

**ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES  
DEPARTMENT OF CHEMISTRY**

**GRADUATE PROJECT (Chem.774)**

**SYNTHESIS AND CHARACTERIZATION OF  
QUINOXALINE-FLUORENE-THIOPHENE  
CONTAINING POLYMERS**

*A Project Presented to the School of Graduate studies of Addis  
Ababa University in Partial Fulfillment of the Requirements for  
the Degree of Master of Science in Chemistry*

By: Zewdu Messele

Advisor: Wendimagegn Mammo (Professor)

July, 2009

---

To: The Chairman,  
Department of Chemistry

From: Wendimagegn Mammo

**Subject: Zewdu Mesele MSc. Project**

This is to testify that **Zewdu Messele** has incorporated all comments of the Examining Board in the final version of his MSc. project.

Thank you

---

## Declaration

I, the undersigned, declare that this MSc. project is my original work and has not been presented for any degree in any other university and that all sources of materials used for this project have been duly acknowledged.

Name: **Zewdu Messele**

Signature: \_\_\_\_\_

This MSc. project has been submitted for examination with my approval as a university advisor.

Name: Wendimagegn Mammo (Professor)

Signature: \_\_\_\_\_

Date and place of submission: Department of Chemistry  
Addis Ababa University  
July, 2009

## Acknowledgment

I would like to express my deepest gratitude to my project supervisor, Prof. Wendimagegn Mammo for his continuous guidance, technical and moral support, running NMR spectra of all compounds, encouraging during the entire project work and providing all necessary materials during paper writing.

I would also like to thank Dr. Shimels Admassie for running UV-Vis spectra, fluorescence spectra and cyclic voltammogram of both polymers.

I also express my thanks to my colleagues for their help and motivation during the entire project work.

The department of chemistry at Addis Ababa University is acknowledged for providing the laboratory space, chemicals and instrumentation to carry out the project work.

I would also like to acknowledge Medawalabu University and the Ministry of Education for sponsoring my studies.

# Tables Content

|   |     |
|---|-----|
| Acknowledgment.....   | i   |
| List of Tables .....  | iii |
| List of Schemes .....   | iv  |
| List of Figures .....   | v   |
| List of Abbreviations.....  | vi  |
| Abstract.....   | vii |
| 1. Introduction .....   | 1   |
| 2. Literature Review .....  | 3   |
| 2.1 Cyclopentadithiophene monomeric sub-units .....   | 4   |
| 2.2 Quinoxaline monomeric sub-units.....  | 9   |
| 2.3 Fluorene monomeric sub-units .....  | 12  |
| 3. Objectives of the Project .....  | 14  |
| 4. Results and Discussion.....  | 14  |
| 4.1 Synthesis of quinoxaline-based monomers .....   | 15  |
| 4.1.1 Synthesis of 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione ( <b>48</b> ).....                                     | 15  |
| 4.1.2 Synthesis of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis-(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine ( <b>51</b> )..... | 19  |
| 4.2 Attempts toward the synthesis of cyclopentadithiophene based monomers.....  | 25  |
| 4.2.1 Synthesis of compounds <b>55</b> and <b>56</b> . .....  | 26  |
| 4.3 Synthesis of copolymers .....   | 30  |
| 5. Conclusion .....   | 35  |
| 6. Experimental.....  | 36  |
| 6.1 Materials and Methods .....   | 36  |
| 6.2 Reagents .....  | 36  |
| 7. Procedures .....   | 36  |
| 8. References .....   | 45  |
| 9. Appendices .....   | 48  |

## List of Tables

|  |    |
|--|----|
| Table 1: $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz) data $\delta_{\text{ppm}}$ : of compounds <b>47</b> and <b>48</b> .....                | 18 |
| Table 2: $^{13}\text{C}$ -NMR (100.6 MHz, $\text{CDCl}_3$ ), data $\delta_{\text{ppm}}$ : of compounds <b>47</b> and <b>48</b> .....           | 19 |
| Table 3: $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz) data $\delta_{\text{ppm}}$ : of compounds <b>49</b> , <b>50</b> and <b>51</b> ....     | 24 |
| Table 4: $^{13}\text{C}$ -NMR (100.6 MHz, $\text{CDCl}_3$ ) data $\delta_{\text{ppm}}$ : of compounds <b>49</b> , <b>50</b> and <b>51</b> .... | 25 |
| Table 5: $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz) data $\delta_{\text{ppm}}$ : of compounds <b>55</b> , <b>56</b> .....                  | 29 |
| Table 6: $^{13}\text{C}$ -NMR (100.6 MHz, $\text{CDCl}_3$ ), data $\delta_{\text{ppm}}$ : of compounds <b>55</b> and <b>56</b> . ...           | 30 |
| Table 7. UV-Vis spectra and cyclic voltammogram of polymers <b>59</b> and <b>61</b> .....  | 34 |

## List of Schemes

|  |    |
|--|----|
| Scheme 1: Synthetic pathway to prepare cyclopentadithiophenes <b>13</b> , <b>3</b> , and poly- <b>3</b> .....                | 5  |
| Scheme 2: Mono- and dialkylation at the 4-position of 4H-cyclopenta[2,1-b;3,4-b']dithiophene ( <b>3</b> ).....               | 6  |
| Scheme 3: Synthetic route to monomer <b>16</b> and polymers <b>17-19</b> .....   | 7  |
| Scheme 4: Preparation of cyclopentadithiophene copolymers with dialkylfluorene. ....   | 8  |
| Scheme 5: Cyclopentadithiophene structures derived from 4H-cyclopenta[2,1b;3,4-b']dithiophene-4-one ( <b>13</b> ).....       | 9  |
| Scheme 6: Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole <b>30</b> and dibromoquinoxaline <b>31</b> .....                   | 10 |
| Scheme 7: Synthesis of some D-A-D copolymers involving thiophene-quinoxaline or 2,1,3-benzothiadiazole monomeric unit. ....  | 11 |
| Scheme 8: Synthesis of PBT and PQBT.....   | 12 |
| Scheme 9: Synthesis of poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF) ( <b>45</b> ). ....                        | 13 |
| Scheme 10: Synthesis of 2-butylthiophene ( <b>47</b> ) and 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione ( <b>48</b> ). .... | 17 |
| Scheme 11: Bromination and reduction of 2,1,3-benzothiadiazole ( <b>28</b> ).....  | 20 |
| Scheme 12: Synthesis of 5,8-dibromo-2,3-bis(5-butylthiophen-2-yl)quinoxaline ( <b>49</b> ). ....                             | 20 |
| Scheme 13: Synthesis of compounds <b>50</b> and <b>51</b> .....  | 22 |
| Scheme 14 General synthetic strategy towards the synthesis of cyclopentadithiophene ( <b>3</b> ).....                        | 26 |
| Scheme 15: Preparation of ethyl formate.....   | 27 |
| Scheme 16: Synthesis of compounds <b>55</b> and <b>56</b> .....  | 28 |
| Scheme 17: Synthesis of copolymers <b>59</b> and <b>61</b> .....   | 31 |

## List of Figures

|   |    |
|---|----|
| Figure 1. Examples of different $\pi$ -conjugated systems. .... | 3  |
| Figure 2. Possible isomers of cyclopentadithiophene. ....       | 4  |
| Figure 3. UV-vis spectrum of polymer <b>59</b> . ....           | 32 |
| Figure 4. Cyclic voltammogram of polymer <b>59</b> . ....       | 33 |
| Figure 5. UV-Vis Spectrum of polymer <b>61</b> . ....           | 33 |
| Figure 6. Cyclic Voltammogram of polymer <b>61</b> .....        | 34 |

## List of Abbreviations

DMF: N,N-Dimethylformamide  
DCM: Dichloromethane  
GPC: Gel permeation chromatography  
PCC: Pyridinium chlorochromate  
DMSO: Dimethyl sulfoxide  
hr: Hour(s)  
NMR: Nuclear Magnetic Resonance  
HOMO: Highest Occupied Molecular Orbital  
LUMO: Lowest Unoccupied Molecular Orbital  
°C: Degree Celsius  
RT: Room temperature  
%: Percentage  
 $\delta$ : Chemical shift  
*J*: Coupling constants  
*d*: Doublet  
*m*: Multiplet  
*dd*: Doublet of doublets  
*t*: triplet  
ppm: Parts per million  
NBS: *N*-Bromosuccinimide  
Pd: Polydispersity  
Mn: Number average molecular weight  
PLED: Polymer light emitting diodes  
PL: Photoluminescence  
EL: Electroluminescence  
FET: Field effect transistor

# SYNTHESIS AND CHARACTERIZATION OF QUINOXALINE-FLUORENE-THIOPHENE CONTAINING POLYMERS

By:Zewdu Messele

Advisor: Wendimagegn Mammo (Professor)

## Abstract

*In the course of this project, the synthesis of polyquinoxaline copolymers was attempted. Monomer 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine (51) was synthesized successfully. Two copolymers based on quinoxaline and fluorene derivatives were synthesized by using Suzuki coupling polymerization reaction. These were, poly(2,3-bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dioctyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (59) and poly(2,3-bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dibenzyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (61). These polymers were characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR spectra, UV-Vis spectra and cyclic voltammetry. Attempts also made to prepare cyclopentadithiophene starting from 3-bromothiophen. However, this synthesis was not accomplished.*

# 1. Introduction

Nowadays, naturally occurring energy sources like coal, oil and natural gas account for the highest source of energy consumption in this world. However, in addition to their negative effect on the environment, their unfair distribution makes this world unstable due to economic imbalance. Synthesis of polymers that can convert solar energy into usable form of energy has its own contribution to solve these problems.

Polymer is a material whose molecules contain a very large number of atoms linked by covalent bonds. Polymers consist mainly of identical or similar units joined together. The unit forming the repetitive pattern is called a monomer. Polymers can be natural or synthetic. Naturally occurring polymers have existed since the beginning of life and include proteins, starch, cellulose, and latex while synthetic polymers are produced commercially on a very large scale and have a wide range of properties and are used for different applications like the synthesis of plastics or insulating materials and, specialized polymers like conducting polymers.

It is a matter of fact that polymeric materials are well known in modern macroelectronics. In the past, however, they were used mainly as passive materials, such as resistance and adhesives. During the last decade, polymers with conjugated units have been developed as active functional materials such as conducting polymers<sup>1</sup>.

Polymers with large  $\pi$ -conjugated systems have attracted much attention as new electronic and optoelectronic substances mainly used for active semiconducting layers in light-emitting diodes, photovoltaic cells and field-effect transistors<sup>2</sup>. One of the most important advantage of conjugated polymers is a rather facile tuning of their optical, spectroscopic, and electronic properties by appropriate design of their chain structure<sup>3</sup>.

Fused ring derivatives of aromatic or heteroaromatic molecules (e.g., fluorene, 3-alkylthiophenes and biphenylene) lead to more extended conjugation in the ground state, more planar molecular geometries and more rigid structures. These tend to increase the degree of conjugation, lower the HOMO-LUMO separation (band gap) and enable closer intermolecular interaction. A band gap is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels in the polymer.

Low-band gap conjugated polymers have attracted considerable interest in recent years to obtain intrinsically conducting materials and enhanced non-linear optical properties. One way to achieve low-band gap in conjugated polymers is to create an alternating arrangement of aromatic and quinoid units along the polymer chain thereby reducing the bond length alteration<sup>4</sup>. Many low-band gap polymers based on thiophene, either as a homopolymer (polythiophene) or in copolymers or as part of fused ring system and electron deficient quinoid-like heterocycles (e.g., benzothiadiazole, quinoxaline) were reported in the literature<sup>5</sup>.

Among the various linear  $\pi$ -conjugated systems developed during the past two decades, poly(thiophene) derivatives (PTs) have become the focus of considerable interest due to a unique combination of original electronic properties, environmental stability and structural versatility<sup>5</sup>. Recent advances in the synthesis and control of the regularity of poly(thiophene) chain have led to considerable progress in terms of structural definition, conjugated length and conductivity. These changes can be correlated to the reduction of the band gap which decreases from 2.20 eV<sup>6</sup> to values in the range of 1.70-1.80 eV<sup>7</sup>. Figure 1 shows some examples of ring systems (e.g., isothionaphthene (**1**), thianapyrazine (**2**)) and  $\pi$ -conjugated systems (bithienyl (**3**) and terthienyl (**4**)) containing the thiophene ring.

Given the interesting properties of polyfluorenes and poly(alkylthiophenes), recent work has focused on polycyclopentadithiophenes. Cyclopenta[2,1-b:3',4'-b']dithiophene (**3**), a bithienyl, was synthesized in the late 1960s by two groups<sup>8</sup>. Cyclopentadithiophene monomeric units can be used to synthesize copolymers with quinoxaline or fluorene to tune the electronic interaction.

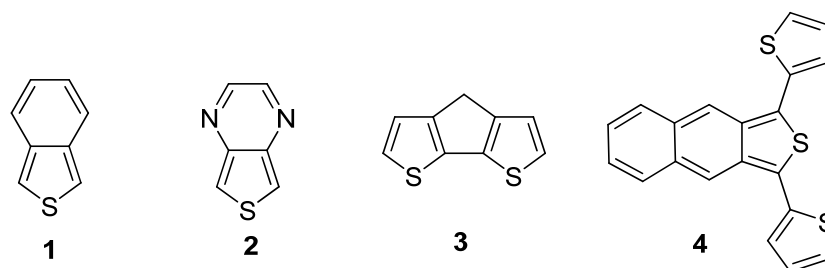


Figure 1. Examples of different  $\pi$ -conjugated systems.

## 2. Literature Review

The ability of chemists to design and synthesize conjugated organic copolymers remain the key to technological breakthrough using polymer materials in electronic and photonic devices and the development of nanoscale devices. The synthesis of low-band gap conjugated copolymers has been particularly rich in the recent past with the main purpose of producing polymers with high intrinsic conductivity.<sup>5</sup> Recently, low-band gap polymers have found for applications in infrared electrochromic displays and solar cells and most of these conducting copolymers are thiophene-based<sup>9</sup>. For example, poly(cyclopentadithiophene) and cyclopentadithiophene based copolymers have been investigated as semiconductor layers in field effect transistors<sup>10</sup>. Moreover, the energy gap can be altered by choosing suitable functional groups attached onto donor and acceptor partners and thus alter the electronic properties. Here, polymers or copolymers based on cyclopentadithiophene, quinoxaline and fluorene have been reviewed.

## 2.1 Cyclopentadithiophene monomeric sub-units

Many applications of polyfluorene copolymers have been discussed in the literature<sup>11</sup>. However, the high band gap energy of polyfluorenes (PFs) of ca. 3.1 eV represents a main disadvantage of this class of  $\pi$ -conjugated materials<sup>11</sup>. Therefore, the search for structurally related materials with lower band gap energy seems to be very challenging and promising. Polycyclopentadithiophenes are structural analogues of polyfluorenes based on thiophene which are important polymers to solve the problem found in polyfluorenes.

The cyclopentadithiophene unit is a combination of structural motif found in fluorene and oligothiophene which has six possible isomers that have been reported<sup>12</sup> (Figure 2).

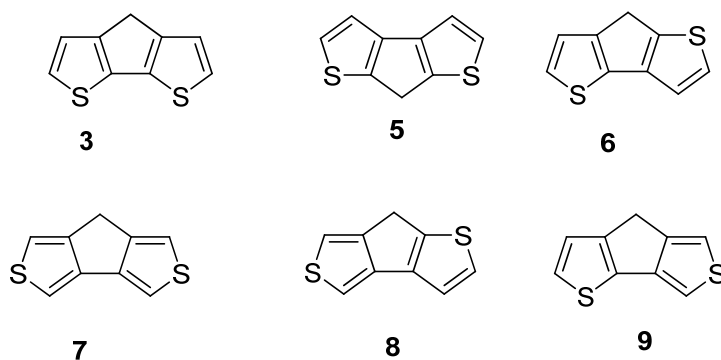
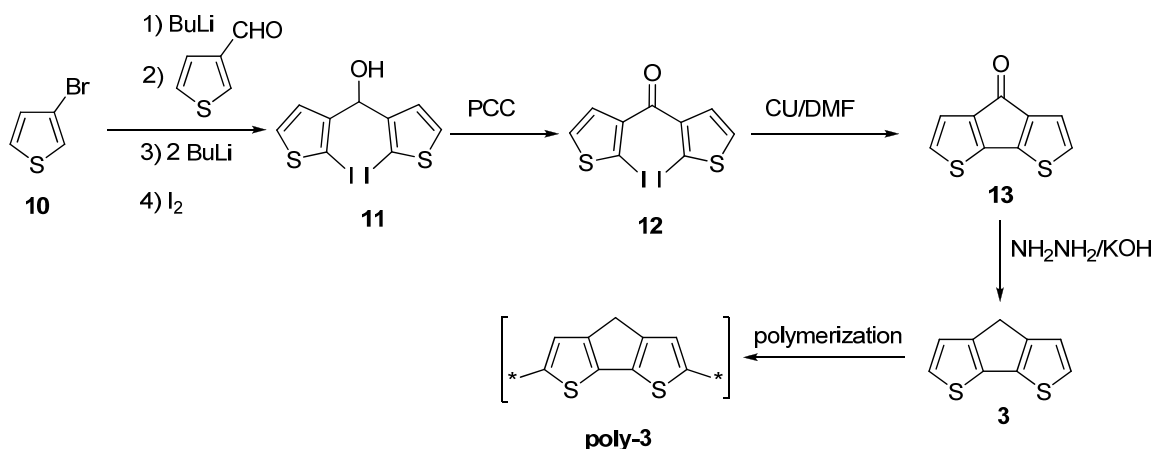


Figure 2. Possible isomers of cyclopentadithiophene.

Synthesis of these isomers was reported in the literature<sup>12</sup>. Scheme 1 shows the synthesis of isomer **3** and its polymerization reaction. The key step in the synthesis of cyclopentadithiophene (**3**) is the two-step one-pot double lithiation and iodination of 3-bromothiophene (**10**) through halogen-lithium exchange that gives the intermediate **11**<sup>12</sup>. Oxidation of **11** in the presence of PCC gives intermediate **12** and this intermediate undergoes coupling of thiophene rings in the presence of Cu/DMF to form 4H-cyclopenta[2,1-b;3,4-b']dithiophene-4-one

(13). Reduction of **13** with hydrazine in the presence of potassium hydroxide gives **3** (Scheme 1).

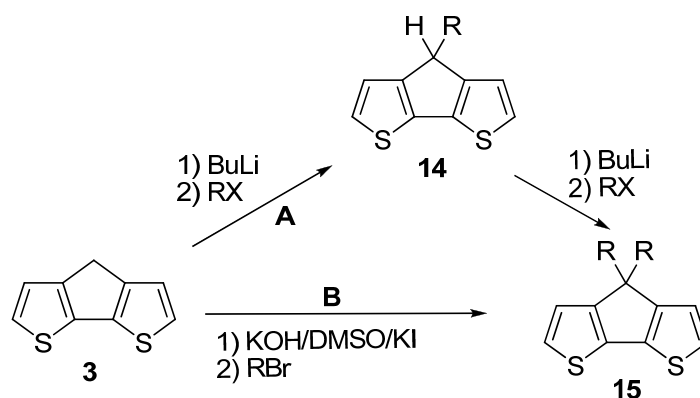


Scheme 1: Synthetic pathway to prepare cyclopentadithiophenes **13**, **3**, and **poly-3**.

Cyclopentadithiophene can be alkylated at the bridging carbon to advance its properties. Alkyl derivatives of **3** can be synthesized by lithiation of the acidic proton at the methylene position followed by quenching with the appropriate alkyl halide. This procedure gives both monoalkyl (**14**) and dialkyl (**15**) cyclopentadithiophene. Dialkylation can also readily be achieved by using potassium hydroxide in dimethylsulfoxide as deprotonating agent <sup>13</sup> (Scheme 2).

Increasing interest in the application of polythiophenes <sup>14</sup> led to the investigation of polymers based on cyclopentadithiophene (**3**). So, monomer **3** was subjected to different types of polymerization techniques.

Electropolymerization of monomer **3** gives a material, **poly-3**, showing a smaller HOMO-LUMO gap than unsubstituted polythiophene <sup>15</sup>. In 1994 Zotti *et al.* reported the electropolymerization of mono- and dialkyl-substituted derivatives of **3** <sup>16</sup>. The monoalkyl-substituted polymers (**poly-14**) proved to be mostly insoluble, while the dialkyl substituted polymers (**poly-15**) (Scheme 2), carrying alkyl chains equal or longer than four carbon units were reported to be soluble in chloroform.



Scheme 2: Mono- and dialkylation at the 4-position of 4H-cyclopenta[2,1-b;3,4-b']dithiophene (**3**)

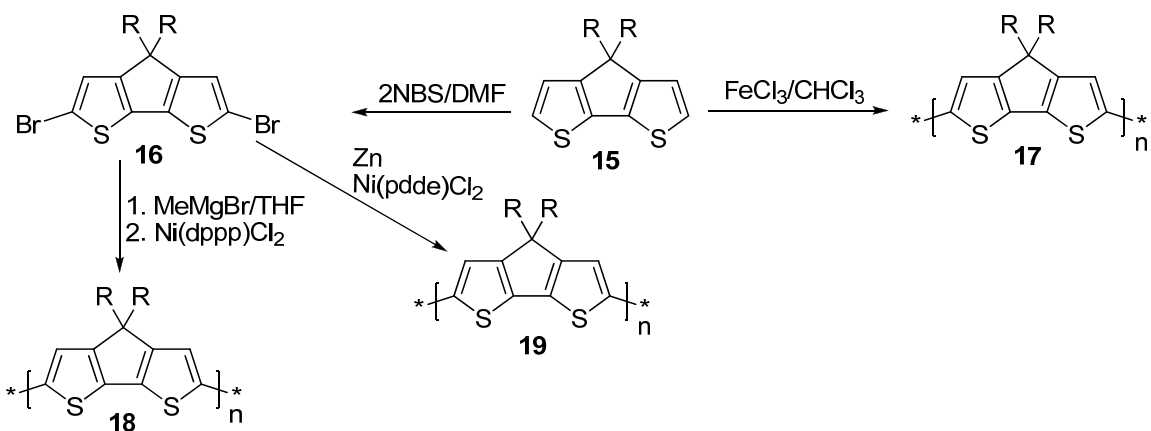
In 2001, Aswapirom and Scherf reported the first chemical polymerization of a dialkyl substituted cyclopentadithiophene, by Yamamoto reductive coupling to give solution processable polymers showing molecular weight in the range of 5-9000 g/mol<sup>17</sup>. These polymers were highly conjugated ( $\lambda_{\text{max}} = 565 \text{ nm}$ ) and showed weak red photoluminescence in solution centered at 639 nm. Having this in mind, three approaches to the synthesis of solution-processable poly(4,4-dialkylcyclopentadithiophenes) were reported<sup>18</sup>.

Oxidative polymerization of **15a-c** by  $\text{FeCl}_3$  gave the oxidized polymers **17a-c** (Scheme 3) as black powders after precipitation. Dedoping with hydrazine, followed by fractionation of the materials by multiple Soxhlet extractions, afforded the final polymers as blue solids that are soluble in chloroform **17a-c** and tetrahydrofuran **17b-c**.

Dibromination of **15a,b** with *N*-bromosuccinimide at room temperature in the dark condition gave **16a,b** in nearly quantitative yield. Monomers **16a,b** were polymerized by a nickel-catalyzed Kumada-type cross coupling<sup>19</sup> (Scheme 3), and involved a Grignard metathesis from methylmagnesium bromide to generate the active thienyl-Grignard intermediate<sup>20</sup>. Low yields of polymers **18a-b** of moderate molecular weight were isolated. The lower molecular weights of

polymers **18a,b** were attributed to incomplete Grignard metathesis and chain capping by residual methylmagnesium bromide.

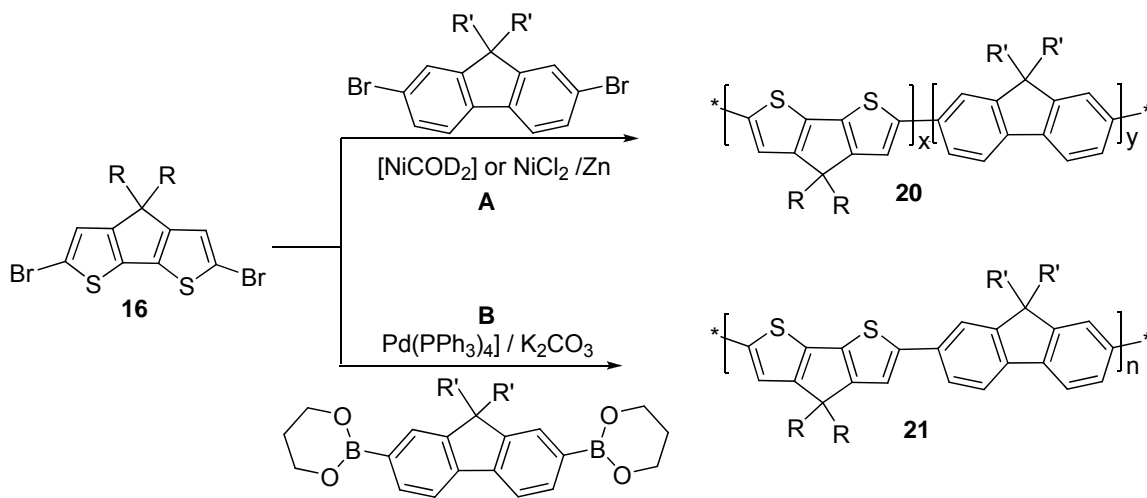
To avoid the undesirable chain-capping reaction, monomers **16a,b** were polymerized by an initial metathesis with Rieke-zinc to generate the thienyl-bromozinc intermediate<sup>21</sup>, and a Negishi-type polymerization catalyzed by Ni(dppe)Cl<sub>2</sub> led to the synthesis of polymers **19a,b** (Scheme 3). Purification by precipitation and repeated Soxhlet extraction gave polymers with moderate molecular weights that are generally lower than those achieved in an analogous preparation of poly-3-hexylthiophene (*M<sub>n</sub>* 12000, *p<sub>d</sub>* 1.3). However, the degrees of polymerization for polymers **19a,b** are higher than those of **18a,b**, suggesting that metathesis with Rieke-zinc is more suitable for the polymerization of 4,4-dialkylcyclopentadithiophenes.



Scheme 3: Synthetic route to monomer **16** and polymers **17-19** (a, R = hexyl; b, R = octyl; c, R = hexadecyl).

Solution processable cyclopentadithiophene can also form a copolymer with other monomers like dialkylated fluorene. Copolymer **20** prepared by Yamamoto reductive coupling (Scheme 4 path A)<sup>16</sup> showed characteristic properties typical of block copolymers with two UV-visible absorption bands, corresponding to segments of the parent homopolymers. Alternating copolymers have been

prepared by Suzuki cross coupling and these polymers (**21**) show a single-band UV-visible absorption.

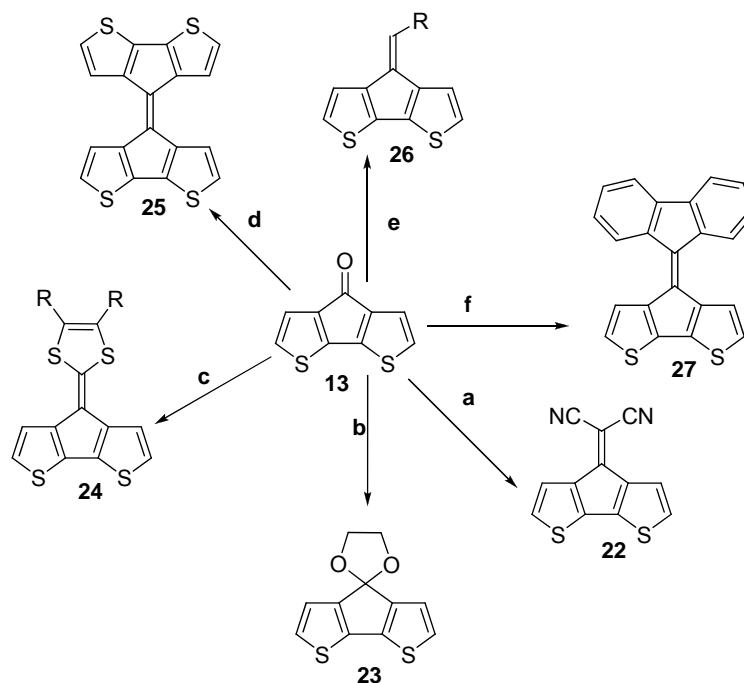


Scheme 4: Preparation of cyclopentadithiophene copolymers with dialkylfluorene.

Cyclopentadithiophene (**3**) can be functionalized at the bridging carbon to tune the HOMO-LUMO gap<sup>5</sup>. This ability to control the chemical nature of the cyclopentadithiophene enables the preparation of functionalized thiophene-based polymers by electropolymerization and therefore, it is possible to introduce a variety of substituents and molecular geometries in this position. Scheme 5 shows different functionalized cyclopentadithiophenes derived from cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-4-one (**13**).

Cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-4-one (**13**) can be treated in a Knoevenagel-like coupling to prepare 4-dicyanomethylene-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**22**) (Scheme 5). Electropolymerization of the resulting monomer forms the corresponding polymer which was first reported by Ferraris *et al.*<sup>22</sup>, and the resulting polymer exhibits a HOMO-LUMO gap of ca. 0.8 eV. It appears that the dicyanomethylene group extends the conjugation outside of the conjugated bithiophene and the presence of these groups lowers the band gap. The above result may lead to the conclusion that a significant reduction of the band gap ( $E_g$ )

in this type of polymer requires introduction of strong electron-withdrawing group at the  $sp^2$ -bridging carbon.



Reaction conditions

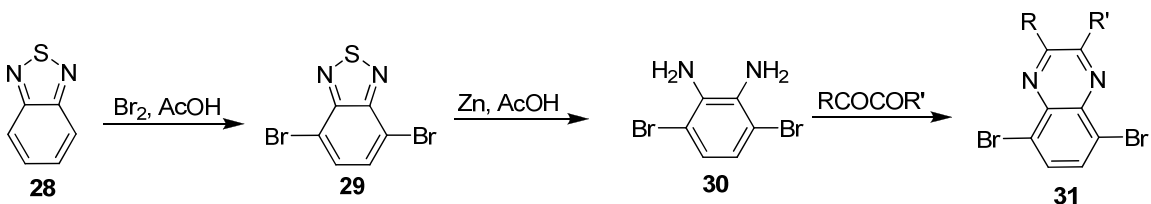
**a**  $CN_2CH_2$ , **b** Ethylene glycol, **c** Wittig-Horner condition, **d** Lawesson's reagent, **e** Wittig condition, **f** 2-lithiobiphenyl.

Scheme 5: Cyclopentadithiophene structures derived from 4H-cyclopenta[2,1b;3,4-b']dithiophene-4-one (**13**).

## 2.2 Quinoxaline monomeric sub-units

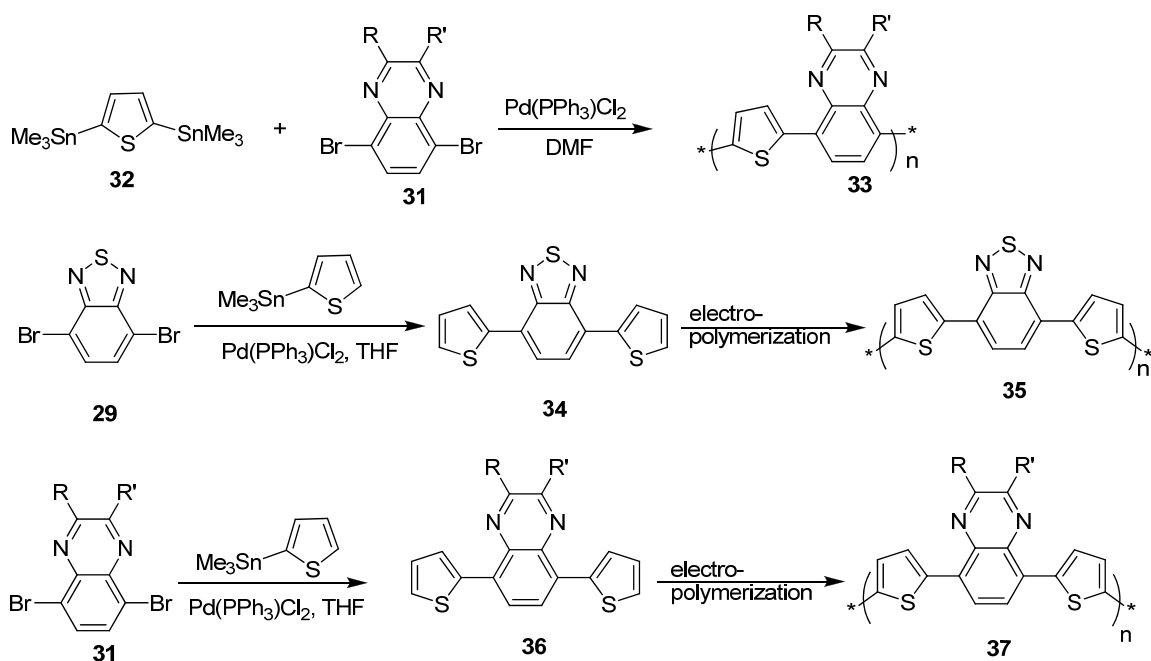
$\pi$ -Conjugated polymers containing electron withdrawing imine nitrogen have electron accepting properties and are susceptible to chemical and electrochemical reduction (or  $n$ -doping) to generate negatively charged carriers in the polymer chain and thus give conducting materials by reduction. Among the  $\pi$ -conjugated polymers with two imine nitrogens, poly(quinoxaline) derivatives are important groups, since the various dibromo-compounds are easily prepared and easily converted into the  $\pi$ -conjugated polymers by dehalogenation-polycondensation using different coupling reactions.

Quinoxaline is a colorless, crystalline, water-soluble powder with two imine groups which are formed by condensation of *o*-phenylenediamine with 1,2-dicarbonyl compounds. Synthesis of quinoxaline starts by bromination of 2,1,3-benzothiadizole (**28**) to form 4,7-dibromo-2,1,3-benzothiadizole (**29**) which can be reduced to dibromo-*o*-phenylenediamine (**30**) by the action of reducing agent like Zn in acetic acid. Reaction of this diamine with a suitable diketone yields dibromoquinoxaline (**31**) (Scheme 6). This building block serves as the starting-point to construct donor-acceptor repeating units by means of organometallic aryl-aryl coupling reactions like Grignard or Stille coupling<sup>23</sup>. Hence, a conjugated polymer with an alternating sequence of the appropriate donor- and acceptor- units in the main-chain may show a decreased band gap<sup>24</sup>.



Scheme 6: Synthesis of 4,7-dibromo-2,1,3-benzothiadizole **29** and dibromoquinoxaline **31**.

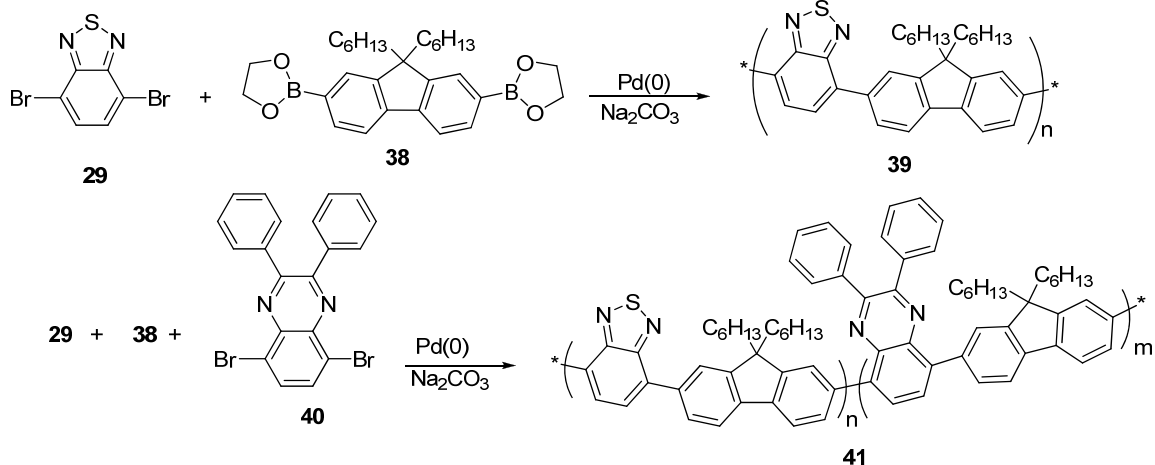
With these precursors, various donor-acceptor polymers containing quinoxaline or 2,1,3-benzothiadiazole as the acceptor and thiophene as the donor have been prepared (Scheme 7). Polymer **33** was prepared by Stille copolymerization of distannylthiophene (**32**) with dibromoquinoxaline (**31**) using a  $\text{Pd}(0)$  catalyst<sup>25</sup>. The Stille coupling, using a  $\text{Pd}(\text{II})$  species as a catalyst, also gives access to monomers **34** and **36** which were electropolymerized to polymers **35** and **37**, respectively.



Scheme 7: Synthesis of some D-A-D copolymers involving thiophene-quinoxaline or 2,1,3-benzothiadiazole monomeric unit.

Quinoxaline and benzothiadiazole can also form copolymers and alternating polymers with other monomers like fluorene. So, poly(benzothiadiazole-co-9,9-dihexylfluorene) (PBT) and poly[(benzothiadiazole-alt-9,9-dihexylfluorene)-co-(quinoxaline-alt-9,9-dihexylfluorene)] (PQBT) were synthesized by the palladium-catalyzed Suzuki cross-coupling reaction. The PBT and PQBT showed excellent solubility in common organic solvents such as chloroform, THF, and N,N-dimethylformamide (DMF)<sup>26</sup>.

Treatment of precursor **29** with fluorene monomeric unit **38** using palladium catalyzed Suzuki cross-coupling reaction provides copolymer, PBT (**39**). An alternating polymer PQBT (**41**), can also be formed by reacting compounds **29**, **38** and **40** (Scheme 8).



Scheme 8: Synthesis of PBT (**39**) and PQBT (**41**).

### 2.3 Fluorene monomeric sub-units

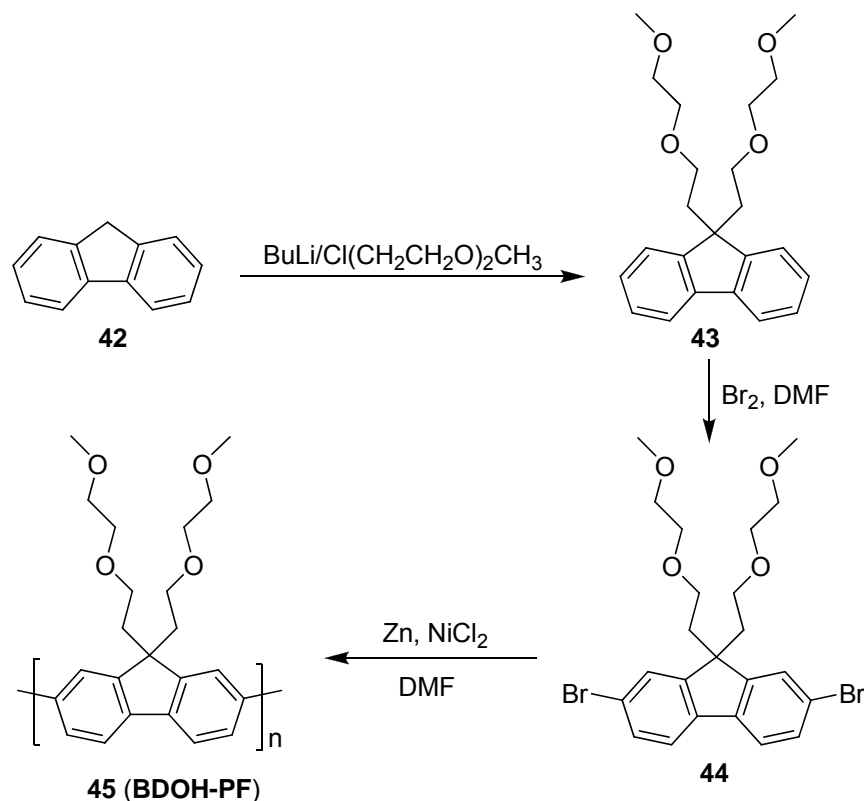
Fluorene is a polycyclic aromatic hydrocarbon that forms white crystals with a characteristic aromatic odor. It is an important starting material for the synthesis of conjugated polyfluorene materials.

Among the various conjugated polymers developed so far, polyfluorene derivatives are currently attracting much attention<sup>27,28</sup>. The high photoluminescence (PL) and electroluminescence (EL) efficiencies of polyfluorene derivatives make them promising candidates for use in PLED applications. The possibility of polymer chain alignment with liquid crystallinity is also a distinctive feature of polyfluorenes<sup>29,30</sup>.

Polyfluorenes were first developed as potential blue-light emitting materials<sup>31,32</sup> with a relatively large band gap. The confinement of the conjugation length has also been known to be a good way of attaining blue light emissions<sup>33</sup>. More recently, the manipulation of the emission wavelength and band gap of polyfluorenes has been achieved through copolymerization with other monomers like cyclopentadithiophene and quinoxaline as discussed in the previous

sections, and this makes polyfluorenes the only family of conjugated polymers that can emit the whole range of visible light.

Synthesis of polyfluorenes starts by functionalizing fluorene at the bridge position. For example, the synthesis of a high efficiency luminescent polymer, poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF) (**45**) starts by reacting fluorene (**42**) with two equivalents of butyllithium at  $-50\text{ }^{\circ}\text{C}$  in THF. The resulting 9-lithiofluorene was reacted with two equivalents of 1-chloro-2-(2-methoxyethoxy)ethane at  $-40$  to  $20\text{ }^{\circ}\text{C}$ , yielding 9,9-bis(3,6-dioxaheptyl)fluorene (**43**). Bromination of **43** with excess amount of bromine in DMF at  $22\text{ }^{\circ}\text{C}$  yields **44**. Reductive polymerization of **44** in DMF using zinc as the reductant and reactive nickel(0) as the catalyst produced light-yellow powders of BDOH-PF (**45**) (Scheme 9) after repeated dissolution in THF and precipitation in methanol<sup>34</sup>.



Scheme 9: Synthesis of poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF) (**45**).

### 3. Objectives of the project

The aim of this project is to synthesize some conjugated, low band gap, quinoxaline-containing copolymers by using palladium-catalyzed Suzuki cross-coupling reactions. Synthesis of quinoxaline and cyclopentadithiophene monomers will be attempted. In addition to these, polymerization reactions like reaction of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-*b*]pyrazine (**51**) with 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl) 9,9-dioctylfluorene and 2,7-bis(4''4''-,5'',5''-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dibenzylfluorene using tetrakis(triphenylphosphine)palladium(0) as a catalyst will be conducted. All reaction products will be characterized by using spectroscopic techniques.

## 4. Results and Discussion

In the course of this work, two polyfluorene copolymers were synthesized based on Suzuki coupling polymerization reactions. These were, poly(2,3-bis-(5-butylthiophen-2-yl)-5-[5-(9,9-dioctyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (**59**) and poly(2,3-bis-(5-butylthiophen-2-yl)-5-[5-(9,9-dibenzyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (**61**).

In addition, attempt was made to synthesize cyclopentadithiophene. The synthetic efforts that were made in this project and the results obtained are described below.

### 4.1 Synthesis of quinoxaline-based monomer

The quinoxaline-based monomer that was prepared is depicted by structure **51**. The synthesis of compound **51** requires the preparation of dione **48** and its condensation with 3,6-dibromo-1,2-phenylenediamine as a crucial step as described below.

#### 4.1.1 Synthesis of 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione (**48**)

Scheme 10 shows the synthesis of compound **48**. Thus, lithiation of thiophene (**46**) with *n*-butyllithium followed by reaction with 1-bromobutane in dry THF under reflux for 3 hours led to 2-butylthiophene (**47**) in 54.2% yield. The resulting compound was characterized by its <sup>1</sup>H- and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H NMR spectrum of compound **47** (Appendix 8) showed seven different proton environments, of which three are in the aromatic region and four are in the aliphatic region. The doublet of doublets at  $\delta$  7.21 integrating for one hydrogen corresponds to H-5 ( $J = 5.2, 0.4$  Hz). The  $J$  value of 5.2 Hz is due to coupling with H-4 which is a vicinal coupling while the four-bond coupling with H-3 has a magnitude of 0.4 Hz. The single hydrogen doublet of doublets at  $\delta$  7.03 can be

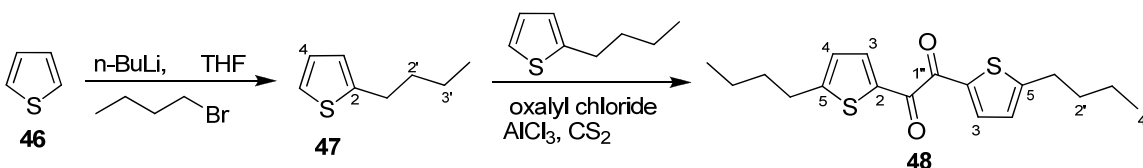
assigned to H-4 ( $J = 5.2$  Hz and  $3.2$  Hz). Another single hydrogen doublet of doublets at  $\delta$  6.89 corresponds to H-3 ( $J = 2.2, 0.8$  Hz) due to coupling with H-4 and allylic coupling with H-1'. The two hydrogens triplet at  $\delta$  2.95 corresponds to H-1' ( $J = 7.6$  Hz) due to coupling with H-2'. The two hydrogens quartet at  $\delta$  1.79 can be assigned to H-2' which has a coupling constant of  $7.6$  Hz due to coupling with H-1' and H-3'. The remaining peaks at  $\delta$  1.52 ( $m, J = 7.6$  Hz, 2H) H-3' and  $1.07$  ( $t, J = 7.6$  Hz, 3H) correspond to H-3' and H-4'.

The  $^{13}\text{C}$ -NMR spectrum of compound **47** (Appendix 7) showed eight carbon resonances, out of which four are in the aromatic region and four are in the aliphatic region. The most down field signal at  $\delta$  145.6 is a quaternary carbon at the substituted position of the thiophene moiety, C-2, which is further confirmed by the absence of peak in the DEPT-135 spectrum (appendix 8). The next most down field signal at  $\delta$  126.7 is due to C-4 of the thiophene ring. The other signals at  $\delta$  124.0 and 122.8 correspond to C-3 and C-5 of thiophene ring, respectively. These results were further confirmed by HH-COSY, HMBC, and HMQC spectra. The carbon signal in the aliphatic region at  $\delta$  34.0 is due to C-2' of the butyl group as was confirmed by HMBC. The resonance peak at  $\delta$  29.7 is attributable to C-1'. Here, the spectrum shows unexpected chemical shift for C-1' and C-2' due to the presence of thiophene group. The remaining carbon resonances at  $\delta$  22.3 and 13.9 are due to C-3' and C-4', respectively (Table 1).

Compound **47** was subsequently transformed to the  $\alpha$ -diketone **48** by treatment with oxalyl chloride and  $\text{AlCl}_3$  in  $\text{CS}_2$  as depicted in Scheme 10.

$\alpha$ -Diones have always attracted a great deal of interest in organic synthesis as versatile intermediates with very useful functional groups undergoing a wide variety of chemical transformations<sup>35</sup>.

The formation of aromatic  $\alpha$ -diketo-compounds through either inter- or intramolecular Friedel-Crafts reaction with oxalyl chloride is limited to only a few examples due to strong tendency of oxalyl chloride to form  $\text{COCl}_2$  or  $\text{COCl}^{\cdot}$  which subsequently substitutes hydrogen atom (aliphatic or aromatic) by chlorocarbonylation<sup>36</sup>.



Scheme 10: Synthesis of 2-butylthiophene (**47**) and 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione (**48**).

The  $^1\text{H-NMR}$  of spectrum of compound **48** (Appendix 9) displayed the presence of six different proton environments. of these, two are in the aromatic region and four are in the aliphatic region. The single hydrogen doublet at  $\delta$  7.85 ( $J = 4.0$  Hz) is assigned to H-3 and the signal at  $\delta$  6.87 ( $J = 4.0$  Hz) can be attributed to H-4. The triplet at  $\delta$  2.87 ( $J = 7.6$  Hz), the multiplet at  $\delta$  1.69 ( $J = 7.6$  Hz), the multiplet at  $\delta$  1.39 ( $J = 7.6$  Hz) and the triplet at  $\delta$  0.93 ( $J = 7.6$  Hz) correspond to H-1', H-2', H-3', H-4' protons of the butyl group, respectively.

The  $^{13}\text{C-NMR}$  spectrum of compound **48** (Appendix 10) displayed nine carbon signals of which three are due to quaternary carbons, two are due to methine carbons, three are due to methylene carbons and one is due to a methyl carbon. The signals at  $\delta$  182.5, 159.9, and 136.5 are due to quaternary carbons corresponding to carbonyl carbon, C-2 and C-5 of the thiophene moieties, respectively as confirmed by the absence of peaks in the DEPT-135 spectrum (Appendix 11). The signal at  $\delta$  137.7 is due to C-3 of the thiophene moieties. This peak appears down field from the corresponding carbon signal in the  $^{13}\text{C}$  NMR of compound **47** due to the attachment of carbonyl group which is an electron-withdrawing group. The other signal at  $\delta$  126.5 can be accounted for C-4. In the

aliphatic regions the carbon signals at  $\delta$  33.34, 30.49, 22.13 and 13.75 can be assigned to C-2', C-1', C-3', C-4', respectively. of the butyl group. The data from  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and DEPT-135 agree with the structure of compound **48** (Table 1).

**Table 1:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) data  $\delta_{\text{ppm}}$ : of compounds **47** and **48**

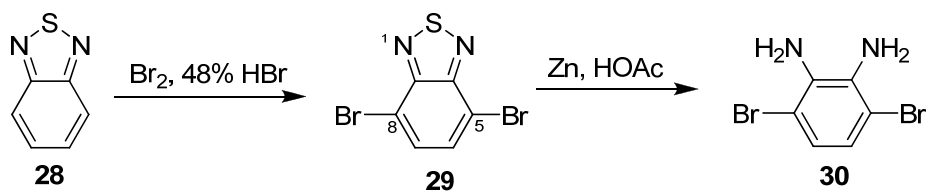
| <b>47</b>   | <b>48</b>                                   |
|---|---|
| 7.21<br>(1H, <i>dd</i> , $J = 5.2$ Hz, 0.4 Hz, H-5) | 7.85<br>(2H, <i>d</i> , $J = 4.0$ Hz, H-3)  |
| 7.03<br>(1H, <i>dd</i> , $J = 5.2$ Hz, 3.2 Hz, H-4) | 6.87<br>(2H, <i>d</i> , $J = 4.0$ Hz, H-4)  |
| 6.89<br>(1H, <i>dd</i> , $J = 2.2$ Hz, 0.8 Hz, H-3) | 2.87<br>(4H, <i>t</i> , $J = 7.6$ Hz, H-1') |
| 2.95<br>(2H, <i>t</i> , $J = 7.6$ , H-1')           | 1.69<br>(4H, <i>p</i> , $J = 7.6$ Hz, H-2') |
| 1.79<br>(2H, <i>p</i> , $J = 7.6$ , H-2')           | 1.39<br>(4H, <i>m</i> , $J = 7.6$ , H-3')   |
| 1.52<br>(2H, <i>m</i> , $J = 7.6$ , H-3')           | 0.93<br>(6H, <i>t</i> , $J = 7.2$ , H-4')   |
| 1.07<br>(3H, <i>t</i> , $J = 7.2$ , H-4')           |   |

**Table 2:**  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ), data  $\delta_{\text{ppm}}$ : of compounds **47** and **48**

| Carbon | <b>47</b> | <b>48</b> |
|--------|-----------|-----------|
| 1'     | 29.7      | 30.5      |
| 2'     | 34.1      | 33.3      |
| 3'     | 22.3      | 22.1      |
| 4'     | 13.9      | 13.7      |
| 1''    | ---       | 182.5     |
| 2      | 145.9     | 126.5     |
| 3      | 124.0     | 137.7     |
| 4      | 126.7     | 126.5     |
| 5      | 122.8     | 159.5     |

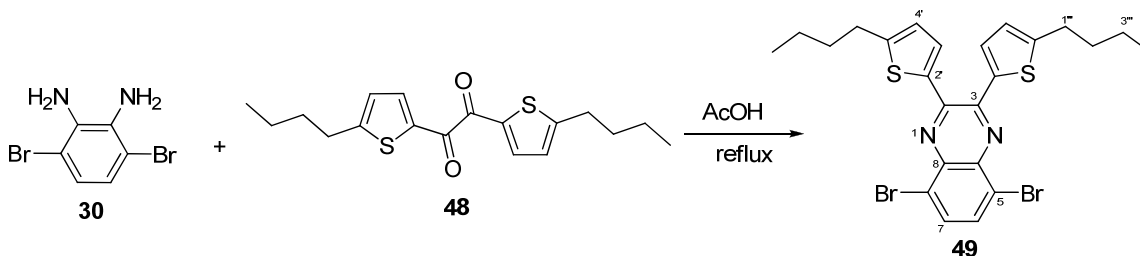
#### 4.1.2 Synthesis of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis-(5-butylthiophen-3-yl)thieno[3,4-*b*]pyrazine (**51**)

The synthesis of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-*b*]pyrazine (**51**) began by bromination of 2,1,3-benzothiadiazole (**28**) (Scheme 11). Thus, treatment of 2,1,3-benzothiadiazole (**28**), with  $\text{Br}_2$  and aqueous HBr (48%) under reflux gave 4,7-dibromobenzo(2,1,3)thiadiazole (**29**) as a gray solid which melted at 175-177  $^{\circ}\text{C}$ . The crude product was recrystallized from isopropanol to give compound **29** in a pure form as revealed by its  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra. Thus, the  $^1\text{H}$ -NMR spectrum of **29** displayed only one singlet at  $\delta$  7.73 in the aromatic region. The  $^{13}\text{C}$ -NMR spectrum showed only three carbon resonances at  $\delta$  152.9, 132.4, 113.9 in the aromatic region of which the signals at  $\delta$  152.9, 132.4 are due to quaternary carbon as evidenced by the DEPT-135 spectrum.



Scheme 11: Bromination and reduction of 2,1,3-benzothiadiazole (**28**).

Reduction of 4,7-dibromobenzo(2,1,3)-thiadiazole (**29**) was accomplished by reacting it with zinc dust in acetic acid<sup>37</sup> for three hours (Scheme 11). Since the resulting diamine was expected to be photochemically degraded, compound **29** was not isolated. As soon as the reduction reaction was completed, which was checked by TLC, the mixture was filtered and to the filtrate was added 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione (**48**). This reaction was done by heating the mixture at 50 °C for four hours. The resulting yellow solid was purified by column chromatography on silica gel using petroleum ether:toluene (4:1) as eluent to afford 5,8-dibromo-2,3-bis(5-butylthiophen-2-yl)quinoxaline (**49**) (Scheme 12) which melted at 125-127 °C.



Scheme 12: Synthesis of 5,8-dibromo-2,3-bis(5-butylthiophen-2-yl)quinoxaline (**49**).

The  $^1\text{H-NMR}$  spectrum of compound **49** (Appendix 12) showed seven signals, of which three are in the aromatic region and four are in the aliphatic region. The two-hydrogen singlet at  $\delta$  7.78 is due to H-6 and H-7. The two hydrogens doublet centered at  $\delta$  7.44 ( $J = 3.6$  Hz) was assigned to H-3'. The other two-hydrogen doublet at  $\delta$  6.74 ( $J = 3.6$  Hz) is attributable to H-4'. The triplet at  $\delta$  2.89 ( $J = 7.4$  Hz), the quintet at  $\delta$  1.76 ( $J = 7.2$  Hz), the multiplet at  $\delta$  1.47 ( $J = 7.4$  Hz) and the

triplet at  $\delta$  0.99 ( $J = 7.2$  Hz) correspond to H-1''', H-2''', H-3''', H-4''' protons of the butyl group, respectively (Table 3).

The  $^{13}\text{C}$ -NMR and DEPT-135 spectra of compound **49** (Appendices 13 & 14) indicate twelve carbon signals. Of which, five are due to quaternary carbon atoms which appeared at  $\delta$  152.0, 147.2, 138.5, 138.3 122.9. The most down field signal is due to the equivalent carbons, C-2 and C-3. This deshielding effect is due to the presence of neighboring electronegative nitrogen atoms. The signal at  $\delta$  147.2 corresponds to C-5' due to the presence of adjacent sulfur which withdraws electron density from C-5'. The carbon resonance at  $\delta$  138.5 is assignable to the equivalent carbons, C-9 and C-10. The remaining signals at  $\delta$  138.3 and  $\delta$  122.9 are due to C-2' and the equivalent carbons, C-5 and C-8, respectively. The last peak is relatively up field because of the presence of bromine as a substituent. Other carbon resonance signals at  $\delta$  132.6, 130.4, 125.0, 33.6, 30.2, 22.3, and 13.9 are due to C-6 and C-7, C-4', C-3', C-2''' C-1''' C-3''', C-4''', respectively (Table 4).

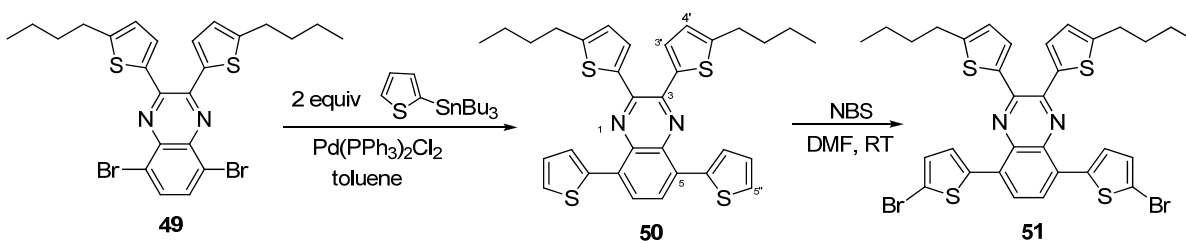
Compound **49** was subjected to Stille coupling reaction with tributyl(thiophen-2-yl)stannane in the presence of bis-(triphenylphosphine)palladium(II) chloride as a catalyst to form compound **50** in 94.5% yield which melts at 111-113 °C. This reaction was done by using high boiling solvent, toluene, to allow high temperature for the reaction. Initial attempt to carryout the reaction in THF failed due to the low boiling point of the solvent that did not allow high enough refluxing temperature.

The  $^1\text{H}$ -NMR spectrum of compound **50** (Appendix 15) shows ten proton signals, six of these are resonate in the aromatic region and the remaining signals are in the aliphatic region. The most down field, two-hydrogen singlet signal at  $\delta$  8.00 is due to H-6 and H-7. The doublet signal at  $\delta$  7.89 ( $J = 3.6$  Hz) integrating for two-hydrogens correspond to H-5''. The two-hydrogen doublet at  $\delta$  7.55 ( $J = 4.80$  Hz) matches up to H-3''. The doublet signals at  $\delta$  7.45 and 6.72 which integrated for

two hydrogens each, belong to H-3' and H-4', respectively. The two-hydrogen doublet of doublet at  $\delta$  7.22 ( $J = 3.6$  Hz) and ( $J = 4.6$  Hz) correspond to H-4'. The triplet at  $\delta$  2.99 ( $J = 7.4$ ), the *pent* at  $\delta$  1.76 ( $J = 7.2$ ), the multiplet at  $\delta$  1.52 ( $J = 7.4$ ) and the triplet at  $\delta$  1.01 ( $J = 7.2$ ) correspond to H-1''', H-2''', H-3''', H-4''' protons of the butyl group, respectively (Table 3).

The  $^{13}\text{C}$ -NMR and DEPT-137 spectra of compound **50** (Appendices 16 & 17) indicate a total of sixteen carbon signals that contain quaternary, methine, methylene and methyl species. Carbon signals at  $\delta$  150.8, 144.8, 139.2, 138.8 and 136.4 are quaternary carbons and correspond to C-2 and C-3, C-5', C-2'', C-9 and C-10, and C-2', respectively. The other carbon signals in the aromatic region, which are methine species, appeared at  $\delta$  130.6, 130.0, 128.5, 126.9, 126.8, 126.7, and 124.7 are attributable to C-5 and C-8, C-6 and C-7, C-4'', C-5'', C-4', C-3'', C-3', respectively. Resonance signals at  $\delta$  33.6, 30.2, 22.3 and 13.9 are due to butyl group (Table 4). The data from  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and DEPT-135 agree with the structure of compound **50**.

Compound **50** was brominated using NBS in DMF and chloroform mixture to provide 5,7-bis(5'-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-*b*]pyrazine (**51**) in 46.9% yield (Scheme 13) as a reddish solid.



Scheme 13: Synthesis of compounds **50** and **51**.

The  $^1\text{H}$ -NMR spectrum of compound **51** (Appendix 18) showed nine proton resonance signals which differ from compound **50** by one hydrogen signal due to

the substitution of hydrogens by bromines on the thiophene rings. The singlet signal at  $\delta$  7.89 integrating for two equivalent hydrogens corresponds to H-6 and H-7. The other hydrogen resonances in the aromatic region at  $\delta$  7.52 (*d*, *J* = 4.0 Hz), 7.41 (*d*, *J* = 3.6 Hz), 7.11 (*d*, *J* = 4.0 Hz) and 6.75 (*d*, *J* = 3.6 Hz) correspond to H-3', H-3'', H-4' and H-4'', respectively.

The  $^{13}\text{C}$ -NMR and DEPT-135 spectra of compound **51** (Appendix 19) displayed a total of sixteen carbon signals attributable to seven quaternary, five methine, three methylene, and one methyl carbons. Carbon signals at  $\delta$  151.3, 145.2, 139.7, 138.7, 135.8, 130.0 and 116.7 are quaternary carbons and corresponds to C-2 & C-3, C-5', C-2'', C-9 & C-10, C-2', C-6 & C-7 and C-3', respectively. The other five signals in the aromatic region at  $\delta$  130.3, 129.2, 125.8, 125.6, 124.8 are methine carbon signals and correspond to C-5 & C-8, C-4'', C-5'', C-4', C-3''. The signals at  $\delta$  33.6, 30.2, 22.3 and 13.9 correspond to C-2''', C-1''', C-3''', C-4''', respectively (Table 4). The data from  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and DEPT-135 agree with the structure of compound **51**.

**Table 3:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) data  $\delta_{\text{ppm}}$  of compounds 49, 50 and 51.

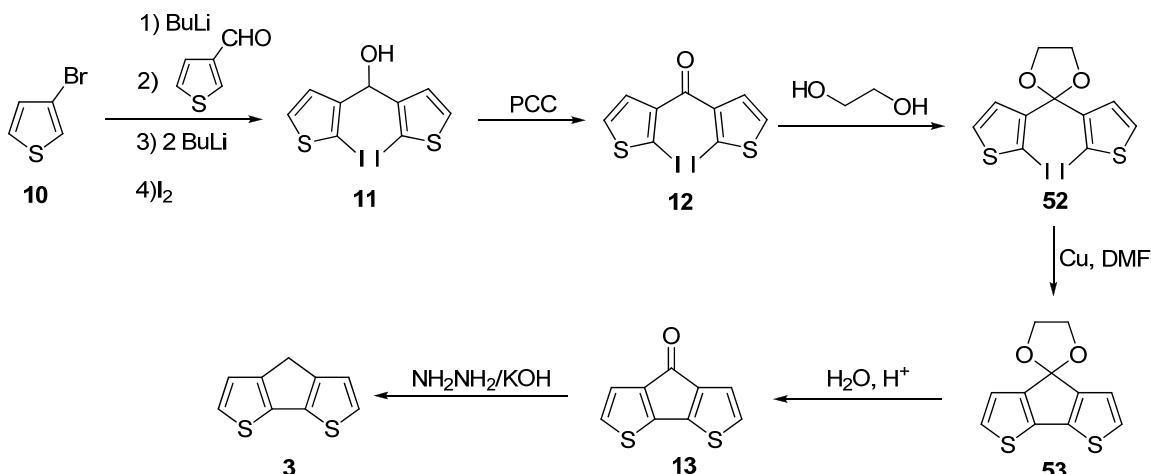
| 49                                      | 50                                    | 51                                    |
|---|---------------------------------------|---------------------------------------|
| 7.78<br>(2H, s, H-6, H-7)               | 7.99<br>(2H, s, H-6, H-7),            | 7.89<br>(2H, s, H-6, H-7)             |
| 7.44<br>(2H, d, $J = 3.6$ Hz, H-3')     | 7.89<br>(2H, d, $J = 3.6$ Hz, H-5'')  | 7.52<br>(2H, d, $J = 4.0$ Hz, H-3')   |
| 6.74<br>(2H, d, $J = 3.6$ Hz, H-4')     | 7.55<br>(2H, d, $J = 4.8$ Hz, H-3'')  | 7.41<br>(2H, d, $J = 3.6$ Hz, H-3'')  |
| 2.89<br>(4H, t, $J = 7.6$ Hz, H-1''')   | 7.45<br>(2H, d, $J = 3.6$ Hz, H-3')   | 7.11<br>(2H, d, $J = 4.0$ Hz, H-4')   |
| 1.76<br>(4H, p, $J = 7.6$ Hz, H-2''')   | 7.22<br>(2H, t, $J = 3.6$ Hz, H-4'')  | 6.75<br>(2H, d, $J = 3.6$ Hz, H-4'')  |
| 1.47<br>(4H, sex, $J = 7.6$ Hz, H-3''') | 6.75<br>(2H, d, $J = 3.6$ Hz, H-4')   | 2.95<br>(2H, t, $J = 7.2$ Hz, H-1''') |
| 0.99<br>(6H, t, $J = 7.2$ , H-4''')     | 2.94<br>(4H, t, $J = 7.6$ Hz, H-1''') | 1.81<br>(2H, p, $J = 7.2$ Hz, H-2''') |
|   | 1.79<br>(4H, m, $J = 7.6$ Hz, H-2''') | 1.51<br>(2H, m, $J = 7.2$ Hz, H-3''') |
|   | 1.49<br>(4H, m, $J = 7.2$ Hz, H-3''') | 1.02<br>(3H, t, $J = 7.2$ Hz, H-4''') |
|   | 1.03<br>(6H, t, $J = 7.2$ Hz, H-4''') |                                       |

**Table 4:**  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ) data  $\delta_{\text{ppm}}$ : of compounds **49**, **50** and **51**

| Carbon | <b>49</b> | <b>50</b> | <b>51</b> |
|--------|-----------|-----------|-----------|
| 2, 3   | 152.0     | 150.8     | 151.3     |
| 5'     | 147.2     | 144.8     | 145.2     |
| 9, 10  | 138.5     | 138.8     | 138.7     |
| 2'     | 138.3     | 136.4     | 135.8     |
| 6, 7   | 132.6     | 130.0     | 130.0     |
| 4'     | 130.4     | 126.8     | 125.6     |
| 3''    | 125.0     | 126.7     | 124.8     |
| 5, 8   | 122.9     | 130.6     | 130.3     |
| 2''    | --        | 139.2     | 139.3     |
| 3''    | --        | 126.7     | 124.8     |
| 4''    | --        | 128.5     | 129.2     |
| 2'''   | 33.6      | 33.6      | 33.6      |
| 1'''   | 30.2      | 30.2      | 30.2      |
| 3'''   | 22.3      | 22.3      | 22.3      |
| 4'''   | 13..9     | 13.9      | 13.9      |

## 4.2 Attempts toward the synthesis of cyclopentadithiophene-based monomers

Attempt was made to synthesize cyclopentadithiophene (**3**) in the course of this project. Scheme 14 shows the general synthetic strategy for the synthesis of compound **3**.



Scheme 14: General synthetic strategy towards the synthesis of cyclopentadithiophene (3).

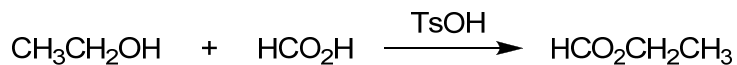
#### 4.2.1 Synthesis of compounds 55 and 56.

The attempted syntheses of cyclopentadithiophene commenced with the synthesis of bis-(3-thienyl)-methanol (55) starting from 3-bromothiophene (10). Since ethyl formate that was required for the reaction was not available, we had to prepare this compound by esterifying formic acid with ethanol in the presence of an acid catalyst (Scheme 15). The reaction product was purified by extraction with sodium hydrogen carbonate and brine solution followed by distillation. This reaction was successful as evidenced by the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the final product.

The <sup>1</sup>H-NMR spectrum of ethyl formate (Appendix 1) showed three signals. The one hydrogen singlet at  $\delta$  7.89 is due to hydrogen directly attached to the ester carbonyl. The two-hydrogen quartet at  $\delta$  4.04 ( $J = 7.2$  Hz) correspond to methylene group and the triplet signal at  $\delta$  1.42 ( $J = 7.2$ ) integrating for three protons is due to the methyl group.

The <sup>13</sup>CNMR and DEPT-135 spectra (Appendices 2 &3) displayed three carbon signals, of which the signal that appeared at  $\delta$  160.9 is due to the ester carbonyl

carbon and the remaining signals at  $\delta$  59.6 and 13.8 correspond to the methylene and methyl carbon, respectively.



Scheme 15: Preparation of ethyl formate.

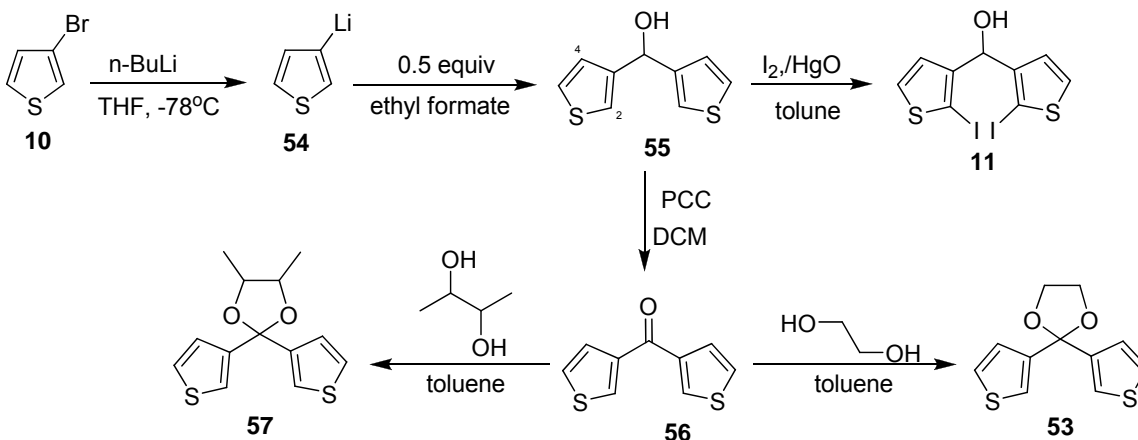
Once we had all starting materials on hand, synthesis of compound **55** was started by treating 3-bromothiophene (**10**) with *n*-butyllithium followed by addition of 0.5 equivalent of ethyl formate. Compound **55** (Scheme 16) was obtained in 29% yield, after purification of the product mixture by column chromatography on silica gel using dichloromethane as eluent.

The  $^1\text{H}$ -NMR spectrum of compound **55** (Appendix 20 and Table 5) signifies the presence of five environmentally different hydrogen signals. In the aromatic region, the most down field signal at  $\delta$  7.32 (*dd*,  $J = 5.0$  Hz, 3.2 Hz) corresponds to H-5. The larger  $J$  value is due to coupling with H-4 and the lower  $J$  value is due to coupling with H-2. The one-proton signal at  $\delta$  7.23 (*dd*,  $J = 1.6$  Hz, 0.8 Hz) is attributable to H-2. The signal at  $\delta$  7.05 ( $J = 5.0$  Hz, 1.2 Hz) is ascribable to H-4. The other signals in the up field region are observed at  $\delta$  5.89 (s) and 2.56 (s). The signal at  $\delta$  5.89 is assigned to the methine proton sitting on the carbon atom carrying the OH group. The most up field peak at  $\delta$  2.56 corresponds to the OH hydrogen.

The  $^{13}\text{C}$ -NMR of spectrum of compound **55** (Appendix 21 and Table 6) showed five carbon signals of which four resonated in the aromatic region while the remaining signal appeared in the aliphatic region. The quaternary carbon resonance at  $\delta$  144.9 is due to C-3 of thiophene ring. The other signals appeared at  $\delta$  126.4 (C-4),  $\delta$  126.3 (C-5), 121.8 (C-2) and  $\delta$  69.1 (C-1').

Compound **55** was subjected to iodination reaction with  $\text{I}_2/\text{HgO}$  mixture to introduce iodine at the 2-position of thiophene ring. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra

of the yellowish compound obtained from this reaction gave no indication of iodination taking place at C-2 of the thiophene rings. It was also not possible to work out the structure of the product based on the available NMR data.



Scheme 16: Synthesis of compounds **55** and **56**.

Treatment of compound **55** with pyridinium chlorochromate as oxidizing agent and dichloromethane as a solvent gave compound **56** in 70% yield. Compound **56** was characterized by its <sup>1</sup>H- and <sup>13</sup>C-NMR as described below.

The <sup>1</sup>H-NMR spectrum of compound **56** (Appendix 23 and Table 6) showed the presence of three signals integrating for one hydrogen each. The doublet of doublets signal at  $\delta$  8.03 corresponds to H-5. The other doublet of doublets at  $\delta$  7.63 corresponds to H-2 and the signal at  $\delta$  7.40 (*dd*) corresponds to H-4.

The <sup>13</sup>C-NMR spectrum of compound **56** (Appendix 23) showed five carbon signals, two of these are quaternary carbon signals at  $\delta$  183.3 and  $\delta$  142.1 as confirmed by the absence of signals in the DEPT-135 spectrum (Appendix 24) and correspond to carbonyl carbon and C-3 of thiophene rings. The other down field signal at  $\delta$  132.7 corresponds to C-4. The signals at  $\delta$  128.3 and  $\delta$  126.4 are assignable to C-2 and C-5, respectively. The data obtained from <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and DEPT-135 agreed with structure **56**.

Attempt was made to protect the carbonyl group in 56 by treatment with ethylene glycol and 2,3-butandiol and an acid catalyst in two different reaction pathways to provide compound **53** and **57**, respectively (Scheme 16). After allowing the reactions to take place for 6 days, the resulting products were isolated and characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR and showed mixtures of the starting materials and product. Since the quantity of reaction product was too small, no further attempts were made to separate the mixture.

**Table 5:** <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) data δ<sub>ppm</sub> of compounds **55**, **56**.

| <b>55</b>  | <b>56</b>  |
|--|--|
| 7.32<br>(2H, <i>dd</i> , <i>J</i> = 5.0 Hz, 3.2 Hz, H-2) | 8.05<br>(2H, <i>dd</i> , <i>J</i> = Hz, Hz, H-5)         |
| 7.23<br>(2H, <i>dd</i> , <i>J</i> = 1.6 Hz, 0.8 Hz, H-4) | 7.63<br>(2H, <i>dd</i> , <i>J</i> = 1.6 Hz, 0.8 Hz, H-2) |
| 7.05<br>(2H, <i>dd</i> , <i>J</i> = 5.0 Hz, 1.2 Hz, H-5) | 7.40<br>(2H, <i>dd</i> , <i>J</i> = Hz, Hz, H-4)         |
| 5.9<br>(1H, <i>s</i> , H-6)                              |  |
| 2.56<br>(1H, <i>s</i> , alcoholic-H)                     |  |

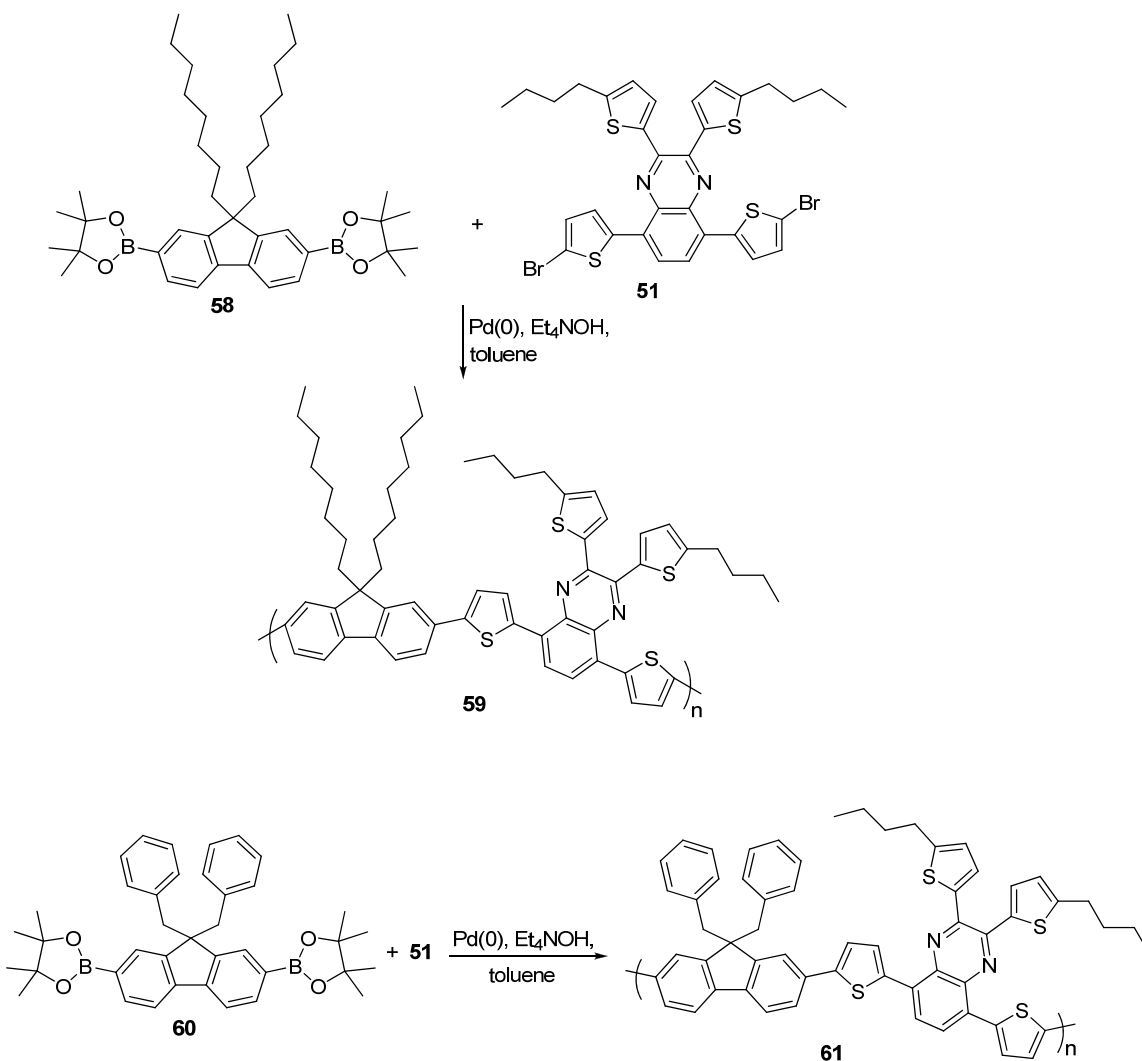
**Table 6:**  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ), data  $\delta_{\text{ppm}}$  of compounds **55** and **56**.

| Carbon | <b>55</b> | <b>56</b> |
|--------|-----------|-----------|
| 2      | 121.8     | 126.4     |
| 3      | 144.9     | 142.1     |
| 4      | 126.4     | 132.7     |
| 5      | 126.3     | 128.3     |
| 6      | 69.1      | 183.3     |

### 4.3 Synthesis of copolymers

Once we have all monomers on hand, the next step would be synthesis of conjugated polymers containing substituted fluorene and quinoxaline moieties. Two polymers were prepared by the reaction of compound **51** with two 9,9-disubstituted fluorine derivatives as discussed below. Scheme 17 showed the synthesis of the polymers. Thus, poly(2,3-Bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dioctyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (**59**) was prepared by reacting compound **51** with **58** and poly(2,3-Bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dibenzyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline) (**61**) which was prepared from monomers **51** and **60**. Monomer **58** was synthesized by Yaddessa Melaku<sup>38</sup> and monomer **60** was synthesized by Zekarias Yakob<sup>39</sup>. The copolymers were synthesized by using a modified Suzuki coupling reaction with tetrakis(triphenylphosphine)palladium(0) as a catalyst and tetraethylammonium hydroxide as the base with bromobenzene and phenylboric acid employing for end capping with phenyl rings. Low molecular weight oligomers were separated by Soxhlet extraction with ether and higher molecular weight polymers were extracted with chloroform. Both polymers are brown powders but the chloroform solution of these polymers is deep red. When

chloroform solutions of the polymers were exposed to 365 nm UV-light they gave red fluorescence.



Scheme 17: Synthesis of copolymers **59** and **61**.

The UV-Vis spectrum of a thin film of polymer **59** (Figure 3) on glass gave an absorption maxima ( $\lambda_{\text{max}}$ ) 547 nm. On the other hand, a chloroform solution of the polymer had an absorption maximum at 531 nm (Table 7). The optical band gap of this polymer, which was the onset of absorption, was determined to be 1.8 eV and 2.0 eV for thin film and solution, respectively.

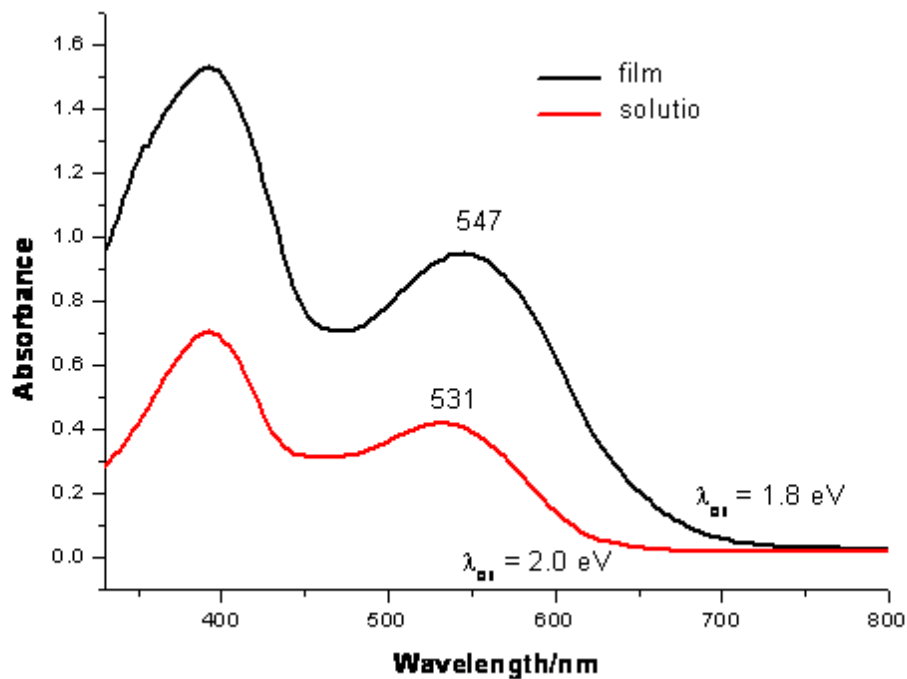


Figure 3. UV-vis spectrum of polymer **59**.

Cyclic voltammetry (CV) was employed to estimate the HOMO and LUMO energy levels of the polymer. The polymer films dip-coated on a Pt electrode were scanned positively and negatively separately in a 0.10 M tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ ) solution in anhydrous acetonitrile. Figure 4 and 6 depicts the CV curves of both the *p*- and *n*-doping processes of the polymers. Thus, cyclic voltammogram of polymer **59** (Figure 4) gave the band gap value of 2.2 eV.

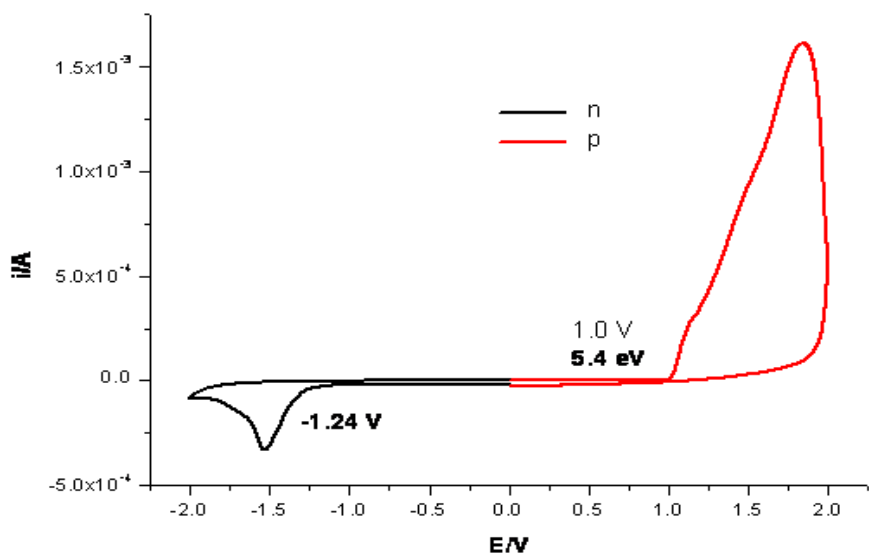


Figure 4. Cyclic voltammogram of polymer **59**.

The UV-Vis spectrum of a thin film of polymer **61** (Figure 5) on glass gave an absorption maxima ( $\lambda_{\text{max}}$ ) showed 533 nm. On the other hand, a chloroform solution of the polymer had an absorption maximum at 522 nm. The optical band gap of this polymer was 1.8 eV and 2.0 eV for film and solution, respectively.

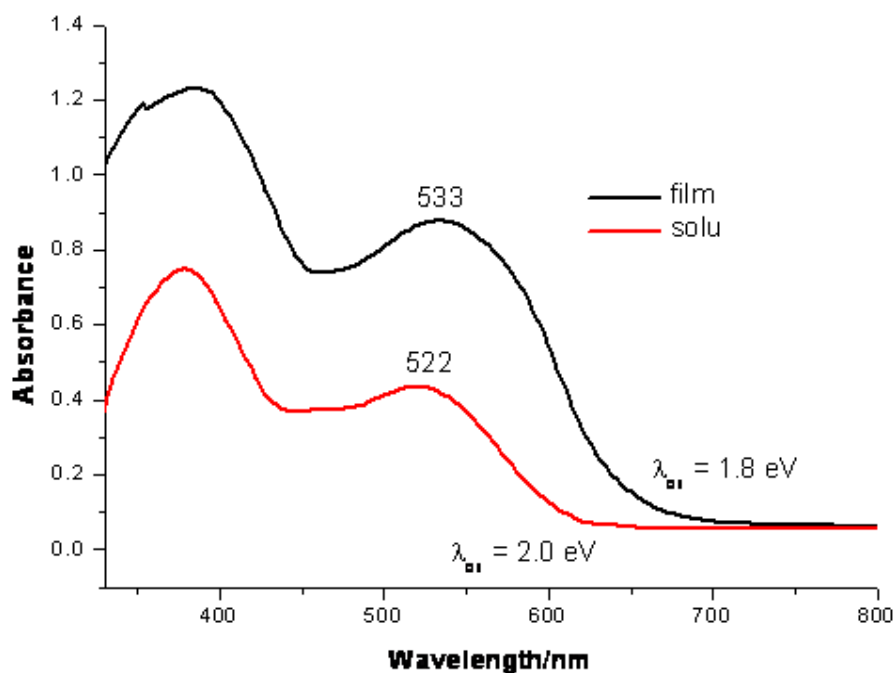


Figure 5. UV-Vis Spectrum of polymer **61**.

Cyclic voltammogram of polymer **61** (Figure 6) gave the electrochemical band gap value of 2.0 eV (Table 7). The difference between optical band gap values of the films and solution samples are due to the presence of more aggregation and conjugation in films than in solution.

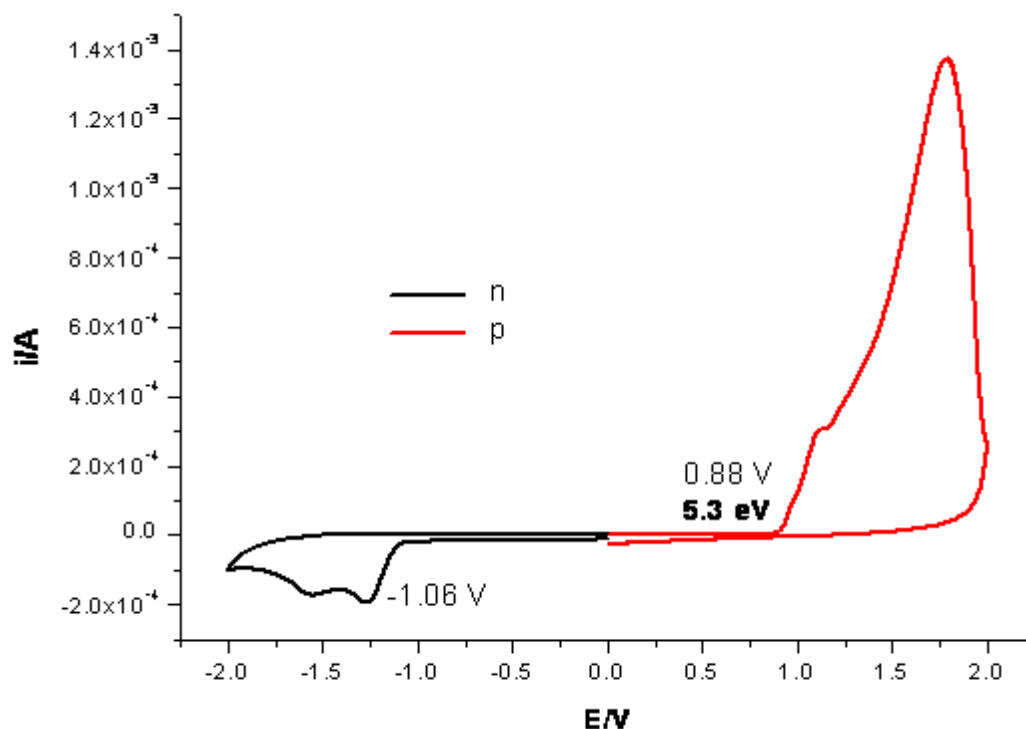


Figure 6. Cyclic Voltammogram of polymer **61**

Table 7. UV-Vis spectrum and cyclic voltammetric results of polymers **59** and **61**.

| Polymer   | Absorption<br>$\lambda_{\max}$ (nm) |          | Optical band gap (eV) |          | Electrochemical band gap (eV) |
|-----------|-------------------------------------|----------|-----------------------|----------|-------------------------------|
|           | Film                                | Solution | Film                  | Solution |                               |
| <b>59</b> | 547                                 | 531      | 1.8                   | 2.0      | 2.2                           |
| <b>61</b> | 533                                 | 522      | 1.8                   | 2.0      | 2.0                           |

## 5. Conclusion

$\pi$ -Conjugated polymers, especially, those consisting of alternating electron-donating and electron-accepting units have been gaining attention due to the ease of both oxidation (p-doping) and reduction (n-doping) and show interesting optical properties. In this study, a thiophene-derivative; 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine was successfully synthesized starting from 2,1,3-benzathiadiazole and 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione. The structure of the former monomer was characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. The monomer was polymerized to form copolymer with fluorene containing monomers. Two polymers, poly(2,3-bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dioctyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline and poly(2,3-bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dibenzyl-9H-fluoren-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline), were synthesized by using modified Suzuki polymerization reaction. Partial characterization of the synthesized polymers was carried out by cyclic voltammetry, absorption and fluorescence spectroscopy.

## 6. Experimental

### 6.1 Materials and Methods

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 and 100.6 MHz, respectively, in  $\text{CDCl}_3$  and DMSO and chemical shifts were reported in  $\delta_{\text{ppm}}$  unit. UV-Vis spectra were recorded in chloroform using SPECTRONIC GENESYS 2PC spectrophotometer. Melting points were measured using Mettler Toledo FP82HT hot stage with FP90 central processor Leica Galen<sup>TM</sup>III microscope apparatus and are uncorrected.

### 6.2 Reagents

NBS, anhyd.  $\text{Na}_2\text{SO}_4$ , ethyl acetate, 2-(tributylstannyl)thiophene, *n*-butyllithium (2.5 M in hexane), 3-bromothiophene,  $\text{CDCl}_3$ , bromine, *bis*-(triphenylphosphine)-palladium(II) chloride, 2,1,3-benzothiadiazole, mercuric oxide, dichloromethane, oxalyl chloride, chloroform, hexane, acetone were bought from Aldrich and were used as received. Toluene, petroleum ether and diethyl ether were bought from BDH and were used as received. Analytical grade chloroform and methanol purchased from BDH were used for the polymerization reactions. Tetrahydrofuran was dried over sodium-benzophenone under nitrogen atmosphere when moisture free reactions needed to be conducted. Silica gel GF<sub>254</sub> pre-coated plates (0.25 mm) were used for thin layer chromatography.

## 7. Procedures

### 7.1 Preparation of ethyl formate

In a 500 mL RB flask, a mixture of formic acid (122 mL, 149 g, 3.23 mol), ethanol (77.4 mL, 71 g, 1.34 mol) and *p*-toluenesulfonic acid (catalytic amount) was refluxed for 22 hrs. The mixture was then distilled below 62 °C and the distillate was extracted with aqueous sodium hydrogen carbonate and then with brine solution. The organic layer was isolated and dried over anhydrous sodium sulfate. Then the solution was filtered with fluted filter paper and the filtrate was distilled over at 50 °C to afford ethyl formate (53.2 g, 46.6%) as a colorless liquid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 7.89 (1H, s, H-C=O), 4.04 (2H, q, *J* = 7.2 Hz, H-2), 1.14 (3H, t, *J* = 7.2, H-3); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 160.9 (C=O), 59.6 (C-2), 13.8 (C-3).

### 7.2 Synthesis of 4,7-dibromobenzo(2,1,3-)thiadiazole (29)

In 1000 mL round bottom flask equipped with reflux condenser and a pressure equalizing dropping funnel, a mixture of 2,1,3-benzothiadiazole (19 g, 0.14 mol) and 48% HBr (76 mL) were heated at 110°C with continuous stirring. Bromine (21 mL) was added to the mixture from the pressure equalizing funnel over 30 min. A white-yellowish solid was deposited on the walls of the flask during refluxing. Additional HBr (66 mL) was added and the mixture was heated for 2 hrs. The reaction progress was checked by TLC in dichloromethane and hexane (1:1) solvent system. The mixture was allowed to cool to room temperature and filtered by suction. The residue was washed with sodium thiosulphate and then with water. The resulting product was recrystallized from isopropyl alcohol and the crystals were collected by suction filtration and allowed to dry in a vacuum oven overnight to afford compound **29** (37.4 g, 91.0%).

Mp 175-177 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub> 7.73 (2H, s, H-5, H-6); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 152.94 (C-4 & C-9), 132.37 (C-6 & C-7), 113.9 (C-5 & C-8).

### 7.3 Preparation of 2-butylthiophene (46)

Thiophene (5 g, 0.059 mol) was dissolved in anhydrous THF (40 mL) and to this was added n-butyllithium (5 M, 0.059 mol) with cooling below -70 °C. After 10 min, *n*-butyl bromide (8.085 g, 0.059 mol) was added. The cooling bath was then removed and the temperature was allowed to rise to room temperature. Yellow orange solution was observed and allowed to stay for 3 hrs. A saturated solution of ammonium chloride was added to the solution and two layers were observed. The organic layer was separated with separatory funnel and washed with water, dried over anhydrous sodium sulphate and the solvent was removed to afford compound **46** (4.5 g, 54.2%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 7.21 (1H, *dd*, *J* = 5.2 Hz, 0.4 Hz, H-5), 7.03 (1H, *dd*, *J* = 5.2 Hz, 3.2 Hz, H-4), 6.89 (1H, *dd*, *J* = 2.2 Hz, 0.8 Hz, H-3), 2.95 (2H, *t*, *J* = 7.6, H-1'), 1.79 (2H, *quintet*, *J* = 7.6, H-2'), 1.52 (2H, *m*, *J* = 7.6, H-3'), 1.07 (3H, *t*, *J* = 7.2, H-4'); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub>: 145.9 (C-2), 126.7 (C-4), 124.0 (C-3), 122.8 (C-3), 34.1 (C-2'), 29.7 (C-1'), 22.3 (C-3'), 13.9 (C-4').

### 7.4 Synthesis of 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione (48)

To 2-butylthiophene (4.5 g, 0.032 mol) dissolved in carbon disulfide (55 mL) under argon atmosphere. AlCl<sub>3</sub> (4.22 g, 0.032 mol) was added and the mixture was stirred at 0°C and oxalyl chloride (2.01 g, 1.4 mL 0.016 mol) was added. Stirring was continued for 18 hrs. The resulting brown mixture was poured to cold water. The organic layer was separated and the aqueous layer was extracted with dichloromethane and the combined organic layers were washed with water, dried over anhydrous sodium sulphate, filtered and concentrated in vacuum. Compound **48** was obtained as brown oil (5.07 g, 94.53%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{ppm}}$ : 7.85 (2H, *d*,  $J = 4.0$  Hz, H-3), 6.87 (2H, *d*,  $J = 4.0$  Hz, H-4), 2.87 (4H, *t*,  $J = 7.6$  Hz, H-1'), 1.69 (4H, *p*,  $J = 7.6$  Hz, H-2'), 1.39 (4H, *m*,  $J = 7.2$  Hz, H-3'), 0.93 (6H, *t*,  $J = 7.2$  Hz, H-4');  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 182.5 (C-1''), 159.7 (C-5), 137.7 (C-3), 136.5 (C-2), 126.5 (C-4), 33.3 (C-2'), 30.5 (C-1'), 22.13 (C-3'), 13.7 (C-4').

## 7.5 Synthesis of 5,8-dibromo-2,3-bis(5-butylthiophen-2-yl)quinoxaline (49)

In 250 mL round bottom flask, 4,7-dibromobenzo(2,1,3)thiadiazole (3 g, 10 mmol), zinc dust (12 g, 0.187 mol) and acetic acid (100 mL) were mixed and heated at 70 °C for 3 hours. The progress of the reaction was followed by TLC using dichloromethane:hexane (1:1) at different intervals of time. After the reaction was complete, the mixture was filtered and the residue was washed with acetic acid. The filtrate was concentrated by rotary evaporator until a small amount of acid remained and to this solution, 1,2-bis(5-butylthiophen-2-yl)ethane-1,2-dione (3.4 g, 0.01 mol) was added. The solution was heated at 50 °C for four hours following the progress of the reaction by TLC in a petroleum ether:toluene (3:2) solvent mixture. After the reaction was complete, the yellow precipitate was collected by filtration and was washed with methanol. This compound was further purified by silica gel column chromatography using petroleum ether:toluene (4:1) as an eluent to afford compound **49** (3.66 g, 64.0%).

Mp 126-128 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{ppm}}$ : 7.78 (2H, *s*, H-6, H-7), 7.44 (2H, *d*,  $J = 3.6$  Hz, H-3'), 6.74 (2H, *d*,  $J = 3.6$  Hz, H-4'), 2.89 (4H, *t*,  $J = 7.6$  Hz, H-1''), 1.76 (4H, *quintet*,  $J = 7.6$  Hz, H-2''), 1.47 (4H, *m*,  $J = 7.6$  Hz, H-3'') 0.99 (6H, *t*,  $J = 7.2$  Hz, H-4'');  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{ppm}}$ : 152.0, (C-2, C-3), 147.2 (C-5'), 138.5 (C-9, C-10), 138.3 (C-2'), 132.6 (C-6, C-7), 130.4 (C-4'), 125.0 (C-3'), 122.9 (C-5, C-8), 33.6 (C-2'''), 30.2 (C-1'''), 22.3 (C-3'''), 13.9 (C-4''').

## 7.6 Synthesis of 2,3-bis(5-butylthiophen-2-yl)-5-8-di(thiophene-2-yl)quinoxaline (50)

5,8-Dibromo-2,3-bis(5-butylthiophen-2-yl)quinoxaline (2.6 g, 4.61 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10.0 mg, 3 mol %), 2-tributylstannylthiophene (2.95 mL, 3.44 g, 9.2 mmol) and toluene (45 mL) were mixed and heated under reflux in an argon atmosphere for 3 hrs. The progress of the reaction was checked by TLC in hexane:dichloromethane (1:1) as a solvent system. After the reaction was complete, the mixture was cooled to room temperature and was treated with saturated ammonium chloride. The organic layer was separated, dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporator to afford a red solid. The solid material was washed with methanol and dried to afford compound **50** (2.5 g, 94.5%).

Mp 111-113 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 7.99 (2H, s, H-6, H-7), 7.89 (2H, d, J = 3.6 Hz, H-5''), 7.55 (2H, d, J = 4.8, H-3''), 7.45 (2H, d, J = 3.6 Hz, H-3'), 7.22 (2H, t, J = 3.6 Hz, H-4''), 6.75 (2H, d, J = 3.6 Hz, H-4'), 2.94 (4H, t, J = 7.6, H-1'''), 1.79 (4H, quintet, J = 7.6, H-2'''), 1.49 (4H, multiplet, J = 7.2 Hz, H-3'''), 1.03 (6H, t, J = 7.2 Hz, H-4'''); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 150.8 (C-2, C-3), 144.8 (C-5'), 139.2 (C-2''), 138.8 (C-9, C-10), 136.4 (C-2'), 130.6 (C-5, C-8), 130.0 (C-6, C-7), 128.5 (C-4''), 126.9 (C-5''), 126.8 (C-4'), 126.7 (C-3''), 124.7 (C-3'), 33.6 (C-1'''), 30.2 (C-2'''), 22.3 (C-3'''), 13.9 (C-4''').

## 7.7 Synthesis of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine (51)

2,3-Bis(5-butylthiophen-2-yl)-5-8-di(thiophene-2-yl)quinoxaline (2.4 g 4.21 mmol) was dissolved in DMF (50 mL) and chloroform (40 mL) and to this solution NBS (1.5 g, 8.42 mmol) was added. The mixture was allowed to stir at room temperature following the progress of the reaction by TLC in hexane:dichloromethane (3:2) as an eluent. After 18 hrs, the red precipitate was

collected by suction filtration and the residue was washed with methanol (3x) and dried to afford compound **51** (1.44 g, 46.9%).

Mp 167-169 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 7.89 (2H, s, H-6, H-7), 7.52 (2H, d, J = 4.00 Hz, H-3'), 7.41 (2H, d, J = 3.6, H-3''), 7.11 (2H, d, J = 4.00, H-4'), 6.75 (2H, d, J = 3.60, H-4''), 2.95 (2H, t, J = 7.2 Hz, H-1'''), 1.81 (2H, quintet, J = 7.2, H-2'''), 1.51 (2H, multiplet, J = 7.2 Hz, H-3'''), 1.02 (3H, t, J = 7.2 Hz, H-4'''); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 151.3 (C-2, C-3), 145.2 (C-5'), 139.7 (C-2''), 138.7 (C-9, C-10), 135.8 (C-2'), 130.3 (C-5, C-8), 130.0 (C-6, C-7), 129.2 (C-4''), 125.8 (C-5''), 125.6 (C-4'), (C-3''), 116.7 (C-3'), 33.6 (C-1'''), 30.2 (C-2'''), 22.3 (C-3'''), 13.9 (C-4''').

## 7. 8 Synthesis of bis-(3-thienyl)-methanol (**55**)

3-Bromothiophene (5.0 g, 0.031 mol) was dissolved in THF (40 mL) and cooled to -78 °C under argon. n-Butyllithium (14.4 mL of a 2.5 M solution in hexane, 0.031 mol) was then added and the resulting suspension was stirred for 15 min. Ethyl formate (1.25 mL, 0.0155 mol) was added and after 20 min the cooling was removed and the mixture was allowed to warm to room temperature. The mixture was stirred for 12 hours at room temperature and then ammonium chloride was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3x). The combined organic layer was dried (anhydrous, Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated and the remaining oily material was chromatographed over silica gel using hexane:dichloromethane (1:9) as eluent. The fastest moving compound was collected and this was recrystallized from hexane and dried to afford compound **55** (1.2 g, 29%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 7.32 (2H, dd, J = 5.0 Hz, 3.2 Hz, H-2), 7.23 (2H, dd, J = 1.6 Hz, 0.8 Hz, H-4), 7.05 (2H, dd, J = 5.0 Hz, 1.2 Hz, H-5), 5.9 (1H, s, H-6), 2.56 (1H, s, O-H); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 144.9, (C-3), 126.4 (C-4), 126.3 (C-5), 121.8 (C-2), 69.1 (C-6).

### 7.9 Attempt towards the synthesis of bis(2-iodothiophen-3-yl)methanol (11)

Bis-(3-thienyl)-methanol (0.2 g, 2.01 mmol) was dissolved in toluene (5.5 ml). The mixture was cooled in an ice water bath and to this was added a mixture of I<sub>2</sub> and HgO portion-wise. The progress of the reaction was followed by TLC in dichloromethane as eluent. The reaction was completed after four hours. The mixture was filtered by suction. The residue was washed with toluene and dichloromethane (3x each). The NMR spectrum of the resulting red powder proved that the desired compound was not synthesized. No further attempt was made to characterize the product.

### 7.10 Synthesis of dithiophen-3-yl-methanone (56)

Pyridinium chlorochromate (1.65 g, 7.65 mmol) was added to a mixture of bis-(3-thienyl) methanol (1 g, 5.1 mmol) and crushed molecular sieve (1.1 g) in dichloromethane (8.0 mL) at 0°C (ice-water bath). The black solution was stirred for 3 hrs following the progress of the reaction by TLC (diethyl ether:hexane, 1:9) as eluent. After the reaction was complete, diethyl ether was added and the mixture was stirred for additional 10 min. The resulting mixture was filtered through celite pad and washed with diethyl ether (3x). The solvent was removed under reduced pressure to afford compound **56** ( 0.7 g, 70.7%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>: 8.05 (2H, *dd*, *J* = 5.0 Hz, 3.2 Hz, H-2), 7.32 (2H, *dd*, *J* = 1.6 Hz, 0.8 Hz, H-4), 7.05 (2H, *dd*, *J* = 5.0 Hz, 1.2 Hz, H-5), 5.9 (1H, *s*, H-6), 2.56 (1H, *s*, O-H); <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 183.3 ( C=O), 142.1 (C-3), 132.7 (C-4), 128.3 (C-5), 126.4 (C-2).

### 7.11 Attempts toward synthesis of 4,5-dimethyl-2,2-di(thiophene-3-yl)-1,3-dioxolane (57)

A mixture of di-3-thienyl ketone (0.7 g, 3.6 mmol) and 2,3-butanediol (0.5 g, 5.46 mmol) in toluene (35 mL) in the presence of catalytic amount of *p*-toluene-sulfonic acid was heated under reflux using a Dean-stark trap as water separator. The mixture was heated for 7 days following the progress of the reaction by TLC (dichloromethane:hexane,1:1) as an eluent. The resulting solution was cooled and washed successively with aqueous sodium hydrogen carbonate and water, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed. Thus reaction was incomplete after 7 days and no further attempt was done to separate the mixture. Another attempt was made by using sulfamic acid as a catalyst. The NMR spectrum of the resulting grey solid proved that the desired compound was not formed.

### 7.12 Synthesis of poly{2,3-bis-(5-butylthiophen-2-yl)-5-[5-(9,9-dioctyl-9H-fluorene-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline} (59)

5,7-Bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine (200 mg, 0.2 mmol) was mixed with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)9,9-dioctylfluorene (0.176 g, 0.2 mmol) and to this was added tetrakis[triphenylphosphine]palladium(0) (7 mg, 6 μmol) and toluene (10 mL) and was refluxed for 15 min. under nitrogen atmosphere. Tetraethylammonium hydroxide (0.6 mL, 20% by weight in water) was added and the mixture was refluxed for two hours. Bromobenzene (0.02 mL) was added and after 1 hr, phenyl boronic acid (0.04 mL) was added. The mixture was allowed to reflux for 1 hr, cooled to room temperature and the polymer was precipitated by slowly adding the mixture into methanol, filtered, washed with methanol and dried. The brown solid was dissolved in chloroform, and was washed with ammonia and water (3x each), concentrated and precipitated from methanol. The resulting solid was collected by membrane filtration, and was Soxhlet extracted with ether and chloroform. The chloroform extract was concentrated to a small volume and the

polymer was precipitated from methanol, dried and filtered to afford polymer **59** (0.21 g).

### **7.13 Synthesis of poly{2,3-bis-(5-butyl-thiophen-2-yl)-5-[5-(9,9-dibenzyl-9H-fluoren-2-yl)-thiophen-2-yl]-8-thiophen-2-yl-quinoxaline} (61)**

5,7-bis(5-bromothiophen-2-yl)-2,3-bis(5-butylthiophen-3-yl)thieno[3,4-b]pyrazine (200 mg 0.2 mmol) was mixed with 2,7-bis(4''4''-,5'',5''-tetramethyl-1,3,2-dioxaborolane-2-yl-9,9-dibenzylfluorene (0.16 g, 0.27 mmol), tetrakis(triphenylphosphine)palladium(0) (7 mg, 6  $\mu$ mol) and toluene (10mL) and was refluxed for 10 min. under nitrogen atmosphere. Tetraethylammonium hydroxide (0.6 mL, 20% by weight in water) was added and then the mixture was refluxed for 1.5 hours. Bromobenzene (0.04 mL) was added and after 1 hr, phenyl boronic acid (0.04 mL) was added. The mixture was allowed to reflux for 1 hr, cooled to room temperature and the polymer was precipitated by slowly adding the mixture into methanol, filtered, washed with methanol and dried. The brown solid was dissolved in chloroform, and was washed with ammonia and water (3x each), concentrated and precipitated from methanol. The resulting solid was collected by membrane filtration, and was Soxhlet extracted with ether and chloroform. The chloroform extract was concentrated to a small volume and the polymer was precipitated from methanol, dried and filtered to afford polymer **61** (0.16 g).

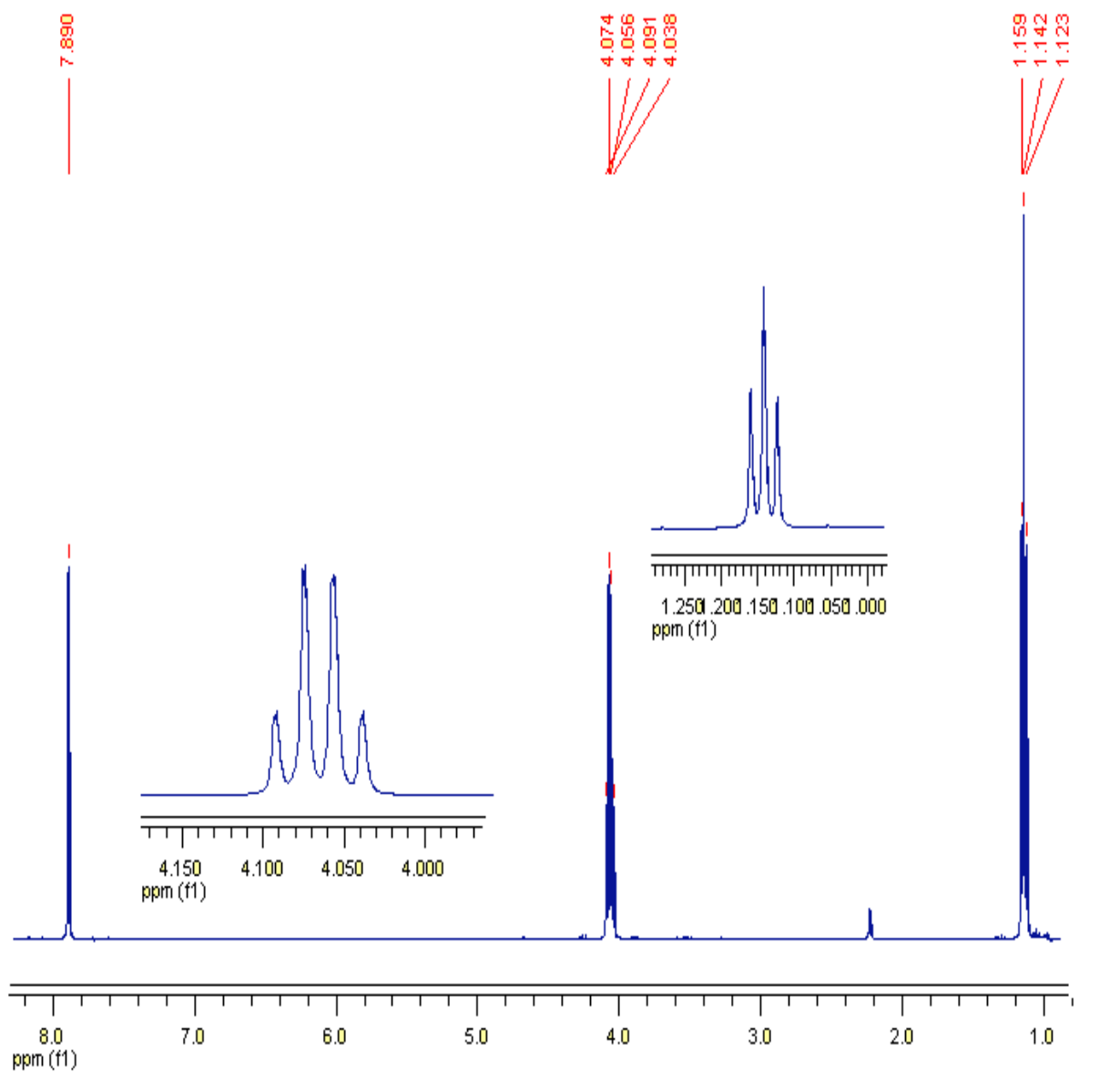
## 8. References

1. S. Janietz, J. Barche, A. Wedel and D. Sainova, *Macromol. Chem. Phys.*, **2004**, 205, 187.
2. S. Nagamatsu, W. Takashima, and K. Kaneto, *Macromolecules*, **2003**, 36, 5252.
3. R. Demadrille, P. Rannou, J. Bleuse, and J. L. Oddou, *Macromolecules*, **2003**, 36, 7045.
4. M. Jayakannan, A. Van Hal, and R. A. J. Janssen, *J. Polym. Sci. Part A: Polym. Chem.*, **2002**, 40, 2360.
5. J. Ronicali, *Chemi. Revj*, **1997**, 97, 173.
6. V. D. Parker *J. Am. Chem. Soc.*, **1976**, 98, 98.
7. J. Ronicali, A. Yassar and F. Garnier, *J. Chem. Soc., Chem Commun.* **1988**, 581
8. A. Kraak, A. K. Weiserma, P. Jordens and H. Weinberg, *Tetrahedron*, **1968**, 24, 3381.
9. A. Dhanabalan, J. L. J. van Dongen, J. K. J. van Duren, H. M. Janssen, P. A. van Hal and R. A. J. Janssen, *Macromolecules* **2001**, 34, 2495.
10. J. P. Ferraris and T. L. Lambert, *J. Chem. Soc., Chem. Commun.* **1991**, 1268.
11. H. Sirringhaus, R. J. Wilson, R. H. Friend, M. Inbasekaran, W. Wu, E. P. Woo, M. Grell and D. D. C. Bradley, *Appl. Phys. Lett.* **2000**, 77, 406.
12. P. Coppo, D. C. Cupertino, S. G. Yeates and G. Pagani *J. Mater. Chem.*, **2002**, 12, 2597.
13. P. Coppo and L. Turner, *J. Mater. Chem.*, **2005**, 15, 1123.
14. R. McCullough, *Adv. Mater.*, **1998**, 10, 93.
15. A. Berlin, E. Brenna, G. A. Pagani and F. Sannicolo, *Synth. Met.*, **1992**, 51, 287.
16. U. Asawapirom and U. Scherif, *Macromol. Rapid. Commun.*, **2001**, 22, 746.
17. G. Zotti, G. Schiavon, A. Berlin, G. Fantana and G. Pagani, *Macromolecules*, **1994**, 27, 1938.

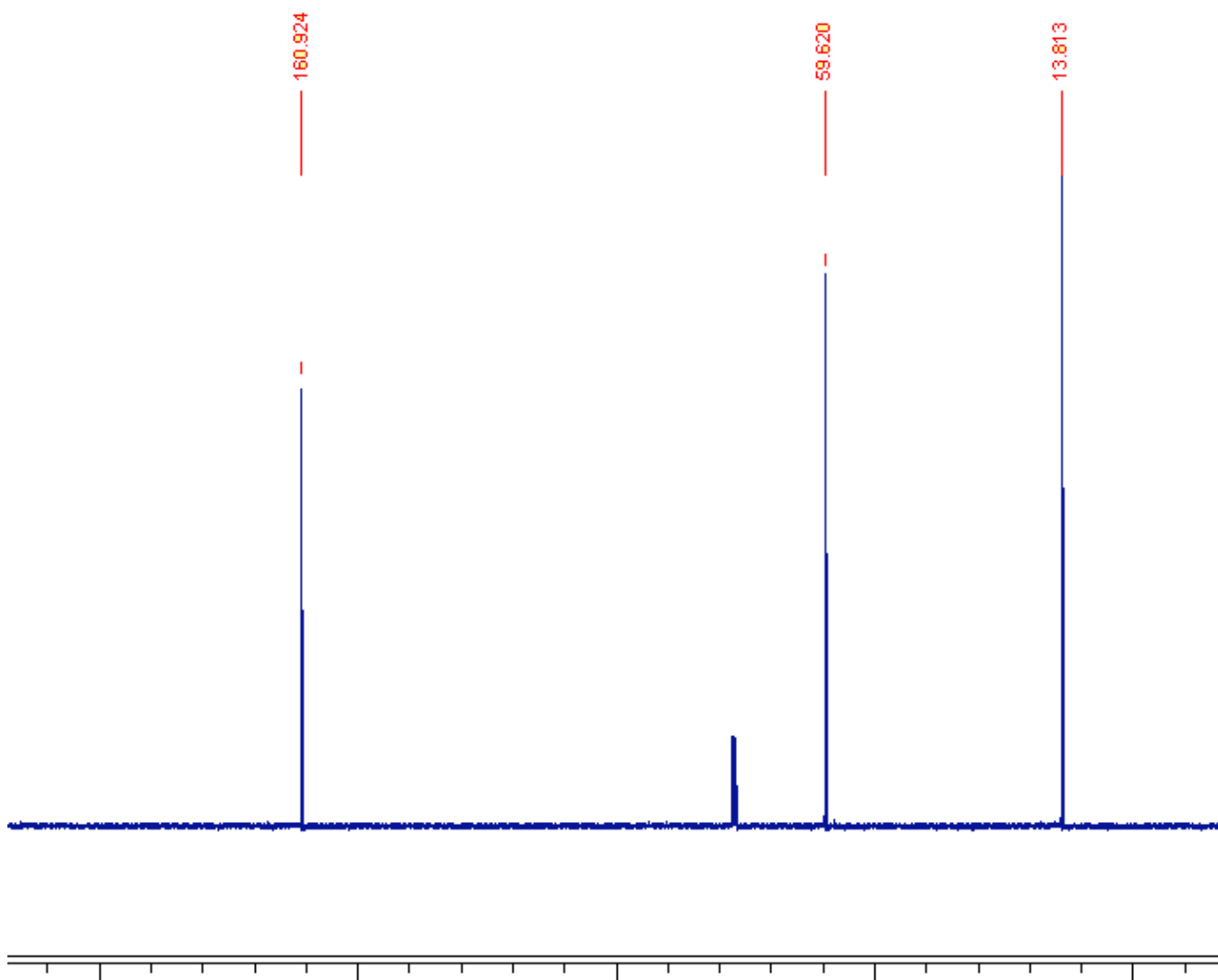
18. P. Coppo, D. C. Cupertino, S. G. Yeates and G. Pagani, *Macromolecules*, **2003**, 36, 2705.
19. K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.* **1972**, 94, 4374.
20. R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.* **1999**, 11, 250.
21. T. A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.* **1995**, 117, 233.
22. J. P. Ferraris and T. M. Lambert, *J. Chem. Soc., Chem. Commun.*, **1991**, 1268.
23. J. K. Stille, *Angew. Chem. Int. Ed*, **1986**, 98, 504.
24. H. A. M. V. Mulkom, J. A. J. M. Vekemans, E. E. Havinga and E. W. Meijer, *Mater. Sci. and Eng.*, **2001**, 32, 20.
25. T. Kanbara, Y. Myazaki and T. Yamamoto, *J. Polym. Sci. Part A: Polym. Chem.*, **1995**, 33, 999.
26. H. J. Kim, J. H. Lee, T. H. Kim, W. S. Lyoo, D. W Kim, C. Lee, Taek and S. Lee, *J. Polym. Sci. Part A: Polym. Chem*, **2007**, 45, 1546.
27. M. Leclerc, *J. Polym. Sci. Part A: Polym. Chem.*, **2001**, 39, 2867.
28. U. Scherf and E. J. W. List, *Adv Mater.*, **2002**, 14, 477.
29. J. Lee, B. J. Jung, S. K. Lee, J. I. Lee, H. J. Cho and H. K. Shim, *J. Polym. Sci: Part A: Polym. Chem.*, **2005**, 43, 1845.
30. D. Neher, *Macromol. Rapid. Commun.*, **2001**, 22, 1365.
31. Q. Peng, M. Xie, Y. Huang, Z. Lu and D. Xiao, *J. Polym. Sci. Part A: Polym. Chem.*, **2004**, 42, 2985.
32. H. J. Cho, B. J. Jung, N. S. Cho, J. Lee and H. K. Shim, *Macromolecules*, **2003**, 36, 6704.
33. N. C. Yang, Y. H. Park and D. H. Suh, *J. Polym Sci. Part A: Polym Chem.*, **2003**, 41, 674.
34. Q. Pei and Y. Yang, *J. Am. Chem. Soc.*, **1996**, 118, 7416.
35. F. Babudri, V. Fiandanese, G. Marchese and A. Punzi, *Tet. Lett.*, **1995**, 40, 7305.
36. B. Mohr, V. Enkelmann and G. Wegner, *J. Org. Chem.*, **1994**, 59, 635.

37. D. Aldakov, M. A. Palacios and P. Anzenbacher, *Chem. Mater*, **2005**, 17, 5238.
38. Yadessa Melaku; *MSc. Project*, Department of Chemistry, Addis Ababa University, Ethiopia, 2007.
39. Zekarias Yakob; *MSc. Thesis*, Department of Chemistry, Addis Ababa University, Ethiopia, 2004.

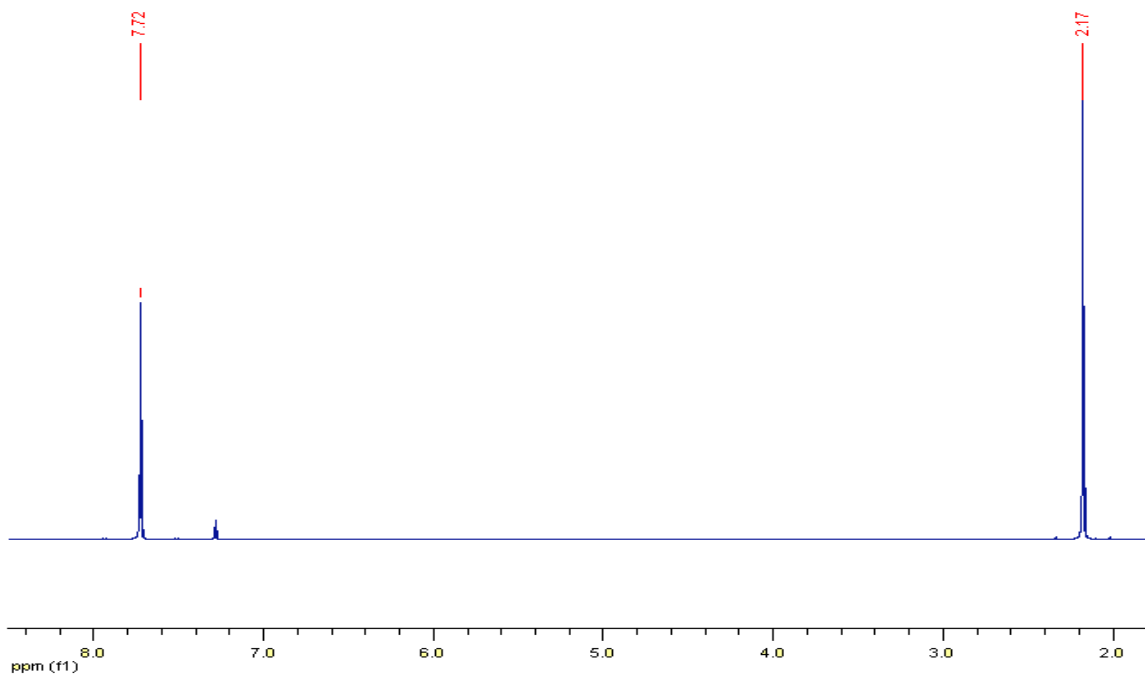
## 9. Appendices



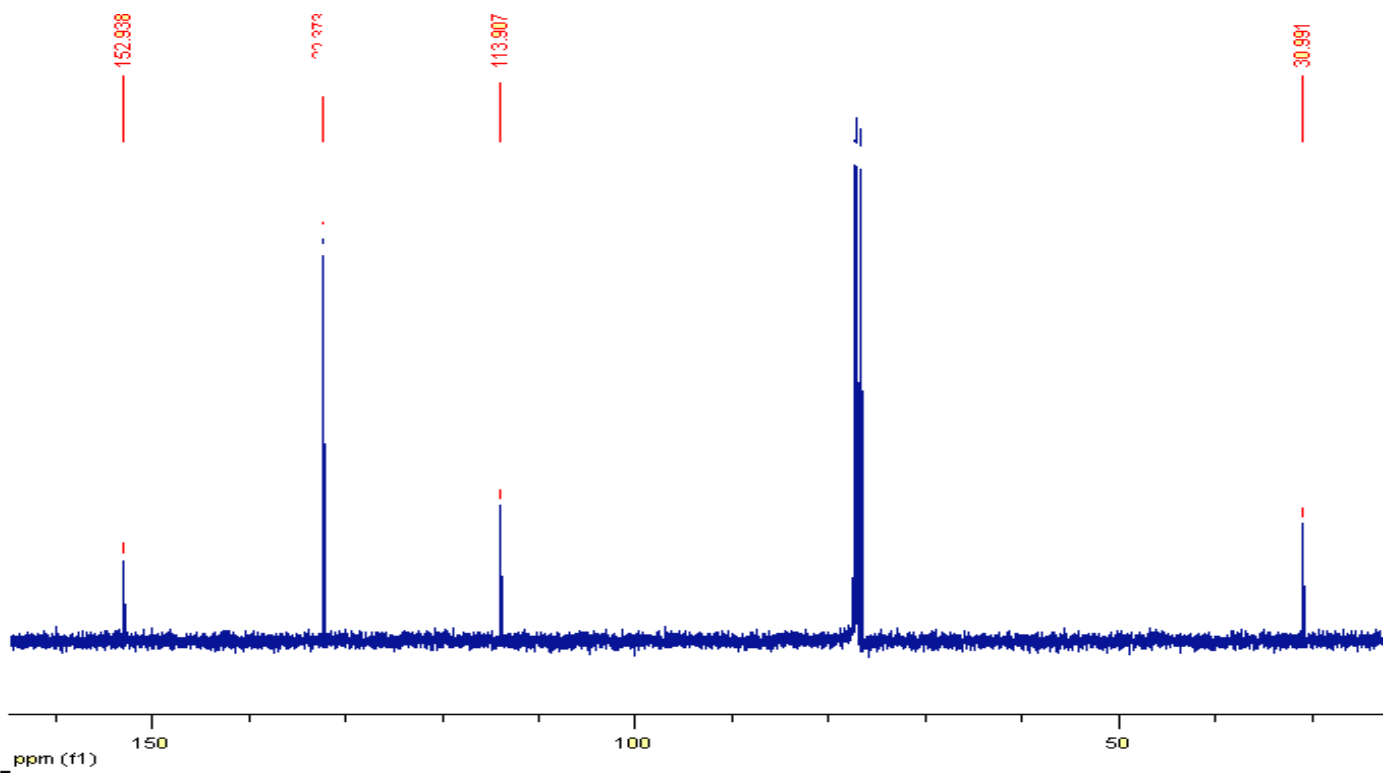
Appendix 1  $^1\text{H-NMR}$  spectrum of ethyl formate.



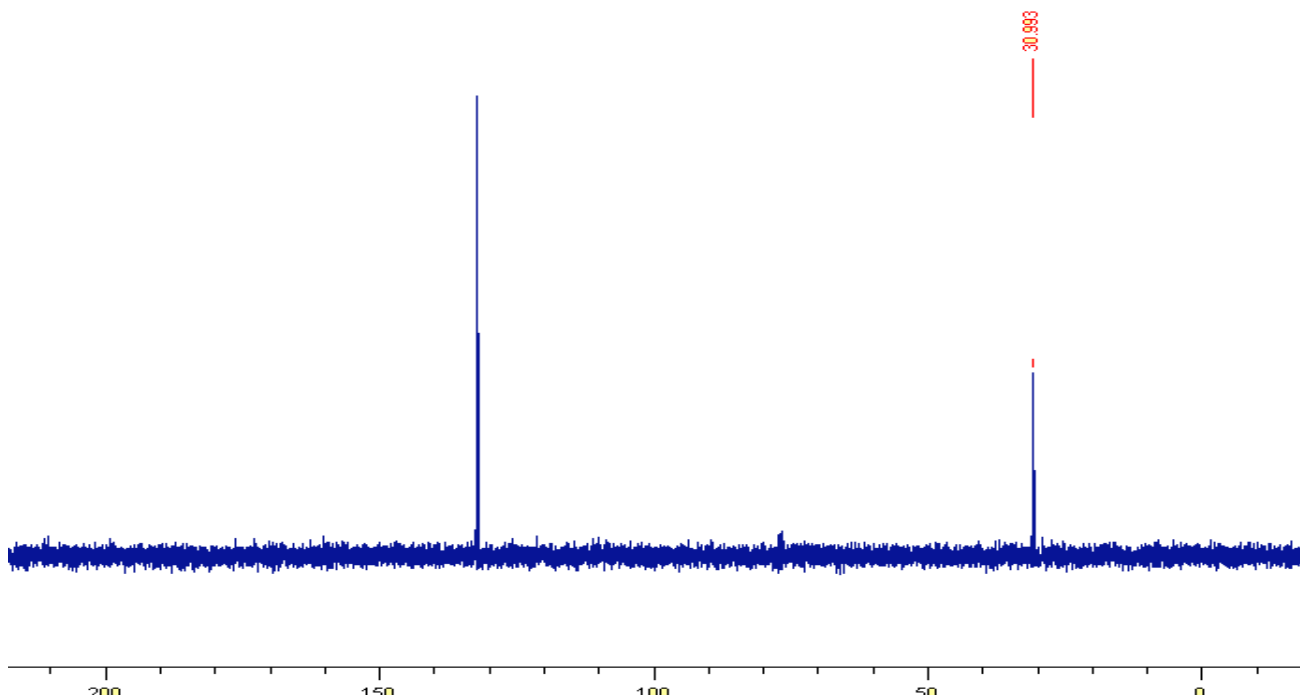
Appendix 2.  $^{13}\text{C}$ -NMR spectrum of ethyl formate.



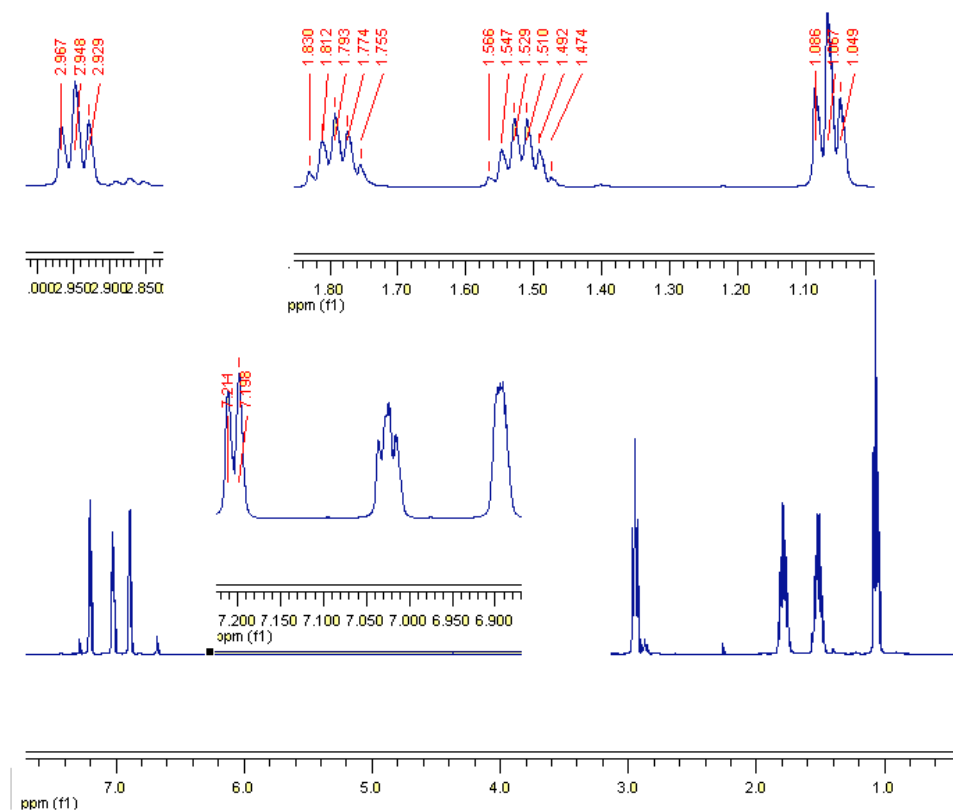
Appendix 3. <sup>1</sup>H-NMR spectrum of 2,1,3-benzothiadiazole.



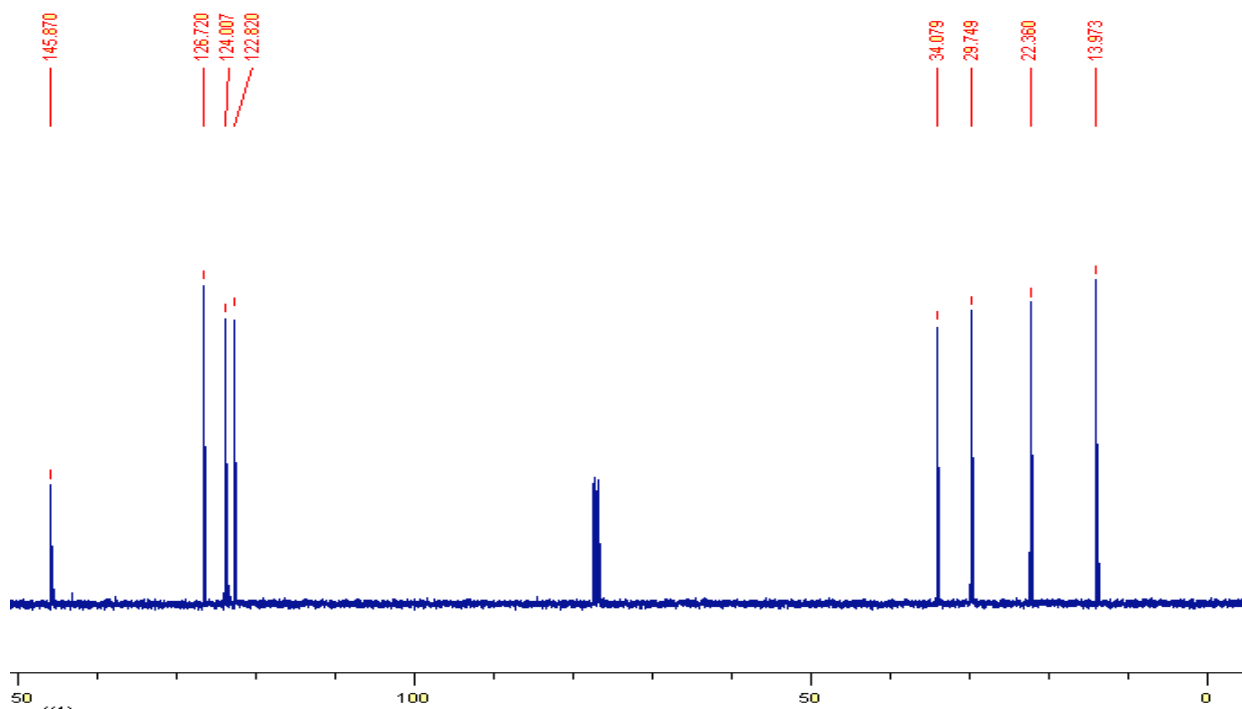
Appendix 4. <sup>13</sup>C-NMR spectrum of 2,1,3-benzothiadiazole.



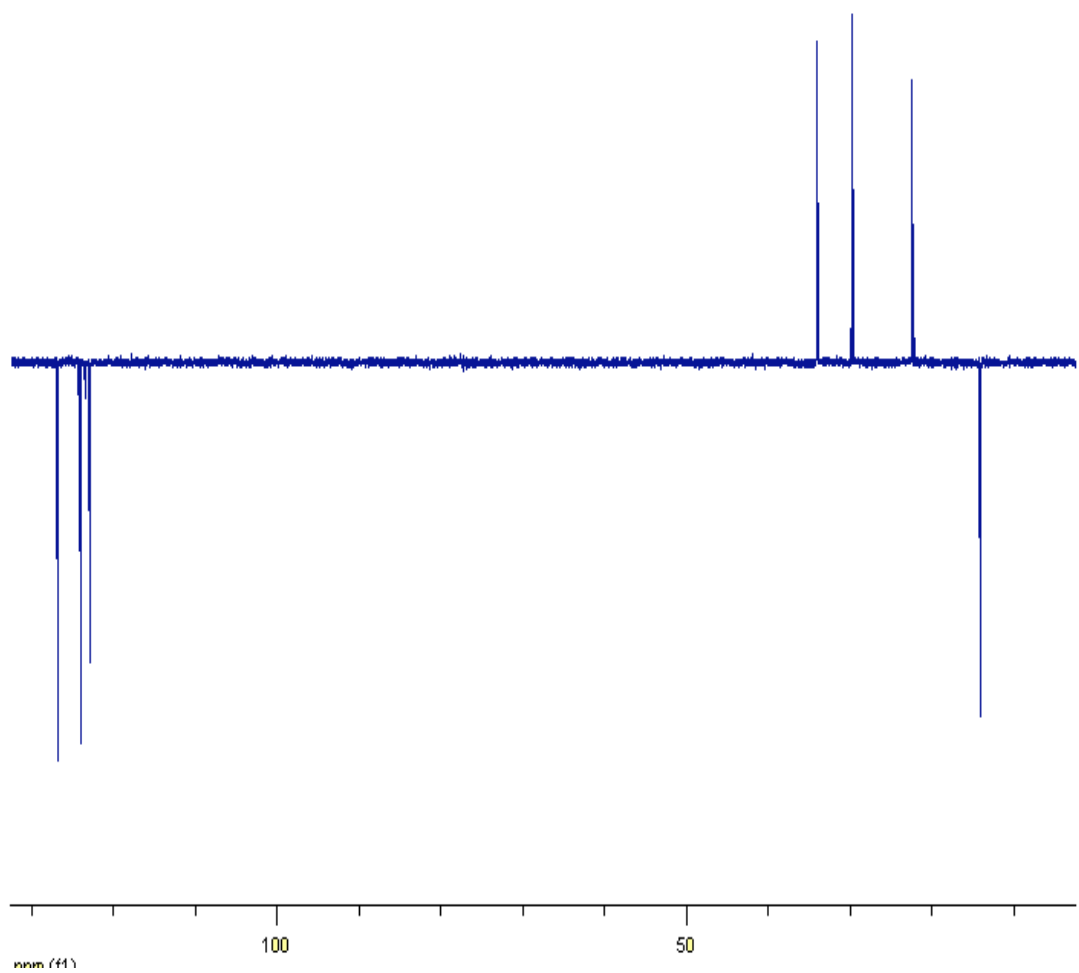
Appendix 5. DEPT-135 spectrum of 2,1,3-benzothiadiazole.



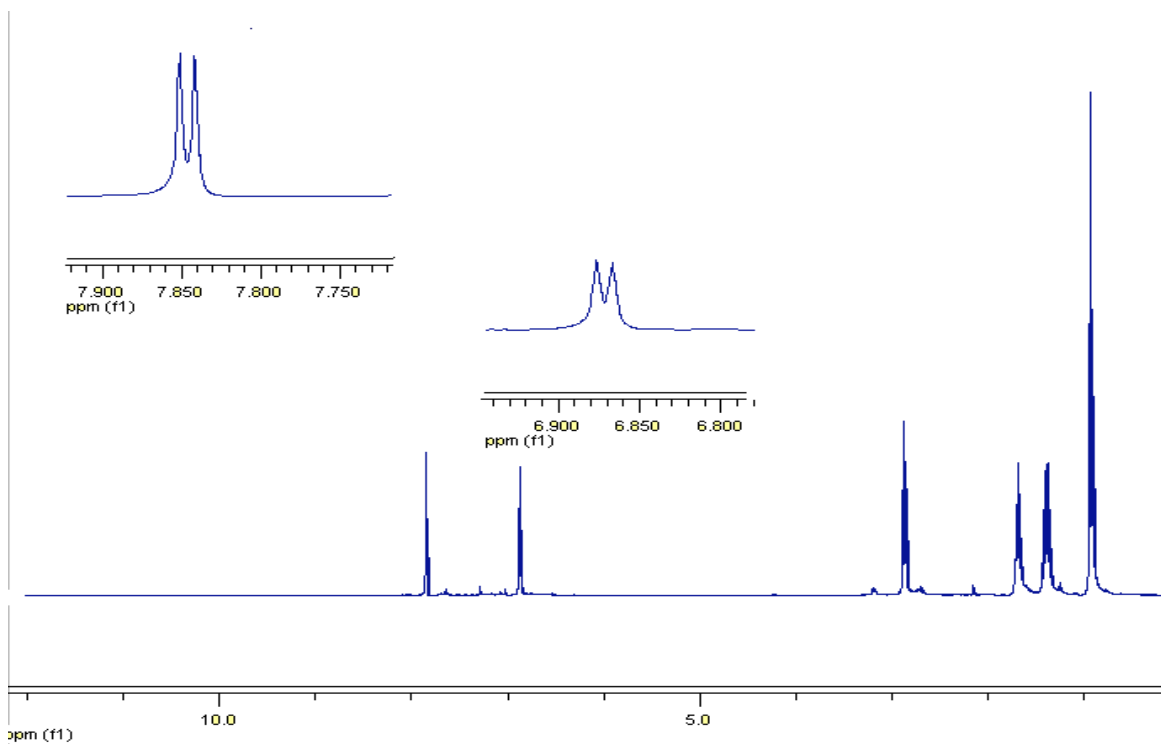
Appendix 6.  $^1\text{H-NMR}$  spectrum of 2-butylthiophene.



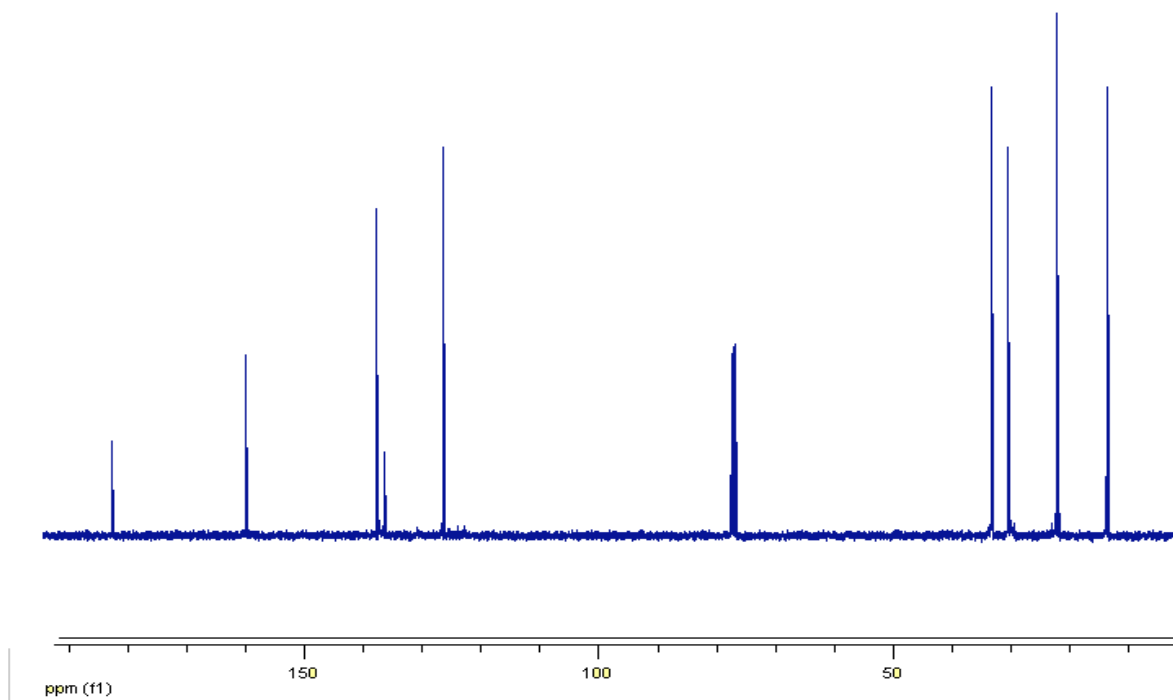
**Appendix 7.**  $^{13}\text{C}$ -NMR spectrum of 2-butylthiophene.



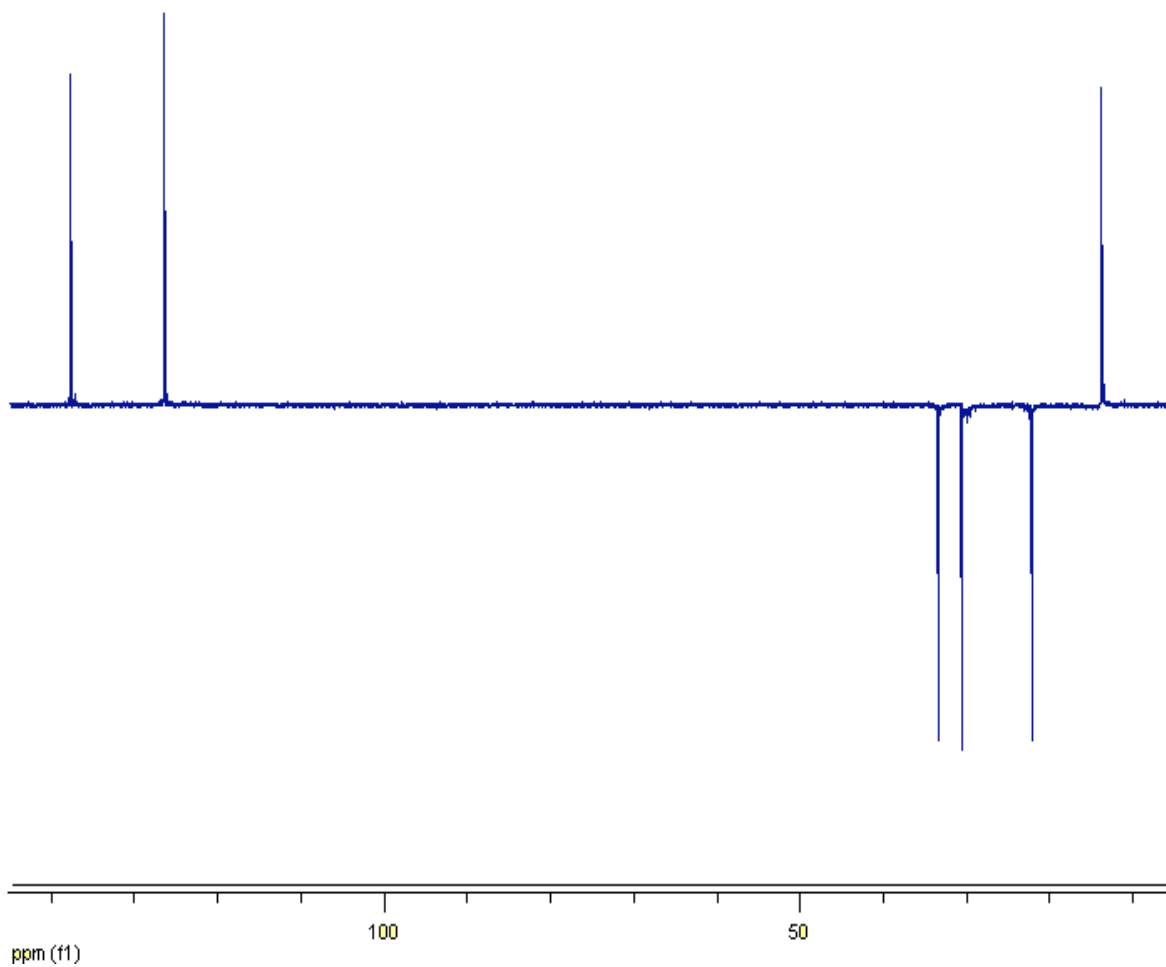
**Appendix 8.** DEPT-135 spectrum of 2-butythiophene.



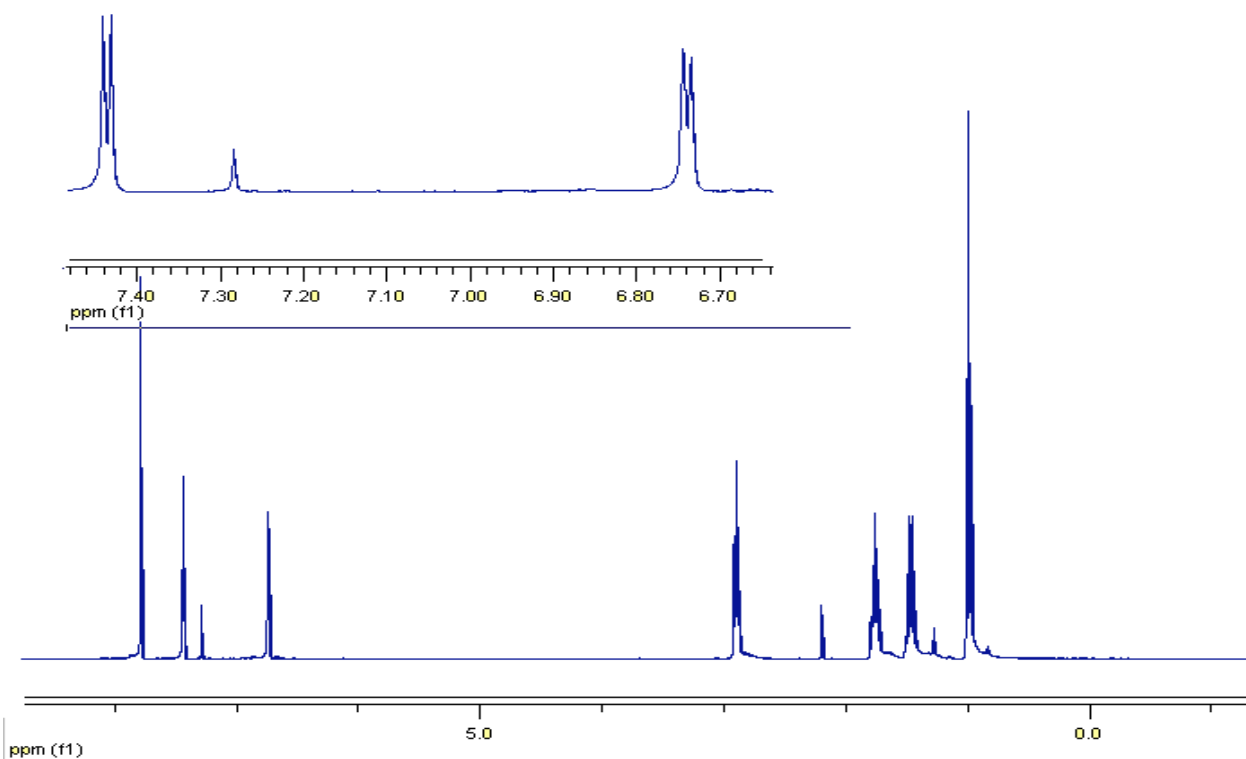
**Appendix 9.**  $^1\text{H}$ -NMR spectrum of compound **48**.



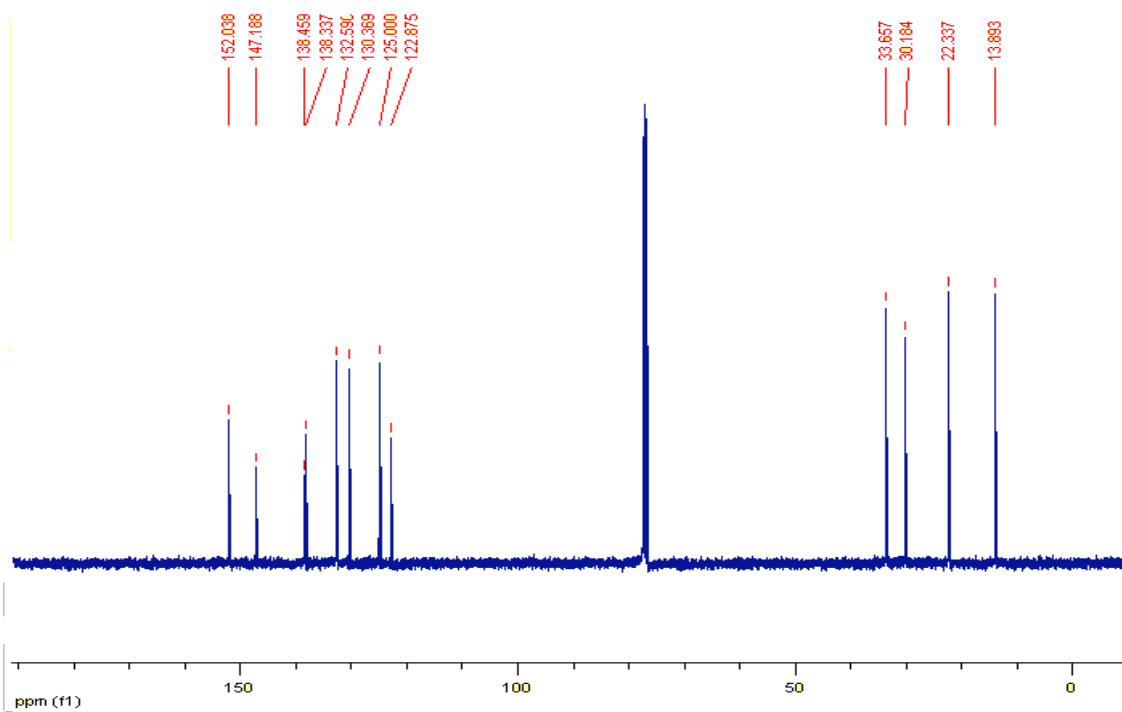
**Appendix 10.**  $^{13}\text{C}$ -NMR spectrum of compound **48**.



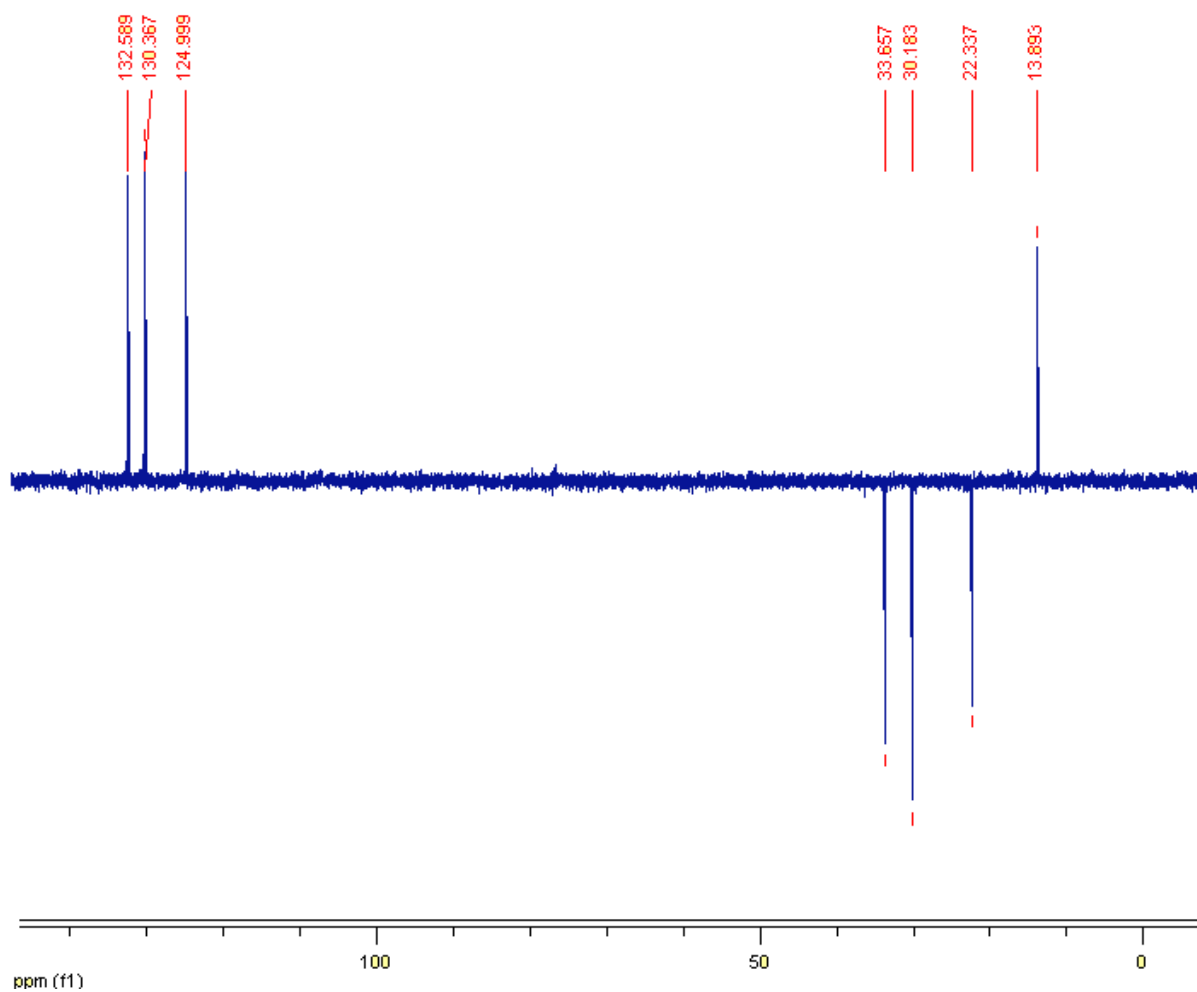
**Appendix 11.** DEPT-135 spectrum of compound **48**.



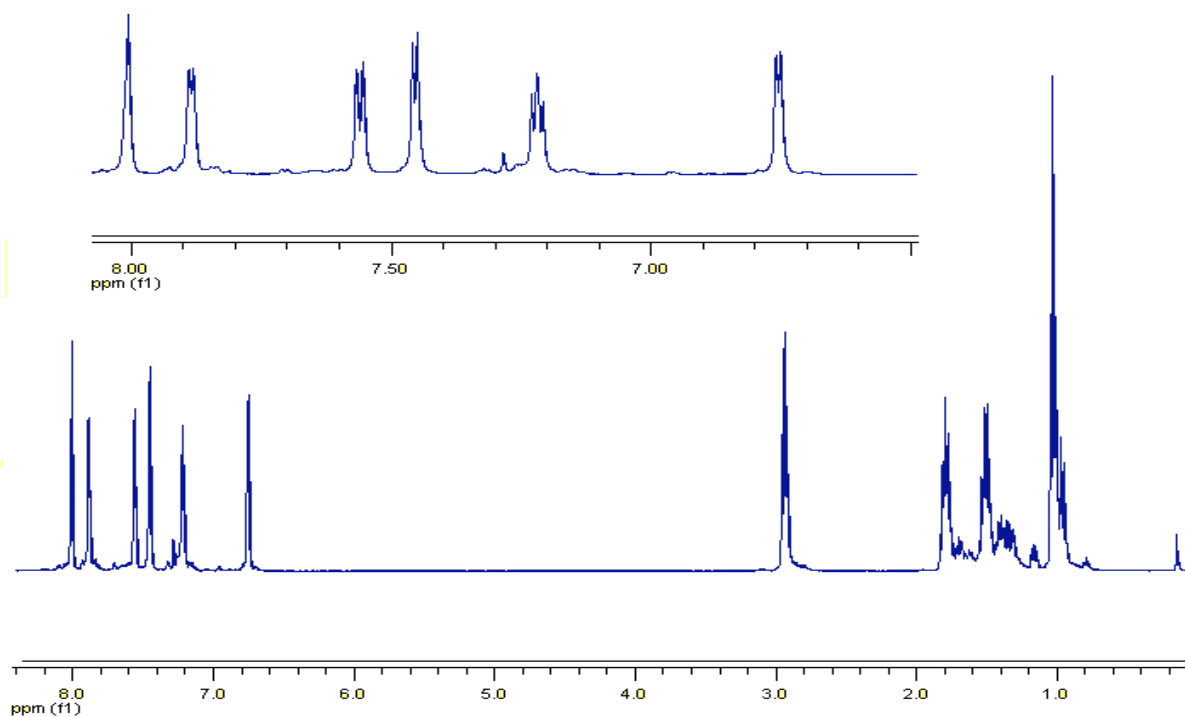
**Appendix 12.**  $^1\text{H-NMR}$  spectrum of compound 49.



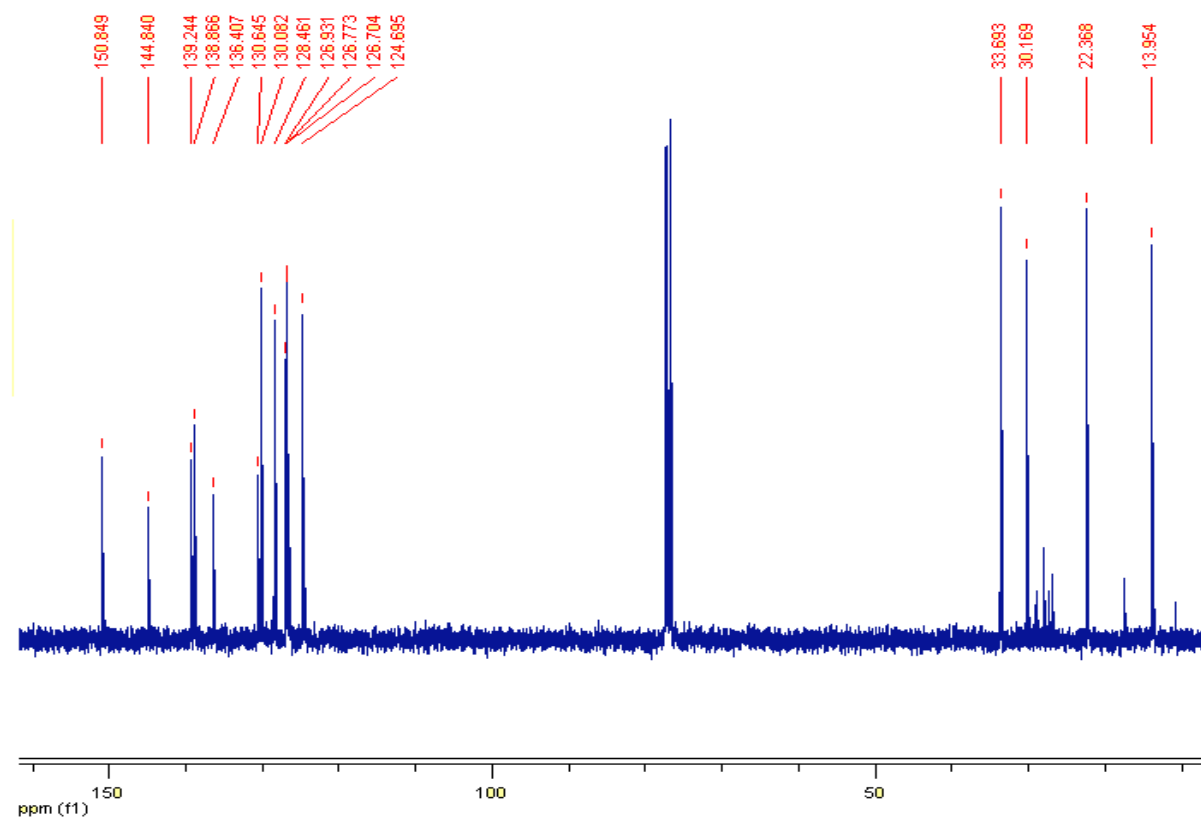
**Appendix 13.**  $^{13}\text{C-NMR}$  spectrum of compound 49.



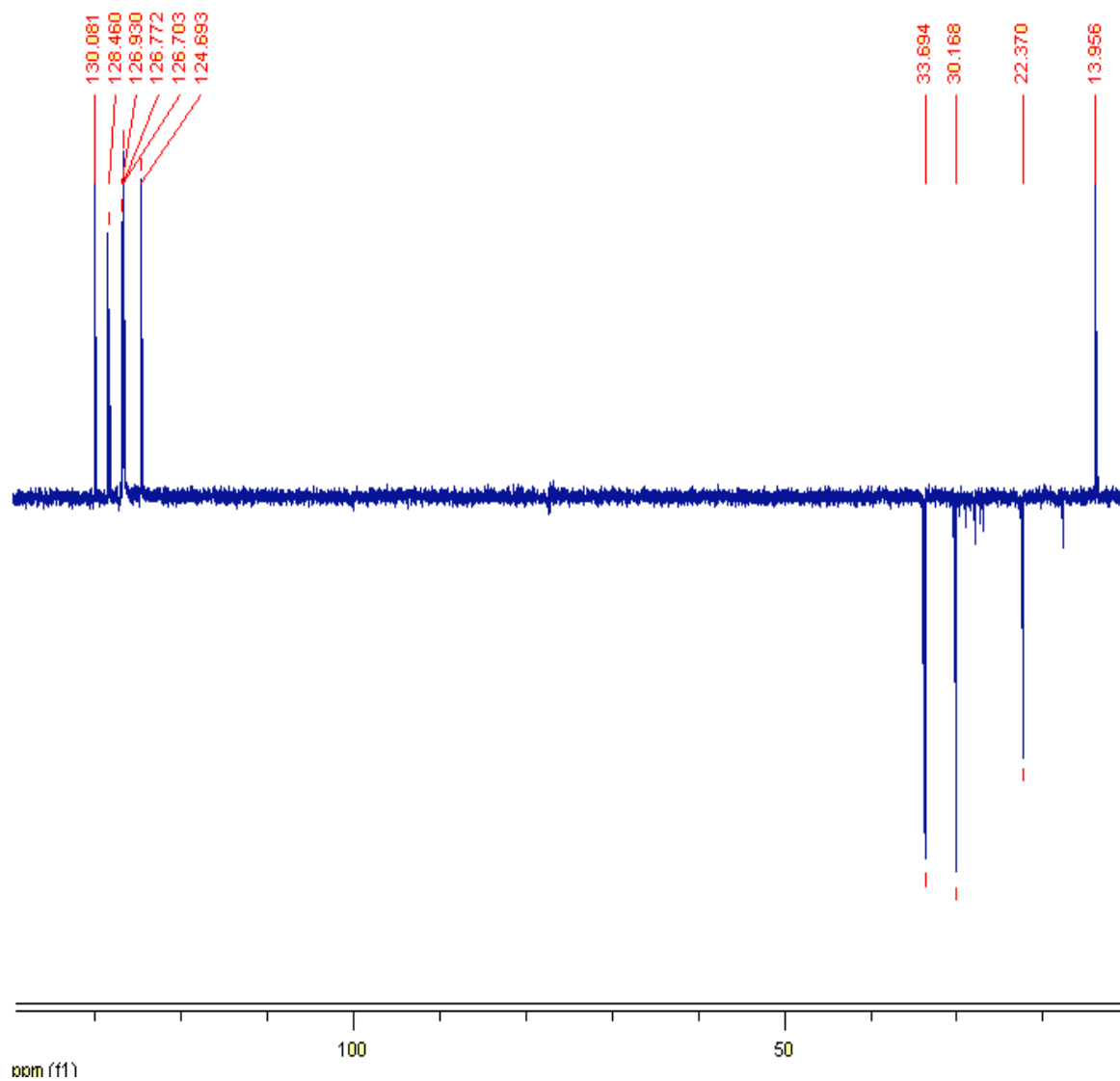
**Appendix 14.** DEPT-135 spectrum of compound **49**.



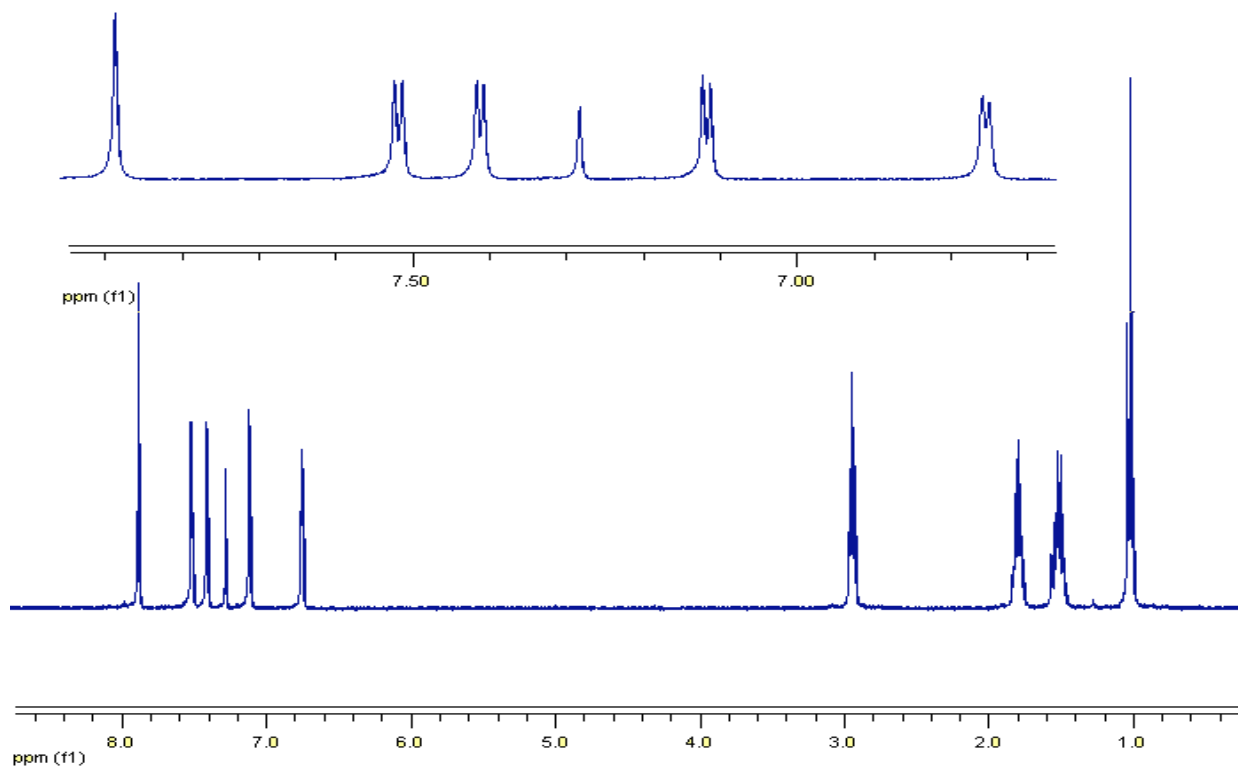
Appendix 15.  $^1\text{H-NMR}$  spectrum of compound 50.



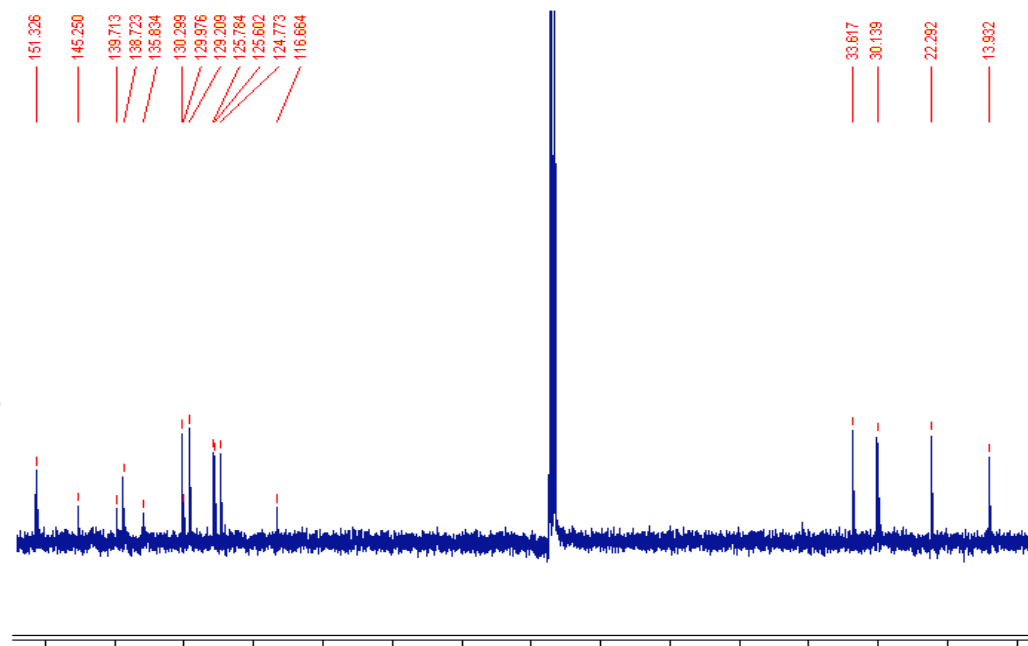
Appendix 16.  $^{13}\text{C-NMR}$  spectrum of compound 50.



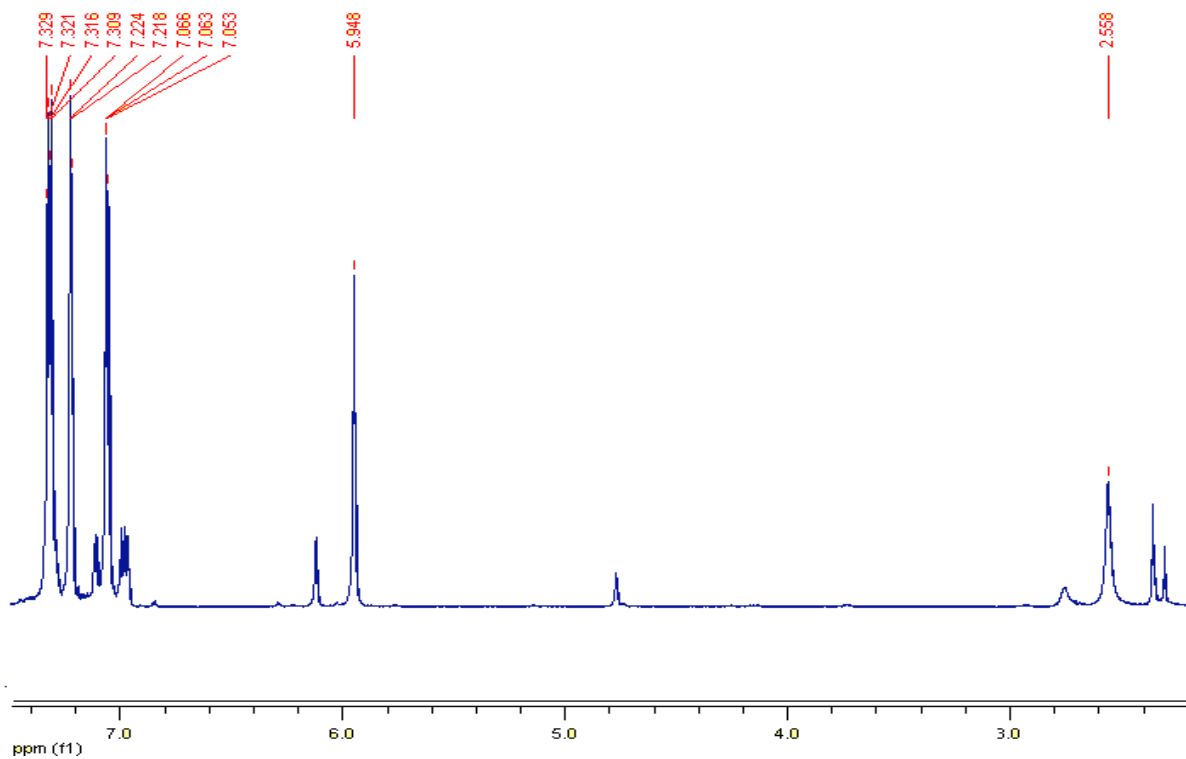
Appendix 17. DEPT-135 spectrum of compound 50.



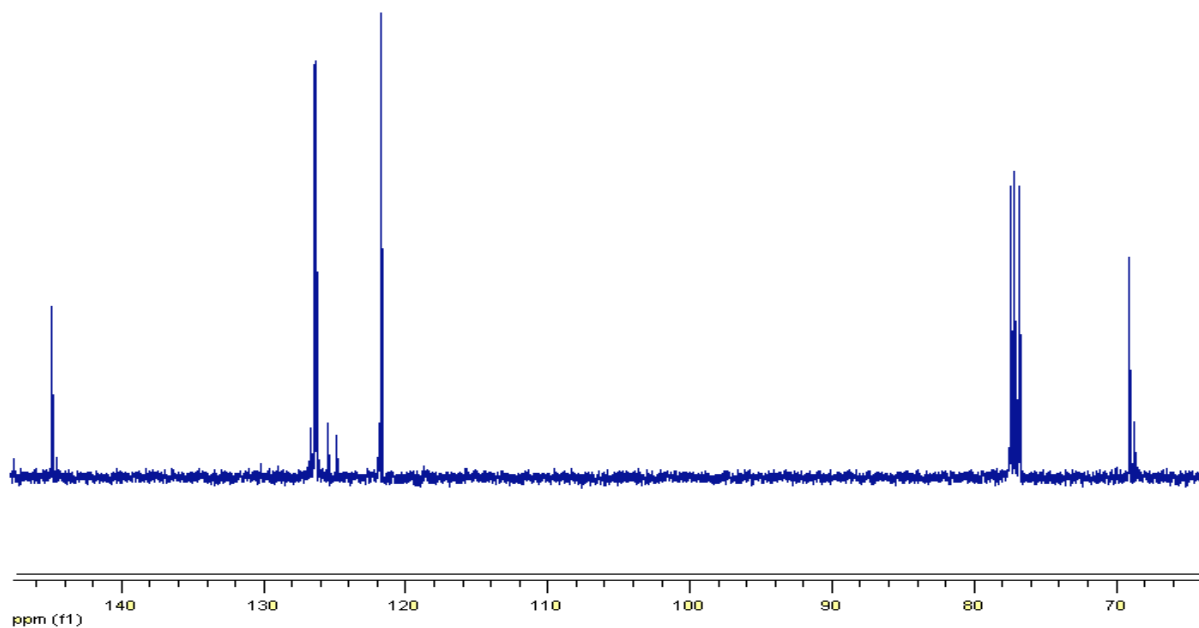
Appendix 18.  $^1\text{H}$ -NMR spectrum of compound 51.



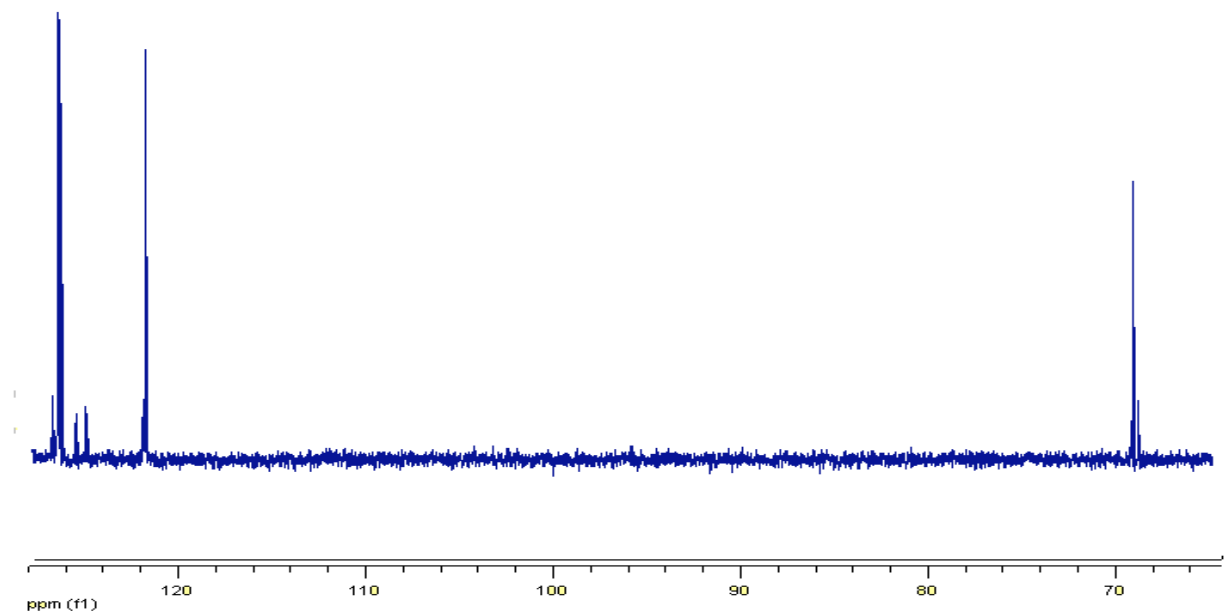
Appendix 19.  $^{13}\text{C}$ -NMR spectrum of compound 51.



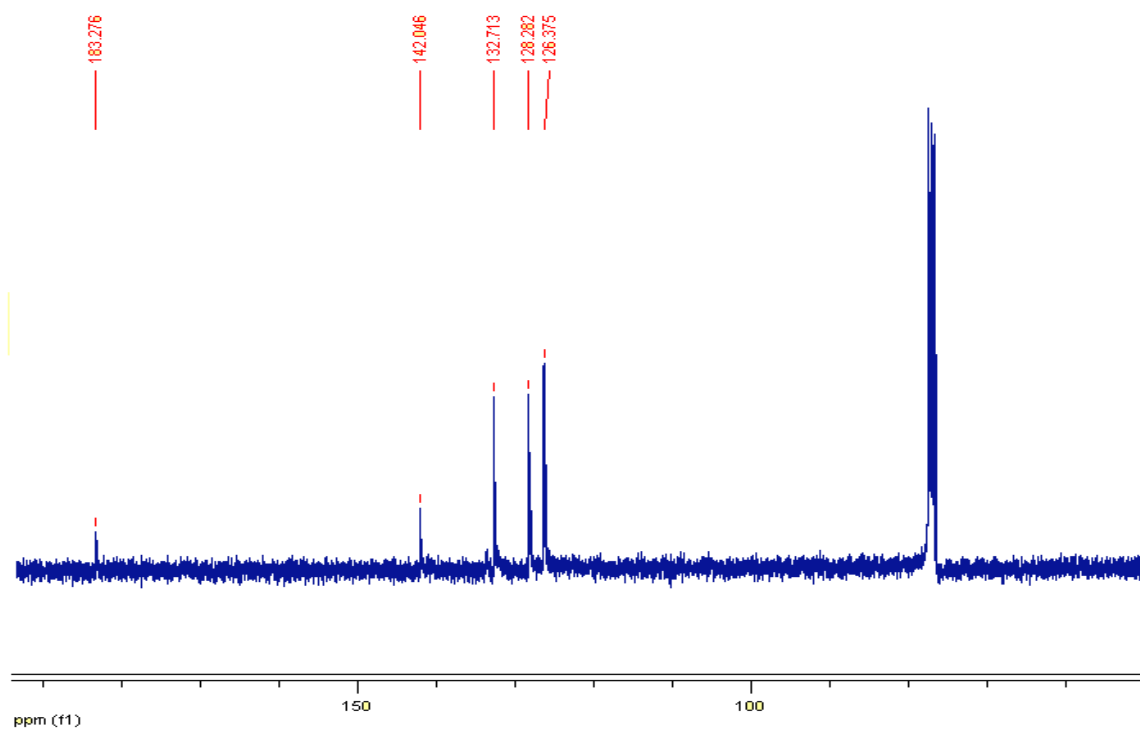
Appendix 20.  $^1\text{H}$ -NMR spectrum of compound 55.



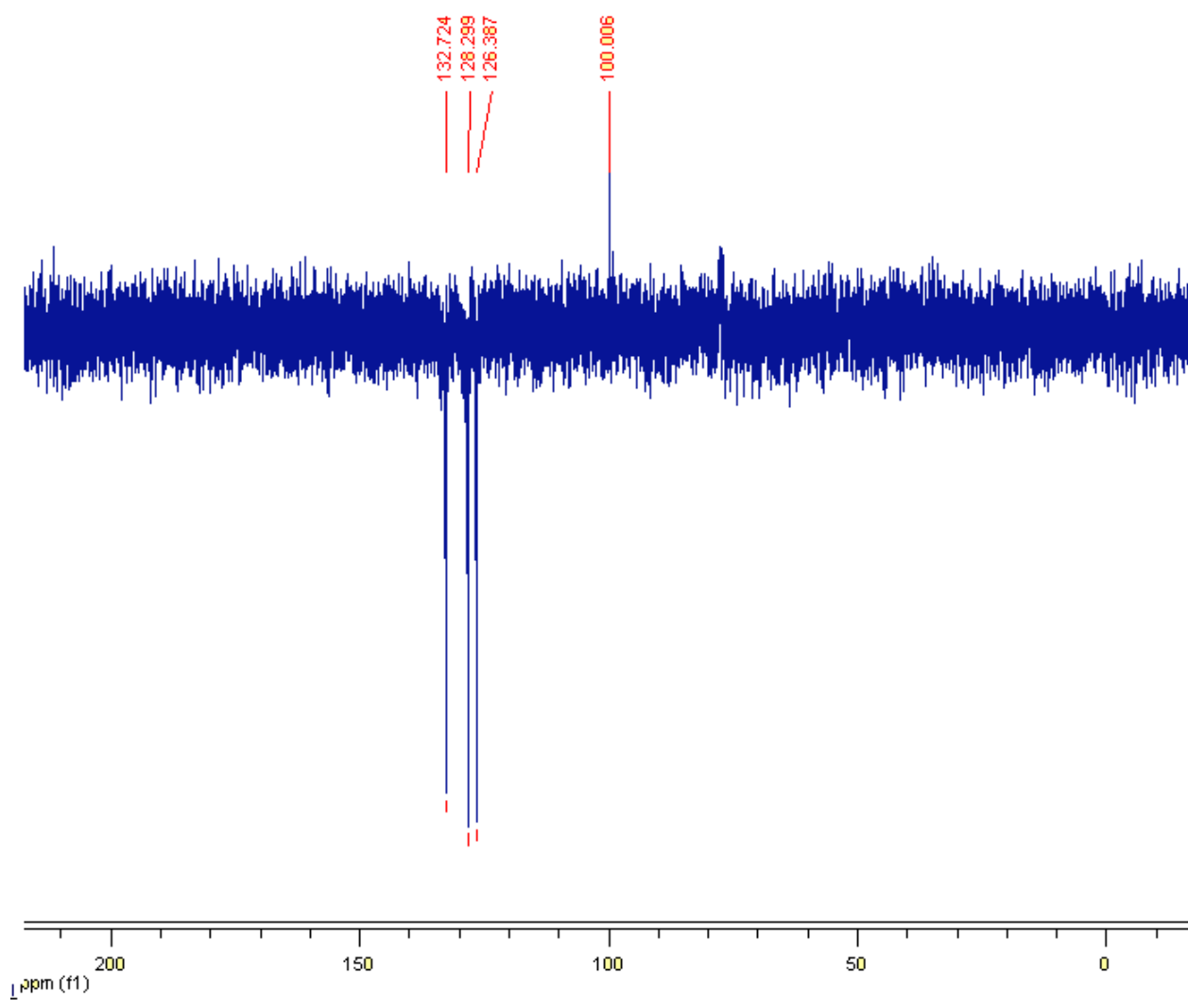
Appendix 21.  $^{13}\text{C}$ -NMR spectrum of compound 55.



Appendix 22. DEPT-135 spectrum of compound 55.



Appendix 23.  $^{13}\text{C}$ -NMR spectrum of compound 56.



**Appendix 24.** DEPT-135 spectrum of compound **56**.