ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF DERIVATIVES OF 3-(4-CYANOPHENYL)THIENO[3,2-b]THIOPHENE AND THEIR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

3-(4-SİYANOFENİL)TİYENO[3,2-B]TİYOFEN TUREVLERİNİN SENTEZİ VE ONLARİN ELEKTRONİK VE OPTOELEKTRONİK UYGULAMALARİ

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Amir Rahimi Varzeghani, **M.Sc.** student of ITU **Graduate School of Science Engineering And Technology** student ID **509131037**, successfully defended the **thesis** entitled **“SYNTHESIS OF DERIVATIVES OF 3-(4-CYANOPHENYL)THIENO[3,2-b]THIOPHENE AND THEIR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS”**, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To My Family,

FOREWORD

This thesis describes the synthesis method of thienothiophens, having phenyl moiety at C-3, substituted with nitrile group (CNPhTT) derivatives and investigation of their applications in electronic and optoelectronic materials.

First of all, I would like to kindly thank my supervisor, Prof. Dr. Turan Öztürk, for giving me the opportunity of being a member of his research group and the patient guidance, encouragement and advice he has provided throughout my time as his student.

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Finally, I would like to thank my parents for their support that was with me all the time. I am so proud to have such friends who cared about me and for their courage and support, such as accommodation, waking up in the middle of the night, or staying up late for my arrival, providing me the peaceful environment..

September 2016 Amir RAHIMI VARZEGHANI

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ABBREVIATIONS

HOMO : Highest occupied molecular orbital
LUMO : Lowest unoccupied molecular orbital
OLED : Organic light emitting diode
ACQ : Aggregation caused quenching
AIE : Aggregation induced emission
LUMO : Lowest unoccupied molecular orbital
TT : Thienothiophene
TPA : Triphenylamine
TPE : Tetraphenylethylene
TT1 : Thieno[2,3-b]thiophene
TT2 : Thieno[3,2b]thiophene
TT3 : Thieno[3,4b]thiophene
TT4 : Thieno[3,4-c]thiophene
THF : Tetrahydrofurane
NBS : N-bromosuccinimide
OFET : Organic field effect transistor
OPV : Organic photovoltaic
UV-vis : Ultraviolet-visible
CV : Cyclic voltammetry
ITO : Indium tin oxide
NMR : Noclear magnetic resonance
FT-IR : Fourier transform infrared
MS : Mass spectroscopy

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SYNTHESIS OF DERIVATIVES OF 3-(4-CYANOPHENYL)THIENO[3,2-b]THIOPHENE AND THEIR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

SUMMARY

In 1936, the phenomenon of electroluminescence (EL), that is a non-thermal generation of light coming up from application of electric current on a inorganic substrate, was first observed by Destriau *et al*. They observed high field electroluminescence from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes. General Electric was the first company that commerciallized light-emitting device which it was based on the inorganic semiconductor GaAsP. Early LED's were able to emit only red light as energy gap of those semiconducting materials were in that region of light. The evolution of further materials allowed access to other colours such as orange, yellow and green, as well as infrared accessible compounds. Future demand for more complex and higher performing circuitry, enabling high-resolution, video-rate displays still requires organic semiconductors with enhanced charge carrier mobility.

There are many organic conjugated materials that are investigated as an active components in order to optimize the performance of OLED's. Among them small organic semiconducting molecules are exhibited to pack closely together with their π-conjugated aromatic rings linked in a planar conformation, allowing efficient intermolecular charge transfer. Owing to the fact that they have unique properties, they are used as active materials in applications, like field-effect transistors, solar cells, light emitting diodes, electrochromic windows, photochromic devices, sensors, lasers. Moreover, they are very convenient in terms of building up electroluminescent devices due to their low molecular weight, allowing them to be vaccum deposited as thin films. However, they are suffering from a phenomenon that is called “aggregation-caused quenching” (ACQ), that becomes a very serious problem in solid state. Hence, it is required to minimize this effect in order to optimize OLED's performance.

A large number of oligomers and polymers are synthesized by using different metal-catalyzed cross-coupling reactions like Suzuki, Stille, Sonogashira, and Kumada-type reactions. These methods have been used to synthesize organic semiconductor materials possesing critical properties such as having appropriate electronic band gap, high charge carrier mobility, low cost starting materials and convenient manufacture of thin films. High fluorescence emitting efficieny in solid state is fundamental aspect for organic light emitting diodes but in the field-effect transistors, low electronic band gap and high charge mobility are crucial.

The purpose of this work is synthesizing low band gap conjugated organic molecules which consist of regular π-electron acceptor and donor groups in order to investigate their optoelectronic applications. Owing to the fact that fused thiophene ring like thienothiophene is electron rich group, therefore it can be served as an electron donor group. In addition, it has phenyl moiety (PhTT) at C-3, substitued by withdrawing group, nitrile, on the contrary triphenylamine (TPA) and tetraphenylethylene (TPE) act as an electron donor groups because of their electron rich structures. Additionally,

tetraphenylethylene has been investigated for aggregation induced emission (AIE) phenomenon that is oppsite of aggregation-caused quenching (ACQ) effect and used to develop OLED materials. In another words, thienothiopehene based π-electron acceptor and π-electron donor TPA or TPE, act as donor-acceptor organic molecules leads to synthesis of suitable materials for electronic and optoelectronic applications.

In this respect, thieno[3,2-*b*]thiophene, having—phenyl moiety (PhTT) at C-3, substitued with nitrile group (CNPhTT) core unit was synthesized by monoketone ring closure route with PPA that was developed by our group. Afterwards, corresponding boronate complex of TPA and TPE were synthesized respectively. Then, final organic materials were synthesized by metal-catalyzed Suzuki cross-coupling reactions.

3-(4-SİYANOFENİL)TİYENO[3,2-B]TİYOFEN TUREVLERİNİN SENTEZİ VE ONLARİN ELEKTRONİK VE OPTOELEKTRONİK UYGULAMALARİ

ÖZET

İlk elektrolüminesans (EL) olayı 1936 yılında Destriau ve arkadaşlarının elektrik akımını inorganik maddeye uygulamasiyla olusan thermal olmayan ışık olarak gözlenmiştir. Izolatöre dağılmış iki elektrot arasında paketlenmiş olan ZnS fosfor tozundan yüksek alan elektrolüminesans elde ettiler. General Electric şirketi inorganik yarı iletken GaAsP'e dayalı ışık yayan cihazı ticaretleştiren ilk firmadır. İlk LED'ler yarı iletken malzemelerin enerji band aralıklarına göre sadece kırmızı ışık yayabilmektedirler. Yeni malzemelerin gelişimi turuncu, sarı ve yeşil gibi diğer renkleri, hemde kızılötesi erişilebilir maddeleri saglamistir. Yüksek çözünürlük ve ekran kare hizini sağlayan daha karmaşık ve daha yüksek performanslı devre için gelecek talep, hala gelişmiş yük taşıyıcı mobilitesine sahip organik yarı iletkenler gerektirmektedir.

OLED'lerin performansını optimize etmek için, aktif bileşenler olarak incelenen birçok konjuge organik maddeler bulunmaktadır. Küçük organik yarı iletken moleküller, moleküller arası etkili yük transferini kolaylaştıran düzlemsel konformasyonda π-konjuge aromatik halkalar ile birlikte istifleme göstermektedir. Onların eşsiz özelliklere sahip olmalari nedeniyle, alan-etkili transistör, güneş hücreleri, ışık yayan diyotlar, elektrokromik, fotokromık cihazları, sensörler, lazer gibi uygulamalarda aktif maddeler olarak kullanılmaktadırlar. Ayrıca, düşük molekül ağırlıkları nedeniyle vakum biriktirme yoluyla ince filmler olarak elektrolüminesans cihazların yapımı için çok uygun maddelerdir.

Buna rağmen, katı halde çok ciddi bir porblem olan "aggregation-caused quenching" (istiflenme ile sonümlenme, ACQ) olarak adlandırılan bir olay yaşanmaktadır. Bu nedenle, OLED performansını en uygun hale getirmek için bu etkiyi en aza indirmek gerekmektedir.

Bu çalışmanın amacı, optoelektronik uygulamaları araştırmak için düzenli π-elektron alıcı ve verici gruplardan oluşan düşük band aralığına sahip konjuge organik molekülleri sentezlemektir. Birlesik tiyofen halkası, mesela, tiyenotiyofen, elektron açısından zengin olmasindan dolayı elektron verici grup olarak davranmaktadır. Buna ek olarak, elektronca zengin yapılarından dolayı elektron donör gruplar olarak trifenilamin (TPA) ve tetrafeniletilenin (TPE) yanı sıra, tiyenotiyofen yapısının C-3 konumunda substitue olan elektron çekici nitril grubunu iceren para-CN-C6H5 bulunmaktadır. Ayrıca, tetrafeniletilen "aggregation-caused quenching" (ACQ)'in aksine "aggregation induced emission (istiflenmeyle ışıma, AIE)" olayını için incelenmekte ve OLED malzemeler geliştirmek için kullanılmaktadir. Başka bir deyişle, tiyenotiyefon iceren π-elektron alıcı ve TPA veya TPE elektron verici donor-akseptor organik moleküller olarak davrandıklarından elektronik ve optoelektronik uygulamaları için uygun malzemelerin sentezinde öncülük edeceklerdir.

Bu bağlamda, TT'nin C-3 konumunda para CNPh tasiyan, CNPhTT, maddenin sentezi grubumuz tarafından geliştirilen PPA monoketon halka kapama yoluyla yapılmıştır. Daha sonra, TPA ve TPE boronat kompleksleri sırasıyla sentezlendi. Daha sonra,

sonuç organik maddeler metal katalizatorlü Suzuki çapraz keletlenme reaksiyonu ile sentezlenmiştir.

Bu bağlamda, tieno [3,2-b] tiofen, nitril grubu (CNPhTT) çekirdek birimi ile ikame olan fenil kısmı C-3 ‘(PhTT), grubumuz tarafından geliştirilen PPA monoketan halka kapama yoluyla sentezlendi. Daha sonra, TPA ve DYP karşılık gelen boronat kompleksi sırasıyla sentezlendi. Daha sonra, nihai organik maddeler, metal katalizli Suzuki çapraz birleştirme reaksiyonları ile sentezlenmiştir.

1. INTRODUCTION

The tremendous research that has been devoted to discovery of efficient electroluminescence in organic and conjugated polymer thin films [1,2] has resulted in a vast literature on organic light-emitting diodes (OLEDs) [1-3]. Reviews of different aspects of the field of OLEDs have appeared, including electroluminescent materials [4] and device physics and engineering [5]. Evidence of the considerable progress that has been made in the field is that flat-panel displays based on OLEDs are emerging in commercial products such as cell phones and digital cameras [6]. Major challenges remain, however, including the need to significantly improve the performance and durability of blue, green, red, and white OLEDs for displays and lighting.

One of the key challenges on the path to developing the next generation of high performance OLEDs is the design and synthesis of readily processible and thermally robust emissive and charge transport materials with improved multifunctional properties. OLEDs are double charge injection devices, requiring the simultaneous supply of both electrons and holes to the electroluminescent (EL) material sandwiched between two electrodes (Figure 1). Since one of the electrodes needs to be semitransparent in order to observe light emission from the organic layer, usually an indium tin oxide (ITO)-coated glass substrate is used as the anode. Electropositive metals with low work functions such as Al, Ca, Mg, or In are used as cathodes in order to guarantee efficient electron injection.

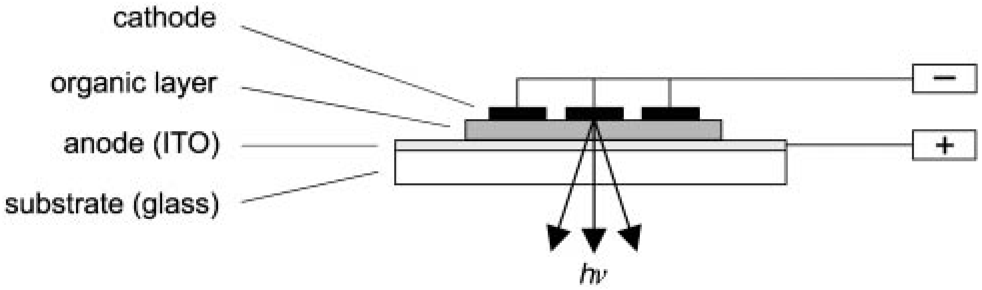


Figure 1.1: Schematic configuration of a single-layer OLED.

If an external voltage is applied at the two electrodes, charge carriers, i.e. holes, at the anode and electrons at the cathode are injected into the organic layer beyond a specific threshold voltage depending on the organic material applied. In the presence of an electric field the charge carriers move through the active layer and are non-radiatively discharged when they reach the oppositely charged electrode. However, if a hole and an electron encounter one another while drifting through the organic layer, excited singlet and triplet states, so-called excitons, are formed. The singlet state may relax by emission of radiation (fluorescence) [7].

To achieve an efficient OLED with the single-layer configuration shown in Figure 1.1, the organic EL material would ideally have a high luminescence quantum yield and be able to facilitate injection and transport of electrons and holes. This demand of multifunctional capabilities from a single organic material is a very difficult one to meet by nearly all current materials. Most highly fluorescent or phosphorescent organic materials of interest in OLEDs tend to have either p-type (hole-transport) or n-type (electron transport) charge transport characteristics [1-5]. A consequence of this is that the simplest OLED configuration, where an organic emitter layer is sandwiched between a transparent anode and a metallic cathode, gives very poor efficiency and brightness. The use of two or more different materials to perform the required functions of efficient light emission and good electron- and hole-injection and transport properties in an OLED has resulted in orders of magnitude improvement in device performance [1-5]. Interestingly, a similar strategy of multilayered device configurations, allowing the independent optimization of organic materials for charge transport, light absorption, and charge photogeneration in photoreceptors, was instrumental to the successful commercial development of organic electrophotographic imaging for copiers and printers [7].

The study of organic electroluminescence is a multidisciplinary field which crosses the traditional boundaries of synthetic chemistry, applied and theoretical physics, materials science and device engineering. A complementary approach involves synthetic chemistry to obtain electron-deficient (n-type) polymeric or low molecular weight materials suitable for incorporation into the devices.

In this regard, thiophene-based π-conjugated systems have been among the most interesting ones in designing organic materials for tuning the electronic and optoelectronic properties, because of their enviromental stability, high charge carrier mobility, low cost and flexibility. However, problem concerning the conventional fluorescent molecules suffer from the aggregation caused quenching (ACQ) due to π-π stacking interactions in the planar fluorophores, which limits their applicability in the efficient OLEDs [8]. The tetraphenylethylene (TPE) has been widely explored for aggregates induced emission (AIE) phenomenon and used to develop OLED materials [9].

This master thesis includes synthesis of thieno[3,2-b]thiophenes, having phenyl moiety at C-3, substituted with nitrile group (CNPhTT) and its derivatives (TPA-CNPhTT-TPA) **P1**, (TPE-CNPhTT-TPE) **P2** and (CNPhTT-TPE) **P3** in order to investigate its electronic and optoelectronic application.

2. THEORETICAL PART

2.1 Heterocyclic chemistry of thiophene

Heterocyclic compounds that have at least one hetero atom such as O, N, S, etc. in a cyclic compound, play crucial role in our life as they are important molecules in nucleic acids. In addition, heterocyclic compounds are one of the main part in naturally occurring pigments, vitamins, and antibiotics. The synthesis of heterocycle compounds is highly demanding as they are used in preparation of drugs, pesticides, dyes, and plastics [10].

Pyrrole, furan, and thiophene possessing nitrogen, oxygen, and sulfur atoms, respectively, in place of CH_2 have aromatic charactericity in spite of doubly unsaturated five-membered homocyclic compound cyclopentadiene. Among these five-membered heterocycles, thiophene is stable liquid compound, which is more reactive than benzene toward electrophiles due to its high π-electron density, has a five membered flat structure owning one sulfur as a heteroatom [11].

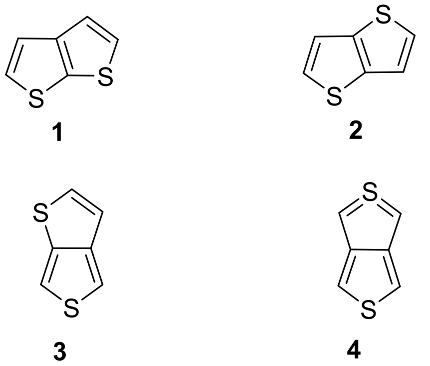
2.1.1 Application of thiophene based materials in OLED's

Conjugated organic materials are anticipated to have significant advantages over their silicon analogues in terms of processing time and cost as they can be deposited from solution providing a fast and large-area fabrication [12]. The main properties used to describe performance of the devices are the charge transfer mobility and the current on/off ratio. Low conductivity in the off-state, together with a charge carrier mobility of higher than 1×10^{-3} cm^2 V^{-1} s^{-1}, is required as a property of a good organic semiconductor. Stability against oxidation is also one of the unavoidable benchmark as device performance deteriorates beginning with oxidation [13]. Extension of the π system in conjugated molecules results in decreasing band gap and often an increased charge carrier mobility. Most of the research in organic electronic materials has been devoted to tune the band gap [14-15].

A convenient way of producing fine-tuning band gaps which is a key factor to fabricate organic semiconductors, involves the utilization of fused thiophene subunits, [16] which incites much more conjugation in the ground state [17]. Having enhanced π-conjugation and more rigid structures, fused thiophenes could be applied for adjusting the band gap of organic materials resulting intermolecular interactions in the solid state [18].

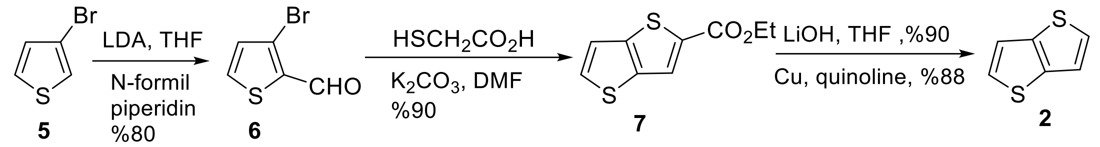
2.2 Thienothiophenes

The simplest fused thiophenes, thienothiophenes (TTs), contain two annulated thiophene rings, with four isomers, thieno[2,3-b]thiophene **1**, thieno[3,2b]thiophene **2**, thieno[3,4b]thiophene **3**, and thieno[3,4-c]thiophene **4** (Scheme 2.1) [18-20].



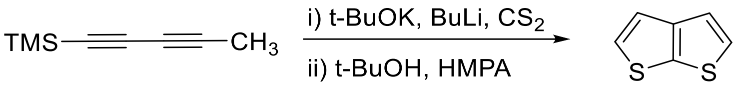
Scheme 2.1 : Thienothiophene isomers.

The first three isomers are referred to as conventional (or classical) thienothiophenes as structures of the type 4 are much less accessible [21]. Synthesis of all the isomers have been investigated comprehensively in literatures. The first three isomers having stable and electron-rich structures, are useful building blocks for the construction of organic semiconductors possessing different conjugation lengths [22]. The lowest band gap and ionization potential belongs to type 2 and it has the most attractive chemical structure [23,14]. The method of synthesis for this isomer was reported by Fuller et al., which had an overall yield of 51% [24]. They treated 3-bromothiophene **5** with lithium diisopropylamide (LDA) and then N-formylpiperidine to obtain 3-bromothiophene-2-carbaldehyde **6** in 80% yield, which was followed by a reaction with ethyl 2-sulfanylacetate to obtain ethyl thieno[3,2-b]thiophene-2-carboxylate **7** in 81% yield. Saponification of the ester 7 with LiOH provided thieno[3,2-b]thiophene-2-carboxylic acid in excellent yield (90%). Finally, the carboxylic acid group was removed using Cu powder in the presence of quinoline at elevated temperature, yielding **2** in 88% yield (Scheme 2.2) [25-29].



Scheme 2.2 : Synthesis of TT **2** from 3-bromothiophene **5** [24].

Thieno[2,3-b]thiophene **1** has been reported to be synthesized by Otsubo et al., (Scheme 2.3) [30].



Scheme 2.3 : Synthesis of TT **1**.

2.2.1 Substitution of thienothiophenes

Thiophene-based π-conjugated systems have been among the most interesting ones in designing organic materials for tuning the electronic and optoelectronic properties, because of their enviromental stability, high charge carrier mobility, low cost and flexibility. One of the main advantage of using thiophene is convenient way of modification resulting change in electron affinity, ionization potential, absorption and emission that allows them to have various applications in organic electronic materials [31-32]. Fusing thiophene rings could also be tuned [33] creating better π-conjugation because of their core skeleton consists of two fused rigid thiophene rings to limit the rotational disorder among the rings [14].

Various substituted TTs and analogues of TT, such as 2,3,5,6-tetrabromothieno[3,2b] thiophene, 3,6-dibromothieno[3,2-b]thiophene, 3-bromothieno[3,2-b]thiophene [24], 3,6-dialkylthieno[3,2-b]thiophene [34-35], 5-bromo-3 chlorothieno[3,2-b]thiophene-2-carbonyl chloride, 6-bromo-3,5-dichlorothieno[3,2-b]thiophene-2-carbonylchloride [36],2-(6-bromo-5-methyl-3-(trifluoromethyl)thieno[3,2-b]thiophen-2-yl)benzo[d] thiazole, 3-chloro-6-methoxy-carbonylnaphtho-[2´,1´:2,3-b]thieno[4,5-d]thiophene-2-carboxylic acid chloride, benzo[b]thieno[3,2-b]thiophene-2-carboxylic acid, 3a,5-dimethyl-3aH-6,7,8,9-tetrahydrobenzo[c]thieno[3,2-b]thiophene,2,3:5,6-thieno [3,2b]thiophene, thieno[2´,3´:4,5]thieno[2,3-c]quinoline, and 2,5-bis(3,5-di-tert-butyl-

4-oxocyclohexa-2,5-dien-2-ylidene)-2,5-dihydro-1,4-dithiapentalene were reported [21].

Based on the report from our research group members for concise synthesis of fused thiophene derivatives [33,37], thieno[3,2-b]thiophenes **2**, having phenyl moiety (PhTT) at C-3, substituted with various groups such as methoxy (MPhTT), bromine (BrPhTT), nitro (NPhTT), amine (APhTT), and dimethylamine (DMAPhTT) [38], I started my master thesis work. The topic was introduced first to synthesize phenyl moiety TT **2** at C-3, substituted with nitrile group (CNPhTT) **9**, then tuning this molecule with electron rich blocks such as triphenylamine (TPA) and (TPE) to investigate their electronic and optoelectronic applications.

2.3 Photophysical Properties of Organic Conjugate Materials

2.3.1 Quantum yield (Φ)

Fluorescence spectroscopy as an optical technique has shown its effective applications in science and engineering. It has been used broadly in different fields such as chemistry, physics and medical science in which these fields need to such a sensitive and specific method.

Quantum yield (Φ) is a parameter that is used to describe the efficiency of the fluorescence process. It can be utilized not only to understand physical characteristic of a substance in specified conditions, but also to calculate of quenching rate constants, lasing ability, radiative behaviour, energy transfer and nonradiative rate constants.

Fluorescence quantum yield Φ_F can be defined by the ratio of the number of emitted photon from a substance to the number of absorbed photon. In other words, it gives the probability of the excited state being deactivated by emitting fluorescence rather than non-radiative mechanism [39].

Williams *et al*. [40], have described the most reliable method to determine fluorescence quantum yield based on use of standard samples with known Φ_F values. Fundamentally, identical absorbance at the same excitation wavelength for test samples and standards considered to be absorbing the same number of photons.

Basically, there are other parameters that needed to be considered while determining fluorescence quantum yield:

- Effect of concentration must to be known in order to avoid self-quenching
- Use of different solvents for test and standard samples
- Checking validity of using the standard sample by cross-calibrating with another sample to ensure both are behaving as expected

However, all the given data above to calculate fluorescence quantum yield is valid when we use dilute solutions. It is common phenomenon that luminescence is often weakened or quenched at high concentrations (concentration quenching) caused by the formation of aggregates which is frequently called “aggregation-caused quenching” (ACQ) [41]. This phenomenon (ACQ) due to π-π stacking interactions in the planar conjugate organic molecules. This effect can be reduced in diluted solution as it is thought that there are no strong intermolecular interactions between molecules in this condition. The ACQ effect is harmful and challenging for organic light-emitting diodes (OLEDs) as luminophores are in solid state and might have a more severe ACQ effect [42]. In the other hand, aggregation induced emission (AIE) has been shown by Tang *et al*. in 2001 that it can dramatically overcome the deficiency of ACQ [43]. This effect will be disscused in the following section.

2.3.2 Aggregation induced emission (AIE)

Since ACQ effect deteriorates efficiency of OLED’s some attempts have been tried to hinder the formation of luminophoric aggregates using chemical reactions, physical methods and/or engineering processes. [44-48]. However, most of the approaches have resulted in non-acceptable effect on obstruct of aggregation: old problem is solved while some other issues are created.

Moreover, the essence of these luminophores is to approach each other forming aggregates in concentrated solutions or in the solid state. Therefore, the way of thinking to overcome this problem needs to be changed fundamentally. Discovery of an unusual luminogen system, in which aggregation worked constructively, rather than destructively as in the conventional systems. A series of silole derivatives were found non-emissive in dilute solutions but became highly luminescent when they were aggregated in concentrated solutions or cast into solid state. The process was termed ‘‘aggregation induced emission” (AIE), because the light emission was induced by aggregate formation [49-50]. The AIE process offers a platform for scientists to look into light emissions from luminogenic aggregates, from which information on structure–property relationships and insights into working mechanisms may be obtained. Structural design for the development of efficient luminogens is illuminating information [51-57].

Mechanism of AIE: Among the first silole derivatives, hexaphenylsilole (HPS) showed the AIE effect. Investigation of its structure reveals that unlike conventional luminophores such as the disc-like planar perylene, HPS is a screw-shaped non-planar molecule. It is believed that this emission bahaviour comes from its unique molecular structure [58]. In a dilute solution, six phenyl rotors in an HPS molecule undergo dynamic intramolecular rotations against its silacyclopentadiene or silole stator, which non-radiatively neutralized its excited state and renders its molecule non-luminescent. In the aggregates, oppositely, the HPS molecules are not able to pack through a π–π stacking process due to its propeller shape, while the intramolecular rotations of its aryl rotors are greatly restricted owing to the physical constraint. This restriction of intramolecular rotations (RIR) is an obstacle for non-radiative pathway and stimulates the radiative channel making the HPS molecules emissive in the aggregate state [59].

Tetraphenylethylene (TPE), has been extensively investigated for AIE phenomenon and used to develop OLED materials [52-57]. TPE, its olefin stator is surrounded by phenyl rotors and the RIR process is known to account for its AIE effect. Therefore, design and synthesis of organic mateials substituted by TPE in order to investigate its applications in OLED’s has much of interest.

In addition, it has been shown that propeller-like structure of triphenylamine (TPA) and electron-donating attribute make it a useful building block for the construction of AIE luminogens. The emission colours can be tuned through astute combinations of the TPA units with other electron-accepting groups. This can be described by the AIE luminogens containing the donor-acceptor (D–A) pairs of TPA–benzaldehyde and TPA–fluorenone, which emit green and red lights, respectively, due to the different extents of push–pull interactions involved in the two systems [60-61].

2.4 Suzuki–Miyaura reaction

The Suzuki–Miyaura reaction is an organic coupling reaction, where the coupling is catalyzed by a palladium$^{(0)}$ complex. Coupling partners are a boronic acid and an organohalide [62-64]. Akira Suzuki published his discovery in 1979 first and afterward in 2010, he and his colleages, Richard F. Heck and Ei-ichi Negishi won Nobel Prize in Chemistry for their achievements in discovery and improvement of palladium-catalyzed cross couplings in organic synthesis [65]. Suzuki–Miyaura coupling reaction is mainly utilized in the synthesis of poly-olefins, styrenes, and substituted biphenyls. There are many scientific reviews published illustrating advancements and the development of the Suzuki reaction [66-68]. The main idea of this coupling reaction is forming a carbon-carbon single bond from a organoboron species (R_1-BY_2) and a halide (R_2-X) using a palladium catalyst and a base. General scheme for the Suzuki reaction is shown in the Scheme. 1.

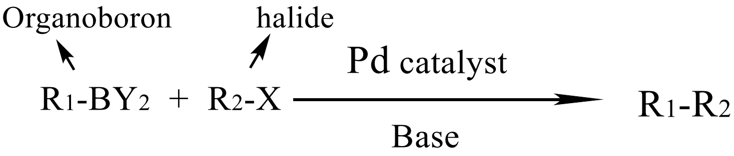


Figure 2.1: General scheme of Suzuki coupling.

Mechanism of the reaction:

The best view in mechanism of Suzuki reaction is based on the perspective of the palladium catalyst (Scheme 2). In the first step oxidative addition occurs where palladium is added to the halide **2** to form theorganopalladium species **3**, followed by reaction with base gives intermediate **4**, which via transmetalation [69] with the boronate complex **6** (that is already produced by reaction of the boronic acid **5** with base) forms the organopalladium species **8**. Finally, reductive elimination happens where the desired product **9** restores the original palladium catalyst **1** which completes the catalytic cycle. Presence of a base is critical in Suzuki coupling and for a long time the role of the base was never fully known. At first it was accepted that base forms a trialkyl borate (R_3B-OR), if an trialkylborane (BR_3) is reacted with alkoxide ($^{-}$OR); this species could be considered as being more nucleophilic and then more reactive towards the palladium complex present in the transmetalation step [70-72]. Duc and coworkers described that base has three roles in the Suzuki coupling reaction: formation of the palladium complex [$ArPd(OR)L_2$], formation of the trialkyl borate and the acceleration of the reductive elimination step by reaction of the alkoxide with the palladium complex [70].

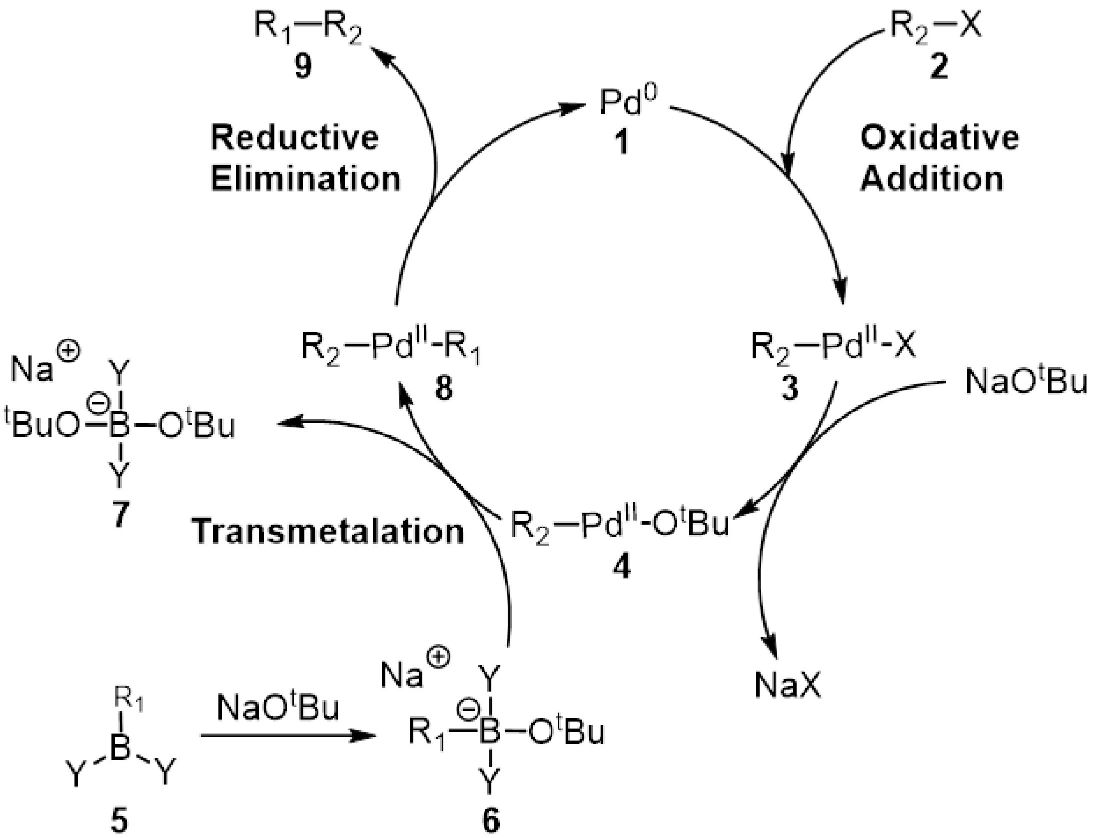


Figure: 2.2: Suzuki-Miyaura reaction mechanism.

Advantages:

Suzuki coupling has some advantages over other coupling reactions; availability of common boronic acids, mild reaction medium, its less toxic nature and water friendly environment for the reaction. Boronic acids are less toxic and safer for the environment than organostannane and organozinc compounds that are used in other coupling reactions. It is also convenient to remove the inorganic by-products from reaction mixture. In another words, this reaction is beneficial for using relatively cheap and easily prepared reagents. In addition, being able to use water as a solvent [73] makes this reaction more economical, eco-friendly, and capable of using wide variety of water-soluble reagents. There are many reagents that can be used for the Suzuki coupling, making suitable for its application in wide variety of chemical synthesis. There are reaction conditions that allow aryl- or vinyl-boronic acids and aryl- or vinylhalides. There are also some other works extending the scope of the reaction to incorporate alkyl bromides [74]. In addition to many different types of halides being possible for the Suzuki coupling reaction, the reaction also works with pseudohalides such as triflates (OTf), as replacements for halides. The relative reactivity for the coupling partner with the halide or pseudohalide is: R_2–I > R_2–OTf > R_2–Br >> R_2–Cl. Besides, palladium nanomaterial-based compounds can be used as catalyst [75]. There is also a report in order to reduce the loading of the catalyst, down to 0.001 mol%, with a novel organophosphine ligand (SPhos) [76]. Suzuki coupling is broadly used in research and has recently been tremendously applied in industrial processes for chemical synthesis as disscused above for advancements and the diverse number of possibilities for coupling partners. Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis have been summarized by Kotha and co-workers [77].

3. EXPERIMENTAL SECTION

3-bromothiophene, 97%,(Across), 2-bromo-4′-cyanoacetophenone(Aldrich), polyphosphoric acid (PPA), n-butyllityum, 4-bromo-N,N-diphenylaniline, sodium sulfate (Merck), palladium catalyst $Pd(PPh_3)_4$ (sigma), dichloromethane (Aldrich), diethyl ether, toluene, and sodium bicarbonate (Merck) were used without further purification except for diethyl ether and THF, which was dried over metallic sodium.

UV measurements were studied on HITACHI U-0080D. ^{1}H and ^{13}C NMR spectra were recorded on a Varian model NMR (500 and 600 MHz). Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments.

3.1 Synthesis Part

3.1.1 Synthesis of 4-(2-(thiophen-3-ylthio)acetyl)benzonitrile 8

To a solution of 3-bromothiophene **5** (15.76 mmol, 2.57 g, 97%) dissolved in dry diethyl ether (50 mL), n- butyllithium (15.76 mmol, 9.9 mL, 1.6 M) was added at −78 °C under nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. Then, S_8 (11.83 mmol, 0.506 g) was added and the mixture was stirred for more 1 h, after which it was placed into an ice bath and 2-bromo-4′-cyanoacetophenone (19.47 mmol, 3.88 g) was introduced into the mixture portion wise and stirring was continued overnight. The reaction mixture was filtered and washed with high amount of water, then followed by extraction with dichloromethane. The organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The crude products were combined and the residue was separated by column chromatography eluting with CH_2Cl_2/hexane (1/3) to give the main product **8** (1.82 g, 44%).

3.1.2 Synthesis of 4-(thieno[3,2-b]thiophen-3-yl)benzonitrile 9

Polyphosphoric acid (PPA) (2.5 g, 23 mmol) and chlorobenzene (5 ml) were placed in a reaction flask, then **8** (0.6 g, 2.3 mmol) that was already dissolved in 10 ml chlorobenzene was added dropwisely to PPA mixture at 135 °C . The reaction was refluxed at this temperature for 6-7 h in order to maximize the yield of ring closure step. The reaction mixture was tested by TLC to make sure the reaction is complete. Then, chlorobenzene was evaporated under fume hood overnight and the residue was dissolved in CH_2Cl_2, then it was neutralized by sodium bicarbonate (30% solution), following by extraction with water several times until water phase was clear. The organic phase was dried over Na_2SO_4 and filtered, then it was crystallized in hexane, finally grey crystals was obtained. The remaining compound (CNPhTT) was separated by coloumn chromatography eluting with CH_2Cl_2/hexane (1/4) to get the closed ring compound **9** (0.39 g, 69%).

3.1.3 Synthesis of 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzonitrile 10

0.2 g (0.83 mmol) 9 was dissolved in 4 ml DMF at -10 °C, then 0.295 g (1.66 mmol) NBS was added to solution in dark. After stirring for 3 h at the same temperature, the reaction mixture was poured into water (50 mL). The precipitated solid was filtrated and purified by column chromatography eluting with hexane to give the titled compound 10 (0.19 g, 57%). ^1H NMR (500 MHz, Chloroform-d) δ 7.81 – 7.75 (m, 4H), 7.24 (s, 1H).

3.1.4 Synthesis of 4-(2-bromothieno[3,2-b]thiophen-3-yl)benzonitrile 11

0.2 g (0.83 mmol) 9 was dissolved in 4 ml DMF at -10 °C, then 0.147 g (0.83 mmol) NBS was added to solution in dark. After stirring for 3 h at the same temperature, the reaction mixture was poured into water (50 mL). The precipitated solid was filtrated and purified by column chromatography eluting with CH_2Cl_2/hexane (1/3) to give the titled compound 11 (0.15 g, 58%). ^1H NMR (500 MHz, Chloroform-d) δ 7.83 – 7.78 (m, 4H), 7.47 (d, 1H), 7.24 (d, 1H).

3.1.5 Synthesis of (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene 12 (Br-TPE)

The method of synthesis was done as [78]. To a solution of diphenylmethane (21 mmol, 3.53 g) dissolved in dry THF (60 ml), n- butyllithium (20 mmol, 12.5 ml, 1.6 M) was added at -10 °C under nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. Then, 4- bromobenzophenone (20 mmol, 5.222 g) was added and the mixture was stirred for more 1 h, after which it was allowed to reach to room temperature and was left overnight. The following day, the reaction was quenched by saturated NH_4Cl solution and the mixture was extracted by DCM (3 times), each time 200 ml. The organic phase was dried over Na_2SO_4 and filtered, followed by evaporation of solvent under reduced pressure. The crude alcohol was dissolved in toluene and refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.6 g) with an azeotropic removal of water using a Dean-Stark trap at 125 °C overnight, followed by evaporation of toluene under reduced pressure and purified by simple crystallization from a mixture of dichloromethane and methanol and finally eluting with pure hexane by column chromatography to get the final product **12** yield (4 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 (dt, *J* = 3.6, 1.8 Hz, 8H), 7.31 – 7.24 (m, 9H) ppm.

3.1.6 Synthesis of 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane 13 (O-B-TPE)

To a solution of **12** (6.44 mmol, 2.65 g) dissolved in dry THF (60 ml), n- butyllithium (6.5 mmol, 4.1 ml, 1.6 M) was added at -78 °C under nitrogen atmosphere and the mixture was stirred for 2 h at the same temperature. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.2 mmol, 1.7 ml) was added and the mixture was stirred for more 1 h, after which it was allowed to reach to room temperature and was left overnight. The following day, the reaction was quenched by saturated NH_4Cl solution and the mixture was extracted by DCM several times. The solvent was evaporated under reduced pressure and the residue was separated by column chromatography eluting with hexane to give the main product. (2.29 g, 76%). ^{1}H NMR (500 MHz, DMSO-d_6): δ= 7.43 (d, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 14.5, 6.7 Hz, 9H), 6.97 (d, *J* = 16.1, 8.0 Hz, 8H), 3.35 (s, 12H) ppm.

3.1.7 Synthesis of N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline 14 (O-B-TPA) [79]

To a solution of 4-bromo-N,N-diphenylaniline (Br-TPA) (18.5 mmol, 6 g) dissolved in dry THF (70 ml), n- butyllithium (25 mmol, 16 ml, 1.6 M) was added at -78 °C under nitrogen atmosphere and the mixture was stirred for 2 h at the same temperature. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24 mmol, 5 ml) was added and the mixture was stirred for more 1 h, after which it was allowed to reach to room temperature and was left overnight. The next day, the reaction was quenched by saturated NH_4Cl solution and the mixture was extracted by DCM several times. The solvent was evaporated under reduced pressure and the residue was separated by column chromatography eluting with hexane to give the main product (4.12 g, 60%).

3.1.8 Synthesis of 4-(2,5-bis(4-(diphenylamino)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P1)

Suzuki–Miyaura coupling reaction: (all the steps were done in saturated N_2 gas atmosphere). (200 mg, 0.501) mmol **10** and (465 mg, 1.25 mmol) **14** were dissolved in 10 ml THF, then the solution was purged for around 10 minutes by N_2. After that, 2.5 ml basic solution (K_2CO_3) 2M was added (10 eq. compared to **10**). Finally, catalytic amount (10%) of $Pd(PPh_3)_4$ was added to the mixture. The reaction vessel was saturated by N_2 and the reaction was settled at 75°C for 48 h. The product was eluted by column chromatography with CH_2Cl_2/hexane (1/3) to obtain targeted compound (260 mg, 71%) as yellow compound, mp 142-144°C. ^{1}H NMR (500 MHz, dmso) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.66 – 7.57 (t, 4H), 7.34 (m, *J* = 8.3, 3.8 Hz, 8H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.14 – 7.02 (m, 12H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, dmso) δ 130.14, 127.02, 134.41, 125.04, 124.44, 123.97, 123.20, 122.09. MS *m/z* calculated for $C_{49}H_{33}N_3S_2$ 727.21, found 728.2.

3.1.9 Synthesis of 4-(2,5-bis(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P2)

Suzuki–Miyaura couplin reaction: (all the steps were done in saturated N_2 gas atmosphere). (150 mg, 0.375 mmol) **10** and (430 mg, 0.94 mmol) **13** were dissolved in 10 ml THF, then the solution was purged for around 10 minutes by N_2. After that, 2.5 ml basic solution (K_2CO_3) 2M was added (10 eq. compared to **10**). Finally, catalytic amount (10%) of $Pd(PPh_3)_4$ was added to the mixture. The reaction vessel was saturated by N_2 and the reaction was settled at 75°C for 48 h. The product was eluted by column chromatography with CH_2Cl_2/hexane (1/3) to obtain targeted compound (220 mg, 65%) as green compound, mp 281-283 °C. ^{1}H NMR (600 MHz, $cdcl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.11 (m, *J* = 15.4, 2.4 Hz, 17H), 7.07 – 7.01 (m, 17H), 6.97 – 6.95 (d, 2H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 132.44, 131.71, 131.31, 129.57, 128.63, 127.90 – 127.49, 126.66. MS *m/z* calculated for $C_{65}H_{43}NS_2$ 901.28, found 901.3.

3.1.10 Synthesis of 4-(2-(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P3)

Suzuki–Miyaura couplin reaction: (As before all the steps were done in saturated N_2 gas atmosphere). (150 mg, 0.262 mmol) **11** and (215 mg, 0.47 mmol) **13** were dissolved in 10 ml THF, then the solution was purged for around 10 minutes by N_2.

After that, 2.5 ml basic solution (K_2CO_3) 2M was added (10 eq. compared to **11**). Finally, catalytic amount (10%) of $Pd(PPh_3)_4$ was added to the mixture. The reaction vessel was saturated by N_2 and the reaction was settled at 75°C for 48 h. The product was eluted by column chromatography with CH_2Cl_2/hexane (1/3) to obtain targeted compound (175 mg, 65%) as green compound, mp 209-211°C. ^{1}H NMR (500 MHz, $cdcl_3$) δ 7.63 – 7.60 (m, 2H), 7.51 – 7.48 (m, 2H), 7.40 – 7.38 (d, 1H), 7.31 – 7.29 (d, 1H), 7.19 – 7.10 (m, 9H), 7.04 (m, J = 8.5, 6.0, 2.9, 1.2 Hz, 8H), 6.99 – 6.96 (m, 2H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 143.59, 142.33, 141.80, 140.66, 132.86, 132.61, 129.58, 129.24, 128.74, 128.20, 118.77, 110.91. MS *m/z* calculated for $C_{39}H_{25}NS_2$ 571.14, found 571.1.

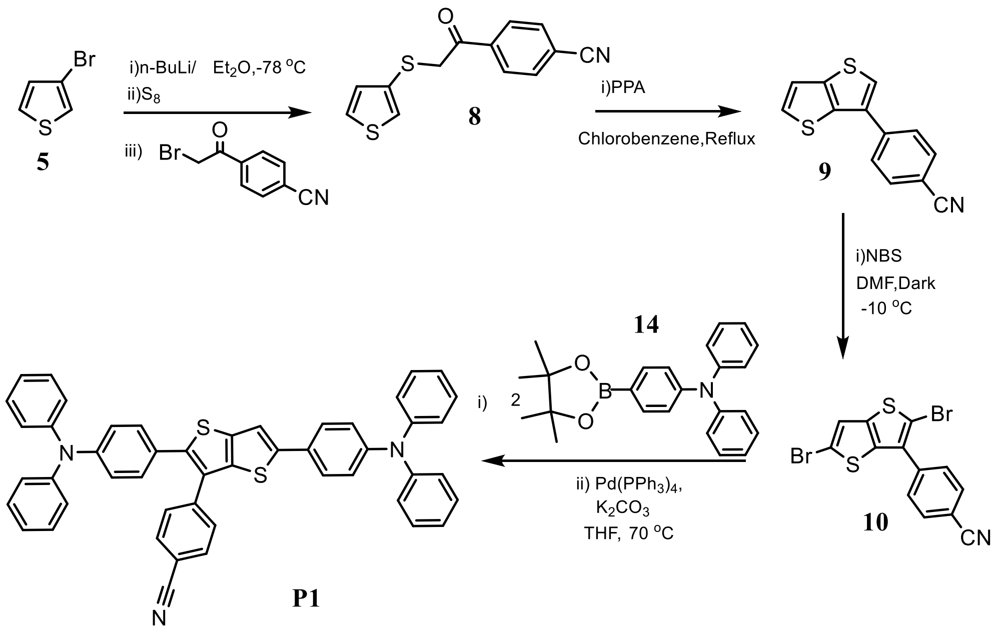
4. RESULTS AND DISCUSSIONS

Thieno[3,2-*b*]thiophene, having phenyl moiety (PhTT) at C-3, substitued with nitrile group (CNPhTT) **(9)** core unit was synthesized successfully with overall moderate to high yield by monoketone ring closure route with PPA. Afterwards, corresponding boronate complex of TPA and TPE were synthesized, respectively. Then, final oligomer products, **P1, P2** and **P3** also were synthesized successfully by metal-catalyzed Suzuki cross-coupling reactions with relatively high yields (65-71%).

4.1 Synthesis 4-(2,5-bis(4-(diphenylamino)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P1)

For the synthesis of thieno[3,2b]thiophene's **(2)** derivative, at first 3-bromothiophene **5** reacted with n-buthyllithium at -78 ^{o}C in diethylether forming 3-lithiothiophene, followed by addition of elemental sulfur and then α-bromoketone to obtain comound **8**.

Then cyclization of **8** was done in the prescence of polyphosphoric acid (PPA) in chlorobenzene furnished the corresponding TT derivative which it was dibrominated by N-Bromosuccinimide (NBS) in DMF. The final compound, 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzonitrile **10** was used for **Suzuki–Miyaura** coupling reaction with boronate tiphenylamine complex **14** as an electrodonating group (Scheme 4.1).

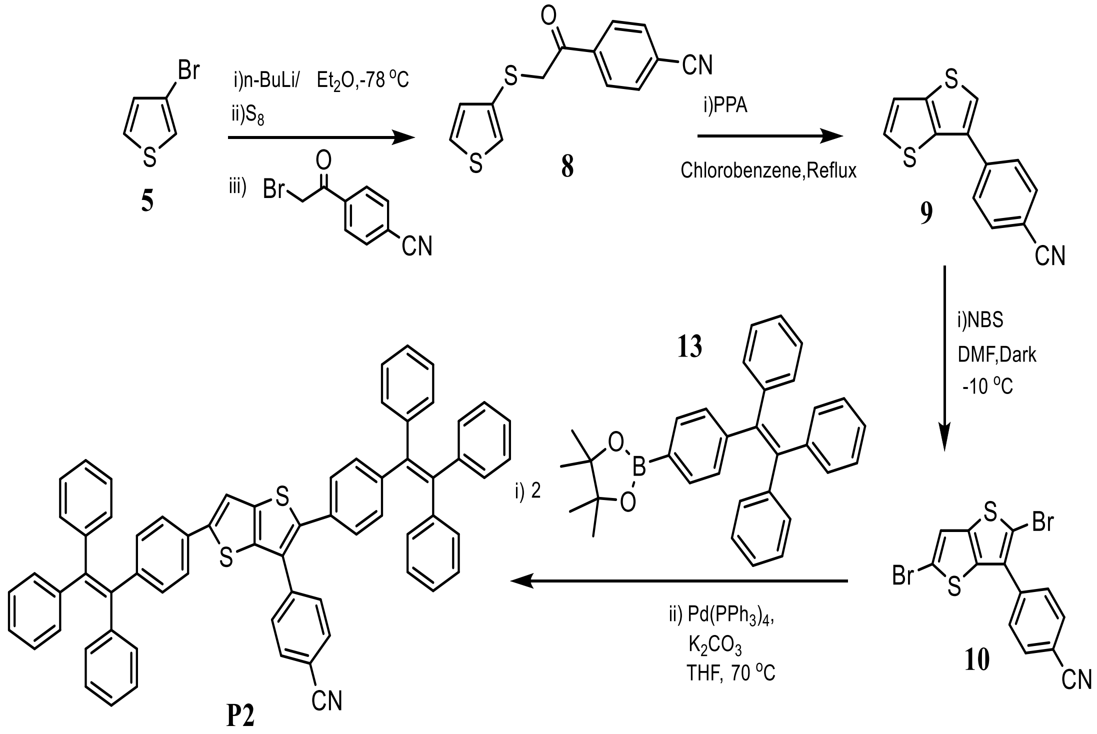


Scheme 4.1: Synthesis route of **P1**.

4.2 Synthesis of 4-(2,5-bis(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P2)

For the synthesis of thieno[3,2b]thiophene's derivative **(2)**, at first 3-bromothiophene **5** reacted with n-buthyllithium at -78 ^{o}C in diethylether forming 3-lithiothiophene, followed by addition of elemental sulfur and then α-bromoketone to obtain comound **8**.

Then cyclization of **8** was done in the prescence of polyphosphoric acid (PPA) in chlorobenzene furnished the corresponding TT derivative which it was dibrominated by N-Bromosuccinimide (NBS) in DMF in dark. The final compound, 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzonitrile **10** was used for **Suzuki–Miyaura** coupling reaction with boronate tetraphenylethylene complex **13** as an electrodonating group (Scheme 4.2).

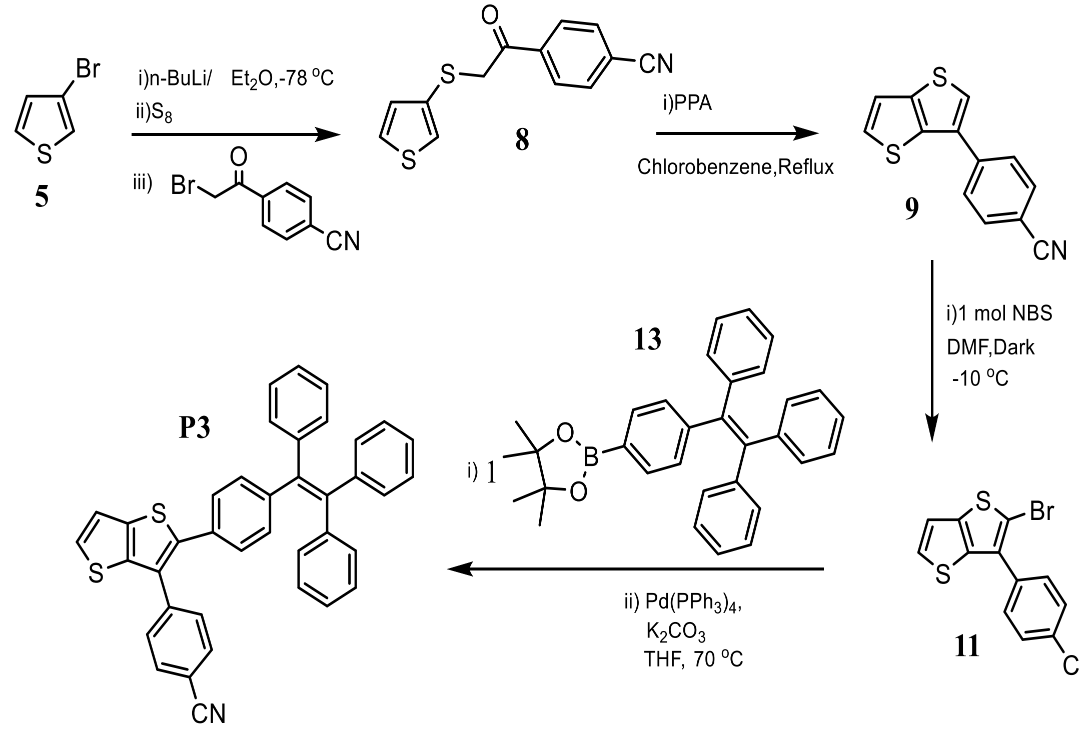


Scheme 4.2: Synthesis route of **P2**.

4.3 Synthesis of 4-(2-(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-3-yl)benzonitrile (P3)

For the synthesis of thieno[3,2b]thiophene's derivative, at first 3-bromothiophene **5** reacted with n-buthyllithium at -78 ^{o}C in diethylether forming 3-lithiothiophene, followed by addition of elemental sulfur and then α-bromoketone to obtain comound **8**.

Then cyclization of **8** was done in the prescence of polyphosphoric acid (PPA) in chlorobenzene furnished the corresponding TT derivative which it was monobrominated by N-Bromosuccinimide (NBS) in DMF. The final compound, 4-(2-bromothieno[3,2-b]thiophen-3-yl)benzonitrile **11** was used for **Suzuki–Miyaura** coupling reaction with boronate tetraphenylethylene complex **13** as an electrodonating group (Scheme 4.3).



Scheme 4.3: Synthesis route of **P3**.

4.4 Photophysical properties of oligomers

The UV-Visible and fluorescence spectra of all three products, **P1, P2, P3** were recorded in a very diluted dichloromethane solution and corresponding data were obtained. The **P1** show broad absorption bands in 350-450 nm region (Figure 4.1). The absorption spectra show multiple absorption peaks corresponding to the absorption of their conjugate system. The electronic transitions in **P1-P3** can be assigned as π-π* transitions. These three molecules are poorly fluorescent in solution. The reason could be due to loss of excited state energy by intramolecular rotations of TPE and TPA unit. In order to see the “aggregation induced emission” (AIC) phenomenon in these three oligomers, they were tested for quantum yield in solid state. The **P1**, **P2** and **P3** are excited at 397, 379 and 296 nm with 0.131, 0.121, and 0.138 quantum yields in solid, respectively. In the following, UV-Vis absorption and fluorescence spectra of all three compounds are shown. In Figure 4.2, it is indicated that all hardly absorbs light at wavelengths longer than 400 nm, showing their high transparency to visible light to ensure a slightly high light collecting efficiency. All the UV-Vis and fluorescence characterization data are followed from the next page.

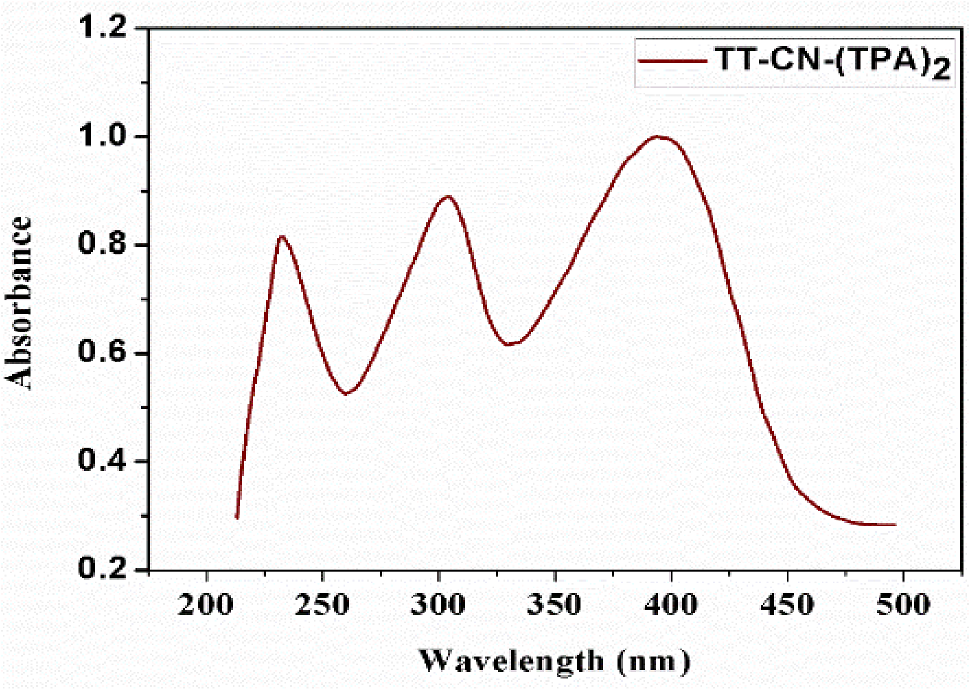


Figure 4.1: UV-Vis spectra of **P1**.

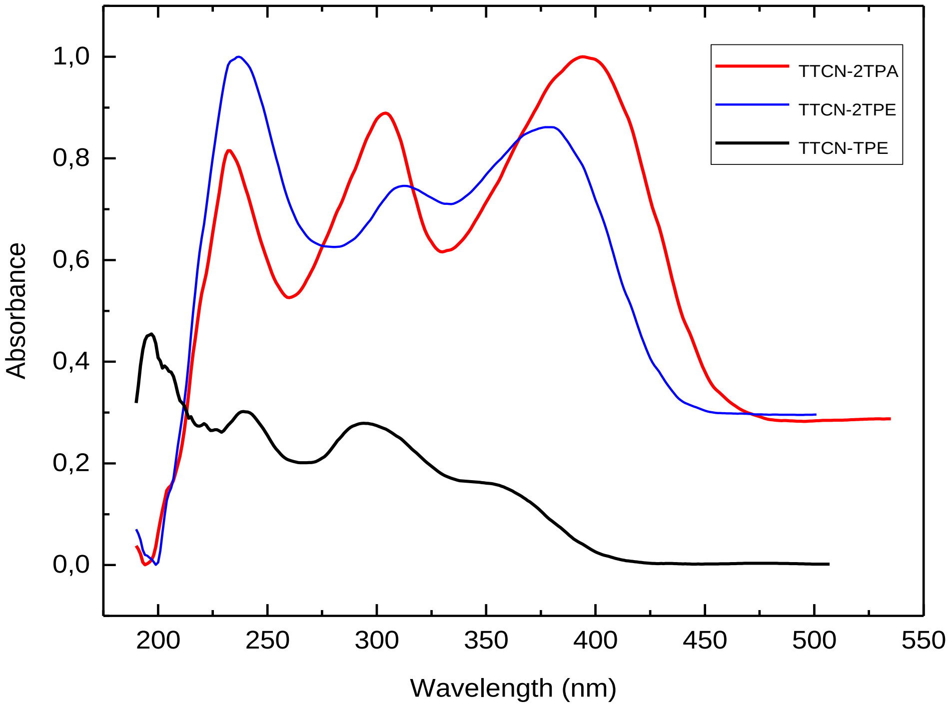


Figure 4.2: UV-Vis absorption spectra comparison **(P1-P3)**.

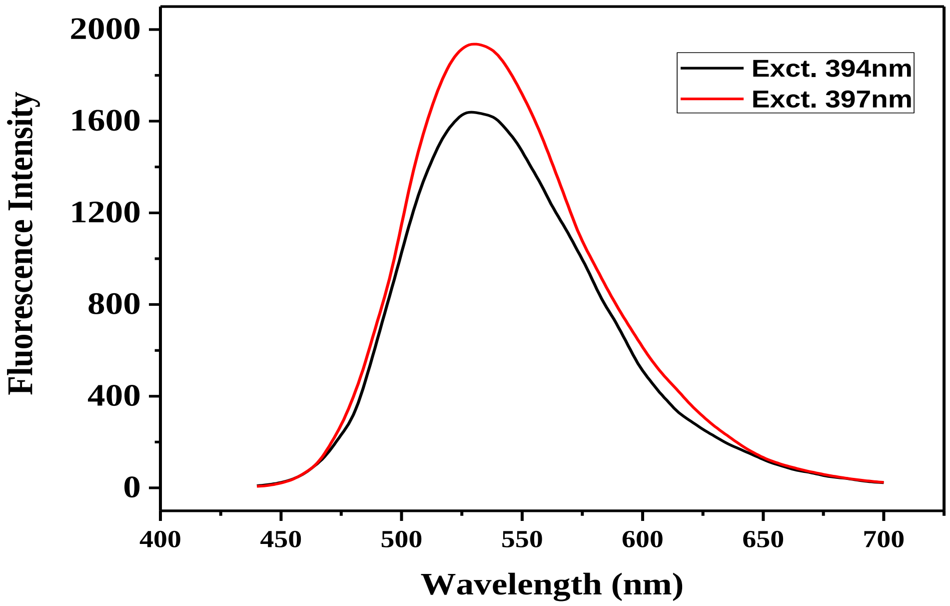


Figure 4.3: Electroluminescence spectra of **P1**.

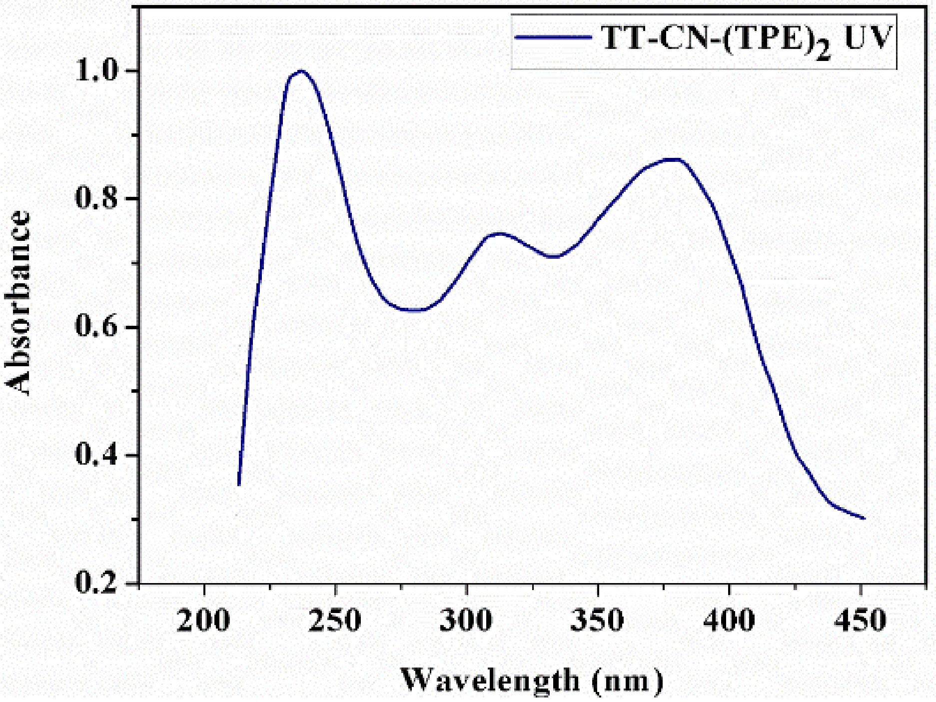


Figure 4.4: UV-Vis spectra of **P2**.

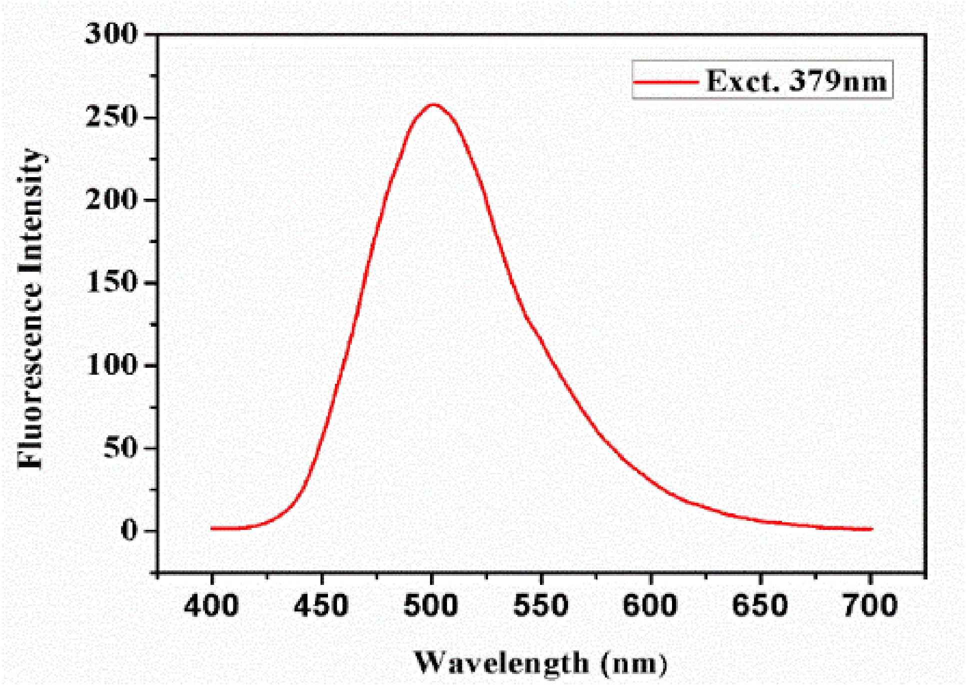


Figure 4.5: Electrolominescence spectra of **P2**.

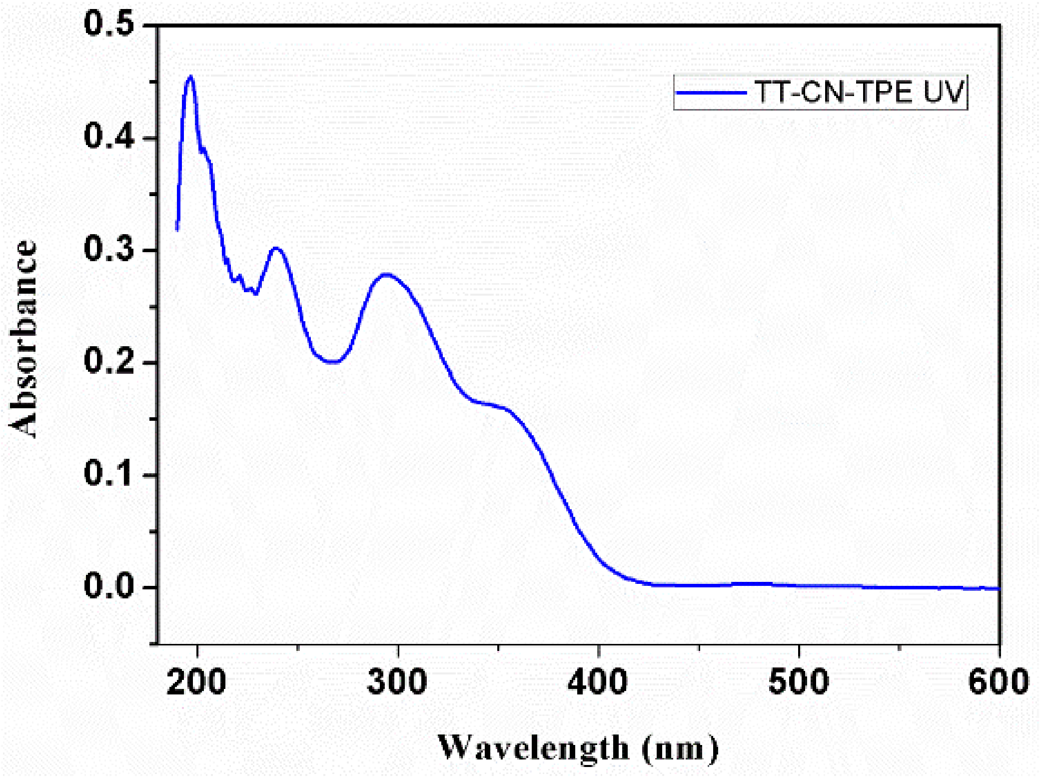


Figure 4.6: UV-Vis spectra of **P3**.

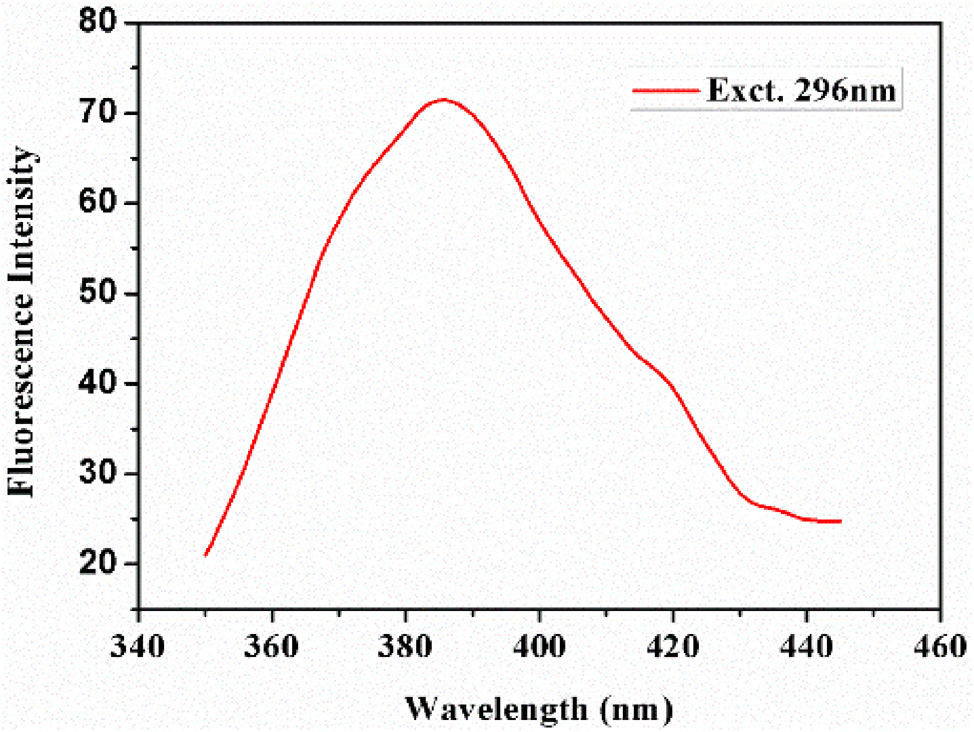


Figure 4.7: Electroluminescence spectra of **P3**

Finally I should mention that these oligomers are under investigation for probability of making OLED devices by Tübitak. In addition, syntheis of other derivatives of 3-(4-cyanophenyl)thieno[3,2-b]thiophene **9** like TPE-TTCN-TPA is interesting which is on the progress by another master student in our research group.

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APPENDIX

A: Characterization data:

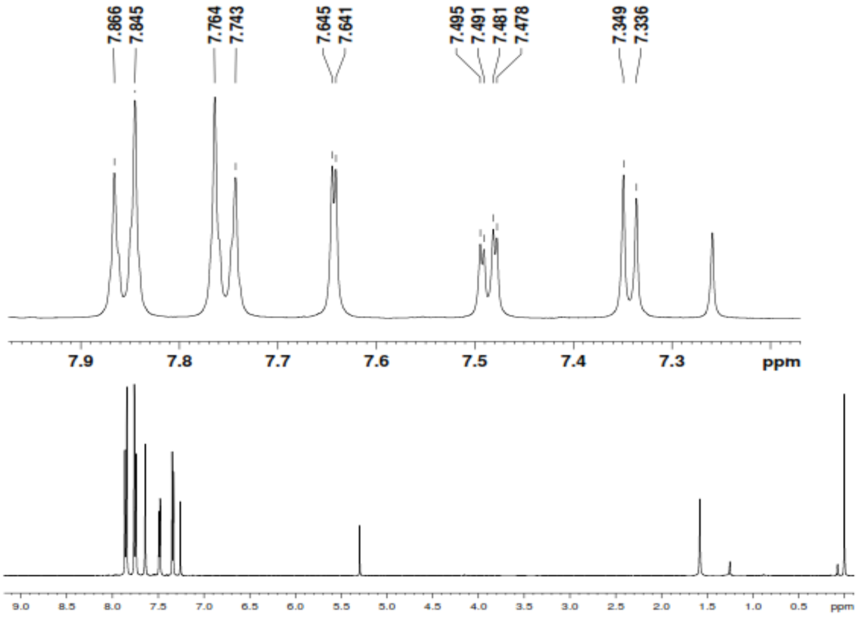

Figure A.1: ^{1}H-NMR (**9**)

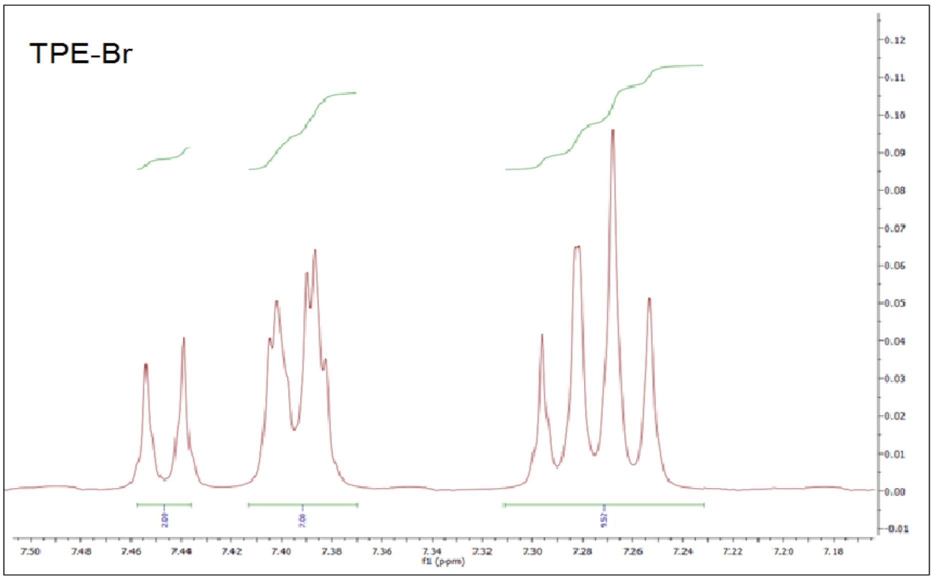

Figure A.2: ^{1}H-NMR (**12**).

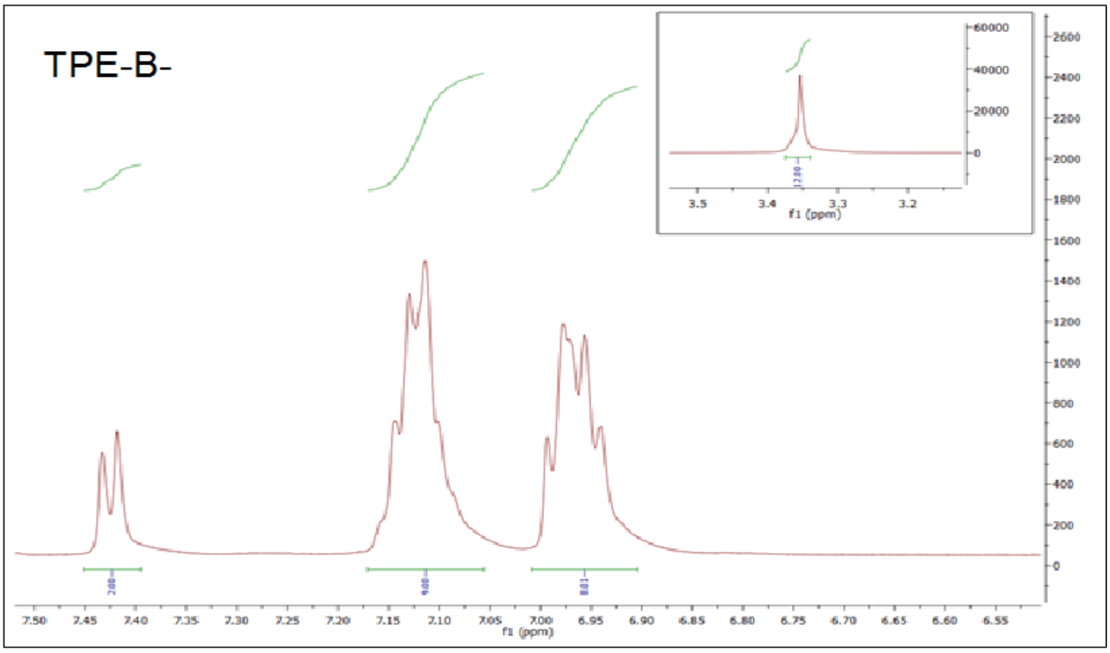

Figure A.3: ^{1}H-NMR (**13**).

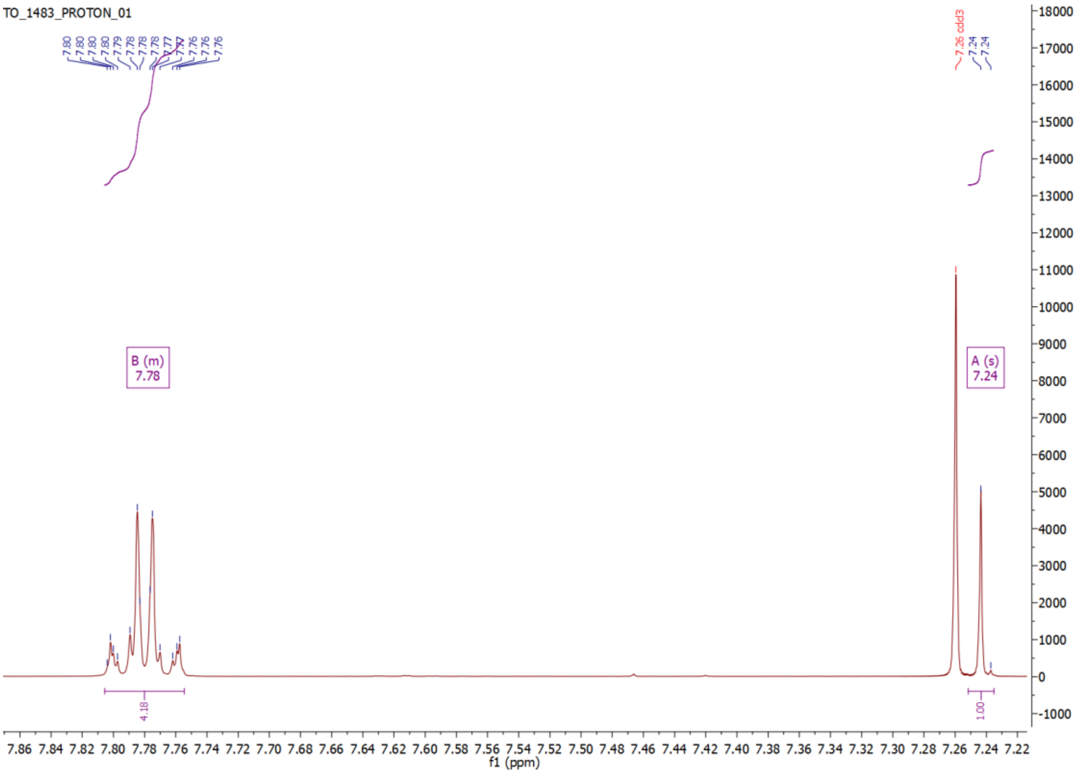

Figure A.4: ^{1}H-NMR (**10**).

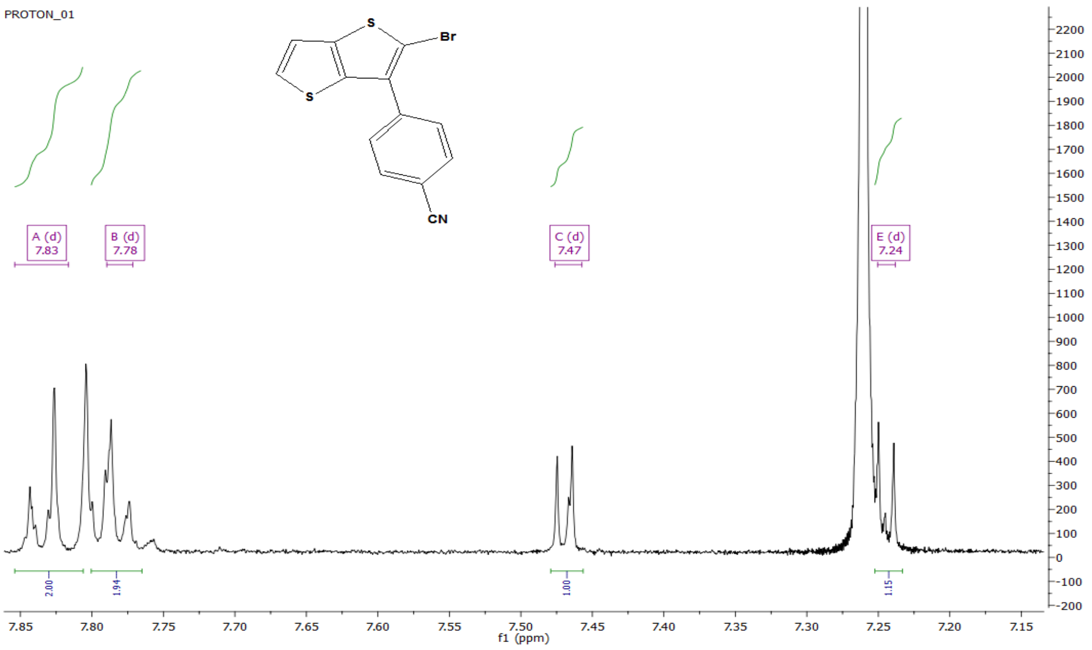

Figure A.5: ^{1}H-NMR (**11**).

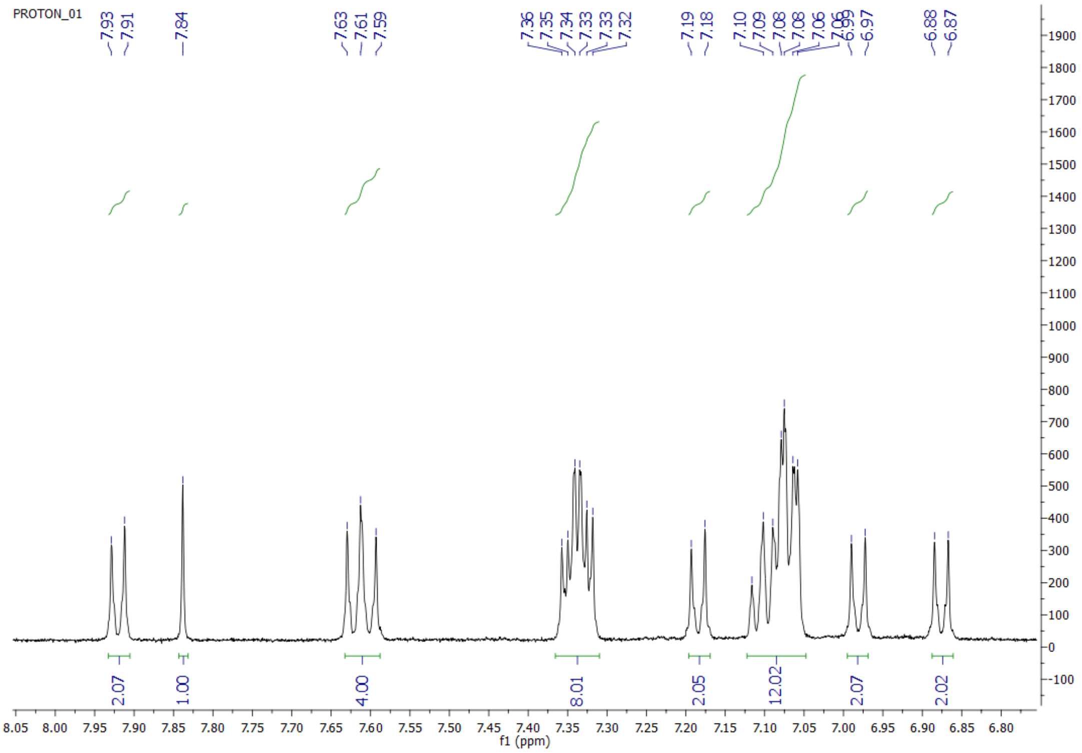

Figure A.6: ^{1}H-NMR **(P1)**.

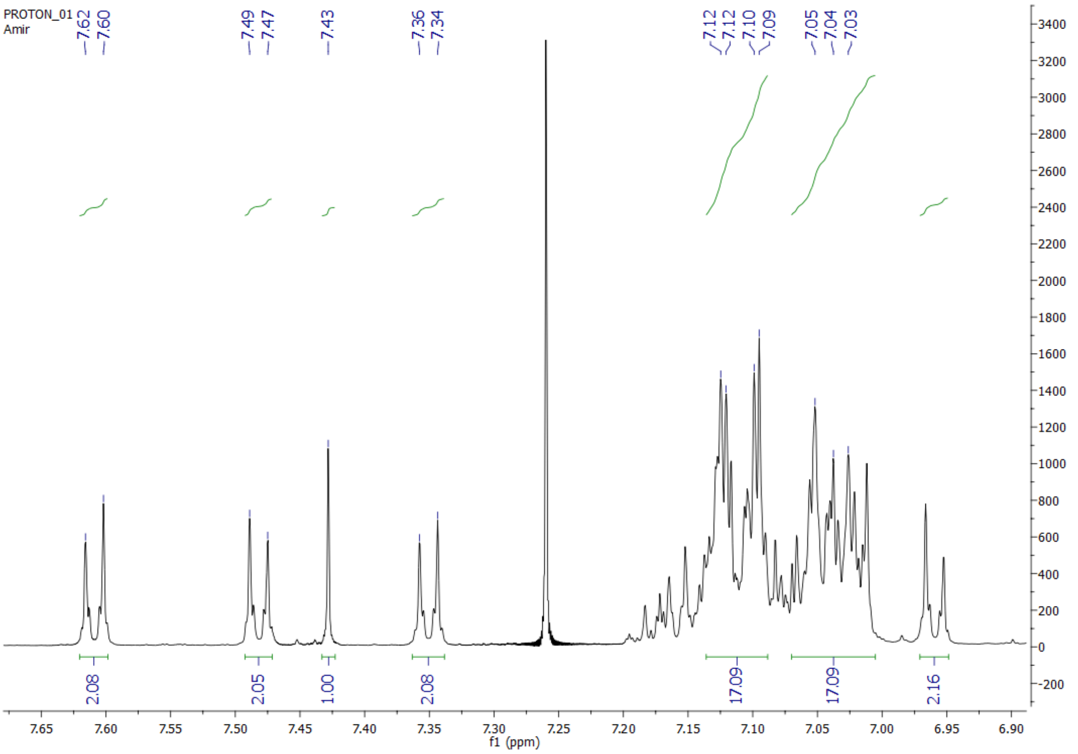

Figure A.7: ^{1}H-NMR **(P2)**.

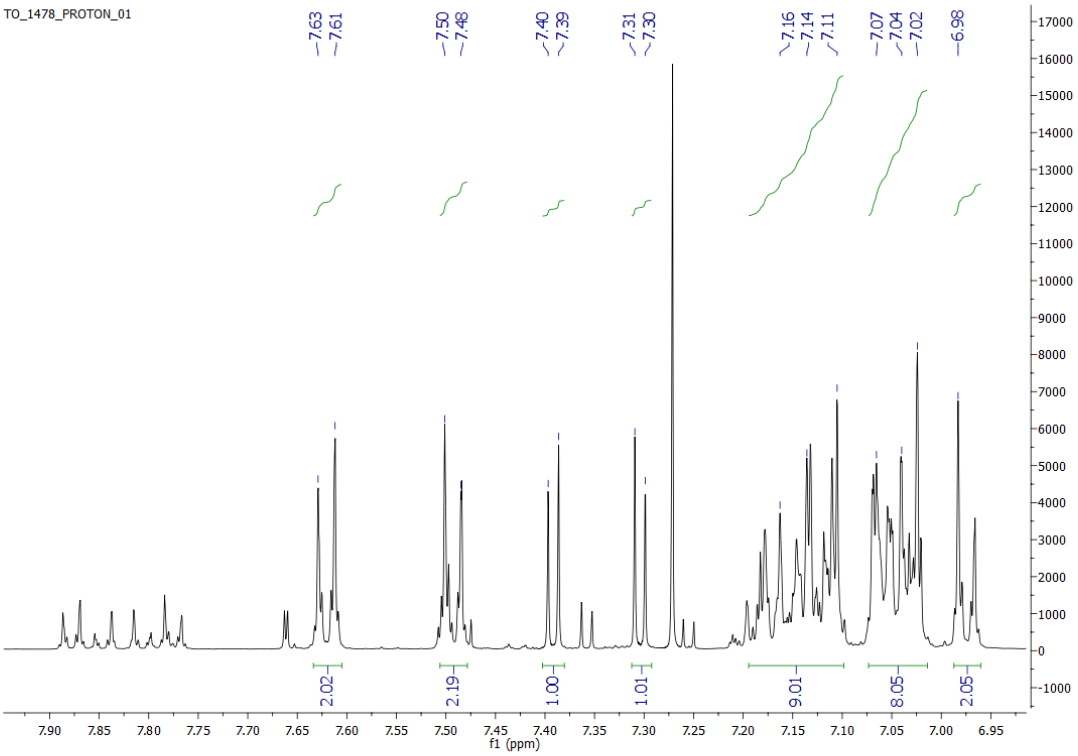

Figure A.8: ^{1}H-NMR **(P3)**.

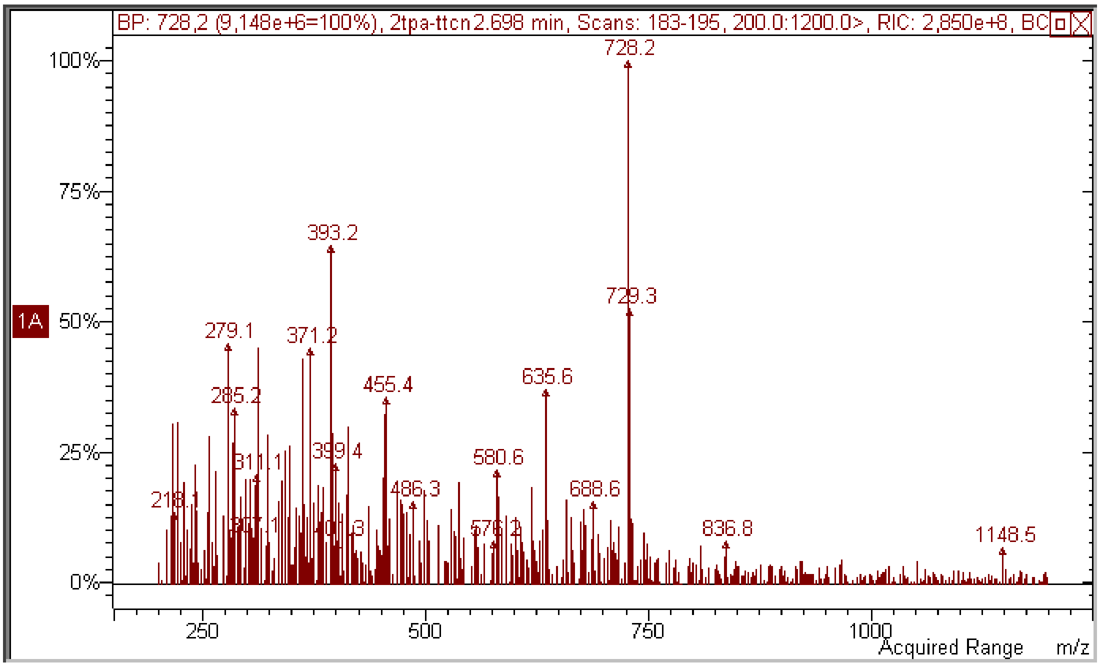

Figure A.9: MS **(P1)**.

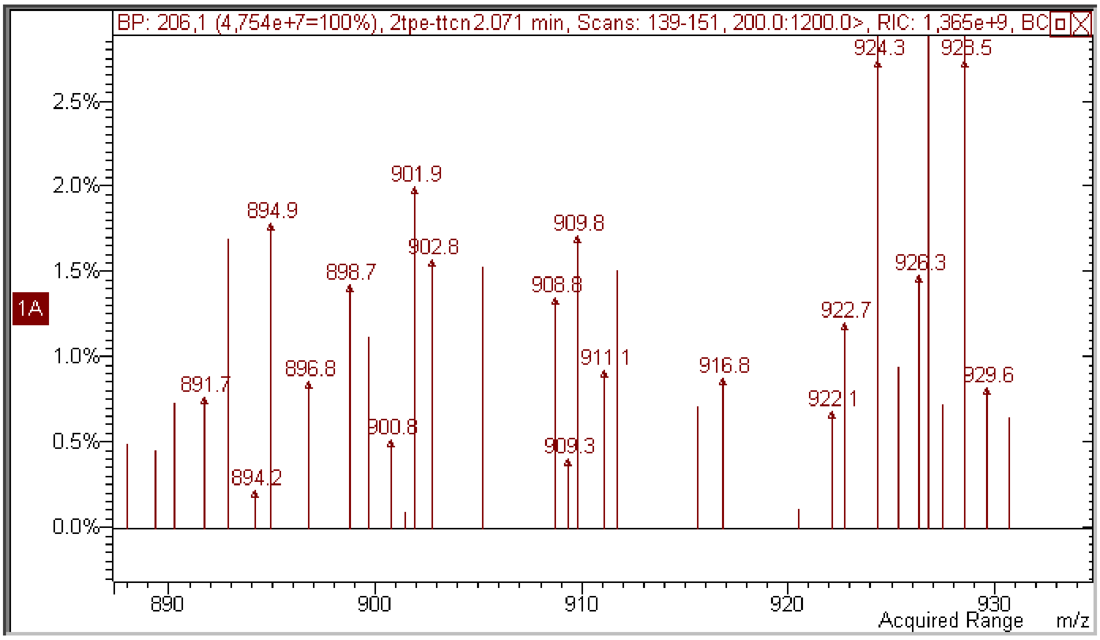

Figure A.10: MS **(P2)**.

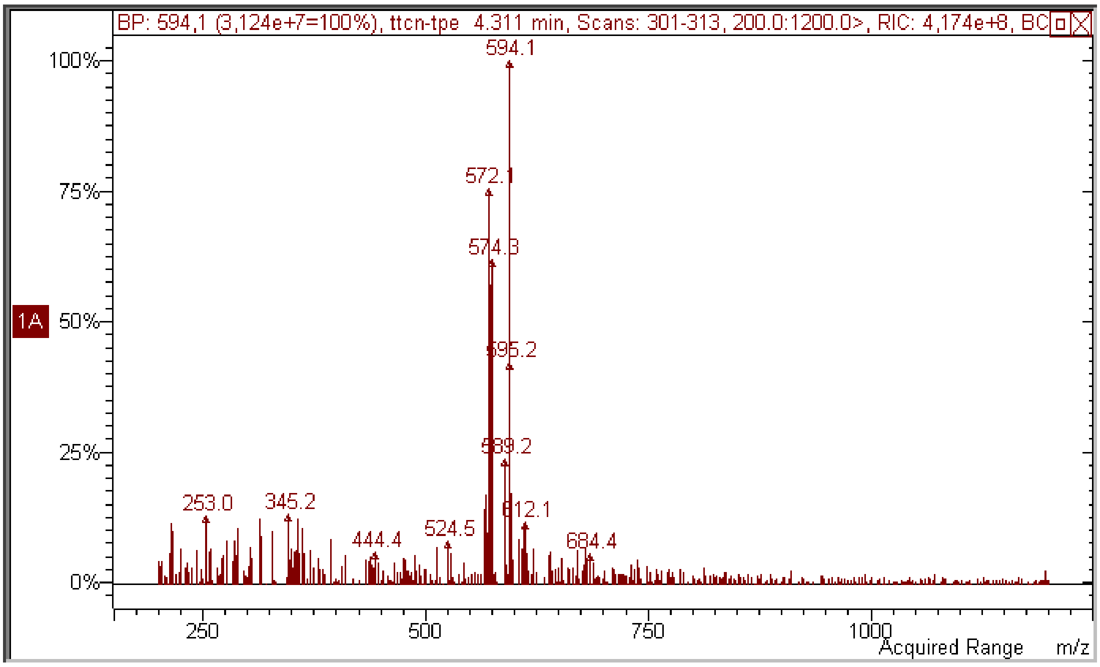

Figure A.11: MS **(P3)**.

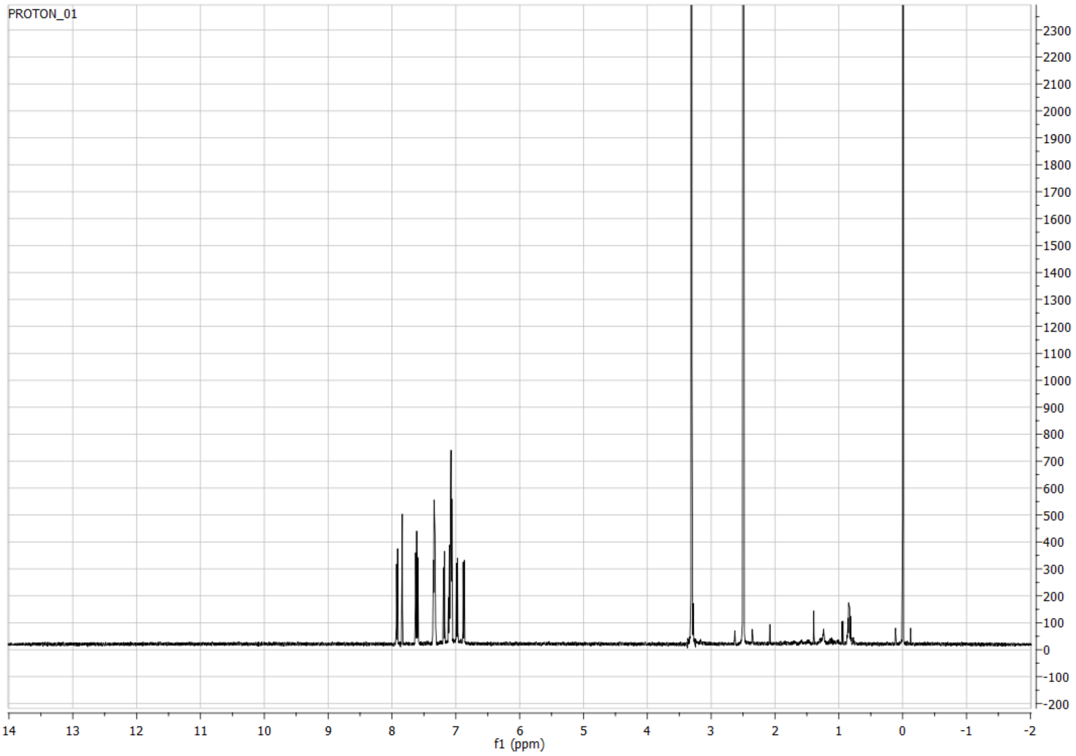

Figure A.12: Full ^{1}H-NMR **(P1)**.

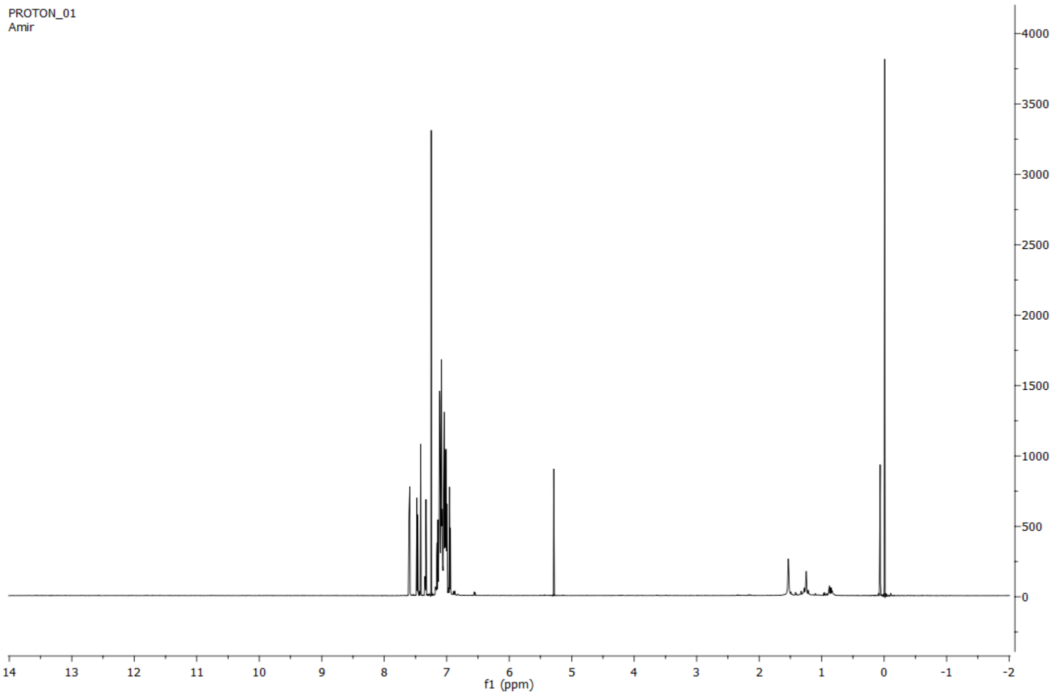

Figure A.13: Full ^{1}H-NMR **(P2)**.

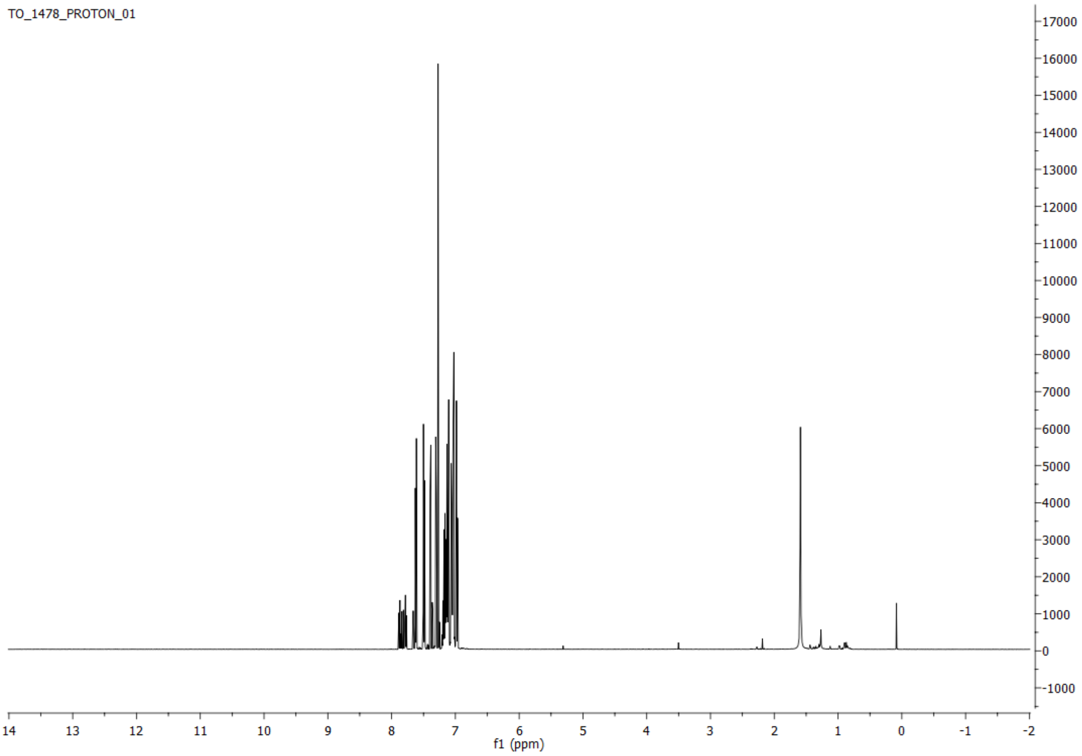

Figure A.14: Full ^{1}H-NMR **(P3)**.

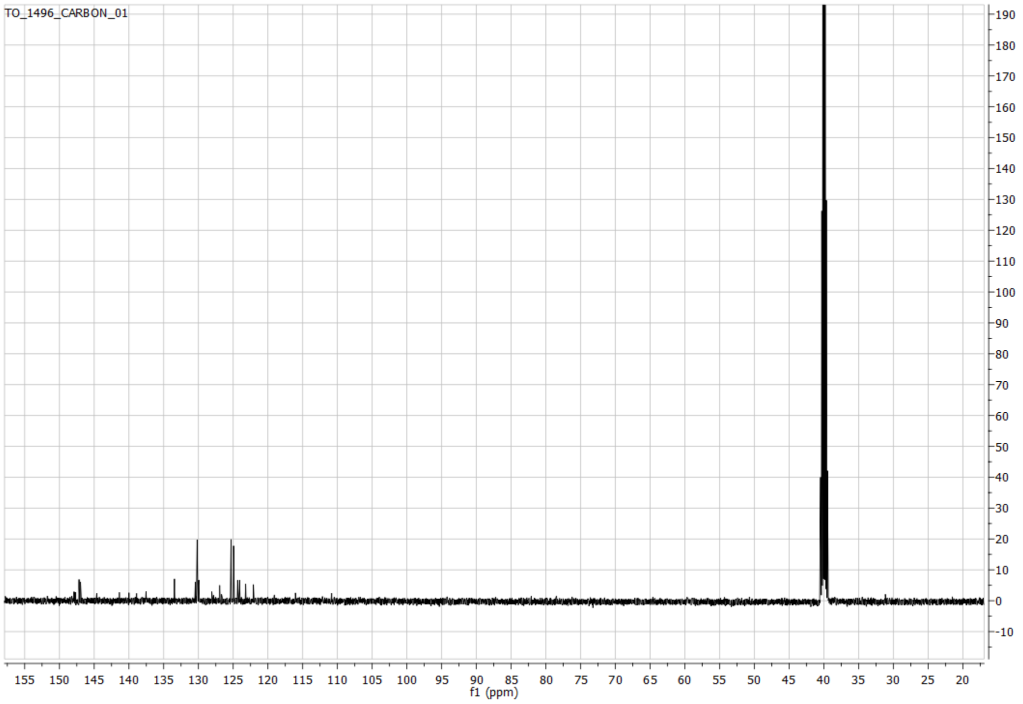

Figure A.15: Full ^{13}C-NMR **(P1)**.

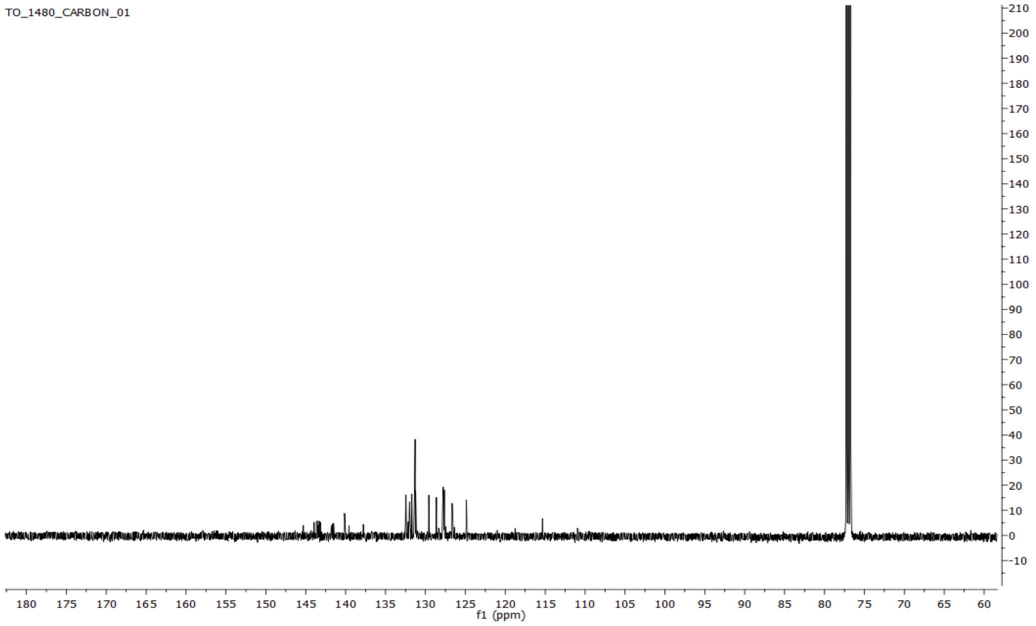

Figure A.16: Full ^{13}C-NMR **(P2)**.

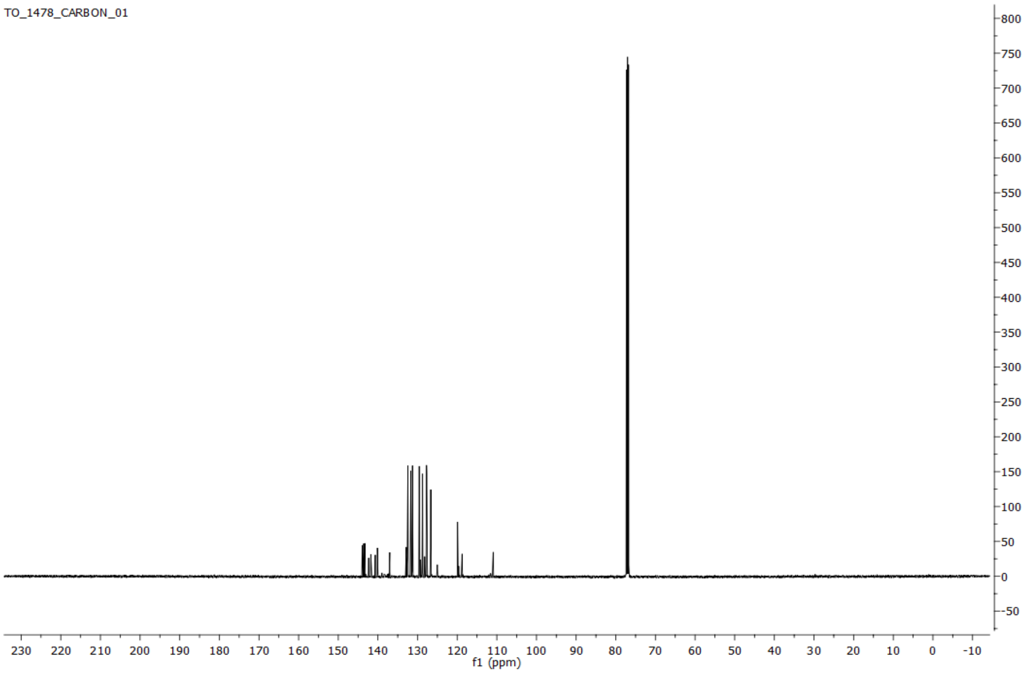

Figure A.17: Full ^{13}C-NMR **(P3)**.

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