1.2 Synthesis of 4-Bromo-7-methylbenzo[*c*][1,2,5]thiadiazole



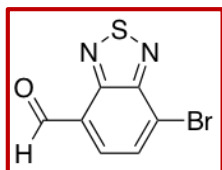
4-Methylbenzo[*c*][1,2,5]thiadiazole (0.36 g, 2.67 mmol) and 48% HBr (2.80 mL) was added to two-necked reaction flask. ³⁸ Br₂ (0.14 mL, 2.67 mmol) was added slowly to the mixture and refluxed for 16 hours. After cooling to the room temperature, saturated Na₂SO₃ solution was added and stirred for 30 minutes. Mixture extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and chloroform (1:4) system with silica. Product obtained as white solid (0.4 g, 60%). ¹H NMR (400 MHz, CDCl₃): 7.72 (d, *J* = 7.4 Hz, 1H), 7.25 - 7.16 (m, 1H), 2.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 155.1, 153.2, 132.1, 131.2, 128.6, 111.2, 17.7.

2.3.1.3 Synthesis of 4-Bromo-7-(dibromomethyl)benzo[*c*][1,2,5]thiadiazole



4-Bromo-7-methylbenzo[*c*][1,2,5]thiadiazole (550 mg, 2.40 mmol), NBS (1.28 g, 7.20 mmol) and benzoyl peroxide (0.12 g, 0.48 mmol) were dissolved in chlorobenzene (5 mL) and heated to 80 °C by stirring overnight. ³⁸ After that, it was cooled to room temperature and filtrated. By adding water to the filtrate, mixture extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and dichloromethane (1:2) system with silica. After, it was recrystallized with ethanol. Product obtained as white solid (0.5 g, 57%). ¹H NMR (400 MHz, CDCl₃): δ 8.01 - 7.86 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 149.8, 133.5, 132.0, 129.6, 116.0, 33.8.

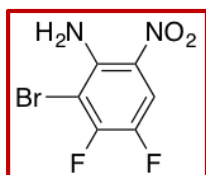
2.3.1.4 Synthesis of 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde



4-Bromo-7-(dibromomethyl)benzo[*c*][1,2,5]thiadiazole (300 mg, 0.78 mmol) was dissolved in 95% formic acid (3 mL) and heated to 110 °C.³⁸ After mixing 2 hours, this mixture was cooled to room temperature and distilled water was added. Precipitate was filtered and washed with distilled water until pH came to the 7. Product obtained as pale-brown solid (0.2 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ 10.72 (s, 1H), 8.16 - 7.99 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 188.4, 154.1, 154.0, 132.2, 131.7, 126.8, 121.9.

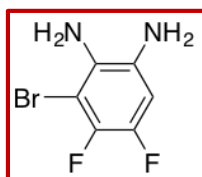
2.3.2 Synthesis of 5,6-Difluorobenzo[*c*][1,2,5]thiadiazole Containing Unit

2.3.2.1 Synthesis of 2-Bromo-3,4-difluoro-6-nitroaniline



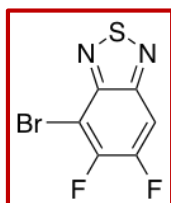
4,5-Difluoro-2-nitroaniline (5.00 g, 28.7 mmol) was dissolved in DCM (100 mL).³⁹ Glacial acetic acid (75 mL) and Br₂ (6 mL) were added to the reaction flask sequentially. Solution was stirred at room temperature for 3 days. At the end of this time, saturated NaHSO₃ was added to reaction mixture to get rid of unreacted Br₂. The color of the solution was turned from red to yellow after addition. Resulting mixture was extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Product obtained as yellow solid (7.0 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ 8.14 - 8.03 (m, 1H), 6.69 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 153.3 (dd, *J* = 258.2, 15.9 Hz), 141.3 (dd, *J* = 245.2, 15.2 Hz), 140.7 (d, *J* = 2.2 Hz), 127.0 - 126.7 (görünürde m), 113.5 (dd, *J* = 21.9, 3.1 Hz), 99.8 (d, *J* = 21.4 Hz).

2.3.2.2 Synthesis of 3-Bromo-4,5-difluorobenzene-1,2-diamine



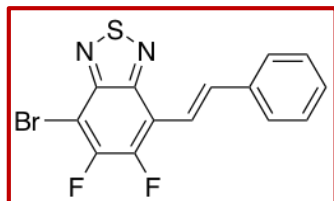
2-Bromo-3,4-difluoro-6-nitroaniline (4.00 g, 16.0 mmol) and SnCl₂ (15 g, 80 mmol) were dissolved in ethyl acetate (35 mL) and ethanol (15 mL).⁴⁰ Resulting mixture was heated to 75 °C and stirred for 3 hours and cooled to the room temperature. By using saturated NaHCO₃ solution, pH was adjusted to around 5. Resulting mixture was extracted with DCM and water twice. Collected organic phase dried by MgSO₄ and condensed. Product were afforded as dark brown solid (3.00 g) and it used for the next step without further purification.

2.3.2.3 Synthesis of 4-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole



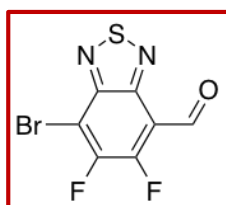
3-Bromo-4,5-difluorobenzene-1,2-diamine (3.00 g, 11.9 mol) was dissolved in chloroform (80 mL).⁴⁰ Triethylamine (6 mL) was added to this solution and stirred for 15 minutes. After, thionyl chloride (2.50 mL) was added dropwise and carefully. The final mixture was heated to 60 °C and stirred overnight. Mixture cooled to the room temperature and concentrated. Resulting mixture was extracted with DCM, brine and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in chloroform and petroleum ether (1:1) system with silica. Product obtained as white solid (2.7 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (dd, *J* = 16.3, 9.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 153.8 (dd, *J* = 261.2, 18.7 Hz), 151.7 (dd, *J* = 258.5, 19.5 Hz), 150.2 (d, *J* = 4.6 Hz), 149.3 (d, *J* = 12.0 Hz), 105.2 (d, *J* = 8.5 Hz), 100.1 (dd, *J* = 21.2, 2.3 Hz).

2.3.2.4 Synthesis of (*E*)-4-Bromo-5,6-difluoro-7-styrylbenzo[*c*][1,2,5]thiadiazole



To a 25 mL Schlenk tube, 4-bromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (0.3 g, 1.2 mmol), Pd(TFA)₂ (9.9 mg, 30 μmol), benzoquinone (12.9 mg, 120 mmol), silver acetate (0.6 g, 3.6 mmol) and benzoic acid (0.4 g, 3.0 mmol) were added under argon atmosphere. This solid mixture was dissolved in anhydrous DMF (16 mL) and styrene (0.25 g, 2.4 mmol) was added. The resulting mixture were stirred overnight at 100 °C. Then, it cooled to room temperature. Resulting mixture was extracted with DCM, brine and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in chloroform and petroleum ether (1:2) system with silica. After, it was recrystallized with hexane. Product obtained as yellow solid (0.3 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ 8.33 (d, *J* = 16.5 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 16.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 149.80 (dd, *J* = 256.7, 20.0 Hz), 147.99 (dd, *J* = 261.8, 18.7 Hz), 147.81 (d, *J* = 5.2 Hz), 146.21 (d, *J* = 8.0 Hz), 136.21 (d, *J* = 7.5 Hz), 134.57 (s), 126.74 (s), 126.55 (s), 124.86 (s), 113.79 (d, *J* = 11.2 Hz), 113.47 (s), 95.02 (d, *J* = 21.9 Hz).

2.3.2.5 Synthesis of 7-Bromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde

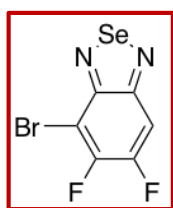


(*E*)-4-Bromo-5,6-difluoro-7-styrylbenzo[*c*][1,2,5]thiadiazole (0.15 g, 425 μmol) and methanol (30 mL) suspended. At 0 °C, for 2 hours, O₂/O₃ passed. After that, at the same temperature, argon passed. Anhydrous Me₂S (0.19 g, 2.97 mmol) was added and stirred for 1 hour. Methanol removed from the reaction medium by using rotary evaporator. Column

chromatography was performed to purify product in chloroform and petroleum ether (3:2) system with silica. After, it was recrystallized with hexane. Product obtained as light-yellow solid (75 mg, 63%). ^1H NMR (400 MHz, CDCl_3): δ 10.73 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.7, 183.7, 183.6, 183.6, 157.4, 157.2, 154.7, 154.5, 152.5, 152.3, 150.0, 150.0, 149.9, 149.7, 146.7, 146.6, 112.7, 112.6, 107.3, 107.2, 107.1, 107.0.

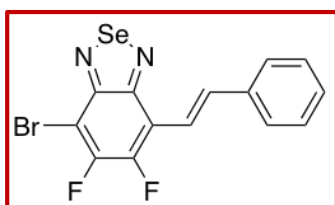
2.3.3 Synthesis of 5,6-Difluorobenzo[*c*][1,2,5]selenadiazole Containing Unit

2.3.3.1 Synthesis of 4-Bromo-5,6-difluorobenzo[*c*][1,2,5]selenadiazole



3-Bromo-4,5-difluorobenzene-1,2-diamine (1.20 g, 5.38 mmol) and selenium dioxide (0.72 g, 6.5 mmol) were dissolved in ethanol (20 mL) and refluxed at 80 °C for 12 hours.⁴¹ At the end of this time, reaction mixture cooled to 0 °C for 30 minutes. After that, precipitate was filtered. Product obtained as brown solid (1.2 g, 75%). ^1H NMR (400 MHz, CDCl_3): δ 7.58 (dd, $J = 9.6, 7.7$ Hz, 1H). MS: 296.8414 [M+H] (calculated 296.8378)

2.3.3.2 Synthesis of (*E*)-4-Bromo-5,6-difluoro-7-styrylbenzo[*c*][1,2,5]selenadiazole

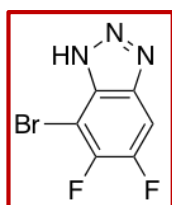


To a 25 mL Schlenk tube, 4-bromo-5,6-difluorobenzo[*c*][1,2,5]selenadiazole (0.30 g, 1.2 mmol), $\text{Pd}(\text{TFA})_2$ (9.90 mg, 30 μmol), benzoquinone (12.90 mg, 120 μmol), silver acetate (0.60 g, 3.6 mmol) and benzoic acid (0.36 g, 3.0 mmol) were added under argon atmosphere. This solid mixture was dissolved in anhydrous DMF (16 mL) and styrene (0.25 g, 2.4 mmol) was added. The resulting mixture were stirred overnight at 100 °C.

Then, it cooled to room temperature. Resulting mixture was extracted with DCM, brine and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in chloroform and petroleum ether (1:2) system with silica. After, it was recrystallized with hexane. Product obtained as yellow solid (0.15 g, 38%). ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, J = 16.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 16.5 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H).

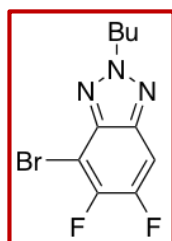
2.3.4 Synthesis of 2-Butyl-5,6-difluoro-2H-benzo[d][1,2,3]triazole Containing Unit

2.3.4.1 Synthesis of 7-Bromo-5,6-difluoro-1H-benzo[d][1,2,3]triazole



3-Bromo-4,5-difluorobenzene-1,2-diamine (1.2 g, 5.4 mmol), acetic acid/water mixture (0.62 mL/25.0 mL) were added to a Schlenk tube. ⁴⁰ After that it heated to 70 °C and mixed for 1 hour. After cooling to room temperature, NaNO₂ (0.39 g, 5.65 mmol) was dissolved in distilled water (5 mL) and added to mixture. After stirring for 1 hour, precipitate was filtered. Product obtained as brown solid (0.9 g) and used for next step without further purification.

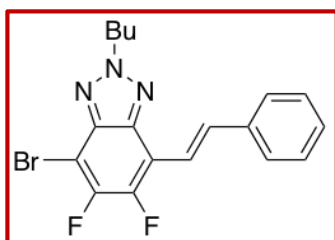
2.3.4.2 Synthesis of 4-Bromo-2-butyl-5,6-difluoro-2H-benzo[d][1,2,3]triazole



7-bromo-5,6-difluoro-1H-benzo[d][1,2,3]triazole (0.75 g, 3.21 mmol) was dissolved in methanol (13 mL) and *t*-BuOK (0.45 g, 4.01 mmol) was added. ⁴⁰ After, 1-bromobutane (0.5 mL, 4.8 mmol) was added under argon atmosphere. Reaction mixture was heated to 65 °C and stirred for 24 hours. Then it was cooled to room temperature. Mixture extracted with EtOAc and water twice. Collected organic phase dried by

MgSO₄ and condensed. Column chromatography was performed to purify product in hexane system with silica. Product obtained as colorless liquid (0.3 g, 33%). ¹H NMR (400 MHz, CDCl₃): δ 7.53 (dd, J = 9.0, 6.7 Hz, 1H), 4.70 (t, J = 7.2 Hz, 2H), 2.06 (dd, J = 14.9, 7.4 Hz, 2H), 1.36 (dd, J = 15.1, 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H).

2.3.4.3 Synthesis of (*E*)-4-bromo-2-butyl-5,6-difluoro-7-styryl-2*H*-benzo[*d*][1,2,3]triazole

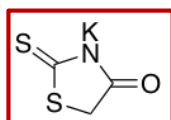


To a 25 mL Schlenk tube, 4-bromo-2-butyl-5,6-difluoro-2*H*-benzo[*d*][1,2,3]triazole (0.10 g, 0.3 mmol), Pd(TFA)₂ (4.0 mg, 12 μmol), benzoquinone (4.3 mg, 40 mmol), silver acetate (0.20 g, 0.9 mmol) and benzoic acid (0.12 g, 1.0 mmol) were added under argon atmosphere. This solid mixture was dissolved in anhydrous DMF (5 mL) and styrene (0.08 g, 0.60 mmol) was added. The resulting mixture were stirred overnight at 100 °C. Then, it cooled to room temperature. Resulting mixture was extracted with DCM, brine and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in chloroform and petroleum ether (1:2) system with silica. After, it was recrystallized with hexane. Product obtained as yellow solid (0.7 g, 48%). ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, J = 16.4 Hz, 1H), 7.63 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 6.3 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 4.77 (t, J = 7.2 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.46 (dt, J = 14.9, 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H).

2.4 Synthesis of Terminal Acceptor Units

2.4.1 Synthesis of Rhodanine Containing Acceptors

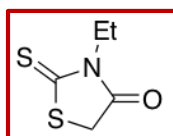
2.4.1.1 Synthesis of Potassium 4-oxo-2-thioxothiazolidin-3-ide



KOH (3.16 g, 56.3 mmol) and 3-H-rhodanine (5.00 g, 37.5 mmol) were dissolved in ethanol (40 mL).⁴² Reaction was refluxed at 80 °C for 2 hours and cooled to room temperature.

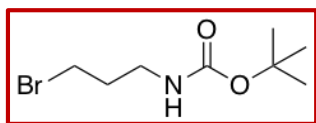
After, it took in ice-bath and crystals were observed. They were filtrated and washed with cold ethanol twice. Product observed as yellow bright solid (4.1 g, 63%). ¹H NMR (400 MHz, DMSO): δ 3.70 (s, 1H). ¹³C NMR (100 MHz, DMSO): δ 214.0, 192.2, 43.3.

2.4.1.2 Synthesis of 3-Ethyl-2-thioxothiazolidin-4-one



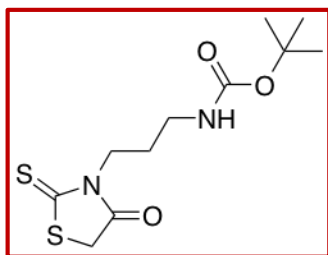
Potassium salt of rhodanine (1.00 g, 5.90 mmol) were suspended in DMF (5 mL).⁴² Ethyl bromide (0.7 mL, 7.3 mmol) was added into suspension dropwise and mixture was heated to 100 °C and stirred for 2 days. At the end of this time, mixture cooled to room temperature and extracted with DCM and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and DCM system (1:3) with silica. Product obtained as red liquid (0.38 g, 40%). ¹H NMR (400 MHz, CDCl₃): δ 4.01 (q, J = 7.1 Hz, 2H), 3.95 (s, 2H), 1.18 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 173.5, 39.7, 35.3, 11.9.

2.4.1.3 Synthesis of *tert*-butyl (3-bromopropyl)carbamate



3-aminopropylhydrobromide (1.80 g, 8.00 mmol) were suspended in DCM (30 mL).⁴³ Temperature was arranged to 0 °C by using water/ice mixture. 3-ethylamine (1.10 mL, 8.90 mmol) was added to reaction mixture. After that, di-*tert*-butyl dicarbonate (1.80 g, 8.00 mmol) by dissolving in DCM (80 mL) was added dropwise. At the end of the adding, reaction mixture is heated to room temperature and stirred overnight. DCM was removed the reaction medium and condensed residue was dissolved in EtOAc (50 mL) and washed with water. Collected organic phase dried by MgSO₄ and condensed. Product obtained as colorless oil (1.8 g, 93%). ¹H NMR (400 MHz, CDCl₃): δ 4.80 (s, 1H), 3.39 (t, *J* = 7.0 Hz, 2H), 3.26 - 3.18 (m, 2H), 2.00 (t, *J* = 6.5 Hz, 2H), 1.39 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 79.3, 39.0, 32.7, 30.8, 28.4.

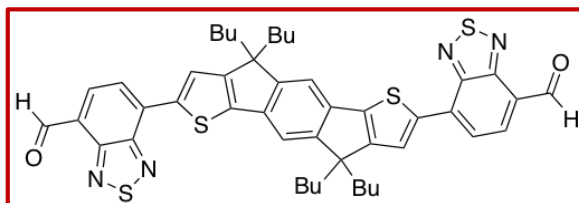
2.4.1.4 Synthesis of *tert*-butyl (3-(4-oxo-2-thioxothiazolidin-3-yl)propyl)carbamate



Rhodanine (0.20 g, 1.50 mmol) and KOH (0.25 g, 2.25 mmol) were dissolved in methanol (5 mL) and stirred for 30 minutes. After that, *tert*-butyl(3-bromopropyl)carbamate (0.56 g, 2.25 mmol) was added dropwise to reaction medium. Then, it heated to 50 °C and stirred overnight. At the end of this time, mixture cooled to room temperature and extracted with DCM and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product. Desired product was not obtained.

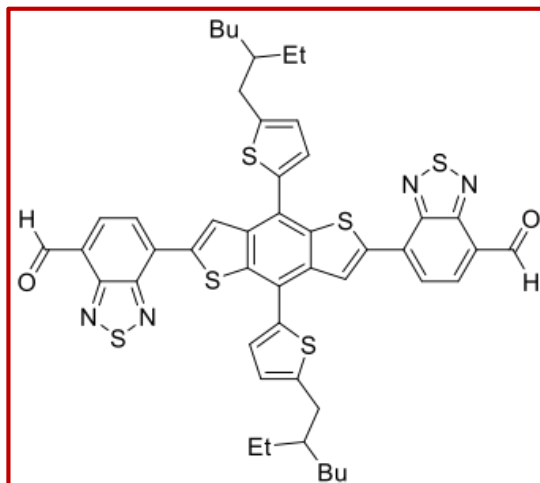
2.5 Stille & Suzuki Cross-Coupling Reactions

2.5.1 Synthesis of 7,7'-(4,4,9,9-tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde)



(4,4,9,9-Tetrabutyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (0.14 g, 0.17 mmol) and 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.095 g, 0.170 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous toluene (10 mL), all solids were dissolved. Tetrakis(triphenylphosphine)palladium(0) (0.009 g, 5%) was added as a catalyst. Mixture was heated to 110 °C and stirred overnight. At the end of this time, mixture cooled to room temperature and extracted with DCM and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with silica. Also, preparative thin layer chromatography was applied. Desired product was not obtained.

2.5.2 Synthesis of 7,7'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde)



1st trial

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.16 g, 0.18 mmol) and 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.16 g, 0.53 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous THF (3 mL), all solids were dissolved. bis(triphenylphosphine)palladium(II) chloride (0.013 g, 5%) was added as a catalyst. Mixture was heated to 75 °C and stirred for 2 hours. At the end of this time, mixture cooled to room temperature and extracted with chloroform and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and chloroform system with silica. Desired product was not obtained.

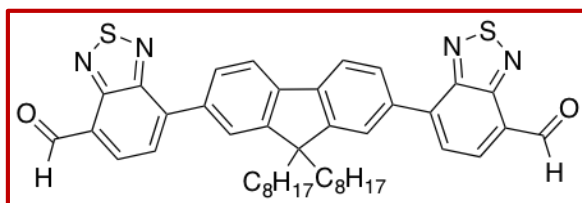
2nd trial

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.25 g, 0.28 mmol) and 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.20 g, 0.82 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous toluene (10 mL), all solids were dissolved. Tetrakis(triphenylphosphine)palladium(0) (0.02 g, 5%) was added as a catalyst. Mixture was heated to 75 °C and stirred overnight. At the end of this time, mixture cooled to room temperature and extracted with DCM and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and DCM (1:2) system with silica. Desired product was not obtained.

3rd trial

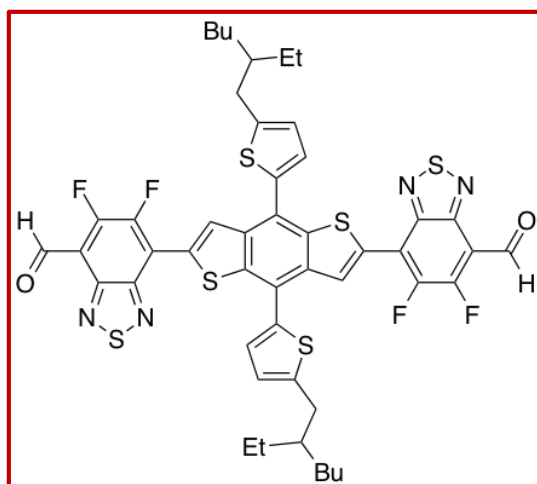
(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.10 g, 0.11 mmol) and 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.08 g, 0.33 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous toluene (6 mL), all solids were dissolved. Tetrakis(triphenylphosphine)palladium(0) (0.013 g, 10%) was added as a catalyst. Mixture was heated to 110 °C and stirred overnight. At the end of this time, mixture cooled to room temperature and extracted with DCM and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in hexane and DCM (1:2) system with silica. Desired product was not obtained.

2.5.3 Synthesis of 7,7'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde)



2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (0.30 g, 0.527 mmol) and 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.30 g, 1.23 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous THF (18 mL), all solids were dissolved. Tetrakis(triphenylphosphine)palladium(0) (0.03 g, 5%) and K₂CO₃ (1M, 2.1 mL) were added as a catalyst and base, respectively. Mixture was heated to 75 °C and stirred overnight. At the end of this time, mixture cooled to room temperature and extracted with DCM and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with water activated neutral alumina. Recrystallization were performed with DCM and hexane. Product obtained as yellow solid (0.21 g, 55%). ¹H NMR (400 MHz, CDCl₃): δ 10.72 (s, 2H), 8.26 (d, *J* = 7.3 Hz, 2H), 8.01 - 7.87 (m, 8H), 2.11 - 2.00 (m, 4H), 1.27 - 0.98 (m, 24H), 0.67 (t, *J* = 6.7 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 189.0, 154.1, 153.9, 152.1, 141.8, 140.8, 135.7, 132.6, 129.0, 126.9, 126.2, 124.5, 120.5, 55.7, 40.1, 31.8, 30.0, 29.2, 24.0, 22.6, 14.1.

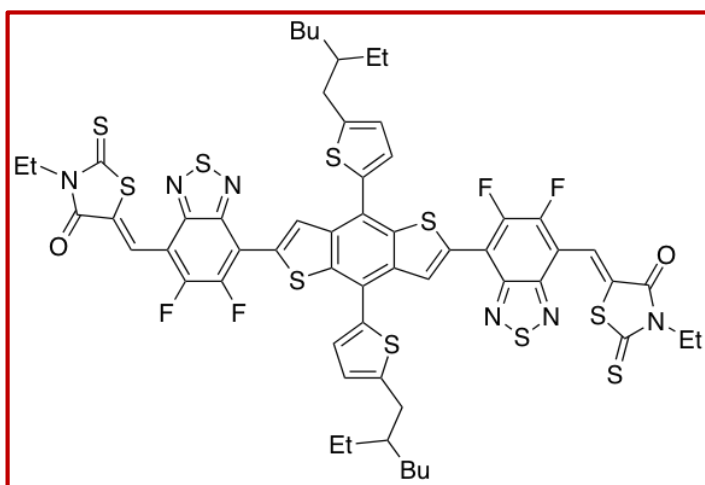
2.5.4 Synthesis of 7,7'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde)



(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.100 g, 0.110 mmol) and 7-Bromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (72 mg, 0.3 mmol) were added to a 25 mL Schlenk tube under argon atmosphere. By adding anhydrous toluene (7 mL), all solids were dissolved. Tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 5%) were added as catalyst. Mixture were heated to 110 °C and stirred for overnight. At the end of this time, mixture cooled to room temperature and extracted with chloroform and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with silica. Product obtained as dark-green solid (0.60 g, 55%). ¹H NMR (400 MHz, CDCl₃) δ 10.76 (s, 1H), 9.11 (s, 1H), 7.50 (d, J = 3.5 Hz, 1H), 7.02 (d, J = 3.5 Hz, 1H), 2.95 (d, J = 6.5 Hz, 2H), 1.78 – 1.74 (m, 1H), 1.44 – 1.31 (m, 8H), 0.99 (d, J = 7.4 Hz, 3H), 0.93 (t, J = 6.7 Hz, 3H). MS: 974.1564 [M+H] (calculated 974.1568)

2.6 Knoevenagel Condensation Reactions

2.6.1 Synthesis of (5*Z*,5'*Z*)-5,5'-(((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]*dithiophene*-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)



1st trial

7,7'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]*dithiophene*-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde) (90 mg, 0.09 mmol) and 3-Ethyl-2-thioxothiazolidin-4-one (140 mg, 0.87 mmol) were added to a 25 mL Schlenk tube. By adding chloroform (20 mL), all solids were dissolved and piperidine (0.1 mL) was added dropwise to the reaction medium.⁴⁴ It was stirred at room temperature for overnight. At the end of this time, mixture cooled to room temperature and extracted with chloroform and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with silica. Desired product could not be obtained.

2nd trial

7,7'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde) (75 mg, 0.08 mmol) and 3-Ethyl-2-thioxothiazolidin-4-one (100 mg, 0.62 mmol) were added to a 25 mL Schlenk tube. By adding chloroform (20 mL), all solids were dissolved, and triethylamine (0.7 mL) was added dropwise to the reaction medium.⁴⁵ It was stirred at room temperature for overnight. At the end of this time, mixture cooled to room temperature and extracted with chloroform and water by three times. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with silica. Desired product could not be obtained.

3rd trial

7,7'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde) (90 mg, 0.09 mmol) and 3-Ethyl-2-thioxothiazolidin-4-one (140 mg, 0.87 mmol) were added to a 25 mL Schlenk tube. By adding chloroform (20 mL), all solids were dissolved and piperidine (0.1 mL) was added dropwise to the reaction medium. It was stirred to 61 °C for overnight. At the end of this time, mixture cooled to room temperature and extracted with chloroform and water twice. Collected organic phase dried by Na₂SO₄ and condensed. Column chromatography was performed to purify product in DCM system with silica. Desired product could not be obtained.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of (4,4,9,9-Tetrabutyl-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane)

IDT core contains five fused aromatic rings and synthesis of this core requires significant number of steps as seen in figure 3.1. The synthesis of the compound has been performed in the literature and the method was followed by slight modifications. Additionally, following the synthesis of the core two additional steps are required: 1) Alkylation to make it soluble in solvents such as chloroform and 2) Stannylation for the Stille Coupling reaction to combine with acceptor units. These synthetic studies are discussed in detail below.

Synthetic pathway was started with commercially available compound **1**. Both methyl groups on compound **1** was oxidized by using KMnO₄ and compound **2** was obtained. Fisher esterification performed on the resulting carboxylic acid groups gave ester **3** successfully. Separately, thiophene (**4**) was processed was stannylated on the alpha position using *n*-buthyllithium in THF and tribuyltin chloride to give compound **5**. After getting compound **3** and **5** successfully, Stille Coupling was performed to give compound **6**. Hydrolysis followed by oxalyl chloride gave the acyl chlorides which was taken directly to double intramolecular Friedel-Craft reaction to give compound **8**. IDT core **9** was synthesized via a high temperature hydrazine-based reduction. Compound **9** was tetra-alkylated with butyl groups. Finally, stannylation was performed to get the central unit **12**.

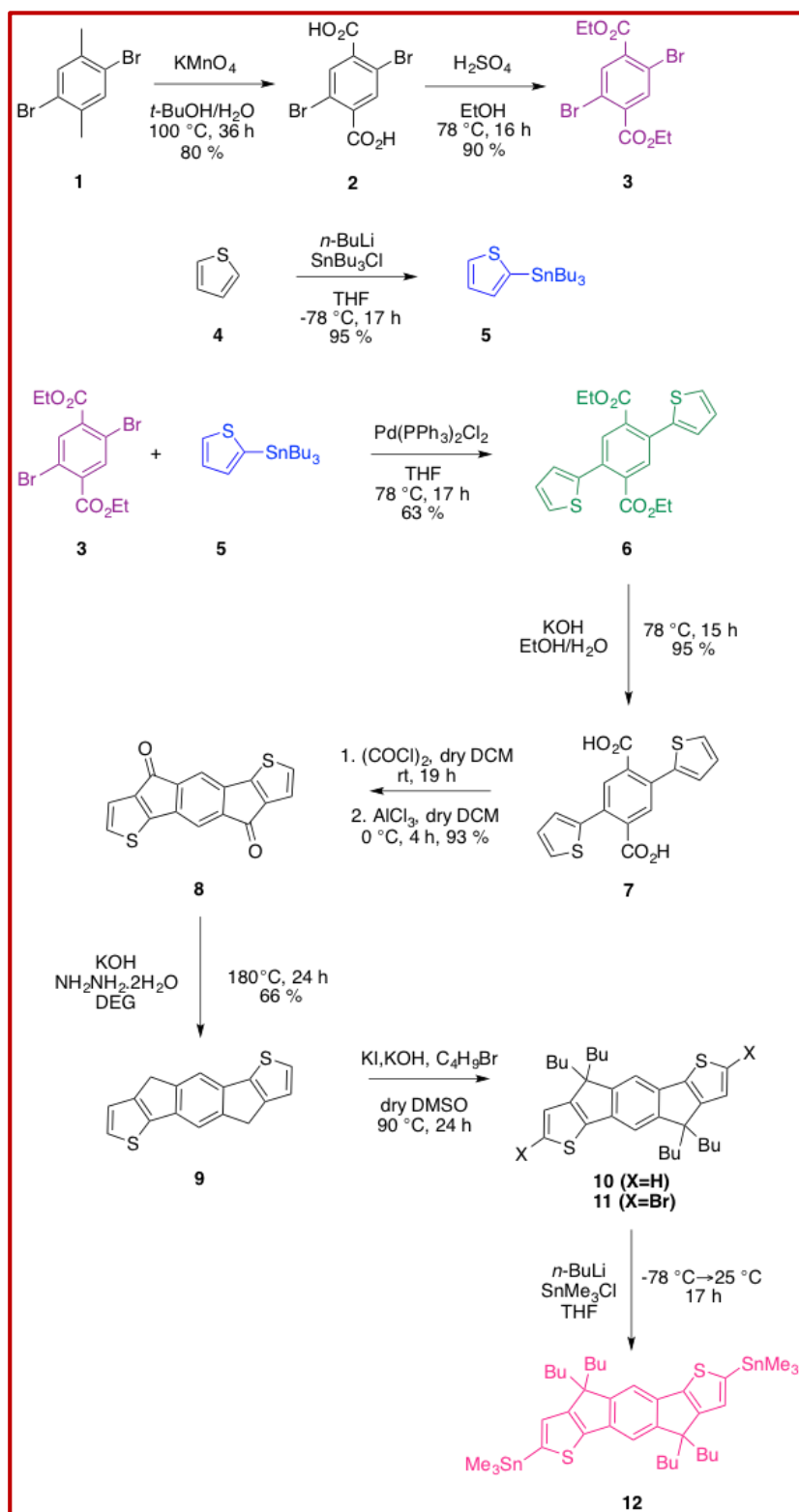


Figure 3.1. General synthetic pathway for compound **12**

3.2 Synthesis of 7-Bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde

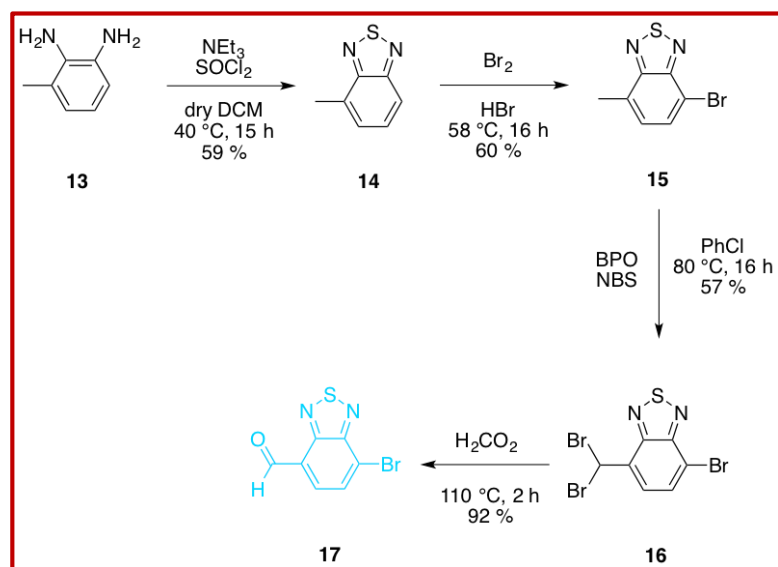


Figure 3.2. General synthetic pathway for compound **17**

Compound **17** is one of the possible candidate bridge unit between core and terminal units. It was synthesized in four steps according to literature procedures. Synthetic pathway started with compound **13** which was commercially available. Thionyl chloride mediated ring closure resulted in benzothiadiazole derivative **14**. Bromination with molecular bromine on the aromatic ring followed by double radicalic bromination of the methyl group gave compounds **15** and **16** respectively. Finally, compound **16** was refluxed in formic acid and after only 2 hours, compound **17** was attained in high yield.

3.3 Synthesis of 7-Bromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde

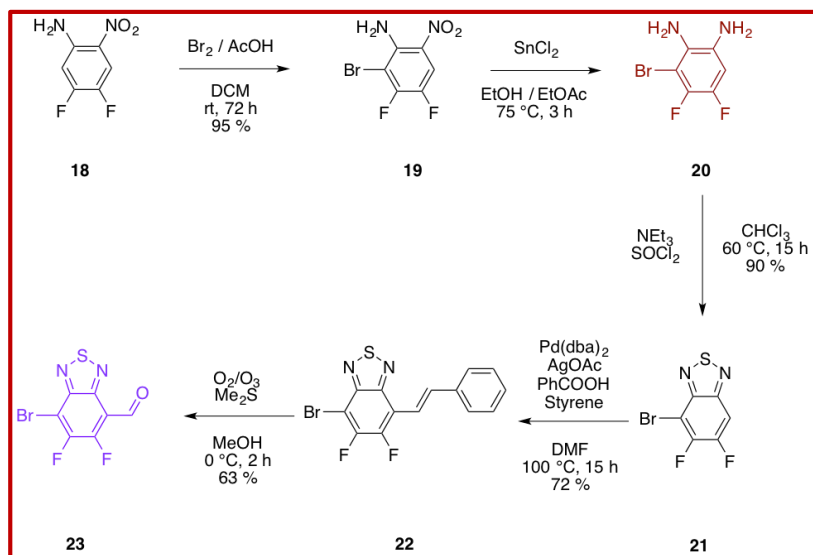


Figure 3.3. General synthetic pathway for compound **23**

Compound **23** is another possible candidate as a bridge unit. Due to electronegative nature of fluorine atoms, difluorinated benzothiadiazole shows better electron accepting properties. This synthetic pathway is a novel method developed in this study, which has fewer number of steps compared to the commonly utilized method in the literature. Moreover, di-fluorinated version cannot be synthesized directly from compound **13**, there is a need for a new commercial which is compound **18**.

Firstly, compound **18** was brominated with bromine and compound **19** was attained as a yellow solid. After, reduction reaction was performed to convert NO_2 group to NH_2 and compound **20** was synthesized. To prevent rapid decomposition of the highly electron rich aromatic rings, next reaction was performed without further purification. A ring closure reaction was applied to get compound **21** with a similar method for the synthesis of compound **14**. A C-H activation reaction that was

developed by Xiao et. al.⁴⁶ Styrene was coupled to compound **21** to yield compound **22**. Lastly, successful implementation of the ozonolysis reaction gave compound **23**.

3.4 Synthesis of 7-bromo-5,6-difluorobenzo[*c*][1,2,5]selenadiazole-4-carbaldehyde and 7-bromo-2-butyl-5,6-difluoro-2*H*-benzo[*d*][1,2,3]triazole-4-carbaldehyde

The successful synthesis of di-fluorinated benzothiadiazole bridge unit (**23**), in a shorter synthesis compared to literature motivated us to demonstrate if similar approach can be utilized with other derivatives. Hence, by starting from compound **20**, first, ring closure reactions with SeO₂ and NaNO₂ were performed to get compound **24** and **27** respectively. Before styrene addition, compound **27** was alkylated by using 1-bromobutane for better solubility. After that, styrene was incorporated with a similar C-H activation reaction to yield compounds **25** and **29**. Due to technical problems with ozone generator in our lab, we weren't able to perform the ozonolysis reactions however we believe reactions would work smoothly to give the target compounds **26** and **30**.

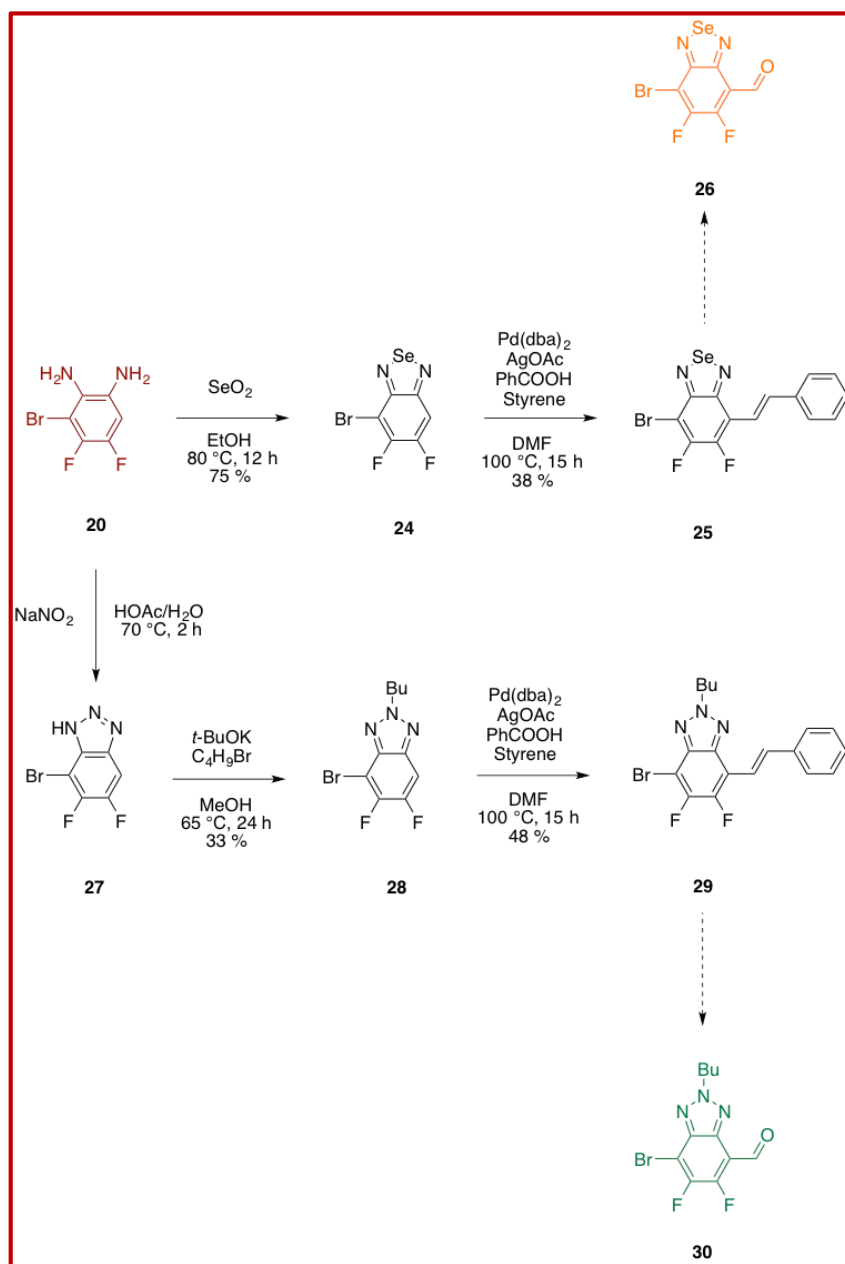


Figure 3.4. General synthetic pathway for compound **26** and **30**

3.5 Synthesis of 3-ethyl-2-thioxothiazolidin-4-one and 3-(3-aminopropyl)-2-thioxothiazolidin-4-one

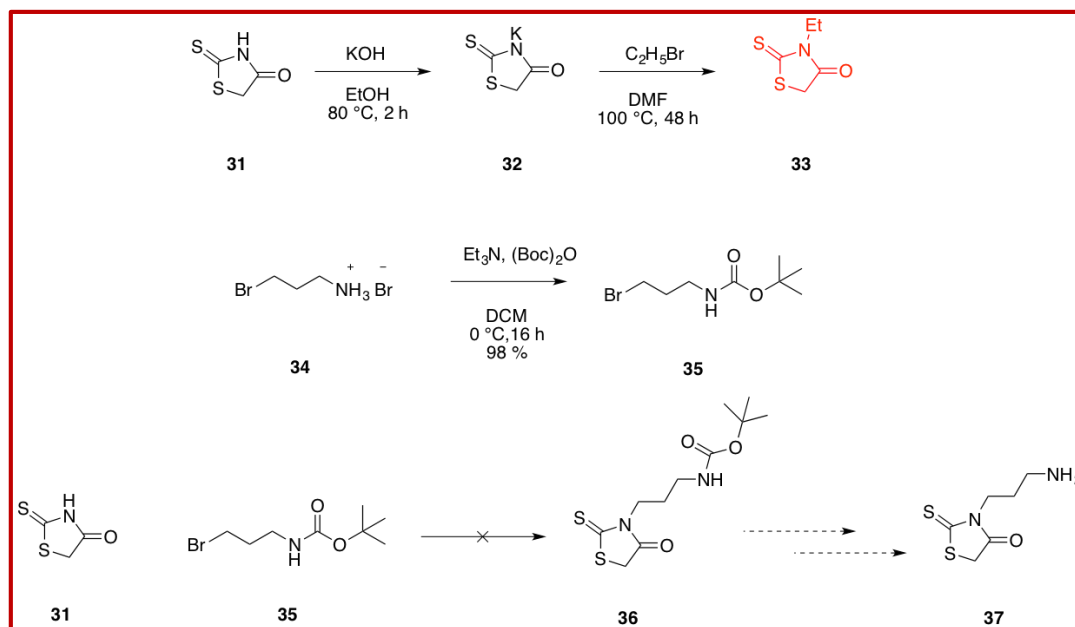


Figure 3.5. General synthetic pathway for compound **33** and **37**

Compound **33** and **37** were designed as possible terminal units for the target molecules. First, terminal unit was synthesized in two sequential steps. In the first step, Commercial compound **31** was deprotonated with KOH to get the potassium salt of rhodanine, compound **32**. After that, **32** was treated with ethyl bromide in DMF to yield the target compound **33** which could be directly utilized in Knoevenagel Condensation reaction.

As mentioned in the motivation part, a terminal amine unit could interact with the transport layers for increasing surface passivation in solar cells. Hence, we aimed to synthesize an amine flanked rhodamine derivative for this purpose. **31** was similarly deprotonated with KOH to get **32**, however alkylation reaction with Boc-protected bromoalkylamine did not yield the expected product. No reaction was observed with similar conditions applied to get compound **33**, and significant decomposition was

observed at higher temperatures. In-situ Finkelstein procedure with added NaI also was not fruitful. We are still working on to solve this puzzling issue on this alkylation reaction.

3.6 Stille & Suzuki Cross-Coupling Reactions

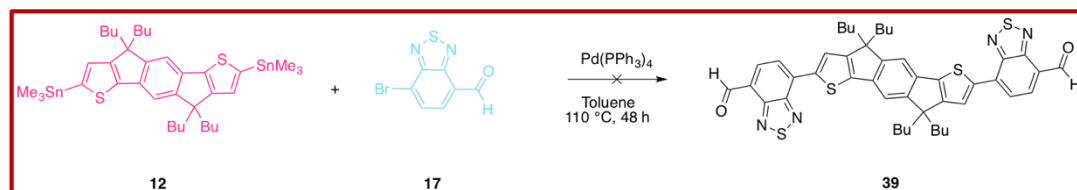


Figure 3.6. Synthetic pathway for compound **39**

First of all, Stille coupling between compound **12** and **17** has been attempted. Pd(0) was utilized as the catalyst and anhydrous toluene was chosen as the suitable solvent. Reaction was taken under reflux and monitored by TLC. During reflux, two new spots (purple and blue colored) were observed. Even though we initially thought these can be the products of the reaction NMR studies revealed that both of these products were not the target compound **39**. The side products formed in this reaction could not be identified however C-Sn bond on compound **12** seemed delicate and easily breaks under reaction conditions with circumvented the desired coupling reaction. Compound **12** contained almost 10 steps with mostly tedious procedures. Hence producing more **12** has been proved difficult, hence additional trials with different catalyst/solvent coupled could not be performed.

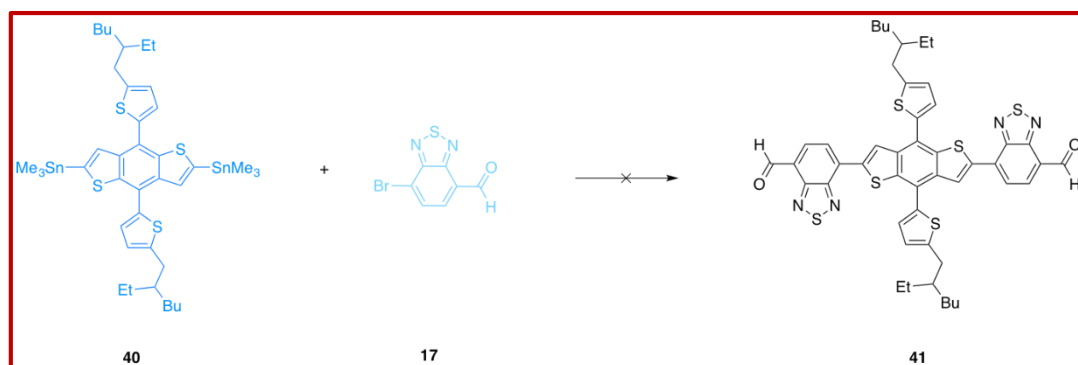


Figure 3.7. Synthetic pathway for compound **41**

To be able to optimize coupling conditions we turned to commercial central units. BDT derivative **40** was chosen as candidate and coupling chemistry has been studied with this model compound. Stille coupling was performed between compound **40** and **17**. Unfortunately, the expected product could not be attained with this compound either even after several attempts as summarized in Table 3.1. Several spots were formed in all tries and separation of the products by silica and alumina column chromatography proved difficult.

Table 3.1. Optimization for Stille Coupling between compound **40** and **17**

number	catalyst	solvent	temperature	time
1	Pd(II), 5%	THF	75 °C	2 h
2	Pd(0), 5%	Toluene	110 °C	overnight
3	Pd(0), 10%	Toluene	110 °C	overnight

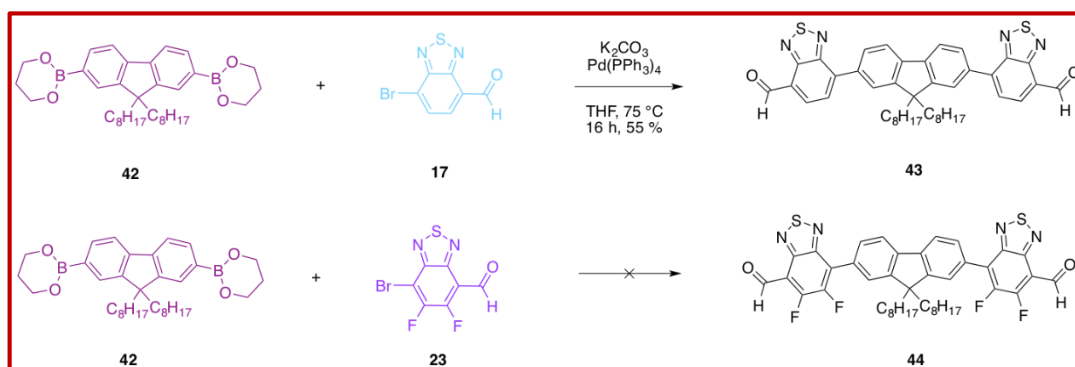


Figure 3.8. Synthetic pathway for compound **43** and **44**

After challenges on Stille coupling, it was decided to try one another coupling method which is Suzuki cross-coupling reaction. A commercial borylated fluorene derivative (compound **42**) was chosen as the model compound. The coupling chemistry which was performed according to the literature was fruitful in this case and the resulting bright yellow spots on TLC was shown to be the title compound **43**. Unfortunately, the coupling chemistry utilizing the di-fluorinated **23** was not successful. Actually, TLC showed a similar spot as it was in the synthesis of compound **43**, however purification of the material was not fruitful. Our work on the lines of purifying this novel derivative is still ongoing.

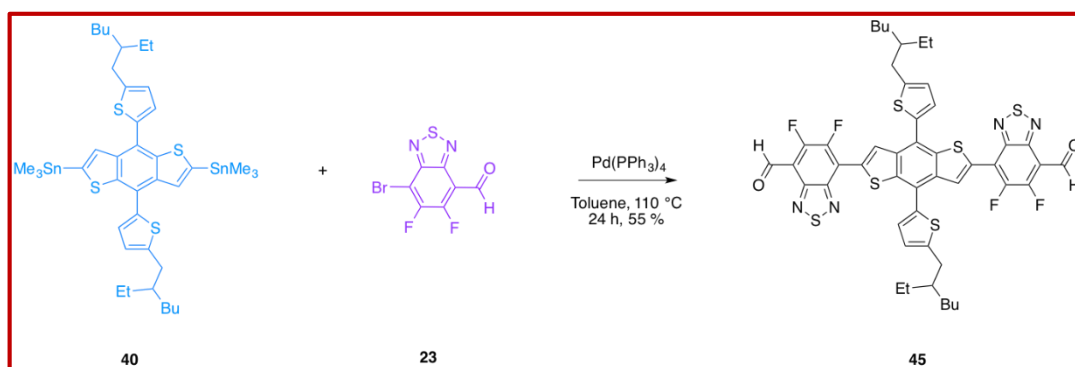
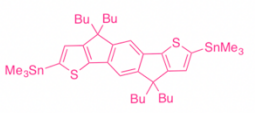
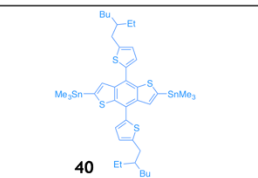
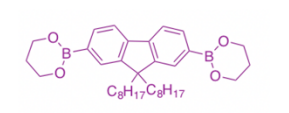
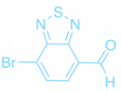
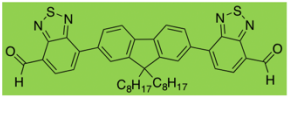
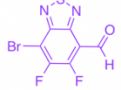
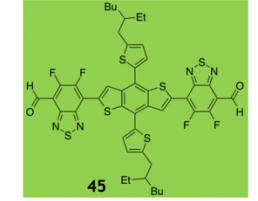


Figure 3.9. Synthetic pathway for compound **45**

At this point it was envisioned that the electronics of the units used for coupling is quite crucial in these reactions and we wondered if Stille coupling of **40** and **23** would yield the target product. Pd(0) was used as a catalyst and anhydrous toluene was preferred as a solvent. This time the reaction was shown to be successful and compound **45** has been synthesized successfully.

Table 3.2. Applied Stille & Suzuki coupling between bridge and central units

<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> <p style="color: green;">central units</p> <p style="color: orange;">↓</p> <p style="color: orange;">bridge units</p> </div> <div style="font-size: 2em;">→</div> </div>	 <p style="text-align: center;">12</p>	 <p style="text-align: center;">40</p>	 <p style="text-align: center;">42</p>
 <p style="text-align: center;">17</p>	X	X	 <p style="text-align: center;">43</p>
 <p style="text-align: center;">23</p>	No Trial	 <p style="text-align: center;">45</p>	X

3.7 Knoevenagel Condensation Reaction

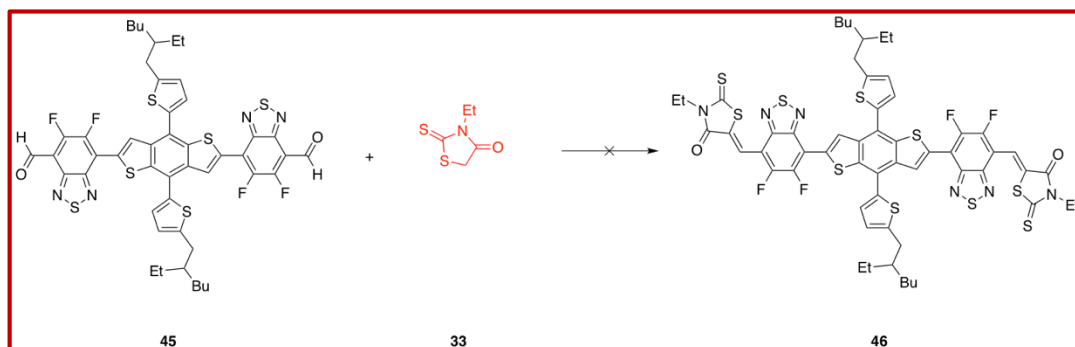


Figure 3.10. Synthetic pathway for compound **46**

The last step was Knoevenagel condensation reaction. Initially we wanted to condense compound **45** and **33**. Several optimizations were performed as given in table 3.2. In the first trial, piperidine was chosen as the catalyst for the reaction and chloroform as the solvent at room temperature. The reaction was monitored by TLC. One major spot was observed in TLC. However, characterization results revealed that target compound **46** was not obtained. Increasing the temperature to reflux also did not give the title compound. Finally, triethylamine was applied as the base however same results were obtained. Our studies on successful implementation of the Knoevenagel condensation is still ongoing.

Table 3.3. Trials for Knoevenagel Condensation Reaction between compound **45** and **33**

number	base	solvent	temperature	time
1	piperidine	CHCl ₃	rt	24 h
2	triethylamine	CHCl ₃	rt	24 h
3	piperidine	CHCl ₃	60 °C	24 h

CHAPTER 4

CONCLUSION

In this study, a novel small molecule targetted as a non-fullerene acceptor for utilization in organic solar cells. Initially demanding synthesis of IDT core was achieved successfully. On the other hand, non-fluorinated benzothiadiazole was synthesized as a bridge unit in four steps. Additionally, di-fluorinated benzothiadiazole was synthesized with a novel synthetic method first time in the literature. Due to challenges in coupling reactions, using IDT core other commercial central unit BDT and Fluorene cores were utilized. We also attempted to synthesize di-fluorinated benzoselenadiazole and benzotriazole derivatives by using the same unique pathway. Studies are still ongoing along these lines. After getting several core and bridge units, Stille and Suzuki cross-coupling reactions were performed. It was observed that di-fluorinated bridge unit and BDT couple was suitable for Stille reaction whereas non-fluorinated BDT and borylated-fluorene was suitable for Suzuki coupling. As a result, compound **45** was obtained adequately. At the same time, successful alkylation of rhodanine was performed with ethyl chain to use in Knoevenagel condensation as a terminal unit. However, the studies and efforts to achieve compound **46** was not fruitful. Our studies on realization of the final target units are still ongoing.

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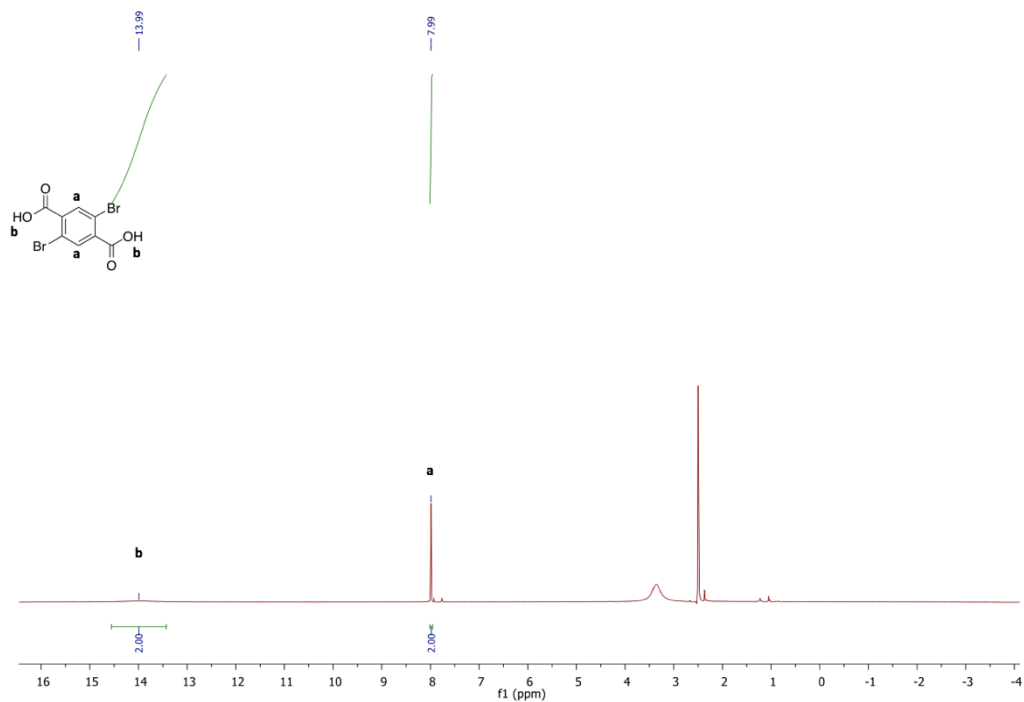
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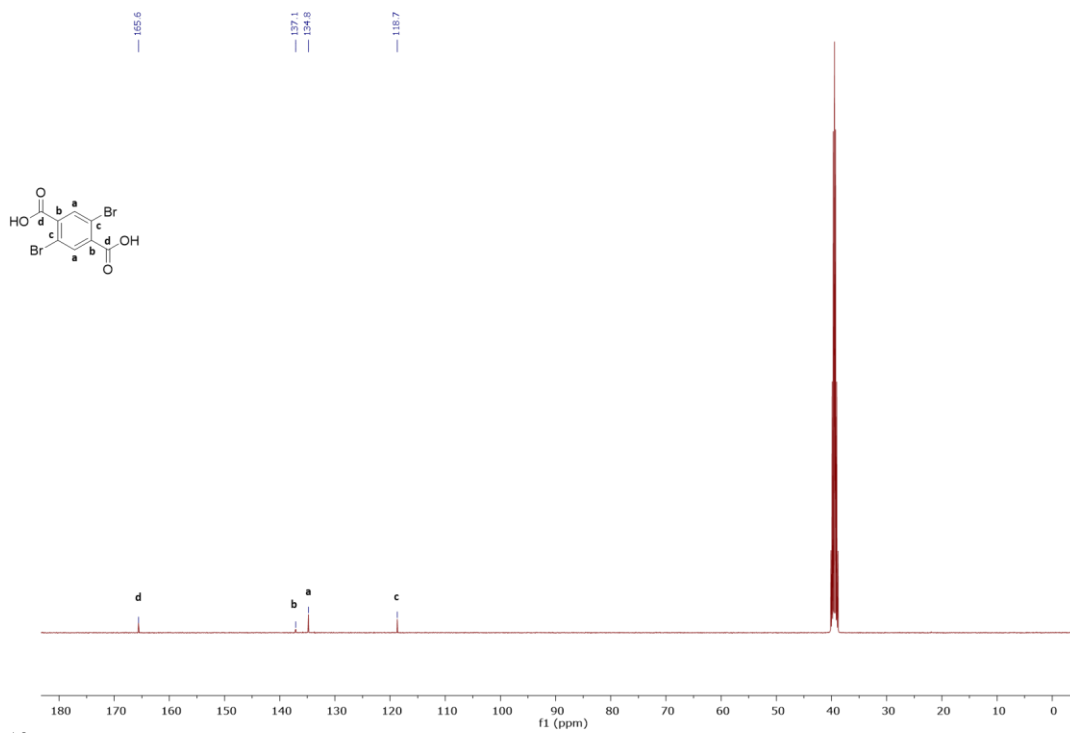
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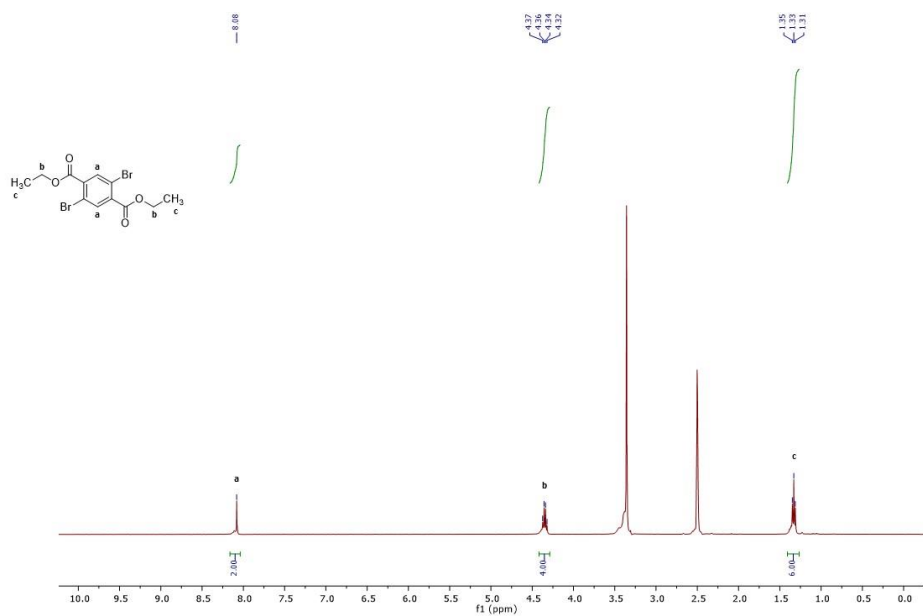
APPENDICES

A. NMR

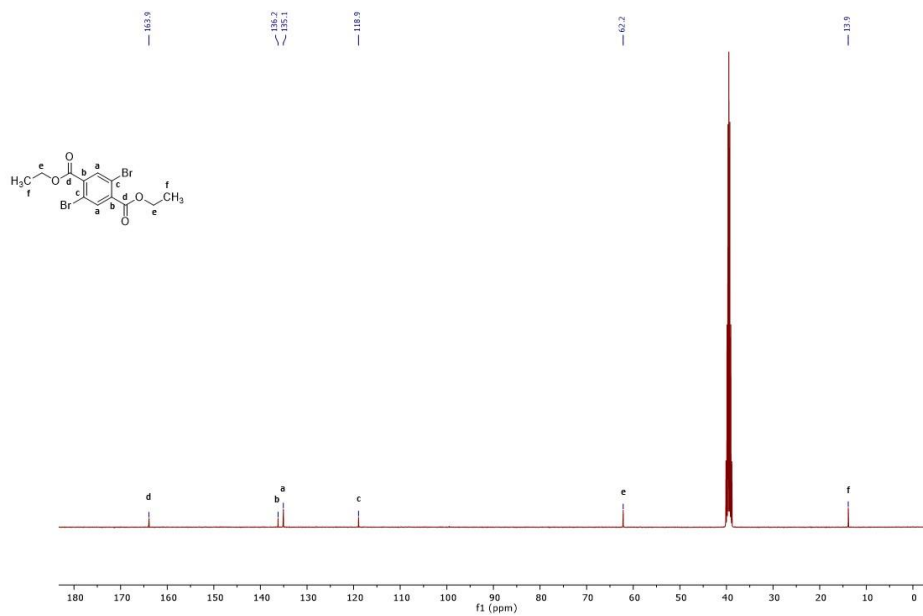


¹³C NMR of compound 2

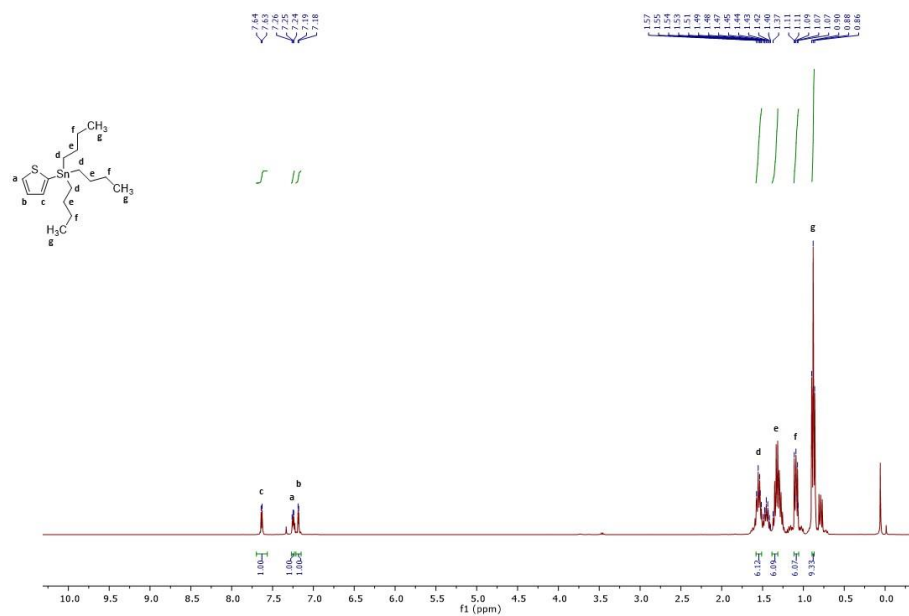




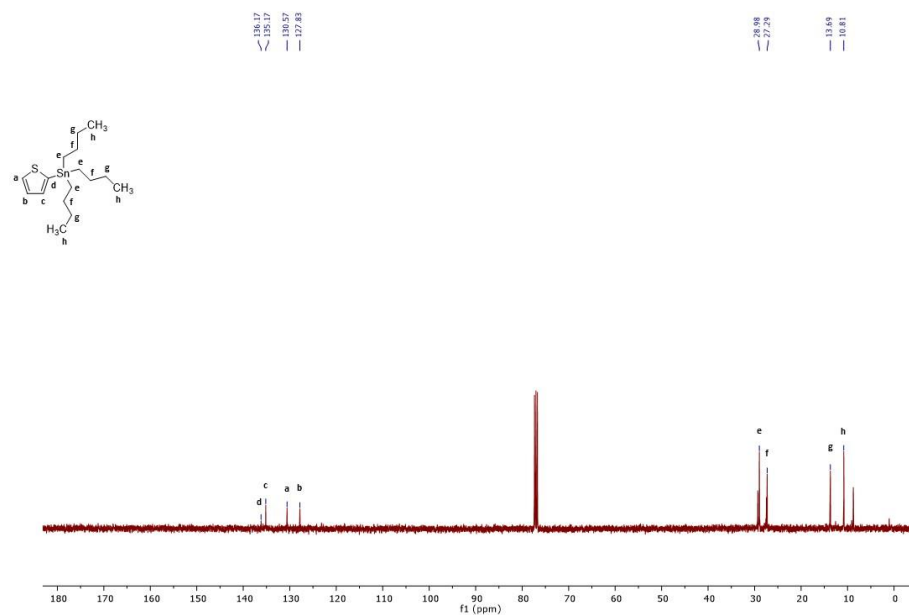
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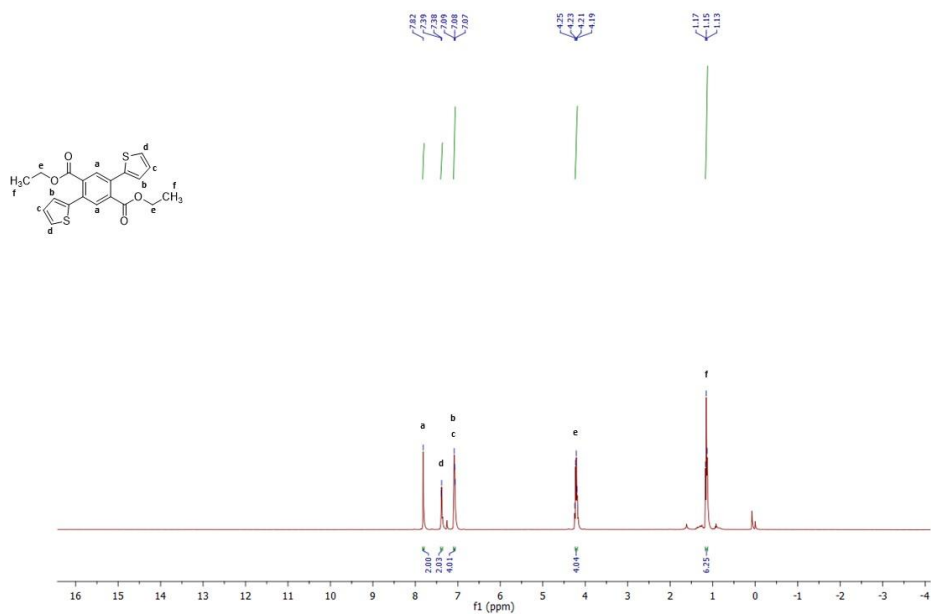
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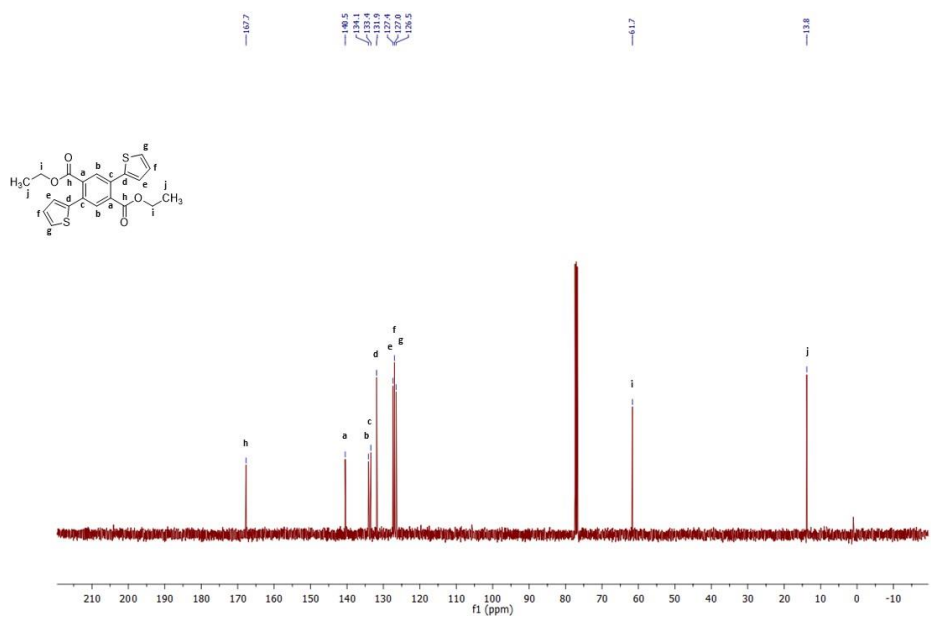
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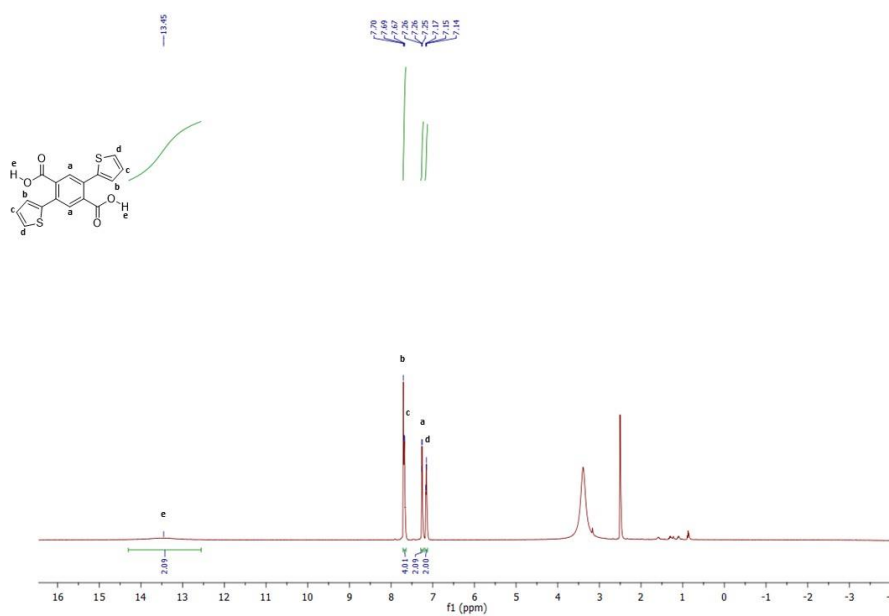
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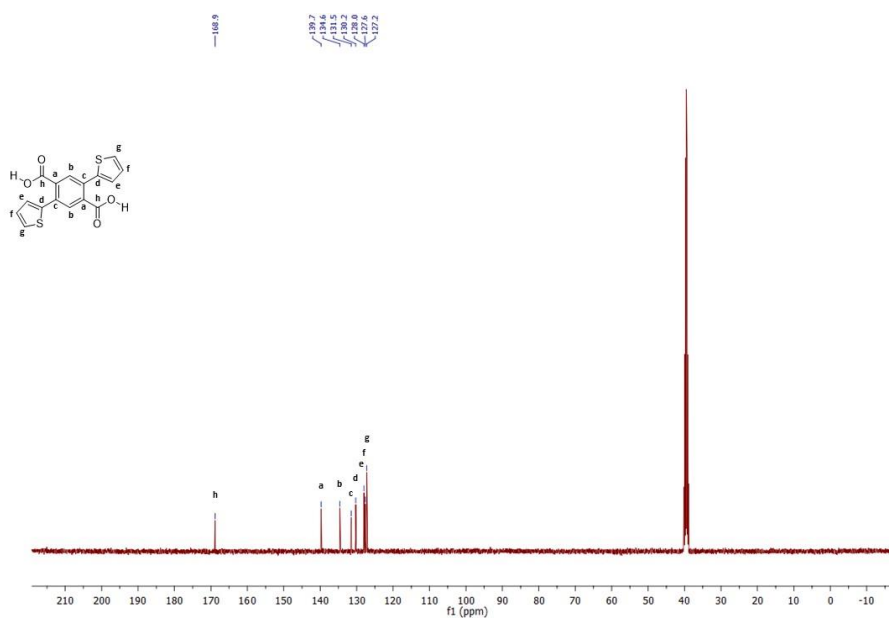
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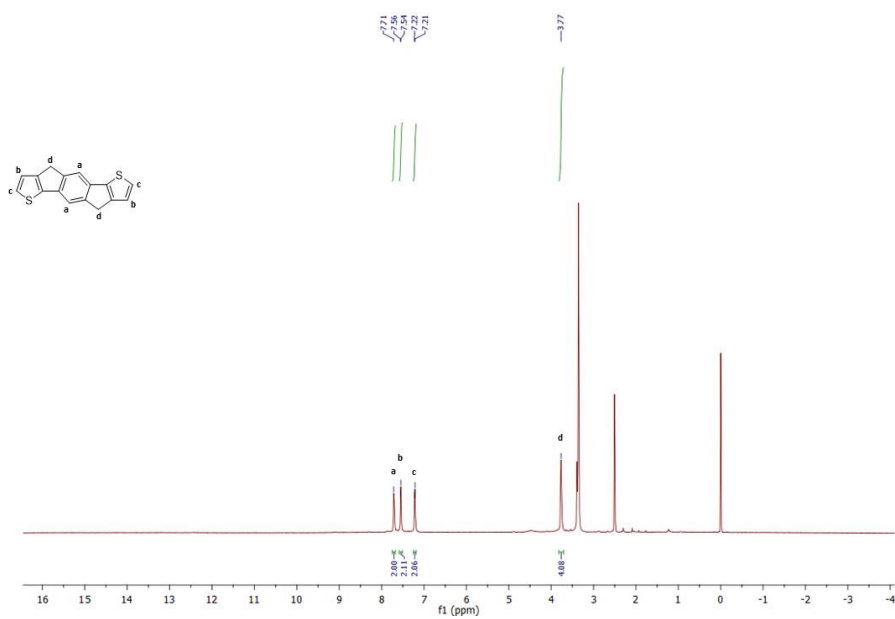
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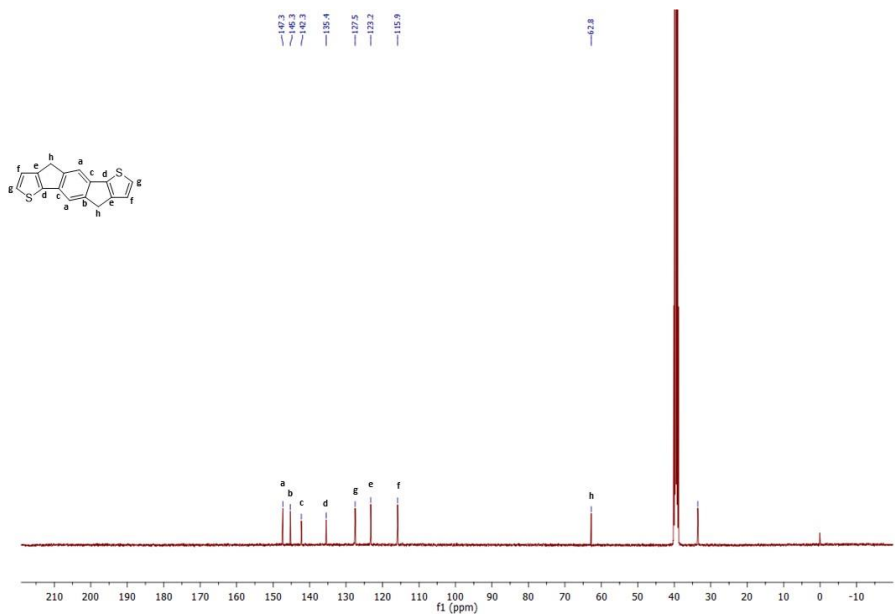
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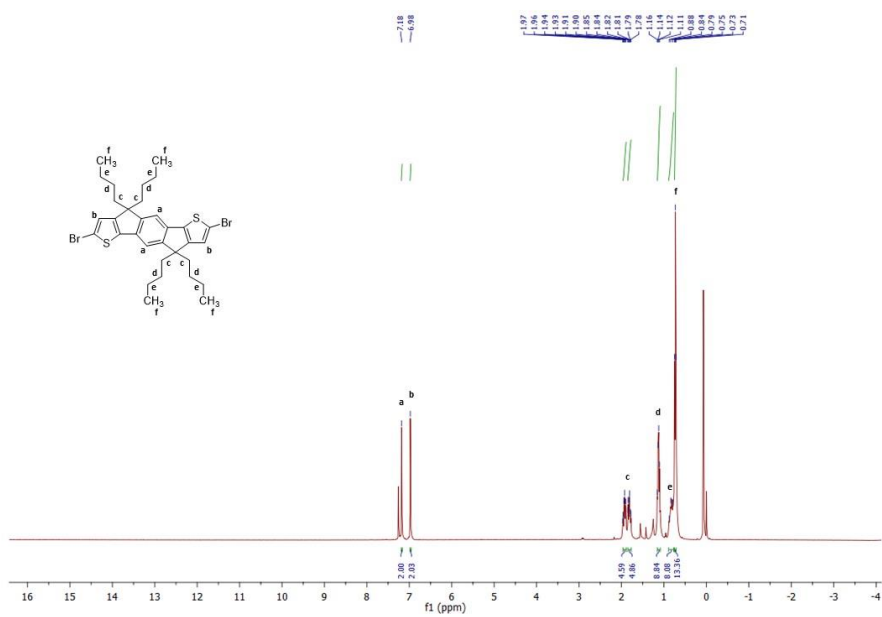
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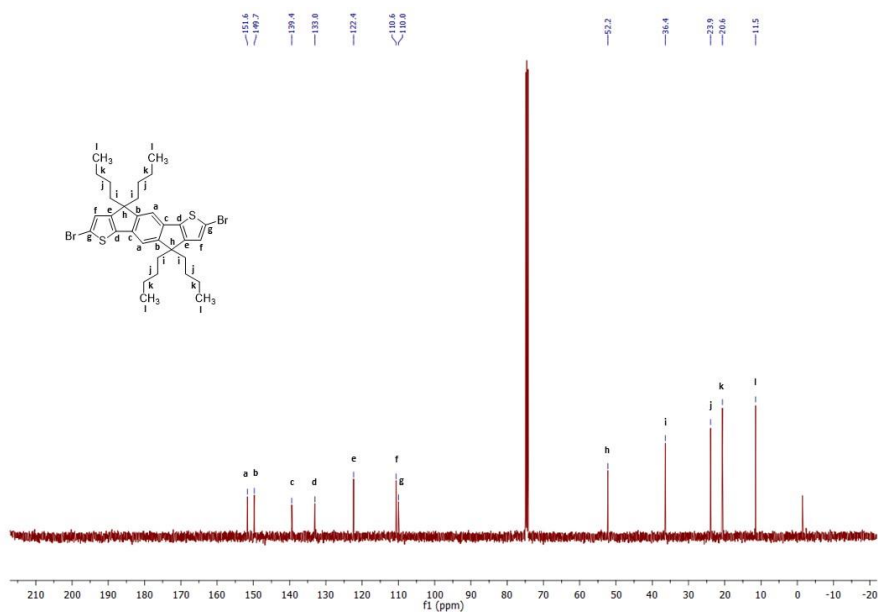
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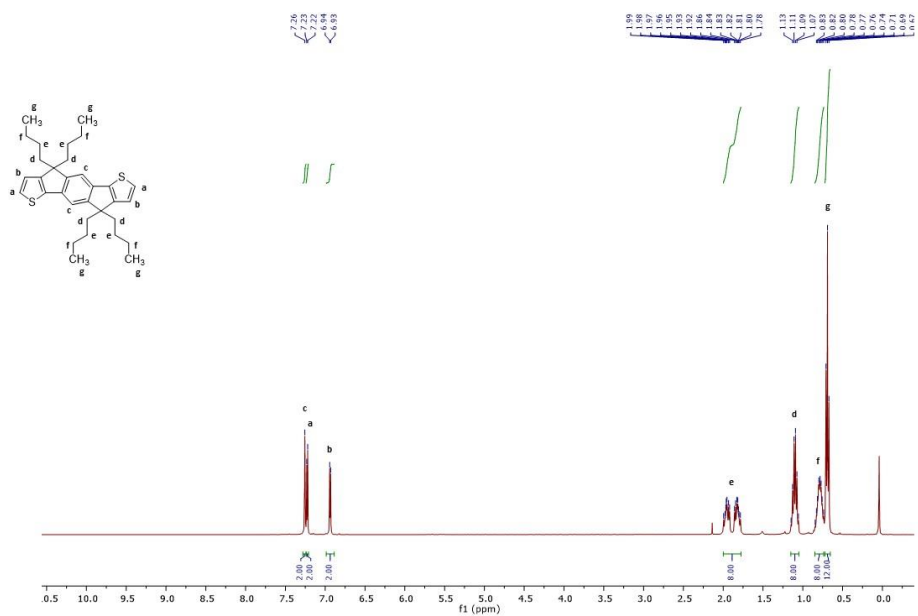
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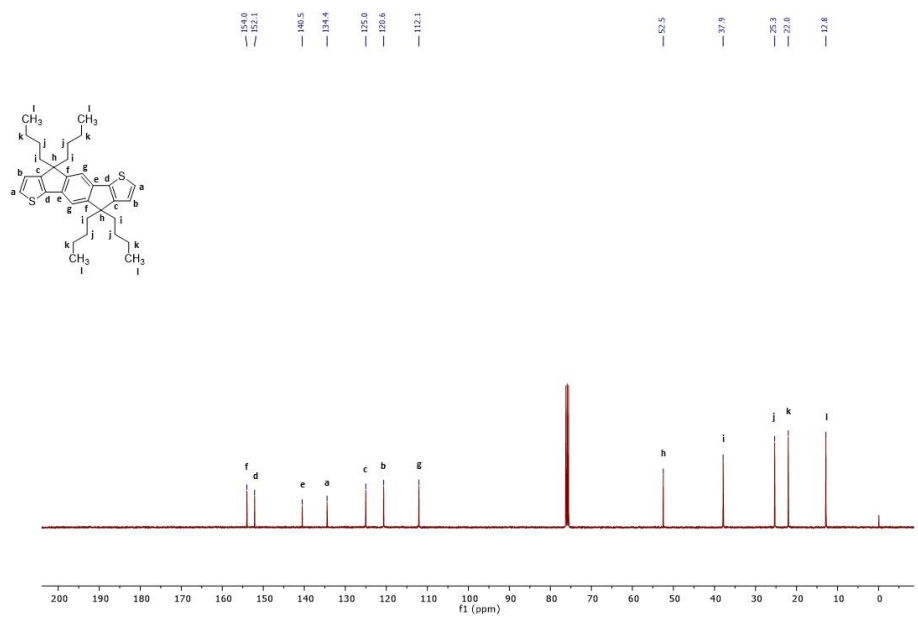
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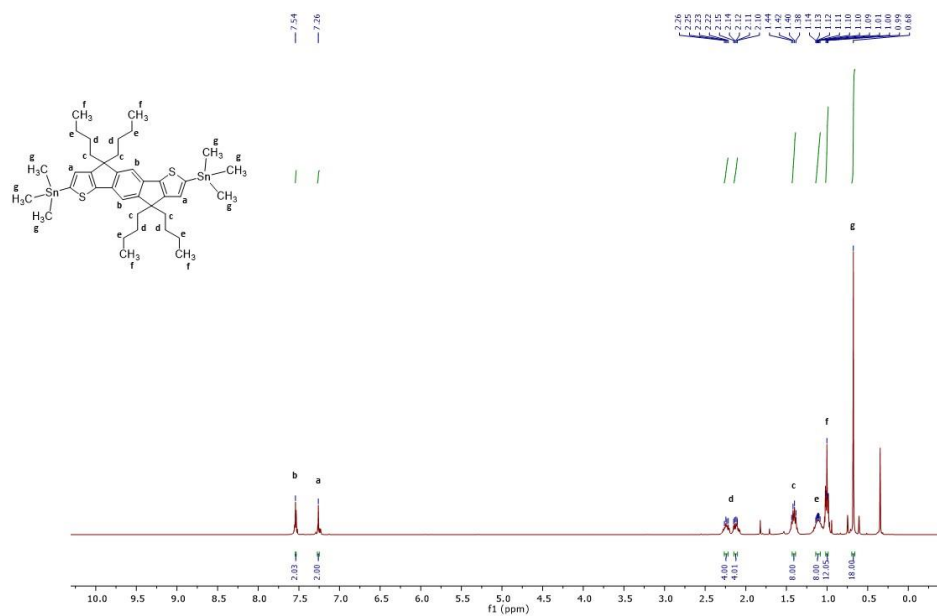
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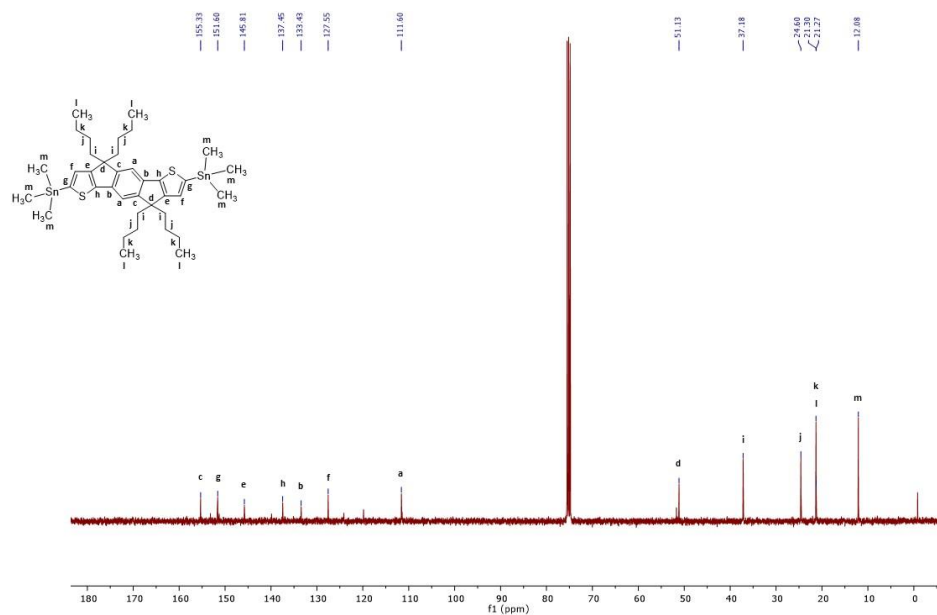
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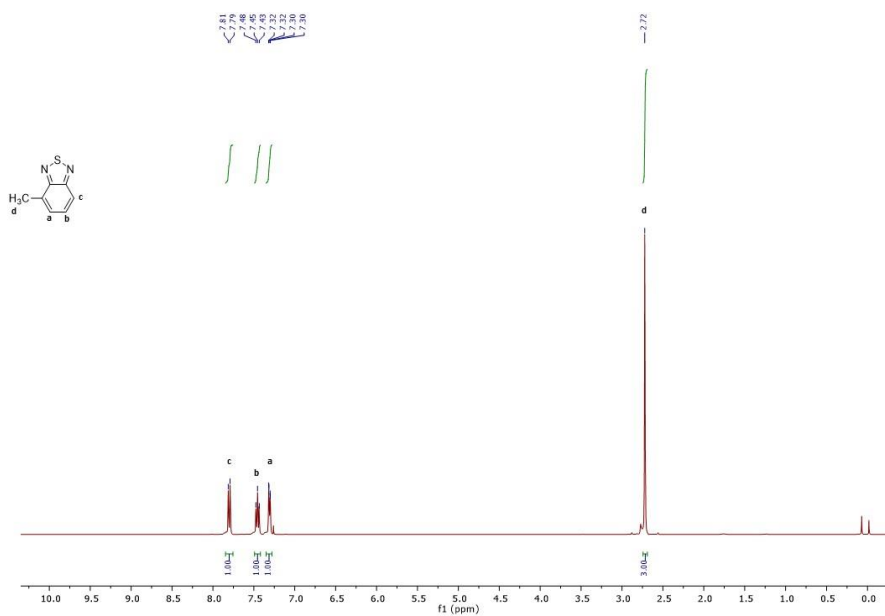
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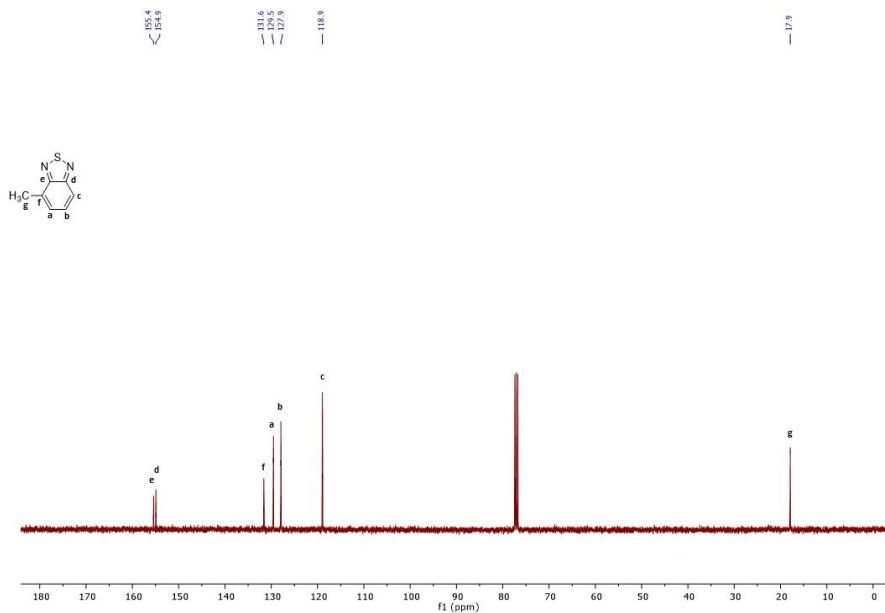
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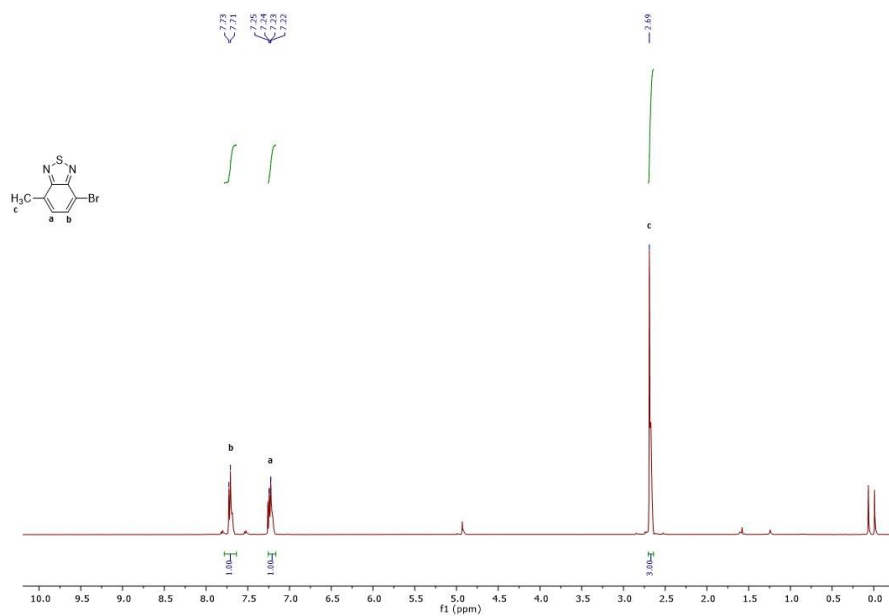
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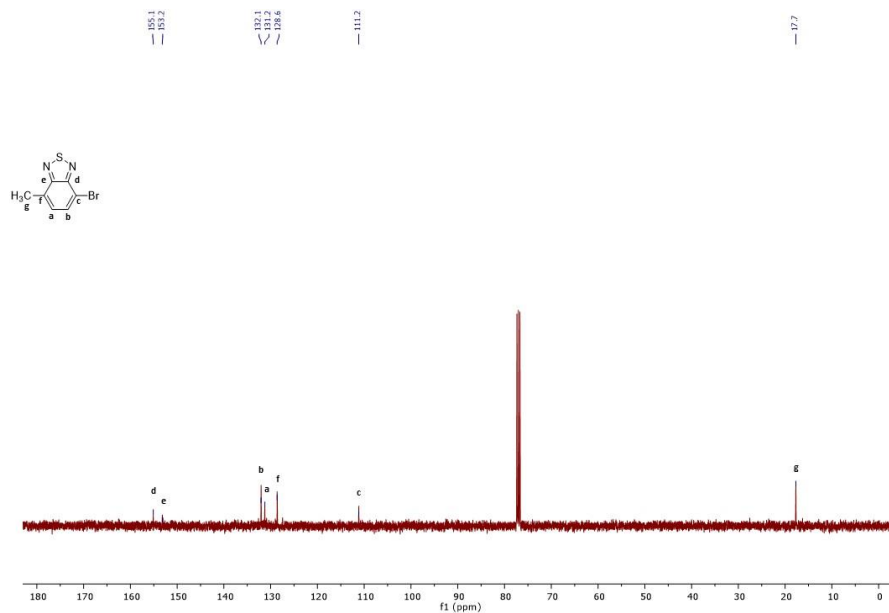
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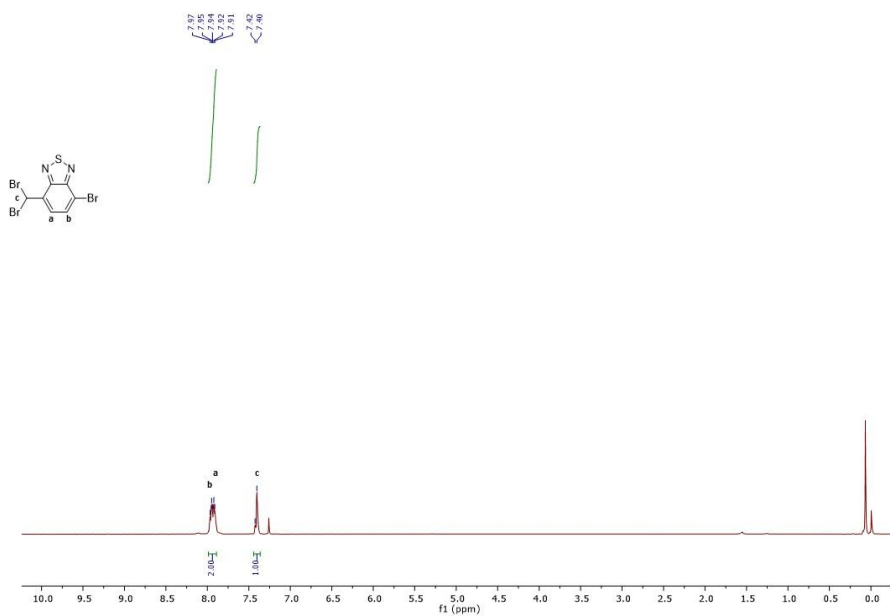
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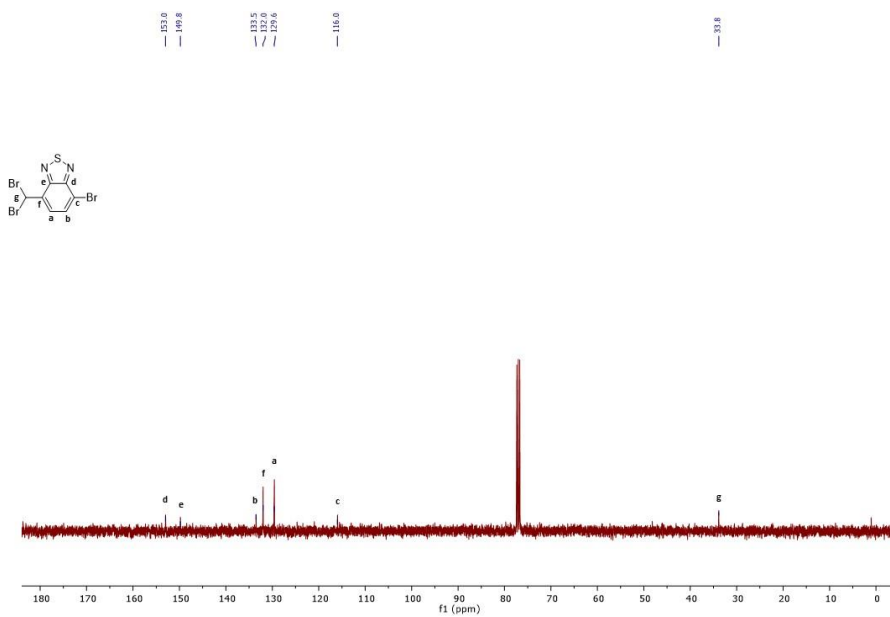
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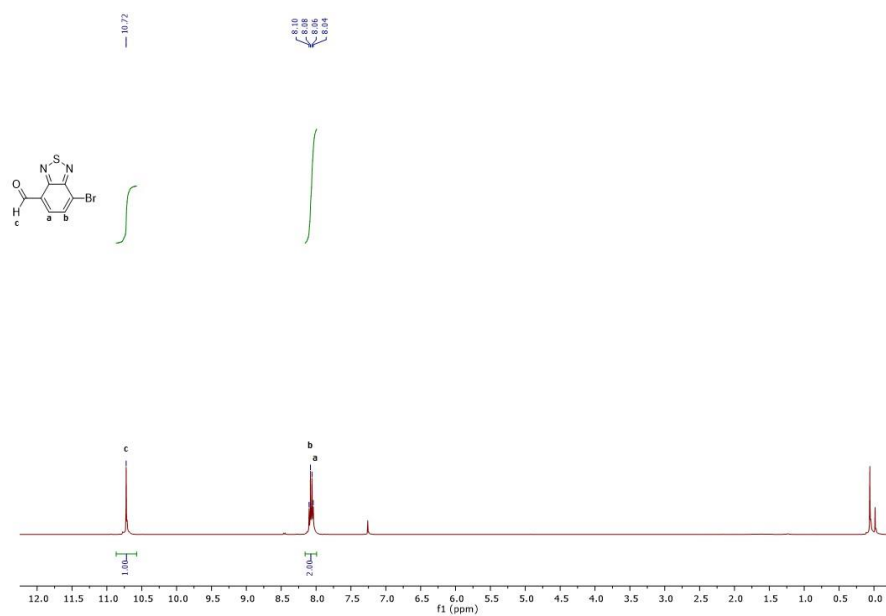
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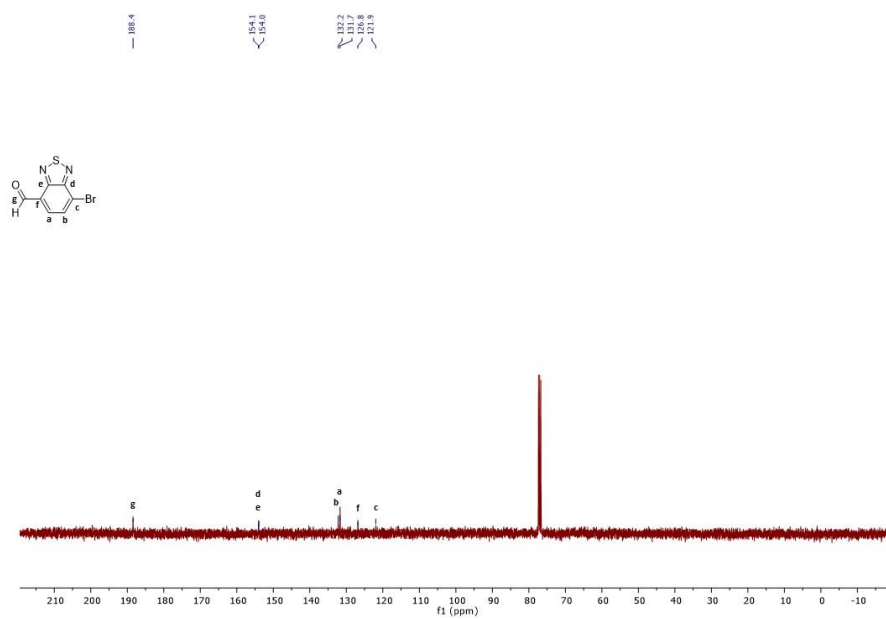
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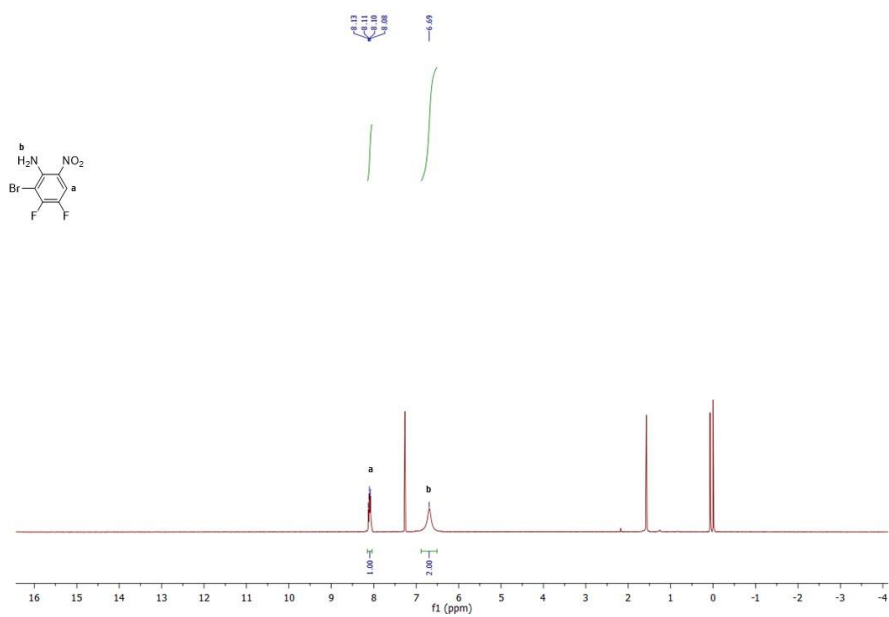
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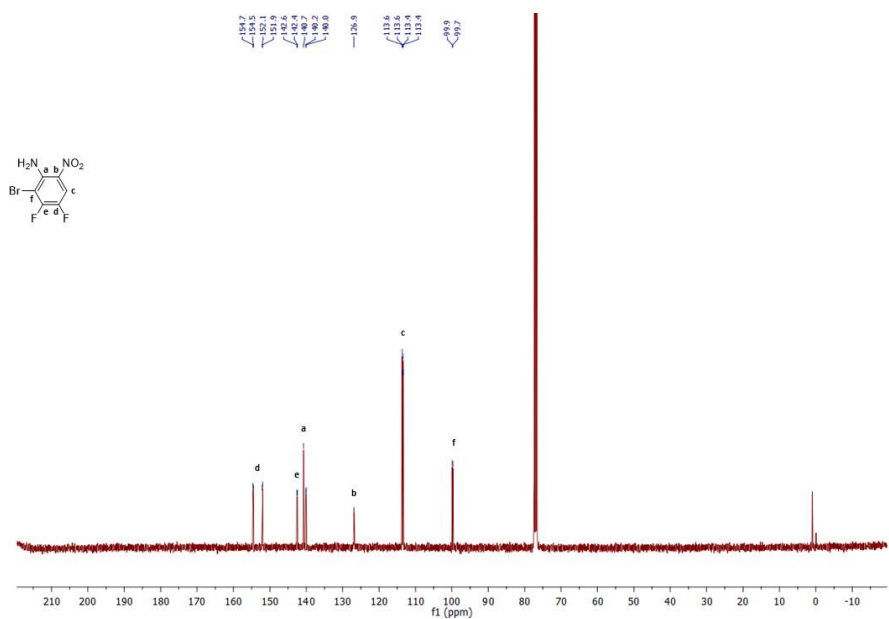
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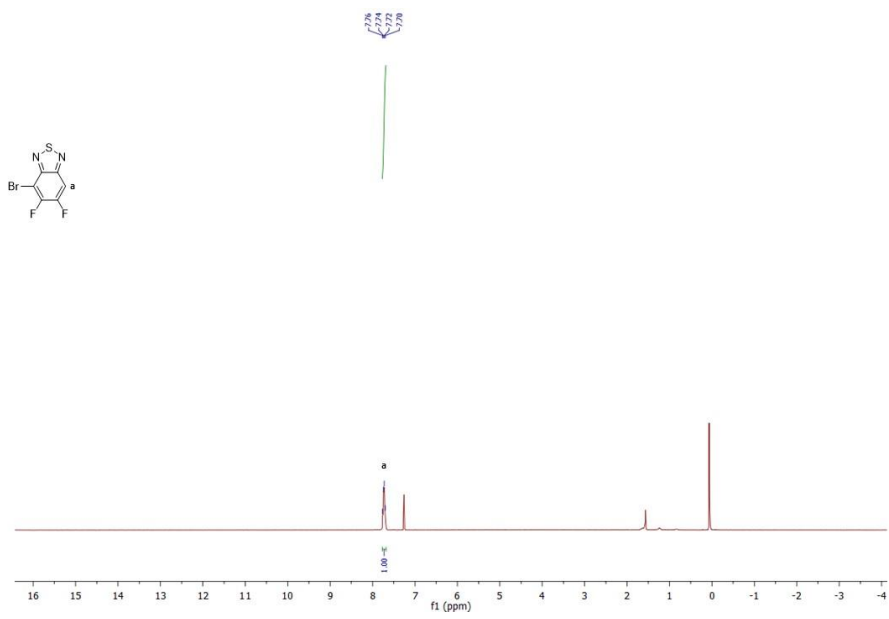
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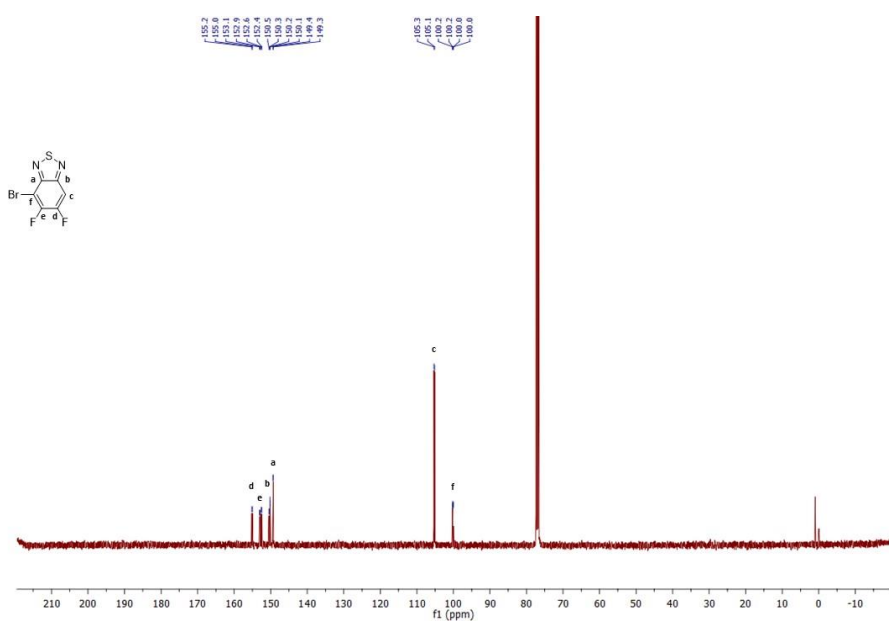
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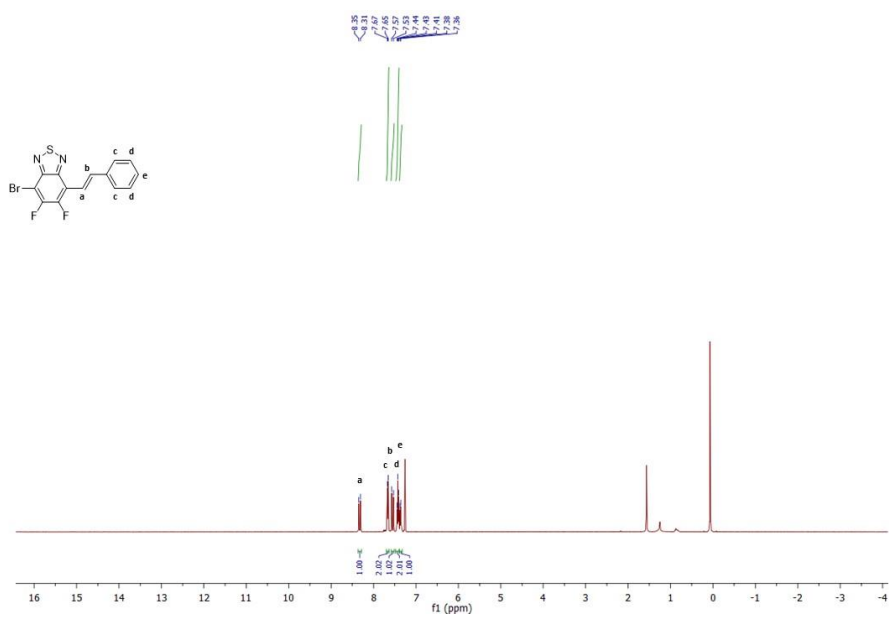
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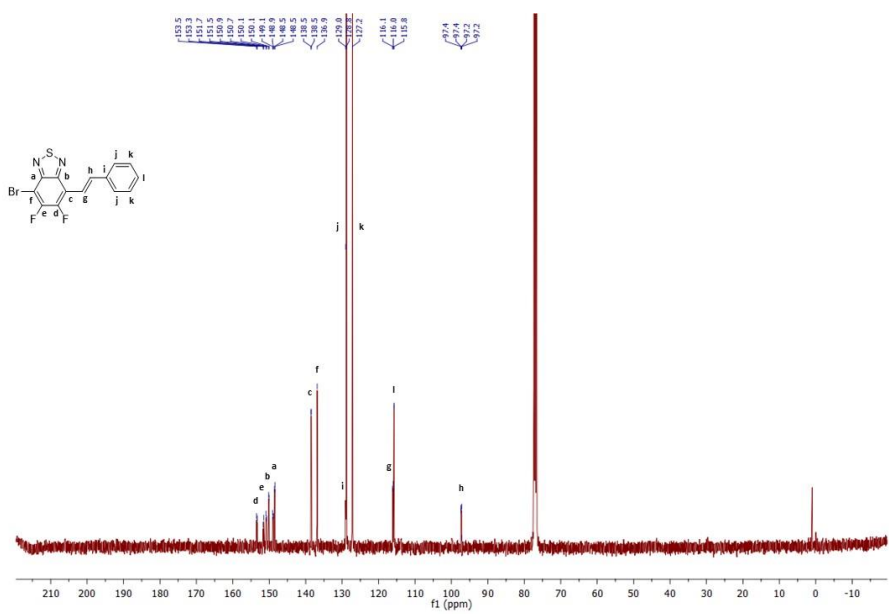
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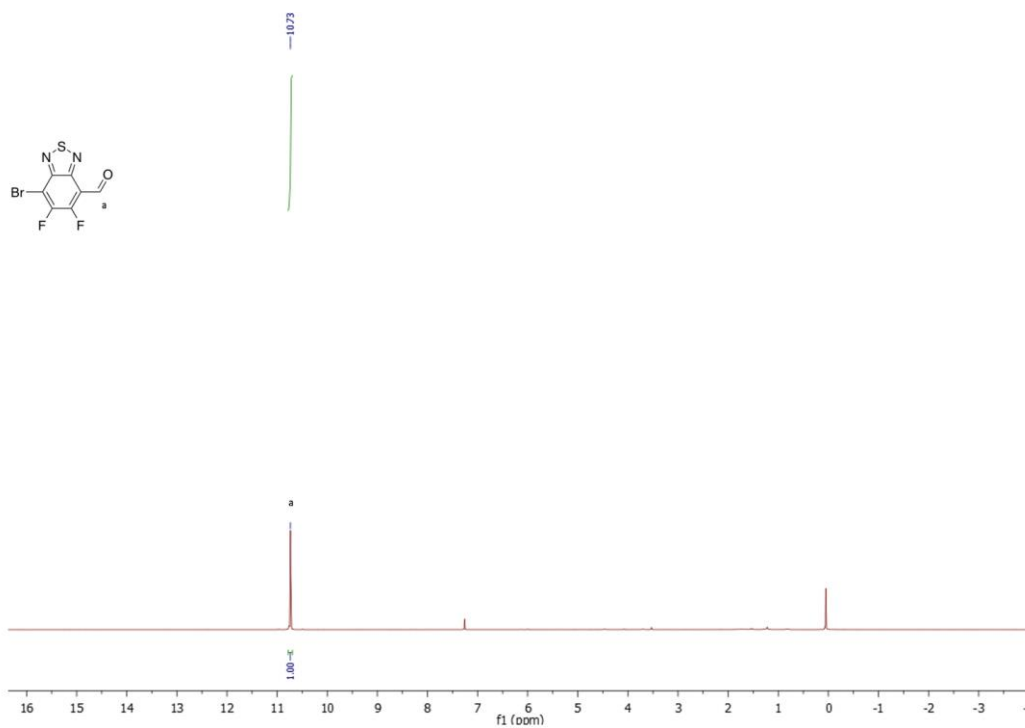
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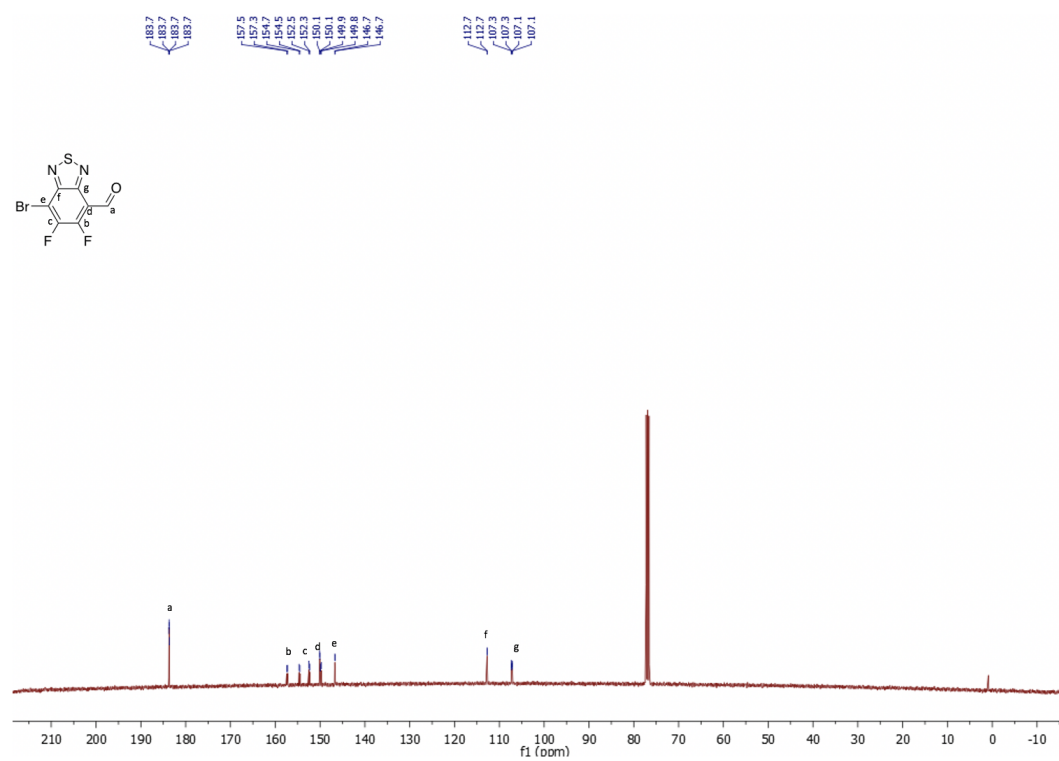
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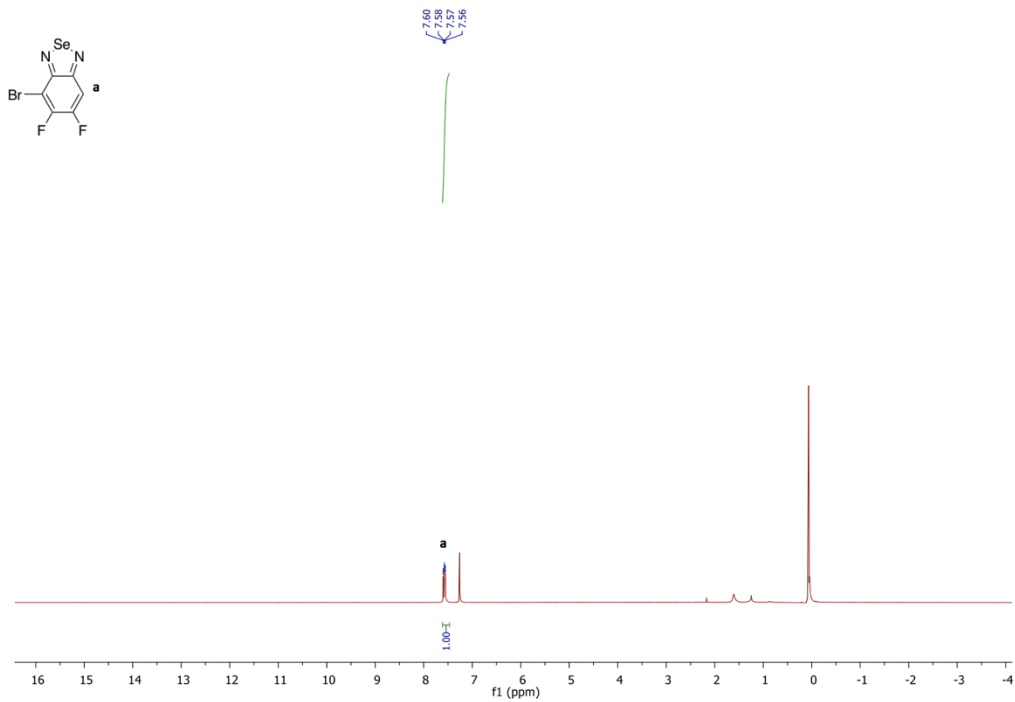
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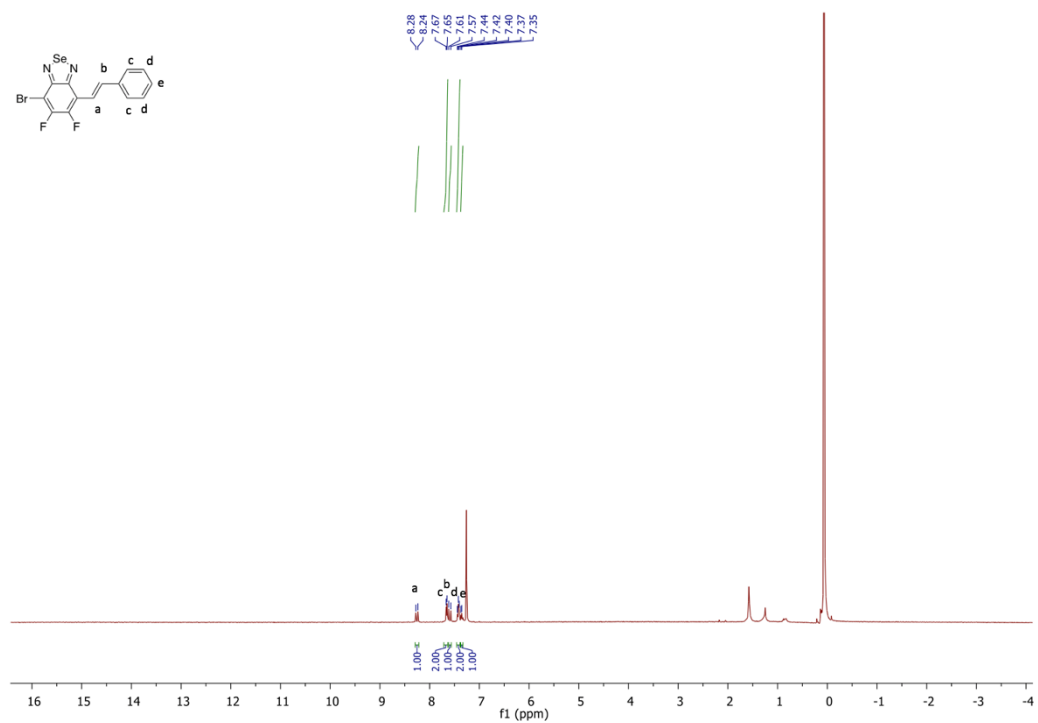
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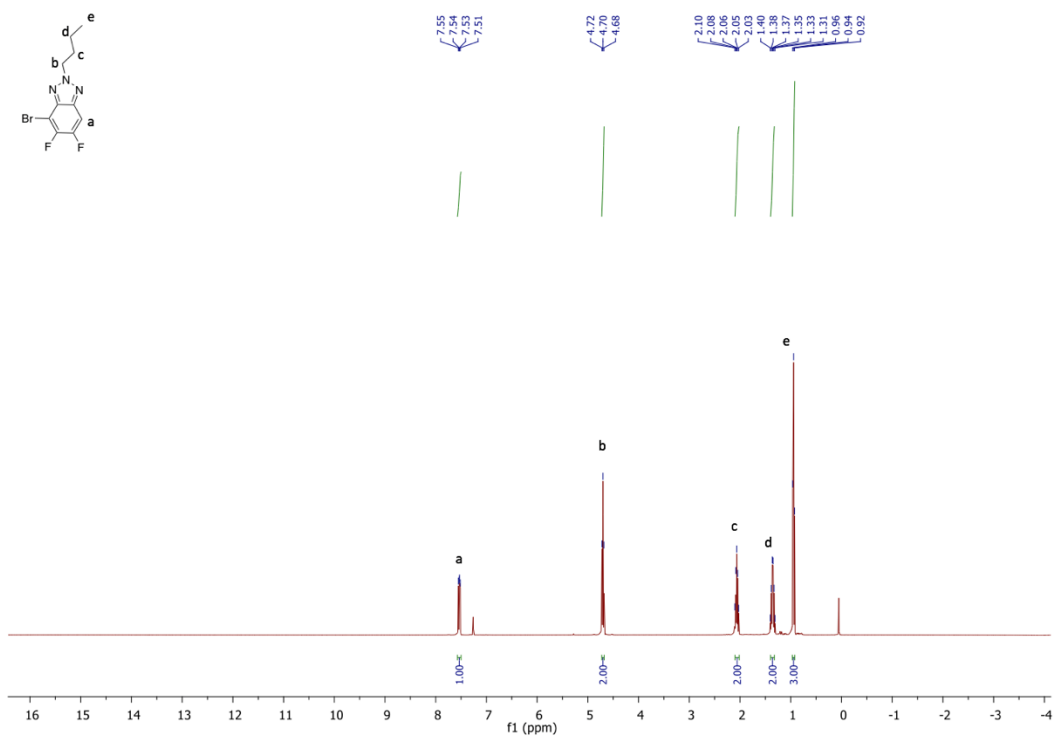
^{13}C NMR of compound **23**



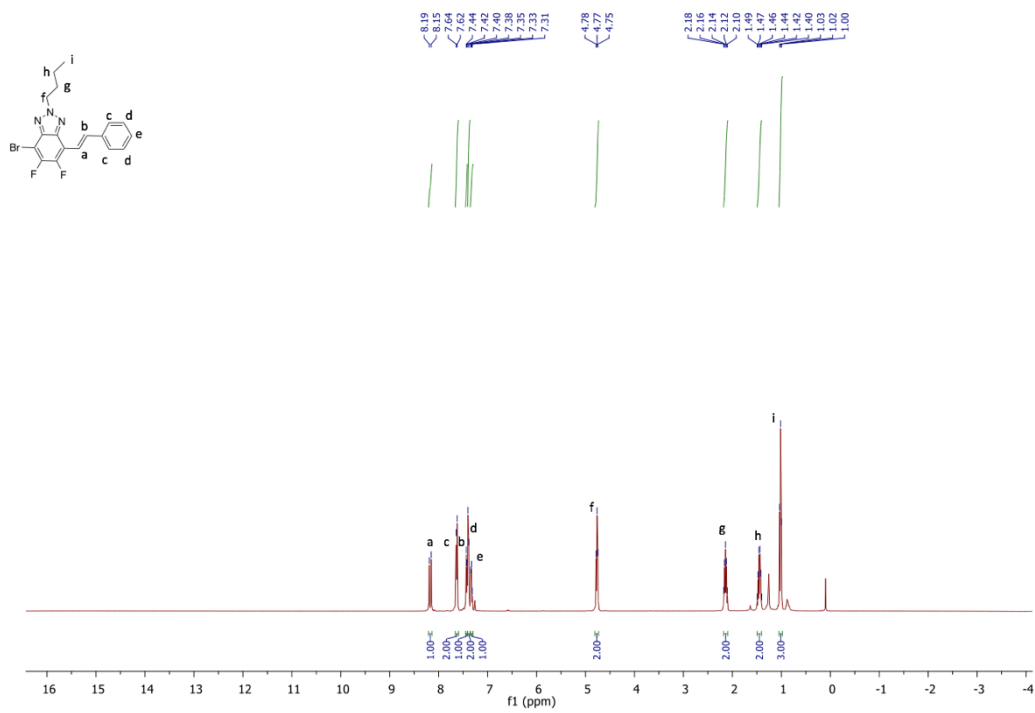
¹H NMR of compound 24



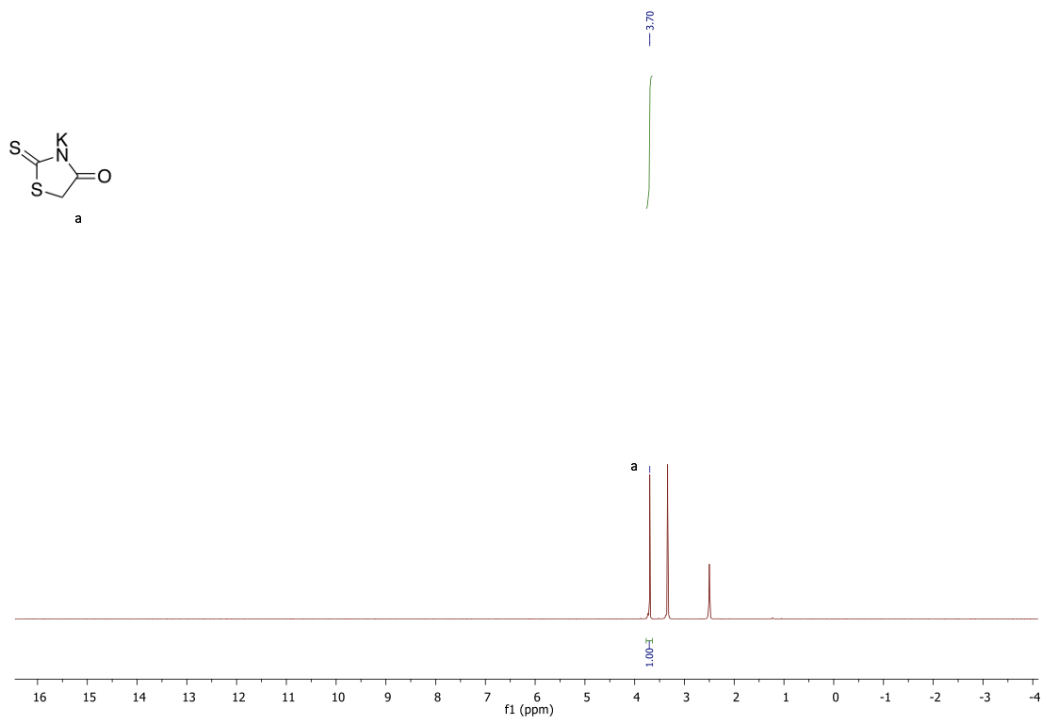
¹H NMR of compound 25



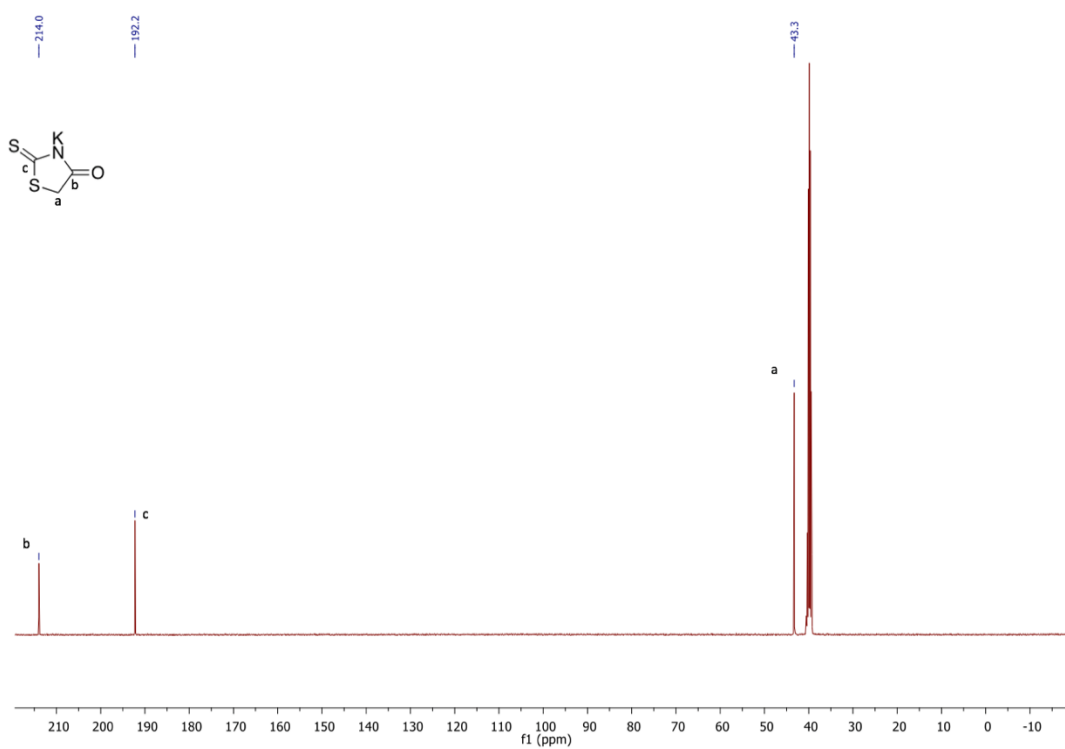
¹H NMR of compound 28



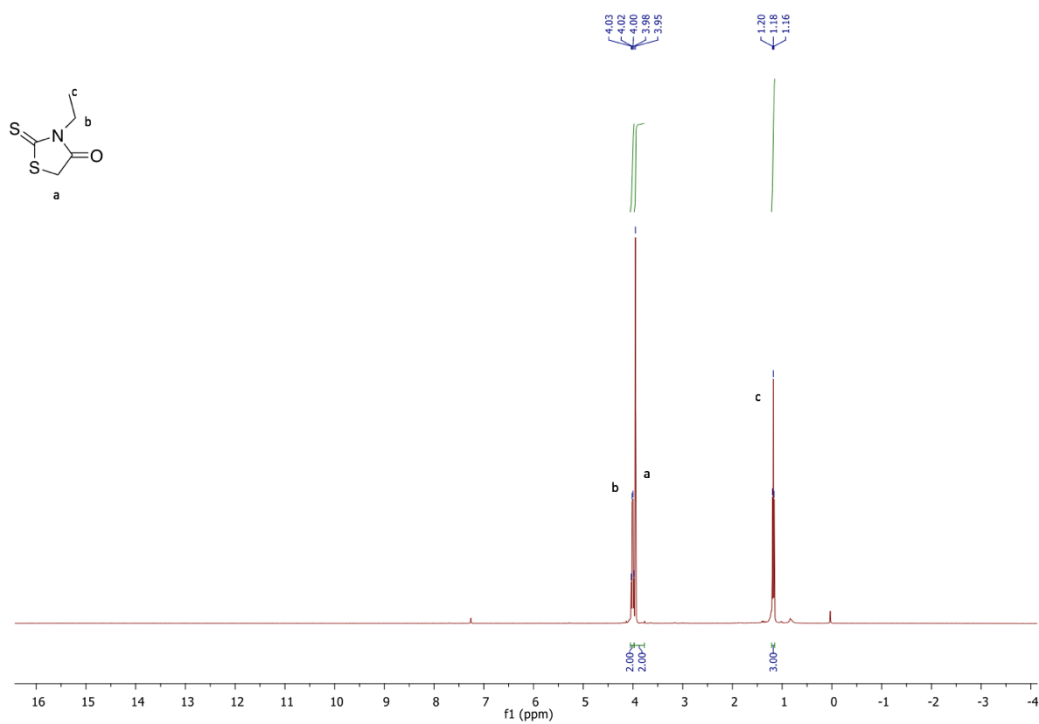
¹H NMR of compound 29



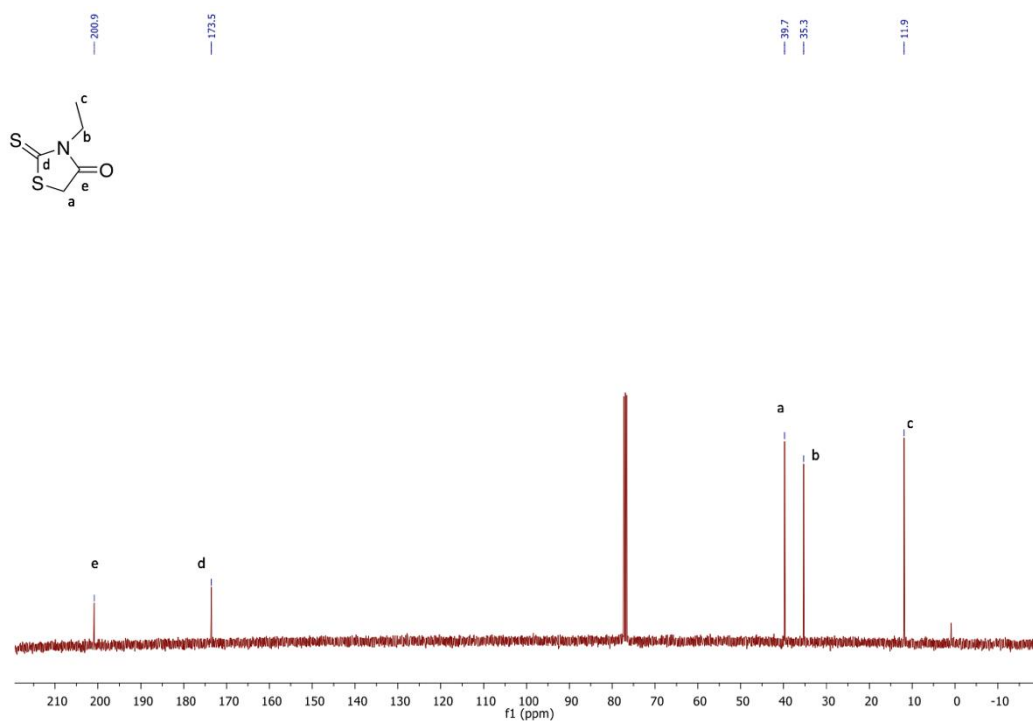
¹H NMR of compound 32



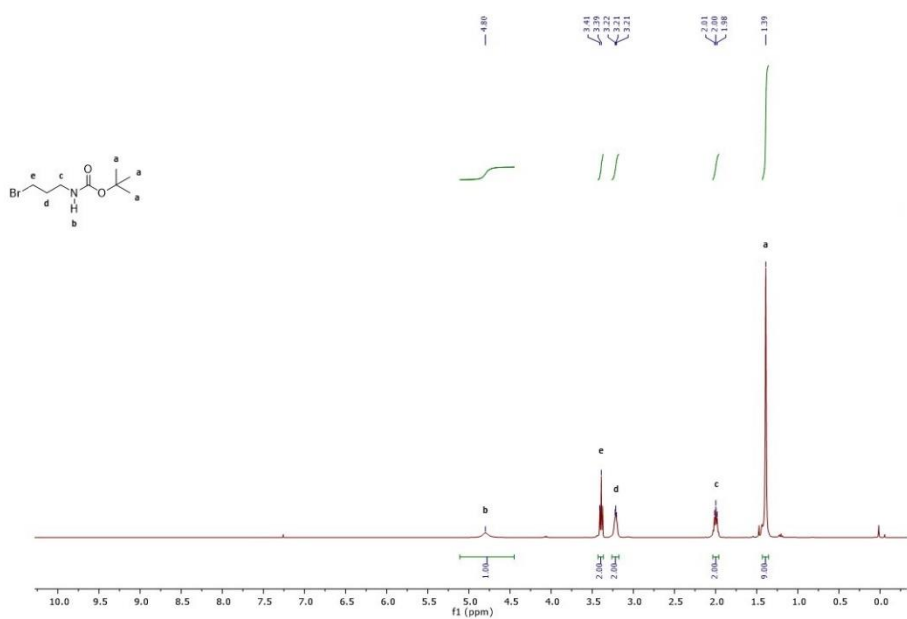
¹³C NMR of compound 32



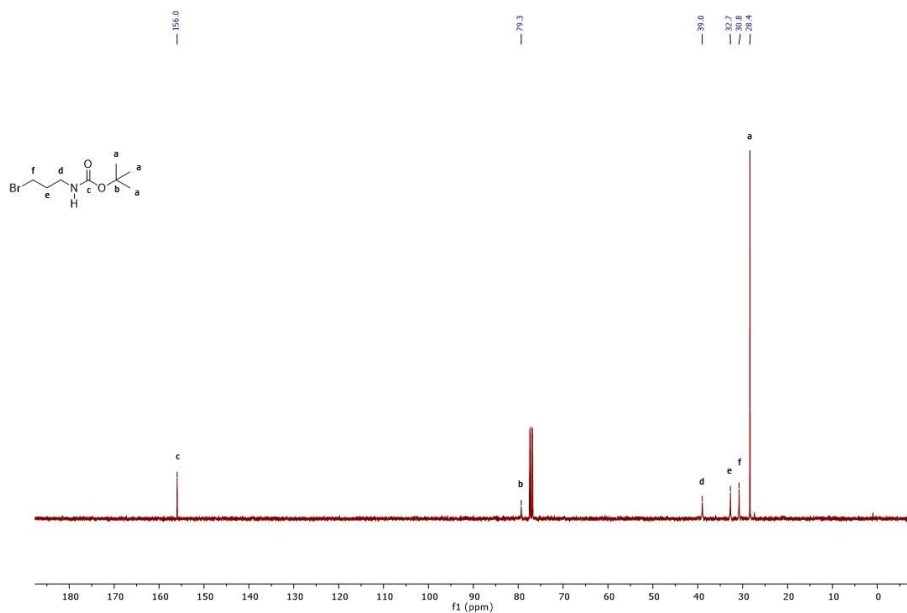
¹H NMR of compound 33



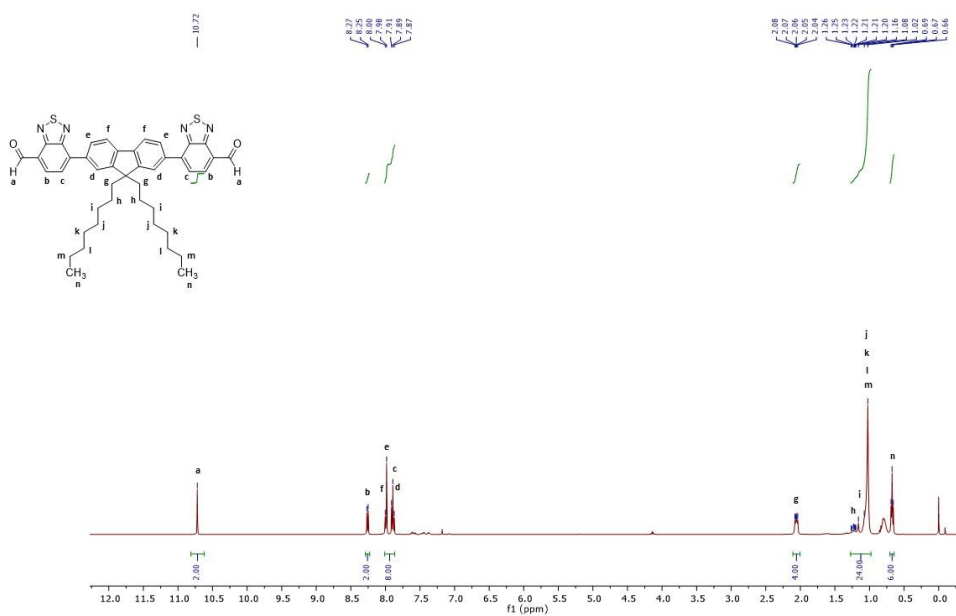
¹³C NMR of compound 33



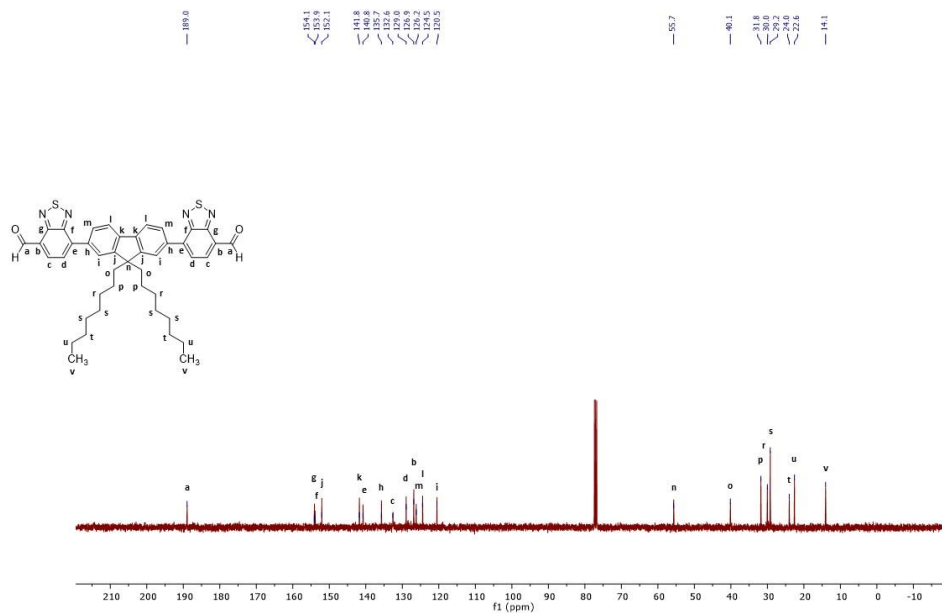
¹H NMR of compound 35



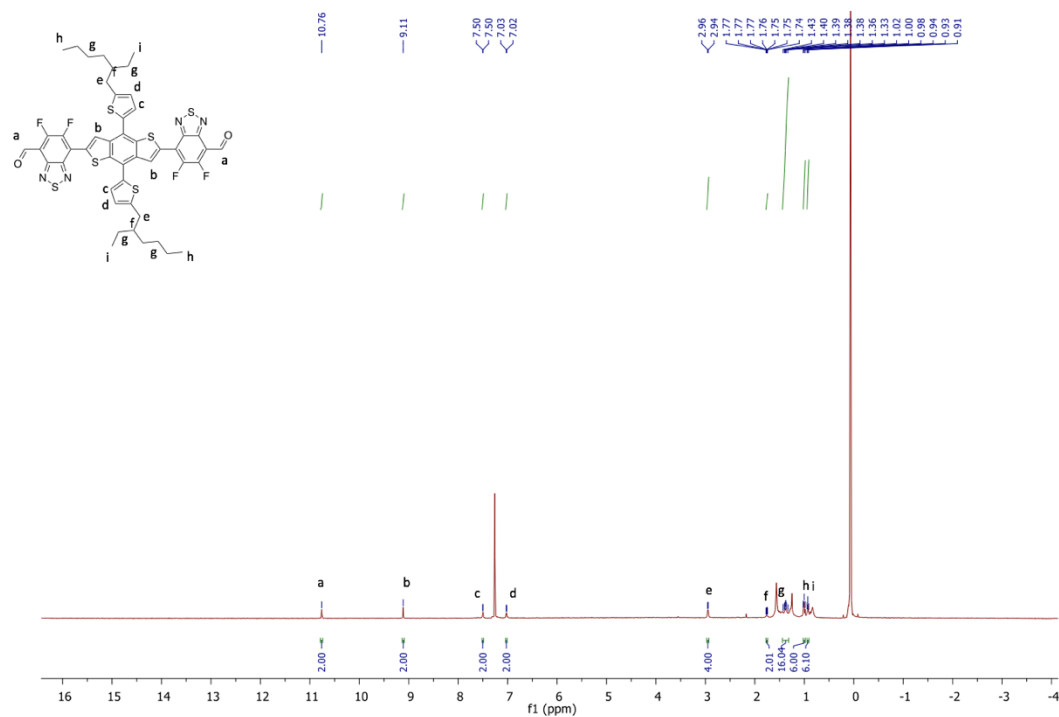
¹³C NMR of compound 35



¹H NMR of compound **43**



¹³C NMR of compound **43**

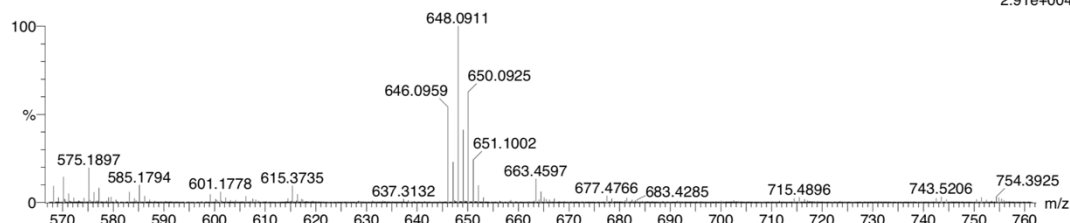


^1H NMR of compound **45**

B. HRMS

Deniz Sen
26360_20190410_01-03 4 (0.172) Cm (1:13)

1: TOF MS ES+
2.91e+004



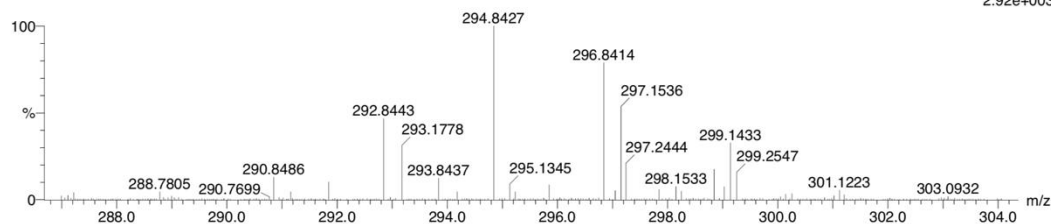
Minimum: -5.5
Maximum: 1000.0 50000.0 1000.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
648.0911	648.0918	-0.7	-1.1	12.0	307.4	0.0	C32 H40 S2 79Br 81Br

HRMS result of compound 11

Deniz Sen
27645_20190911_01-N02 5 (0.206) Cm (1:9)

1: TOF MS ES-
2.92e+003



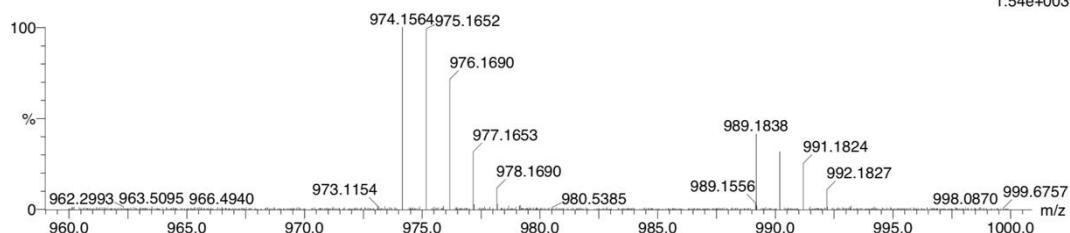
Minimum: -5.5
Maximum: 1000.0 5000.0 1000.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
296.8414	296.8378	3.6	12.1	7.5	276.3	0.0	C6 N2 F2 Se Br

HRMS result of compound 24

Deniz Kardelen
32077_20210319_01-03 20 (0.775) Cm (9:20)

1: TOF MS ES+
1.54e+003



Minimum: -5.5
Maximum: 1000.0 1000.0 1000.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
974.1564	974.1568	-0.4	-0.4	28.0	134.2	0.0	C48 H42 N4 O2 F4 S6

HRMS result of compound 45