ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS OF QUINOXALINE- AND BENZIMIDAZOLE-BASED MONOMERS

A PROJECT PRESENTED TO

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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JULY, 2008

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HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

OLEDs: Organic light emitting diodes

LEDs: light emitting diodes

FET: Field effect transistor

D-A-D: Donor-Acceptor-Donor

AcOH: Acetic acid

THF: Tetrahydrofuran

n-BuLi: n-Butyllithium

DMF: Dimethyl formamide

IR: Infrared

UV-Vis: Ultra violet-Visible

P(5,8)-Qx): Poly(5,8-quinoxaline)

DEE: Diethyl ether

DCM: Dichloromethane

^{o}C: degree Celsius

%: percentage

dd: doublet of doublets

d: doublet

DEPT: Distortionless enhancement by polarization transfer

DMSO: Dimethyl sulfoxide

J: coupling constants

m: multiplet

NBS: *N*-Bromosuccinamide

NMR: Nuclear Magnetic Resonance

s: singlet

t: triplet

Acknowledgement

I would like to express my deepest gratitude to my research supervisor, Prof. Wendimagegn Mammo, for all his unreserved guidance.

My gratitude also goes to Yoseph Atilaw and Medanit Mamo for measuring spectra.

Above all, boundless thanks to God.

I would also like to extend my gratitude to the Department of Chemistry, AAU.

Abstract

Synthesis of quinoxaline- and benzimidazole-based monomers

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2,3-Bis(4-(hexyloxy)phenyl)-5,8-di(thiophene-2-yl)quinoxaline has been synthesized by the condensation reaction between 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione and 3,6-di(thiophen-2-yl)benzene-1,2-diamine. This monomer has been characterized based on its ^{1}H-NMR, ^{13}C-NMR and IR spectra. Syntheses of benzimidazole-based monomers were attempted by the reaction between *o*-phenylenediamine and heptanal.

1. Introduction

A polymer is a large molecule built up from smaller molecules called monomers. These smaller molecules are linked to each other by conventional chemical bonds. Polymers can be classified in to natural and synthetic polymers based on their origin. Cellulose and its derivatives, starch and rubber are naturally occurring polymers. In addition, a number of important biological materials, most notably the proteins, DNA, and RNA are polymers which occur in nature. The synthetic polymers include materials that are considered as plastics, fibres, elastomers, synthetic rubber and specialized polymers like conducting polymers. Prior to the discovery of conducting polymers, all synthetic polymers were considered to be insulators and uninteresting from the electronic point of view.

Nowadays, conducting polymers are used for the manufacture of electronic device such as light emitting diodes, photovoltaic cells, field effect transistors, sensors, electronic coatings, actuators (artificial muscles), electromagnetic shields, batteries, non-linear optical devices, high quality self-emissive displays and similar devices which are applicable on numerous kinds of portable and stationary utensils [1].

The modern era of conducting polymers started at the end of the 1970s when Heeger and MacDiarmid discovered the first conducting polymer, polyacetylene [2], which was made to conduct electricity by doping with iodine vapour. Since then, the science of conjugated polymers has developed in to an intense research field and hence Heeger, MacDiarmid, and Shirakawa were awarded Nobel Prize in chemistry in the year 2000 for their great contribution to the field [2-4]. Polyacetylene, the first conjugated conducting polymer synthesized, has certain limitations such as improcessability and instability toward air oxidation in the doped

state. Search for alternative conjugated polymers with superior stabilities led to the discoveries of aromatic polymers such as, polythiophenes **(1),** polypyrroles **(2),** polyanilines **(3),** and poly(*p*-phenylenevinylenes) **(4)** (Figure 1) [5] and their copolymers.

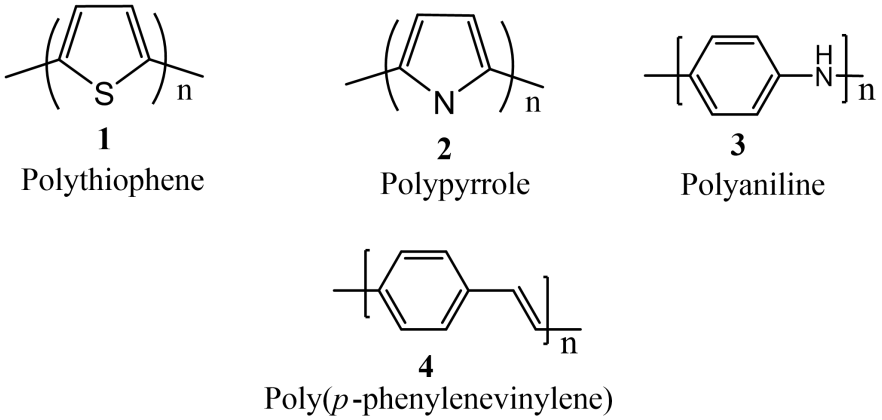
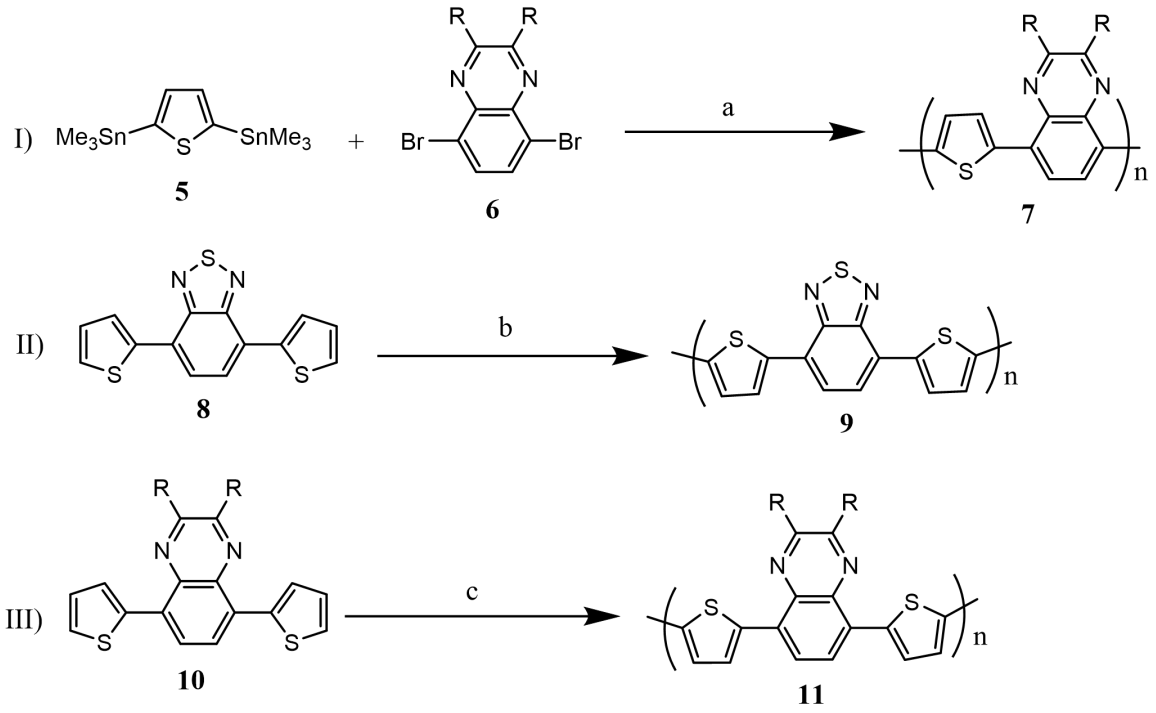


Figure 1. Some aromatic conjugated polymers.

Recently, low band gap conjugated polymers have attracted considerable interest to obtain intrinsically conducting materials [6]. Because low optical band gap conjugated polymers may improve the efficiency of organic photovoltaic devices by increasing the absorption in the visible and near infrared region of the solar spectrum, the synthesis of low band gap material is of interest for the development of plastic solar cells. These polymer solar cells are becoming attractive because they show potential advantages over silicon based solar cells [7]. The main limitations to their applications are lower power conversion efficiency and instability compared to silicon-based solar cells, but their cost of production is low.

There are several factors that influence the band gap of conjugated polymer material. Among these are; intra-chain charge transfer, bond length alternation, aromaticity, substituent effect, intermolecular interaction and π-conjugation length. Thus considerable attention has been given to design methods, which take one or more of the above

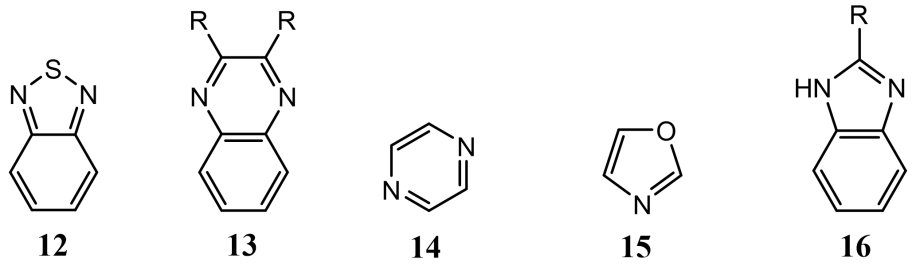
factors into account in order to achieve low band gap polymers, in turn extending wide range of spectral coverage. One of the approaches to low band gap polymers is the alternation of strong electron donating and electron accepting moieties along the polymer back bone [8,9]. The alternating donor-acceptor arrangement causes a strong interaction of the highest occupied molecular orbital (HOMO) of the donor with the lowest unoccupied molecular orbital (LUMO) of the acceptor and, hence reduction in the band gap of the materials [10,11]. Following this strategy a number of low band gap polymers have been synthesized. As an illustration, the polymers **7**, **9**, **11** indicated in scheme 1, were reported [12].



Scheme 1. Synthesis of polymers (a) $Pd(PPh_3)_4$, DMF, (b) electrochemical Polymerization, (c) electrochemical polymerization

If the HOMO level of the donor and the LUMO level of the acceptor are close in energy, it results in a low band gap. Therefore, reduction of band gap can also be efficiently achieved by copolymerization of electron-deficient quinoids like benzothiadiazole **(12)**, quinoxaline **(13)**, pyrazine

(14) and oxazole **(15)** (Figure 2) with aromatic electron-rich rings such as phenylene, thiophene, and pyrrole [13-15]. In these copolymers, the nature of the two monomers affords a novel means to design materials with functional, optical and electrical properties that are not present in the corresponding homopolymers. In this regard, it has been found that quinoxaline and benzimidazole **(16)** are the promising electron-deficient building blocks since they are known to have high electron affinity and good thermal stability and have been successfully incorporated in polymers for use as electron-transport materials in multilayer organic light-emitting diodes (OLEDs) [16,17,18] **.**



12 **13** **14** **15** **16**

Figure 2. Some electron-deficient species.

2. Literature Review

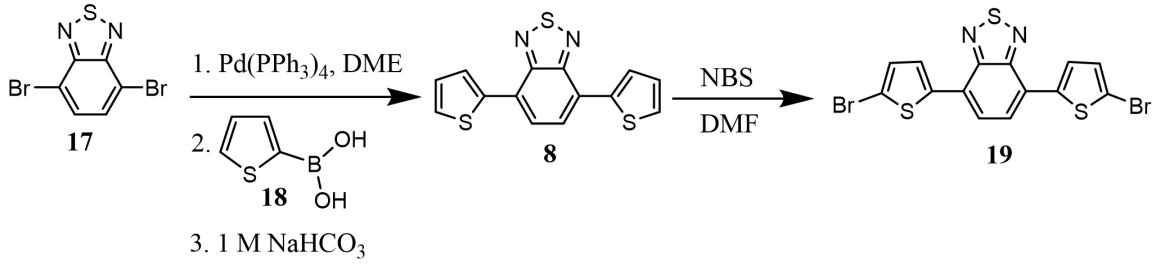
It has recently been found that π-conjugated polymers containing electron withdrawing imine nitrogen(s) (C=N) possess electron-accepting properties and are susceptible to chemical and electrochemical reduction (n-doping). They generate negative charge carriers in the polymer chain and thus give conducting materials by reduction. The increase in the number of imine nitrogens enhances the electron accepting ability of polymers. Thus, monomers with two imine nitrogens seem to be more suited to make electric devices using the n-type electrically conducting

polymers because of their higher electron accepting ability [19]. Quinoxaline is one of the materials that contain two imine nitrogens.

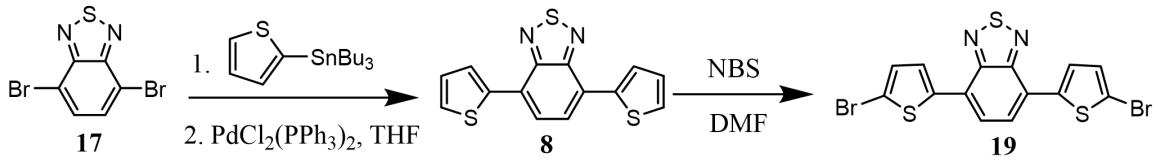
2.1 The quinoxaline monomeric sub-units

Quinoxalines are weakly basic, bicyclic compounds, made by condensing the *o*-phenylenediamine with 1,2-diketones. Monomers with quinoxaline moieties were first synthesized using a condensation between aromatic bis(*o*-diamines) and bis(1,2-dicarbonyls) [20]. The polymers prepared from such monomeric units were initially used as heat-resistant and chemical-resistant materials [16]. Polymers of this type have been later used as the electron transporting materials in polymer light emitting diodes [16].

Most conjugated polymers synthesized to date have low electron affinity, despite the advantages of high electron affinity for many applications. One example is in light-emitting diodes (LEDs), where high electron affinity allows the fabrication of LEDs with good electron injection from stable cathodes such as aluminium, rather than the low work function metals [16]. Other possible applications are n-type field effect transistors (FET) or as the electron accepting material in photodiodes or solar cells. One way to achieve high electron affinity is to attach electron-withdrawing groups to the polymer, for example nitro and CN groups. Another way to synthesize polymers with high electron affinities is to introduce an electron deficient heterocyclic unit such as pyridine, pyrimidine, quinoline, oxadiazole and quinoxaline in the polymer backbone [6]. Quinoxaline is one of the most promising heterocycles for this type of conjugated polymers. The syntheses of donor-acceptor monomeric units have been achieved by Suzuki coupling reactions (Scheme 2) and Stille coupling reactions (Scheme 3).



Scheme 2. Synthesis of a D-A-D monomer using Suzuki coupling reaction.



Scheme 3. Synthesis of a D-A-D monomer using Stille coupling reaction.

2.2 The fluorene monomeric sub-unit

Polyfluorene-based materials have been investigated extensively because of the many attractive properties they possess, as active components of organic light emitting diodes [21, 22] and because of their thermal and chemical stability [22]. Polyfluorene-based materials can emit color across the entire visible range, possess high thermal stability, and can easily be functionalized at the methylene bridge for fine tuning of emissive properties. The polyfluorene backbone provides planarity; side groups at C-9 can give polymer processablity and solubility [22]. These characteristics make polyflorene homo- and co-polymers attractive components for luminescent materials in organic light emitting diodes. Thus, polyfluorenes are considered as one of the most promising classes of electroluminescent polymers.

The ability to functionalize polyfluorene at the methylene bridge, without distorting the conjugation between monomer units, has been utilized as a method to help control undesirable properties and improve thermal properties of the polymer along with processibility [23]. Copolymerization of fluorene monomer derivatives with different aromatic moieties allows for color tuning through the modification of the band gap. To extend the optical absorption to longer wavelengths, synthesis of alternating fluorene copolymers, which contain blocks of electron accepting and electron donating moieties along the polymer backbone, have been developed [24, 25]. Following this, alternating polyfluorene copolymers **20**, **21**, **22**, **23** and **24** with a D-A-D backbone structure (Figure 3) have been synthesized [5, 26].

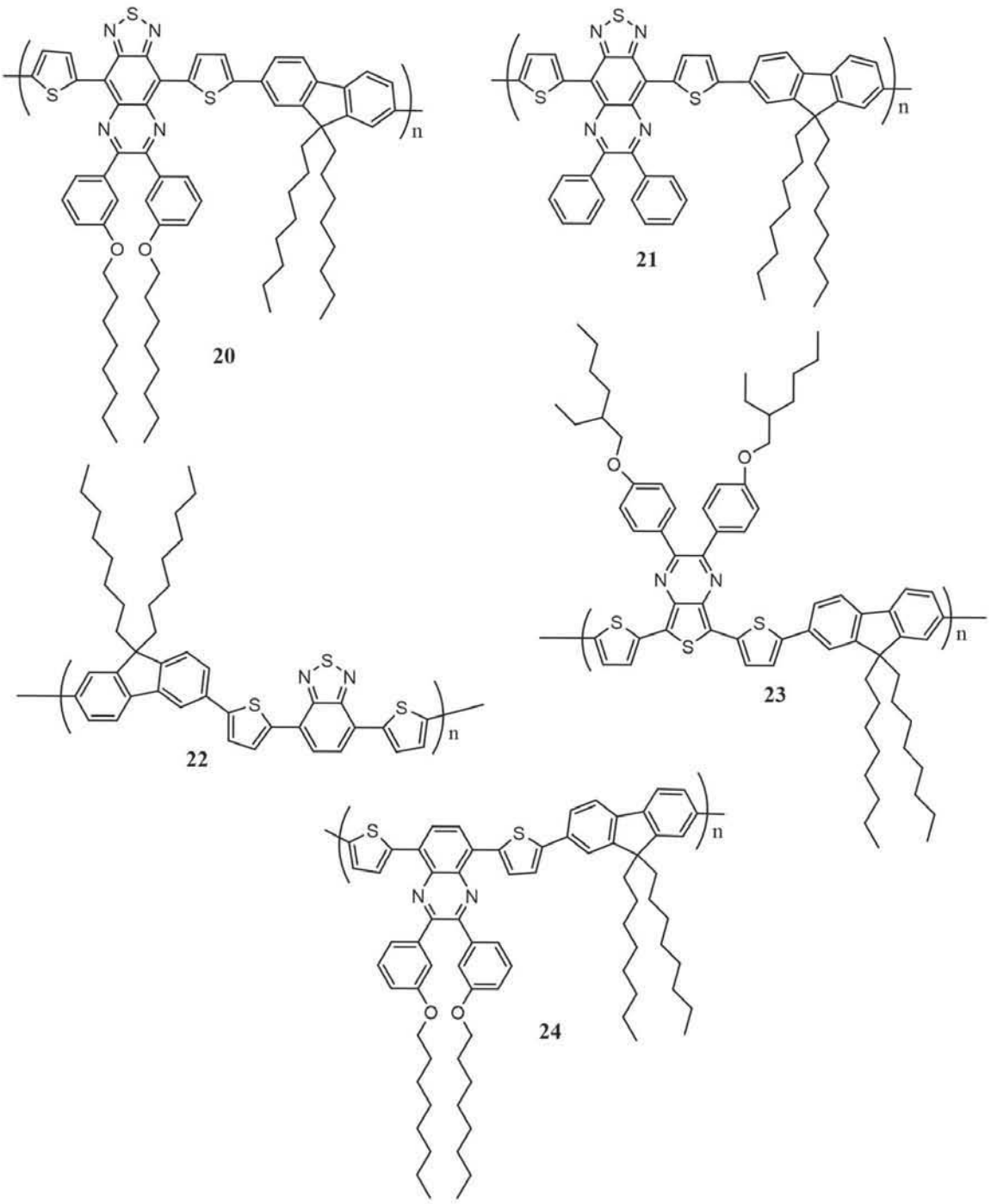
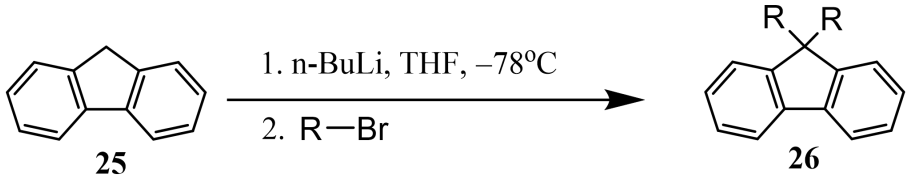


Figure 3. Some low band gap polyfluorene copolymers.

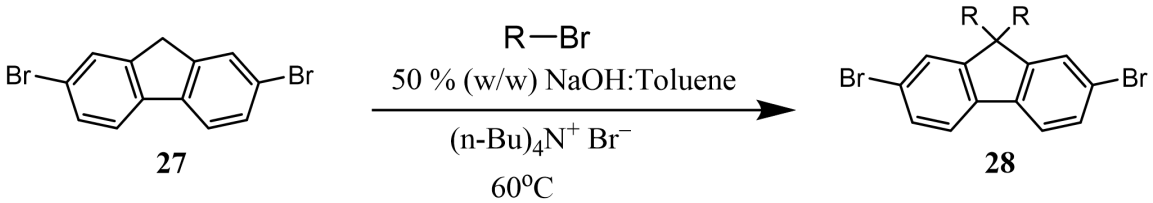
The 9,9-dialkyl-substituted fluorene can be synthesized by using different types of reactions. Among the principal and most commonly

used reactions are nucleophillic substitution using an alkyllithium reagent (Scheme 4), and the phase transfer catalysis reactions (Scheme 5). The former uses a strong base like n-butyllithium (n-BuLi) in THF at -78^{0}C for sequential abstraction of the protons from the benzylic position, and the consequent reactions of the resulting alkyllithium anion with an alkylhalide in nucleophilic manner [27, 28].



Scheme 4. Syntheis of 9,9-dialkylflourene using n-BuLi.

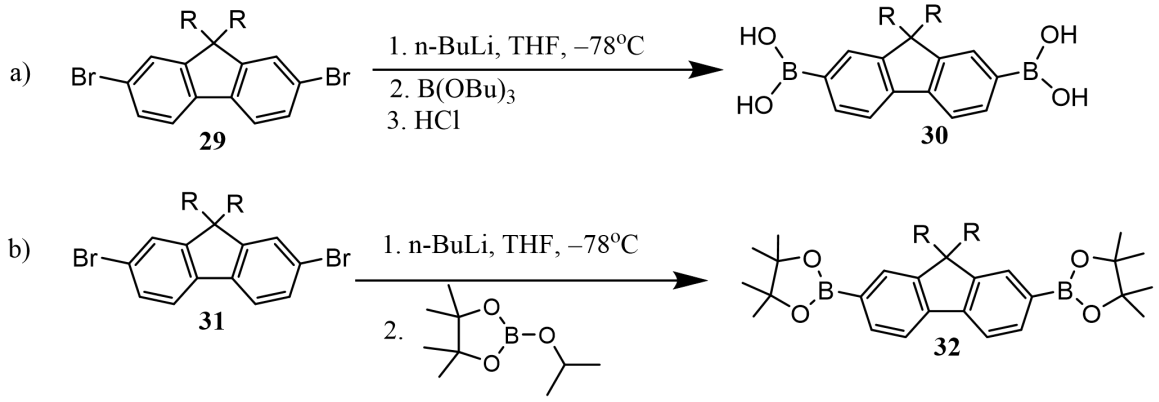
Another pathway that has been used for the synthesis of 9,9-dialkyl substituted fluorenes is the phase transfer catalysis reaction. This reaction involves the use of a two-phase system composed of equal volumes of toluene and 50% (w/w) aqueous NaOH and tetrabutylammonium bromide as a phase transfer catalyst (Scheme 5). Agitating the mixture of fluorene and an alkylbromide at reflux in the two-phase system results the 9,9-dialkylated fluorene [29]. The advantage of this reaction is that it can be implemented on a 2,7-dihalogenated fluorene. Thus, it eliminates the risk of halogenating the side chain or functional groups on the side chain.



Scheme 5. Synthesis of 9,9-dialkylfluorene by phase transfer catalysis.

The subsequent step, after the synthesis of 2,7-dibromo-9,9-dialkylfluorene, is preparation of the respective 2,7-diboronic acids or

boronate esters (Scheme 6) for the consecutive Suzuki type polymerization with the dihaloaryls. The synthesis of 2,7-diboronic acids or boronate esters uses a very strong base like n-BuLi for the formation of the aryllithium through metal-halogen exchange. Subsequent treatment of the aryllithium with tributylborate affords the fluorene-2,7-diboronic acid **(30)** after an acid work up whereas treatment with pinacolborane affords fluorene-2,7-diborate ester **(32)** [30] as indicated in Scheme 6.

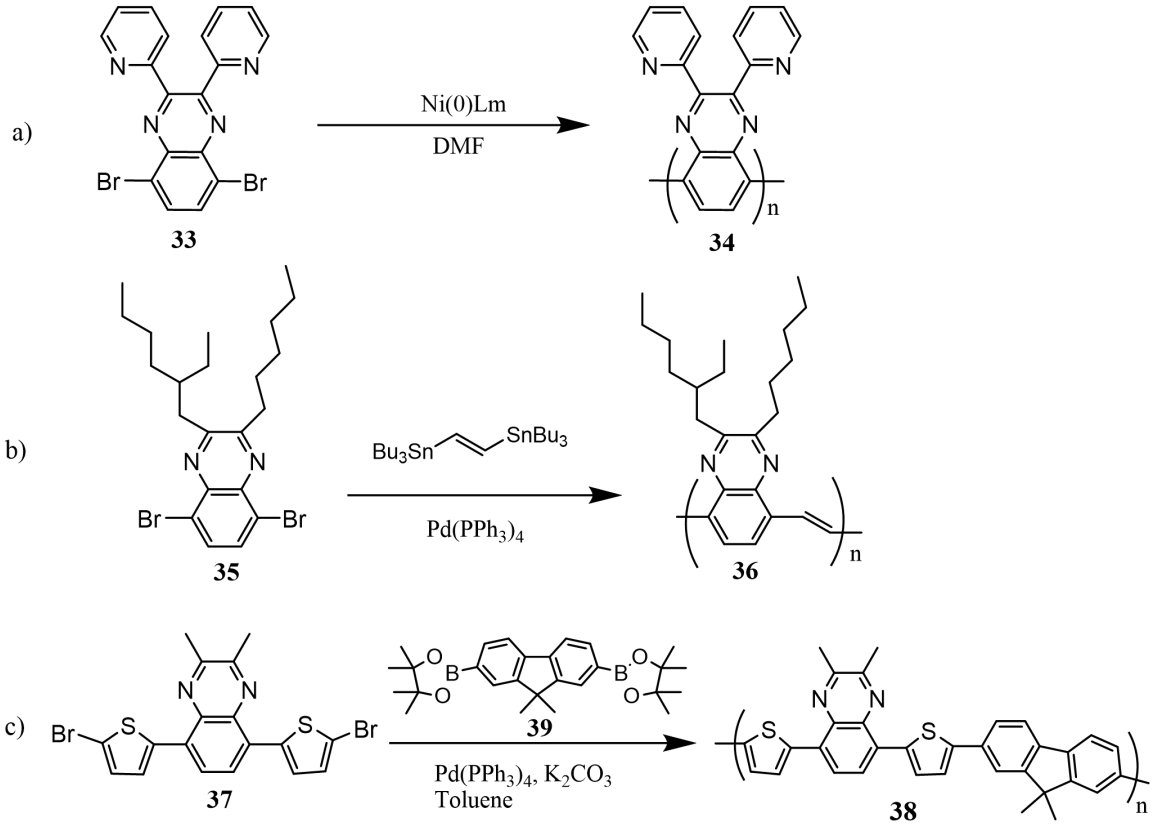


Scheme 6. Synthesis of boronic acid (a), and boronate ester (b).

2.3 Polymerization reaction of quinoxaline monomer unit

In general polymers are mostly prepared by two methods; (1) electrochemical polymerization, where a potential is applied to a solution containing the monomer and an electrolyte, this results in the formation of polymers at anode. (2) Chemical polymerization using Stille, Negishi, Kumada, Suzuki cross coupling reactions, oxidative ferric chloride polymerizations and Yamamoto, Knoevenagel or Horner-Wadsworth-Emmons condensation polymerization have been documented [31]. Thus, quinoxaline monomer units form homopolymers or copolymers with

other monomer units using either of the above two methods. As an illustration, it was reported that polymers **34**, **36**, **38** were prepared by the dehalogenation polycondensation using nickel complex, Stille coupling and Suzuki coupling reactions, respectively (Scheme 7) [16, 32, 33].



Scheme 7. Polymerization through (a) Yamamoto polymerization, (b) Stille coupling reaction, (c) Suzuki coupling reaction route.

2.4 Application of quinoxaline-containing polymers in light emitting diodes

Since the discovery of poly(*p*-phenylenevinylene), electroluminescent polymers have been the subject of considerable academic and commercial interest. Much effort has been directed towards the preparation of materials with improved properties such as wide tunability of emission wave length, high photoluminescence and electroluminescence efficiency. The colour of emission is directly dependent on the extent of conjugation along the π-system and the chemical structure of the polymer. While synthesizing and designing light emitting polymers, considerable attention has been given to tailoring the monomer units as well as the conjugated building blocks in order to achieve the desired device characteristics. Short conjugation gives blue-shifted emission and long conjugation gives red-shifted emission from the polymer. Introducing of electron withdrawing or electron donating groups into the main chain tunes the electron affinity of the conjugated polymer. Bulky side groups can twist the conjugated π-system out of planarity thereby increasing the optical band gap which affects the desired characteristics of the polymer.

As the spectral region of polymer LEDs is being expanded into the ultraviolet and near IR regions, areas of applications besides displays extends to variable optical attenuators, camouflage materials, thermal emission detectors, and sensor and communication technologies [34, 35]. It has been reported that different polyquinoxalines, which have found applications in the fabrication of light emitting diodes, have been synthesized [19]. Their optical, electrical, and electrochemical properties are manipulated by their substituents.

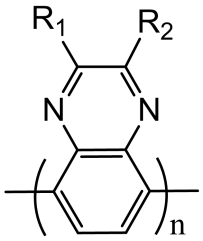


Figure 4. Structure of polyquinoxaline.

It has been found that unsubstituted polyquinoxaline is soluble in trifluoroacetic acid and formic acid, and insoluble in other organic solvents. Introduction of methyl, ethyl, phenyl, *p*-tolyl, substituents does not cause a distinct increase in solubility, whereas introduction of *p*-phenylpheyl and 2-pyridyl substituents make the polymer soluble in organic solvents such as halogenated solvents (chloroform and tetrachloroethane). Polymers containing long alkyl chains are soluble in various organic solvents. The P(5,8-Qx) absorbs UV-Vis radiation at 258 and 324 nm. Other polyquinoxaline polymers with various substituents show the UV-Vis absorption peaks near that of P(5,8-Qx), despite the π-π* absorption peaks of the polymers with aromatic substituents show shifts to longer wave lengths due the formation of longer π-conjugation systems. Since polyquinoxalines having aromatic substituents show strong fluorescence, the polymers are expected to be useful materials to make light emitting diodes [19].

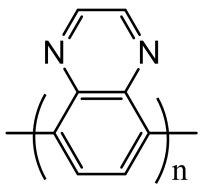


Figure 5. Structure of poly(5,8-quinoxaline).

3. Objective of the Project

The aim of this project is to synthesize monomers based on quinoxaline and benzimidazole derivatives, which can be used as electron-deficient building blocks for the construction of copolymers along with other monomeric units. The monomers will be characterized based on their ^{1}H-NMR, ^{13}C-NMR, IR and UV-Vis spectral data.

4. Results and Discussion

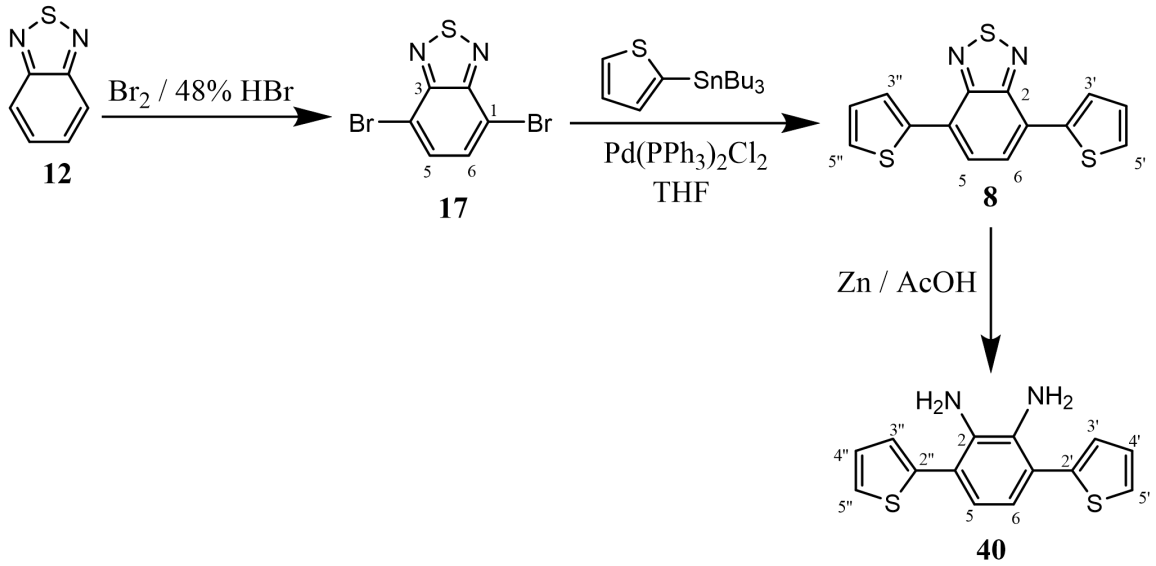
In the course of this work, attempt was made to synthesize a 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**. The synthesis of this compound is described below.

4.1 Synthesis of 3,6-di(thiophen-2-yl)benzene-1,2-diamine (40)

Bromination of 2,1,3-benzothiadiazole **(12)**, with bromine and 48% aqueous HBr resulted in formation of 4,7-dibromobenzo[1,2,3]thidiazole **(17)** in 97% yield as a yellowish crystalline solid, which melted at 246-248^{0}C. The ^{1}H-NMR spectrum of this compound showed only one singlet at δ 7.75 in agreement with the chemically equivalent protons H-5, H-6 in the molecule. Three carbon resonances appeared in the ^{13}C-NMR spectrum of compound **17** of which two are quaternary carbon atoms. The quaternary carbon resonance at δ 113.9 is accountable to C-4 and C-1 which are attached to bromines. The other quaternary carbon resonance at δ 152.9 is due to the carbon atoms connected to the nitrogen at C-3 and C-2. The resonance at δ 132.4 is due to C-5 and C-6. The FT-IR spectrum of **17** displayed the C-Br bond stretching band at 586 cm^{-1}, aromatic C-H stretching at 3078 cm^{-1}and 3046 cm^{-1} , carbon-nitrogen double bond stretching at 1637 cm^{-1}, and aromatic modes at 1476 cm^{-1}.

Compound **17** was subjected to Stille coupling reaction with 2-(tributyl stannyl)thiophene in the presence of $Pd(PPh_3)_2Cl_2$ to afford 4,7-di(thiophene-2-yl)benzo[c]thiadiazole **(8)** in 71.7% yield, which melted at 125^{0}C. Subsequent reduction of **8** with zinc in acetic acid resulted in the formation of 3,6-di(thiophen-2-yl)benzene-1,2-diamine **40** in 93.8% yield

(Scheme 8). Compounds **8** and **40** were characterized based on their spectroscopic behaviors as discussed below.



Scheme 8. Synthesis of compound **40**.

The ^{1}H-NMR spectrum of compound **8** (Table 1) showed four signals in the aromatic region. The downfield doublet at δ 8.15 (J = 3.6 Hz), integrating for two hydrogens, corresponds to H-5' and H-5". The two-proton singlet centered at δ 7.91 is due to H-5 and H-6. The two hydrogens do not couple with each other on account of being chemically equivalent. The two-proton doublet of doublets at δ 7.25 corresponds to H-4' and H-4". The remaining two-proton doublet of doublets at δ 7.49 is due to H-3' and H-3".

Compound **8** contains fourteen carbons but only seven carbon signals appeared in the ^{13}C-NMR spectrum and four in the DEPT-135 spectrum. The signals at δ 152.7, 139.4 and 126.0 are due to quaternary carbon atoms and can be accounted for C-2', C-3 and C-4, respectively. The remaining four signals are due to methine groups on the thiophene rings and the equivalent carbons (C-5 and C-6) in the central aromatic ring. These signals appeared at δ 125.8, 126.8, 127.5 and 128.0 and

correspond to C-4', C-3', C-5', and C-6, respectively. The data obtained from ^{1}H-NMR and ^{13}C-NMR along with DEPT-135 agree with the structure of compound **8**.

The FT-IR spectrum of compound **8** showed aromatic C-H stretching band at 3000 cm^{-1}, carbon-nitrogen double bond stretching band at 1637 cm^{-1}, aromatic modes at 1482, 1421 cm^{-1} and C-S stretching vibration at 690 cm^{-1}.

Table 1. ^{1}H-NMR (400 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **17**, **8** and **40.**

17	**8**	**40**
7.75 (2H, *s*, H-5, H-6)	8.15 (2H, *d, J* = 3.6 Hz, H-5', H-5")	7.41 (2H, *dd, J* = 1.1, 5.2 Hz, H-5", H-5')
-	7.91 (2H, *s*, H-5, H-6)	7.22 (2H, *dd, J* = 1.2, 3.6 Hz, H-3', H-3"
-	7.49 (2H, *d, J* = 4.9 Hz, H-3', H-3")	7.18 (2H, *dd, J* = 3.5, 5.2 Hz, H-4', H-4")
-	7.25 (2H, *dd, J* = 4.0, 8 Hz, H-4', H-4")	6.91 (2H, *s*, H-5, H-6

The ^{1}H-NMR spectrum of compound **40** (Table 1) indicated an upfield singlet centered at δ 6.91 which integrates for two protons, corresponding to H-5 and H-6. The doublet of doublets that appeared at δ 7.41 (*J* = 1.1, 5.2 Hz) is assignable to H-5" and H-2. The remaining two signals have also doublet of doublets multiplicity. The one at δ 7.18 (*J* =

3.5, 5.2 Hz) that integrates for two protons belongs to H-4' and H-4". The other signal centered at δ 7.22 (J = 1.2, 3.6) is due to H-3' and H-3".

Table 2. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **17**, **8** and **40**.

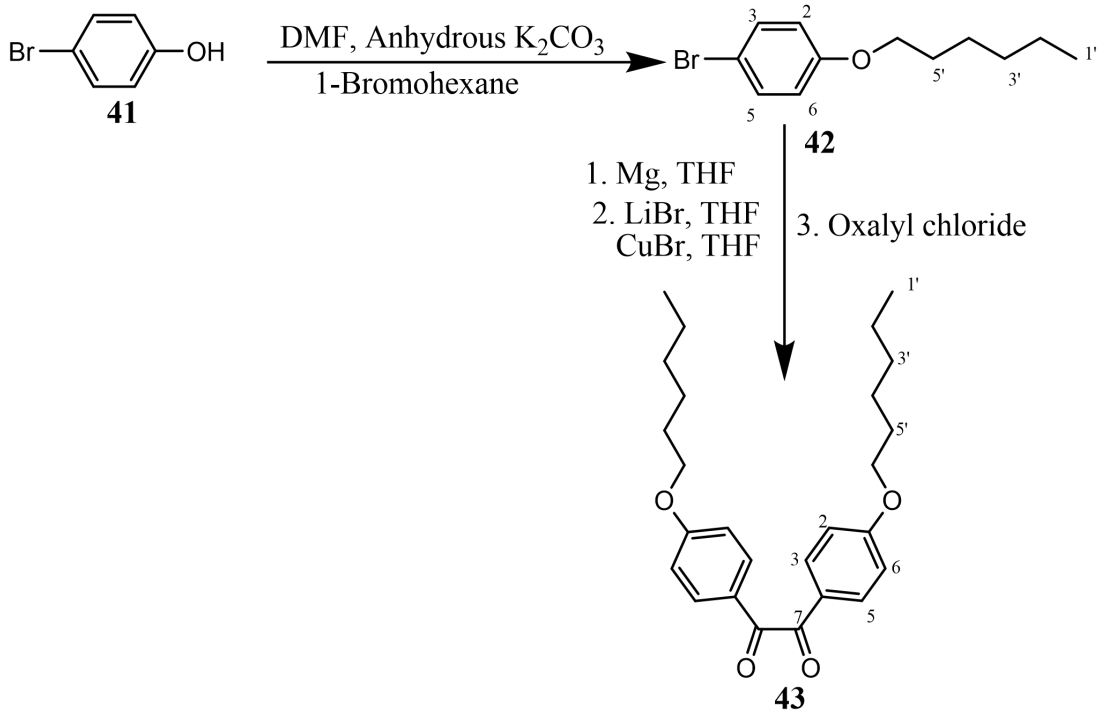
Carbon	**17**	**8**	**40**
1	113.9	126.0	141.0
2	152.9	152.7	132.9
3	152.9	152.7	132.9
4	113.9	126.0	141.0
5	132.4	128.0	121.2
6	132.4	128.0	121.2
1'	-	-	-
2'	-	139.4	121.5
3'	-	126.8	126.1
4'	-	125.8	125.6
5'	-	127.5	127.6

The ^{13}C-NMR spectrum of **40** showed seven carbon signals confirming that the compound is symmetrical. Of which three are quaternary carbons. The signals at δ 141.0, 132.9, 121.5 are due to quaternary carbons and can be accounted to C-1, C-2, and C-2', respectively. The remaining four carbon signals appeared at δ 121.2, 125.6, 126.1, and 127.6 and correspond to C-5, C-4', C-3', and C-5', respectively. Thus, the data obtained from ^{1}H-NMR and ^{13}C-NMR along with DEPT-135 agree with the structure of compound **40**.

4.2 Synthesis of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione (44)

One of the essential precursors to build compound **44** was 1,2-bis-(4-(hexyloxyphenyl)-ethane-1,2-dione **(43)**, which was synthesized starting from *p*-bromophenol **(41)** (Scheme 9). The reaction began by alkylating *p*-bromophenol using 1-bromohexane in the presence of anhydrous K_2CO_3

in DMF and resulted in formation of *p*-bromohexyloxybenzene **(42)** in 91% yield. Compound **42** was subjected to Grignard reaction with Mg in THF and the resulting Grignard reagent was added to a suspension of LiBr/CuBr mixture. Up on adding oxalyl chloride to the above mixture, 1,2-bis–(4-hexyloxyphenyl)-ethane-1,2-dione **(43)** was obtained, which was purified by silica gel column chromatography using 4.5:0.5 pet ether:ethyl acetate as eluent. The above two compounds **42** and **43** were characterized based on their spectra of ^{1}H-NMR, ^{13}C-NMR, and DEPT-135.



Scheme 9. Synthesis of compound **43**.

The ^{1}H-NMR spectrum of **42** (Table 3) showed two doublets in the aromatic region. The doublet at δ 6.79 (J = 8.9 Hz) integrates for two protons and corresponds to H-2 and H-6. The two protons are *ortho* to the oxygen and are shielded due to the electron donating resonance effect of the oxygen. The doublet centered at δ 7.38 (J = 9.0 Hz) is due to H-3 and H-5. All the remaining signals are in the aliphatic region. The signal at δ 3.94 (J = 6.6 Hz), which is downfield compared to other signals in

aliphatic region, belongs to H-6' on the oxygenated carbon. The quintet at δ 1.82 and the sextet at δ 1.52, which integrate for two protons each, are attributable to H-2' and H-5', respectively. The multiplet centered at δ 1.36, which integrates for two hydrogens, is accountable to H-3' and H-4'. The signal due to the terminal methyl groups appeared at δ 0.95.

Table 3. ^{1}H-NMR (400 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **42** and **43**.

42	**43**
7.39 (2H, *d, J* = 9.0 Hz, H-2, H-6)	7.95 (4H, *d, J* = 8.9 Hz, H-2, H-6)
6.79 (2H, *d, J* = 8.9 Hz, H-3, H-5)	6.97 (4H, *d, J* = 8.9 Hz, H-3, H-5)
3.94 (2H, *t*, *J* = 6.6 Hz, H-6')	4.05 (4H, *t, J* = 6.5 Hz, H-6')
1.82 (2H, *quintet*, *J* = 6.9 Hz, H-5')	1.84 (4H, *quintet*, *J* = 6.7 Hz, H-5')
1.49 (2H, *sextet*, J = 7.0, H-2')	1.50 (4H, *sextet*, *J* = 7.0 Hz, H-2')
1.36 (4H, *m*, H-3', H-4')	1.36 (8H, *m*, H-3', H-4')
0.95 (3H, *t*, *J* = 6.2 Hz, H-1')	0.93 (6H, *t, J* = 7.0 Hz, H-1')

The ^{13}C-NMR spectrum of compound **42** (Appendix 5) showed four resonances in the aromatic region. The quaternary carbon signals at δ 158.3 and 112.6, respectively, are attributed to C-1 and C-4. The methine signals at δ 132.2 is due to C-3 and C-5, where as the signal at δ 116.3 is due to C-2 and C-6. In the aliphatic region of the spectrum, there are six signals. The signal at δ 68.3 is due to C-6' and the

remaining signals at δ 14.1, 22.6, 31.6, 25.7, and 29.2 are due to C-1', C-2', C-3', C-4',and C-5', respectively. Thus, the data obtained from ^{1}H-NMR and ^{13}C-NMR along with DEPT-135 agrees with the structure of compound **42**.

The ^{1}H-NMR spectrum of compound **43** (Table 3) showed two doublets in the aromatic region. The signal at δ 7.95 (J = 8.9 Hz), integrating for four protons corresponds to H-2 and H-6, which couple with their neighboring *ortho* protons. The remaining doublet at δ 6.97 (J = 8.89 Hz) integrated for four protons and is accounted to H-3 and H-5. In the aliphatic region of the spectrum, there are five signals. The one that appeared at δ 4.05, which integrates for four protons, is due to the methylene protons on the carbon atoms attached to the oxygen. The two-proton quintet at δ 1.84, which integrates for four hydrogens, is due to protons at C-5'. The sextet at δ 1.5 integrating for four protons is attributed to the methylene protons at C-2'. The unresolved multiplet at δ 1.36 integrating for eight protons is due to two methylene groups at position 3' and 4'. The six-proton triplet at δ 0.93 is due to the terminal methyl groups.

The ^{13}C-NMR and DEPT-135 spectra of compound **43** revealed the presence of three quaternary carbons, two non-equivalent methine, five methylene and one methyl groups. The signal at δ 193 is assigned to the two equivalent carbonyl groups. The resonance at δ 68 is due to the oxygenated methylene groups and the signal at δ 14.0 is due to the terminal methyl groups. The carbon signals at δ 126.2 and 164.5 are accountable to two quaternary carbons and correspond to H-4 and H-1, respectively. The remaining signals at δ 114.7, 132.4, 22.6, 31.5, 25.6, and 28.9 are assignable to C-2, C-3, C-2', C-3', C-4', and C-5', respectively.

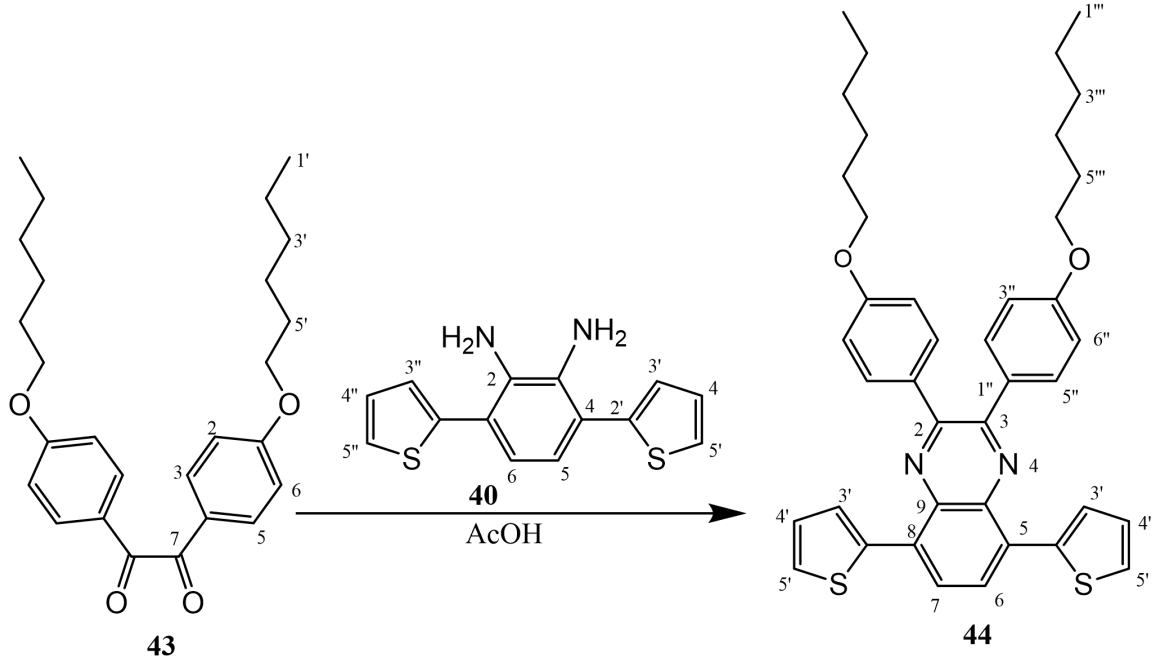
Table 4. ^{13}C-NMR (100.6 MHZ, $CDCl_3$) data (δ_{ppm}) of compounds **42** and **43.**

Carbon	**42**	**43**
1	158.3	164.5
2	116.2	114.7
3	132.2	132.4
4	112.6	126.1
5	132.2	132.4
6	116.2	114.7
7	-	193.6
1’	14.1	14.0
2’	22.6	22.6
3’	31.6	31.5
4’	25.7	25.6
5’	29.2	28.9
6’	68.3	68.5

The FT-IR spectrum of compound **43** showed bands at 2943 and 2853 cm^{-1} due to stretching vibrations of the CH_3 and CH_2 groups, respectively. The carbonyl-stretching band appeared at 1664 cm^{-1}. In addition, the bands at 1604 and 1510 cm^{-1} are attributed to the C=C ring stretching vibration. The asymmetric and symmetric C-O-C stretching bands appeared at 1262 and 1164cm^{-1}, respectively. The IR data along with the ^{1}H-NMR and ^{13}C-NMR data agree very well with structure **43**.

4.3 Synthesis of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline (44)

Compounds **43** and **40** are essential building blocks for the construction of compound **44**. The condensation of diamine **40** with 1,2-bis-(4-hexyloxyphenyl)-ethane-1,2-dione **(43)** in acetic acid resulted in formation of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)** in a pure form in 71% yield, which melted at 124°C. The structure of this compound was confirmed based on its spectroscopic data as discussed below.



Scheme 10. Synthesis of compound **44**.

The ^{1}H-NMR spectrum of compound **40** (Table 5) showed six proton resonances in the aromatic region. Among these, three of them are due to thiophenic protons and the remaining two are assignable to the protons on the benzene rings. The most downfield singlet at δ 8.11, which integrated for two protons, is due to H-6 and H-7. The doublets at δ 7.75 (J = 8.8 Hz) and 6.93 (J = 8.8 Hz) are due to equivalent protons H-2", H-6", H-3" and H-5", respectively. The three-proton doublet of doublets at δ

7.89 (*J* = 1.0, 4.0 Hz), 7.54 (*J* = 1.0, 5.2 Hz) and 7.21 (*J* = 4.0, 5.2 Hz) are due to thiophene ring protons H-5', H-3' and H-4', respectively. The methylene protons attached to the oxygenated carbon (H-6'") resonate at δ 4.04 (*J* = 6.6 Hz) with triplet multiplicity. The quintet at δ 1.86 (*J* = 6.8 Hz) and the sextet at 1.54 (*J* = 6.8 Hz) are due to H-5'" and H-2'", respectively. The multiplet at δ 1.39 integrating for eight protons is due to H-3'" and H-4'". The signal due to the methyl protons appeared at δ 0.96 as triplet.

In the ^{13}C-NMR spectrum of compound **44** (Table 6) a total of eighteen carbon resonances appeared, of which six are in the aliphatic region and twelve are in the aromatic region. The ^{13}C-DEPT-135 spectrum revealed the presence of six quaternary carbons. The signals at δ 131.1, 159.9 are attributed to C-1", C-4", respectively. The other quaternary carbon signals are due to equivalent carbon atoms. The resonance at δ 136.9 is due to two equivalent carbons C-2' while the signal at 138.9 is assignable to equivalent carbon atoms C-9 and C-10. The remaining quaternary carbon signal at 131.16 corresponds to C-5 and C-8. The resonances at δ 14.0, 22.6, 25.8, 29.2, 31.6 and 68.1 correspond to C-1', C-2', C-4', C-5', C-3' and C-6', respectively.

The UV-Vis spectrum of compound **44** was recorded in ethyl acetate and showed two absorption bands at 310 and 403 nm. The FT-IR spectrum of compound **44** displayed the C=C bond stretching band at 1606 cm^{-1}. The bands at 2928 and 2830 cm^{-1} are due to stretching vibrations of the CH_3 and CH_2 groups, respectively. In addition, the bands at 1229, 1262, 1072, and 1045 cm^{-1} are attributed to C-O-C stretching vibration. The IR data along with the ^{1}H-NMR and ^{13}C-NMR data agree very well with structure **44**.

Table 5. ^{1}H-NMR (400 MHz, $CDCl_3$) data (δ_{ppm}) of compound **44**.

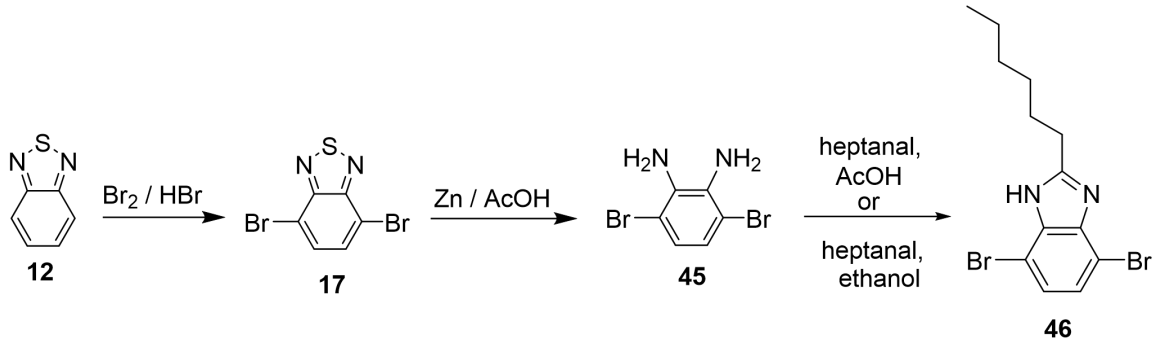
44
8.11 (2H, *s*, H-6, H-7)
7.89 (2H, *dd, J* = 1.0, 4.0 Hz, H-5')
7.75 (4H, *d, J* = 8.8 Hz, H-2,H-6)
7.54 (2H, *dd, J* = 1.0, 5.2 Hz, H-3')
7.21 (2H, *dd, J* = 4, 5.2 Hz, H-4')
6.93 (4H, *d, J* = 8.8 Hz, H-3", H-5")
4.04 (4H, *t, J* = 6.6 Hz, H-6"')
1.86 (4H, *quintet*, *J* = 6.5 Hz, H-5"')
1.54 (4H, *sextet, J* = 6.8 Hz, H-2"')
1.39 (8H, *m*, H-3"', H-4"')
0.96 (6H, *t, J* = 6.9 Hz, H-1"')

Table 6. ^{13}C-NMR (100.6 MHz, $CDCl_3$) (δ_{ppm}) of compounds **44**.

Carbon	**44**
1	-
2	151.3
3	151.3
4	-
5	131.2
6	128.7
7	128.7
8	131.2
9	138.9
10	138.9
1’	-
2’	136.9
3’	126.5
4’	126.2
5’	126.6
1”	131.1
2”	131.9
3”	114.2
4”	159.9
5”	114.2
6”	131.9
1”’	14.0
2”’	22.6
3”’	31.6
4”’	25.8
5”’	29.2
6”’	68.1

4.4 Attempted synthesis of 4,7-dibromo-2-hexyl-1*H*-benzo[d]imidazole

In the course of this project work, attempt was made to synthesize compound **46.** The original synthetic plan is shown in Scheme 11**.**

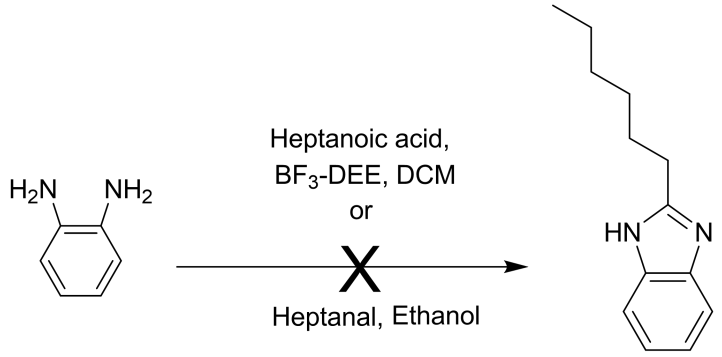


Scheme 11. Synthesis towards compound **46**.

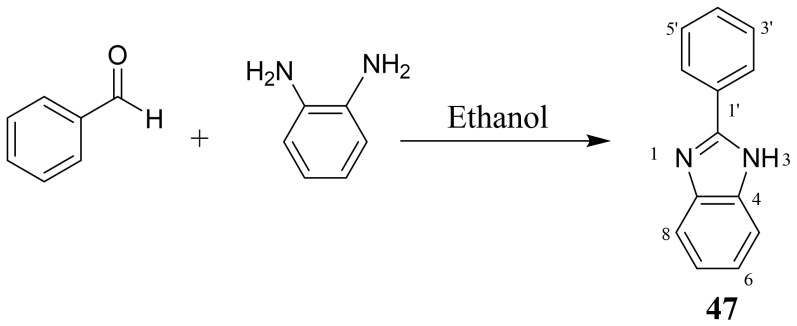
Benzothiadiazole (**12**) was brominated and subsequently reduced to 3,6-dibromobenzene-1,2-diamine (**45**) with zinc in acetic acid and filtered. Without work-up, heptanal was directly added to the filtrate and allowed to stir at room temperature following the progress of reaction by TLC. Five diffused spots appeared on TLC. The mixture was separated by column chromatography using dichloromethane:hexane (1:1) as eluent. None of the separated compounds turned out to be the desired benzimidazole **46**. In case of the second attempt, before adding heptanal to the filtrate the solvent was removed to obtain the diamine **45**. Heptanal was added to a solution of compound **45** in ethanol and stirred for seven days. This also failed to afford the desired product.

Some more attempts were made to explore the condensation reactions of heptanal with *o*-phenylenediamine. Thus, the condensation of *o*-phenylenediamine with heptanal failed to give the required product. A similar attempt to effect a condensation between *o*-phenylenediamine and heptanoic acid in the presence of boron trifluoride-diethylether complex gave no condensation product (Scheme 12). However, the condensation of *o*-phenylenediamine with benzaldehyde (Scheme 13) resulted in the formation of 2-phenyl-1*H*-benzo[d]imidazole **(47)**, which is insoluble in most organic solvents except DMSO. The structure of this

compound was confirmed based on its spectroscopic data as discussed below.



Scheme 12. Attempted synthesis of 2-hexyl-1*H*-benzo[d]imidazole.



47

Scheme 13. Synthesis of compound **47**.

The ^{1}H-NMR spectrum of compound **47** revealed four signals in the aromatic region. A two-hydrogen doublet of doublets centered at δ 8.31 (*J* = 2.9, 6.7 Hz) is due to H-2' and H-6', which are equivalent and couple with H-4' and H-3'. Another two-proton doublet of doublets at δ 7.81 (*J* = 3.1, 6.1 Hz) integrating for two hydrogens corresponds to H-5 and H-8. The multiplet signal at δ 7.71 is accountable to H-3', H-4' and H-5'. The remaining doublet of doublets signal which appeared at δ 7.51 (*J* = 3.1, 6.1Hz) and integrating for two protons is due to H-6 and H-7.

The ^{13}C-NMR and DEPT-135 spectra of compound **47** showed seven carbon signals, of which the signals at δ 149.8 and 133.1 are quaternary and belong to C-2 and C-1', respectively. The remaining five signals are

due to methine groups of benzene ring at δ 114.7, 125.6, 128.2, 129.9, and 133.1 and can be accounted for C-6, C-5, C-2', C-4', and C-3', respectively. The FT-IR spectrum of compound **47** showed the carbon-nitrogen double bond stretching band at 1636 cm^{-1}. The bands at 1463, 1445 and 1412 cm^{-1} are due to aromatic mode of vibrations. Aromatic C-H stretching band appeared at 3050 cm^{-1}.

Table 7. ^{1}H-NMR (400 MHz, DMSO) data (δ_{ppm}) of compound **47**.

47
8.31 (2H, *dd, J* = 2.9, 6.7 Hz, H-2', H-6')
7.81 (2H, *dd, J* = 3.1, 6.1 Hz, H-5, H-8)
7.71 (3H, *m*, H-3', H-4', H-5')
7.51 (2H, *dd, J* = 3.1, 6.1Hz, H-6, H-7)

Table 8. ^{13}C-NMR (100.6 MHz, DMSO) data (δ_{ppm}) of compound 47.

Carbon	**47**
1	-
2	149.8
3	-
4	-
5	125.6
6	114.7
1’	133.9
2’	128.2
3’	133.0
4’	129.9
5’	133.1
6’	128.2

5. Conclusion

In this project work a quinoxaline-based monomer was synthesized and characterized. This monomer can be an important building block for the construction of homo- and copolymers with other monomeric unit like fluorene. Attempts were also made to prepare benzimidazole-based monomers by the reaction between *o*-phenylenediamine and heptanal. However, these attempts did not lead to the desired products. The reaction between benzaldehyde and *o*-phenylenediamine afforded 2-phenyl-1H-benzo[d]imidazole.

6. Experimental Section

6.1. Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer with $CDCl_3$ and DMSO as solvents and are reported in δ units. The solvent signal was used as internal standard. The UV-Vis spectrum was recorded in ethyl acetate using SPECTRONIC GENESYS 2PC spectrometer with a 1 cm cell at room temperature. Infrared spectra were obtained using a Perkin Elmer Bx FT IR spectrophotometer. FT-IR spectra of the crystalline compounds were obtained as KBr pellets. Melting points were measured using a Mettler FP85HT hot stage with FP90 processor melting point apparatus.

6.2. Reagents

Diethyl ether (Riedel-de Haën), hexane (Riedel-de Haën), petroleum ether bromine (BDH), 2,1,3-benzothiadiazole (Aldrich), hydrochloric acid (Riedel-de Haën), hepthanal (Fluka), heptanoic acid (Aldrich), methyl benzoate (BDH), iodine crystal (BDH), benzaldehyde (NICE), magnesium sulphate (Aldrich), 48% hydrobromic acid (Fisher), dichloromethane (Aldrich), borontriflouride-ether complex (Fluka), potassium carbonate (Aldrich), sodium sulfate (Aldrich), $PdCl_2$ (BDH), *N*-bromosuccinimide (NBS) (Aldrich), 1-bromohexane (Aldrich), DMF (Aldrich), $CHCl_3$ (BDH), methanol (BDH), diethyl ether (BDH), acetone (BDH), ethyl acetate (Aldrich), n-pentane (BDH), magnesium (Aldrich), *p*-bromophenol (Aldrich), oxalyl chloride (Aldrich), NaOH (Aldrich), toluene (BDH), propan-2-ol (BDH), CuBr (Aldrich), 2-(tributylstannyl)thiophene (Aldrich), *o*-phenylenediamine (Sigma), ethanol (Analar), acetic acid (Analar), iron

(Fluka) were bought and used as received. Tetrahydrofuran (THF) was dried over Na-benzophenone under nitrogen atmosphere. Silica gel 60 (43-63 μm) was used as a stationary phase for column chromatography. 0.25 mm silica gel pre-coated plates (Fluka) were used for thin layer chromatography.

7. Procedures

7.1 Bromination of 2,1,3-benzothiadiazole (12)

A mixture of 2,1,3-benzothiadiazole (10 g, 73.4 mmol) and aqueous HBr (48 %) (40 mL) was heated at 110°C with stirring while adding bromine (34.3 g, 214 mmol,) slowly with in 30 minutes. When heated, the mixture became pasty solid and HBr (48 %) (35 mL) was added. The mixture was allowed to heat at the same temperature following the progress of reaction by TLC (dichloromethane and hexane 1:1). After 2 h the mixture was allowed to cool to room temperature and filtered using suction filtration and washed with water and sodium thiosulphate ($Na_2S_2O_3$). The product was dried overnight in vacuum oven to afford compound **17** as yellowish solid (21.14g, 97%). Mp. 188-190°C. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.75 (2H, *s*, H-5, H-6); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 113.9 (C-1), 152.9 (C-2), 152.9 (C-3), 113.9 (C-4), 132.4 (C-5), 132.4 (C-6).

7.2 Synthesis of 4,7-dithien-2-yl-2,1,3-benzothiadiazole (8)

A mixture of 4,7-dibromobenzo(2,1,3)thiadiazole **(17)** (6.47 g, 0.022 mol), 2-(tributylstanyl)thiophene (18.8 g, 0.05 mol), $Pd(PPh_3)_2Cl_2$ (300 mg) (2% mol) and THF (200 mL) was refluxed for 7 h. The mixture was then cooled to room temperature and recrystallized from isopropyl alcohol. Red brown crystals were collected using suction filtration to afford compound **8** (4.73 g, 71.7 %). Mp. 125°C. ^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ 8.15 (2H, *d, J* = 3.6 Hz, H-5', H-5"), 7.91 (2H,*s*, H-5, H-6), 7.49 (2H, *d, J* = 4.9 Hz, H-3', H-3") 7.25 (2H, *dd, J* = 4.0, 8 Hz, H-4', H-4"); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 126.0 (C-1), 152.7 (C-2), 152.7 (C-3), 126.0 (C-4), 128.0 (C-5), 128.0 (C-6), 139.4 (C-2'), 126.8 (C-3'), 125.8 (C-4'), 127.5 (C-5'). FT-IR (KBr) ν_{max} (cm^{-1}): 2990, 1636, 1560, 1481, 825, 690.

7.3 Synthesis of hexyloxy-*p*-bromobenzene (42)

In a three-necked round bottom flask, *p*-bromophenol (10 g, 57.8mmol) was dissolved in DMF (80 mL). To this solution, anhydrous potassium carbonate (35 g, 250 mmol) was added. The mixture was stirred while heating to 100°C. 1-Bromohexane (9.5 g, 57.73 mmol) was then added slowly from a pressure equalizing dropping funnel after the temperature reached 100°C. The reaction mixture was heated at the same temperature under nitrogen atmosphere following the progress of reaction by TLC using diethylether:hexane (3:2) as solvent system. After six hours the reaction mixture was cooled to room temperature and filtered. The filtrate was acidified by 2 M HCl and extracted with diethyl ether. The ether extract was washed with 1 M NaOH and brine solution consecutively. The organic layer was dried over anhydrous Na_2SO_4 to afford compound **42** (13.52 g, 91%).^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.39 (2H, *d, J* = 9.0 Hz, H-2, H-6), 6.79 (2H, *d, J* = 8.9 Hz, H-3, H-5), 3.94 (2H, *t, J* = 6.6 Hz, H-6'), 1.82 (2H, *quintet, J* = 6.9 Hz, H-5'), 1.49 (4H *m*, H-3', H-4'); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 158.3 (C-1), 116.2 (C-2), 132.2 (C-3), 112.6 (C-4), 132.2 (C-5), 116.2 (C-6), 14.1 (C-1'), 22.6 (C-2'), 31.6 (C-3'), 25.7 (C-4'), 29.2 (C-5'), 68.3 (C-6').

7.4 Synthesis of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione (43)

In a three-necked round bottom flask, containing a pressure equalizing dropping funnel and a condenser, a Grignard reagent was prepared by drop-wise addition of 1-bromo-4-hexyloxybenzene (7.2 g, 0.028 mol) in THF (10 mL) from pressure equalizing dropping funnel to a suspension of magnesium (0.8 g, 0.033 mol) in THF (18 mL). Small amount of iodine crystals were added to activate the magnesium. When reaction started, the flask became hot due to the exothermic reaction. The aryl bromide was added drop-wise and when the addition was complete, the reaction mixture was heated to reflux for one hour and cooled to room temperature.

In a separate round bottom flask (500 mL), a solution of LiBr (5.17 g, 59 mmol) in THF (20 mL) was added to a stirred suspension of CuBr (4.28 g, 29.7 mmol) in THF (20 mL). The mixture was stirred until it became homogenous and was cooled to a temperature of -30^{o}C.

The Grignard reagent was then transferred to the LiBr/CuBr suspension using cannula. Oxalyl chloride (1.89 g, 14.88 mmol) was quickly added by using a syringe. After 30 minutes the reaction mixture was quenched with saturated NH_4Cl. The organic layer was separated and washed with NH_4Cl. It was then dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporator to afford light red product (5 g) which was further chromotographed on silica gel using petroleum ether:ethyl acetate (4.5 : 0.5) to afford compound **43** as yellowish solid (1.5 g). Mp. 55^{o}C. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.95 (4H, *d, J* = 8.8 Hz , H-2, H-6), 6.97, (4H, *d, J* = 8.9 Hz, H-3, H-5), 4.05, (4H, *t, J* = 6.5 Hz, H-6'), 1.84, (4H, *quintet*, *J* = 6.7 Hz, H-5'), 1.5, (4H, *sextet*, *J* = 7 Hz, H-2'), 1.36, (8H, *m*, H-3', H-4'), 0.93, (6H, *t, J* = 7.0 Hz, H-1'); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 164.5 (C-1), 114.7 (C-2), 132.4 (C-3), 126.1 (C-4), 132.4 (C-5),

114.7 (C-6), 193.6 (C-7), 14.0 (C-1'), 22.6 (C-2'), 31.5 (C-3'), 25.6 C-4'), 28.9 (C-5'), 68.5 (C-6'). FT-IR (KBr) ν_{max} (cm^{-1})**:** 2943, 2853, 1664, 1604, 1573, 1510, 1261.

7.5 Synthesis of 3,6-di(thiophen-2-yl)benzene-1,2-diamine (40)

A mixture of 4,7-dithien-2-yl-2,1,3-benzothiadiazole (3 g, 10 mmol) and zinc dust (13.3 g, 203 mmol) in acetic acid (150 mL) was allowed to heat at 80^0C. The reaction progress was monitored by TLC (dichloromethane: hexane (1:1) plus one drop of ammonia solution). After 4 h, the reaction mixture was filtered and the residue was washed with acetic acid. The solvent was then removed under reduced pressure until small amount of solvent remained and to this diethylether was added. This solution was washed with 5% NaOH and brine solution consecutively. The organic layer was dried over $MgSO_4$ and then filtered. The solvent was removed by rotary evaporator to afford yellowish solid (2.55 g). It ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 7.41, (2H, *dd, J* = 1.1, 5.2 Hz, H-5", H-2), 7.22, (2H, *dd, J* = 1.2, 3.6 Hz, H-4', H-4"), 7.17, (2H, *dd, J* = 3.5, 5.2 Hz, H-3', H-3"), 6.91, (2H, *s*, H-5, H-6); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 141.0 (C-1), 132.9 (C-2), 132.9 (C-3), 141.0 (C-4), 121.2 (C-5), 121.2 (C-6), 127.6 (C-2'), 125.6 (C-3'), 126.1 (C-4'), 121.5 C-5').

7.6 Synthesis of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline (44).

Diamine **40** (1 g, 3.68 mmol) and 1,2-diketone **43** (1.5 g, 3.68 mmol) were dissolved in acetic acid (87 mL) and was allowed to heat at 60^0C. The progress of reaction was monitored by TLC (petroleum ether:toluene (3:2)). After 6 h the reaction mixture was cooled to room temperature and

the yellow precipitate was collected by suction filtration. The precipitate was washed with acetic acid, methanol, and water consecutively and dried under vacuum oven to afford compound **44** (1.7 g, 76 %). Mp. 124^0C. ^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.11 (2H, *s*, H-6, H-7) 7.89 (2H, *dd, J* = 1.0, 4.0 Hz, H-5'), 7.75 (4H, *d, J* = 8.8 Hz, H-2", H-6"), 7.54 (2H, *dd, J* = 1.0, 5.2 Hz, 3'), 7.21 (2H, *dd, J* = 4.0, 5.2 Hz, H-4'), 6.93 (4H, *d, J* = 8.8 Hz, H-3", H-5"), 4.04 (4H, *t, J* = 6.6 Hz, H-6'"), 1.86 (4H, *quintet,J* = 6.5 Hz, H-5'"), 1.54 (4H, *sextet, J* = 6.8 Hz, H-2'"), 1.39 (8H, *m,* H-3'", H-4'") 0.96 (6H, *t, J* = 6.9 Hz, H-1'"); (^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 151.3 (C-2), 151.3 (C-3), 131.2 (C-5), 128.7 (C-6), 128.7 (C-7), 131.2 (C-8), 138.9 (C-9), 138.9 (C-10) 136.9 (C-2'), 126.5 (C-3'), 126.2 (C-4'), 126.6 (C-5'), 131.1 (C-1"), 131.9 (C-2"), 114.2 (C-3"), 159.9 (C-4"), 114.2 (C-5"), 131.9 (C-6"), 14.0 (C-1'"), 22.6 (C-2'"), 31.6 (C-3'"), 25.8 (C-4'"), 29.2 (C-5'"), 68.1 (C-6'"). FT-IR (KBr) ν_{max} (cm^{-1})**:** 2928,1606,1670,1560, 1248, 700.

7.7 Synthesis of 2-phenyl-1*H*-benzo[d]imidazole (47)

Benzaldehyde (0.371 g, 3.5 mmol) was added to *o*-phenylenediamine (0.324 g, 3 mmol) in ethanol (15 mL). This mixture was allowed to stir for two days at room temperature. No clear spots were observed while monitoring the reaction progress by TLC. It was then allowed to heat at 80^0C for 1 h and cooled to room temperature. The reaction mixture was washed with chloroform and dried under vacuum oven to afford compound **47** (50 mg). Mp. 230^0C.^{1}H-NMR (400.13 MHz, $CDCl_3$): δ 8.31, (2H, *dd, J* = 2.9, 6.7 Hz, H-2', H-6'), 7.81, (*dd, J* = 3.1, 6.1 Hz, H-5, H-8), 7.71, (3H, *m*, H-3', H-4', H-5'), 7.51, (2H, *dd, J* = 3.1, 6.1 Hz, H-6, H-7); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 149.8 (C-2), 125.6 (C-5), 114.7 (C-6),

133.9 (C-1'), 128.2 (C-2'), 133.1 (C-3'), 129.9 (C-4'), 133.1 (C-5'), 128.2 (C-6'). FT-IR (KBr) ν_{max} (cm^{-1})**:** 3050, 1634, 1463, 1445, 1412.

7.8 Attempted synthesis of 2-hexyl-1*H*-benzo[d]imidazole

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (0.3 g, 1 mmol) and zinc dust (1.33 g, 20.33 mmol) in acetic acid (15 mL) was heated at 60^0C following the progress of reaction by TLC (dichloromethane: hexane (1:1) plus one drop of ammonia solution). After 20 minutes the reaction mixture was filtered. To the filtrate was added heptanal (0.175 g, 1.535 mmol) and stirred at room temperature. The solvent was removed with rotary evaporator to afford green pasty substance which was chromatographed using dichloromethane and hexane (1:1) as eluent. The desired product was not obtained.

7.9 Attempted synthesis of 2-hexyl-1*H*-benzo[d]imidazole

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (1 g, 3.3 mmol) and zinc dust (4.4 g, 67.67 mmol) in acetic acid (45 mL) was heated at 60^0C for 30 min. The reaction mixture was filtered followed by washing the residue with diethyl ether. To the filtrate was added additional diethyl ether. The solution was washed with 5% NaOH and brine consecutively. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, 2,3-diamino-*p*-dibromobenzene (0.83 g) was obtained. To a solution of 2,3-diamino-*p*-dibromobenzene (0.83 g, 3.12 mmol) in ethanol (25 mL) was added heptanal (0.5 mL, 3.7 mmol) and stirred for 7 days at room temperature. The solvent was the removed under reduced pressure. The residue was washed with hexane. The desired product was not obtained.

7.10 Attempted synthesis of 2-hexyl-1*H*-benzo[d]imidazole

A mixture of *o*-phenylenediamine (0.324 g, 3 mmol) and heptanal (0.399 g, 3.5 mmol) in of ethanol (24 mL) was stirred for 7 days at room temperature following the progress of reaction by TLC (dichloromethane:hexane in (1:1)). After seven days the solvent was removed under reduced pressure. The residue was washed with hexane. The desired product was not obtained.

8. **References**

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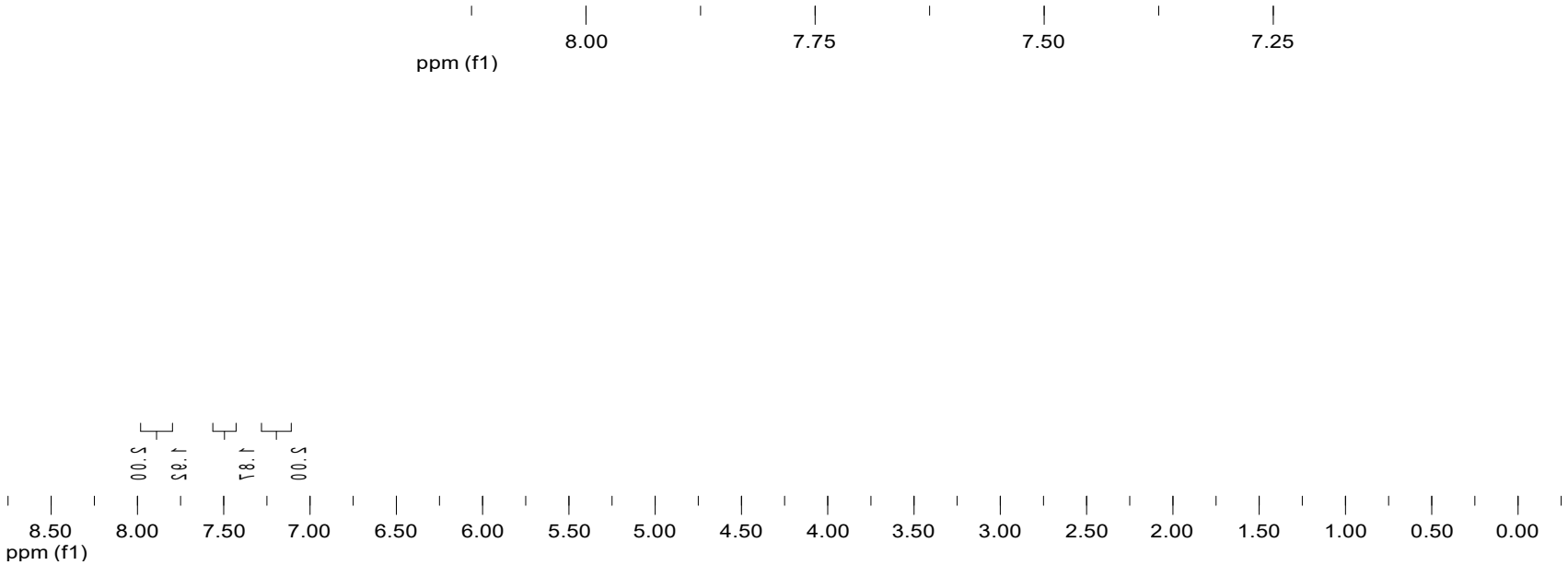
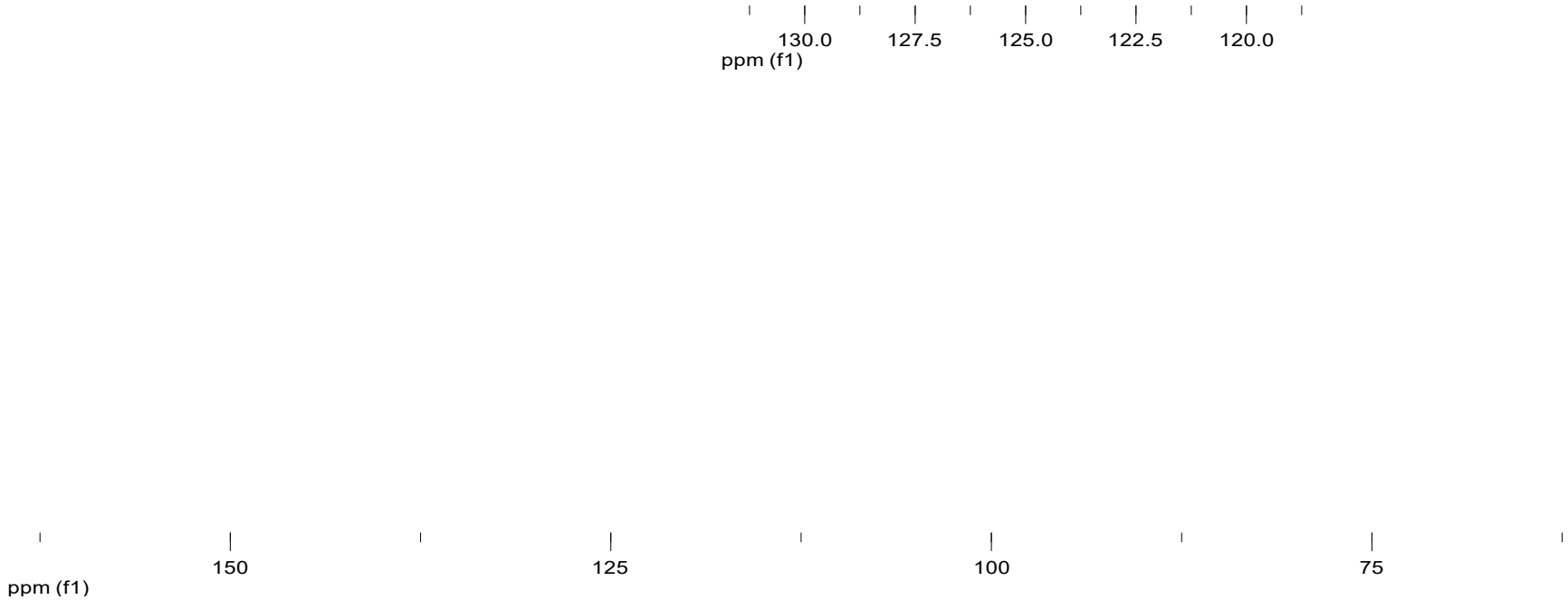
9. Appendices

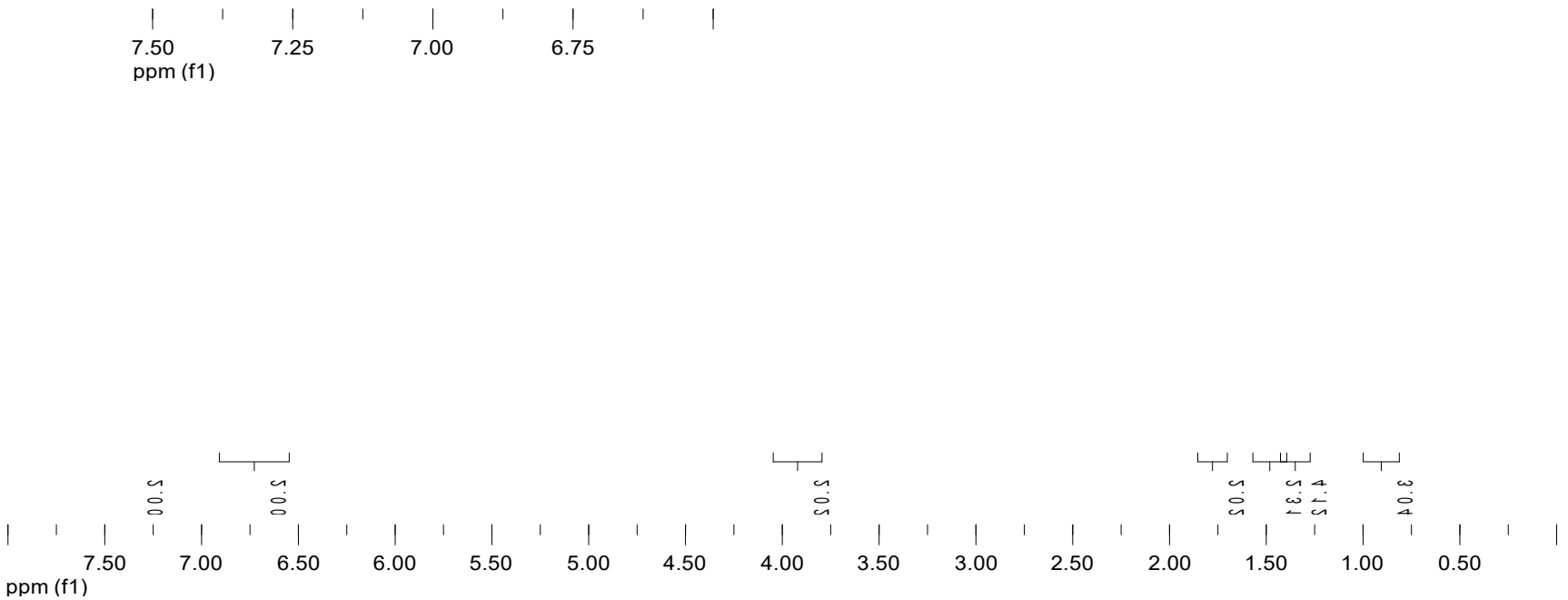


Appendix 1.[1]H-NMR spectrum of 4,7-dithien-2-yl-2,1,3-benzothiadiazole **(8)**.

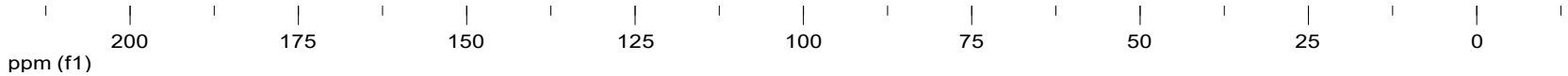


Appendix 2. ^{13}C-NMR spectrum of 4,7-dithien-2-yl-2,1,3-benzothiadiazole **(8)**.

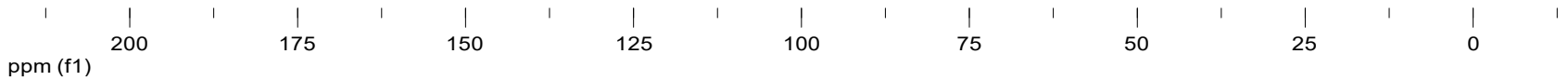
Appendix 3. DEPT-135 spectrum of 4,7-dithien-2-yl-2,1,3-benzothiadiazole **(8)**.



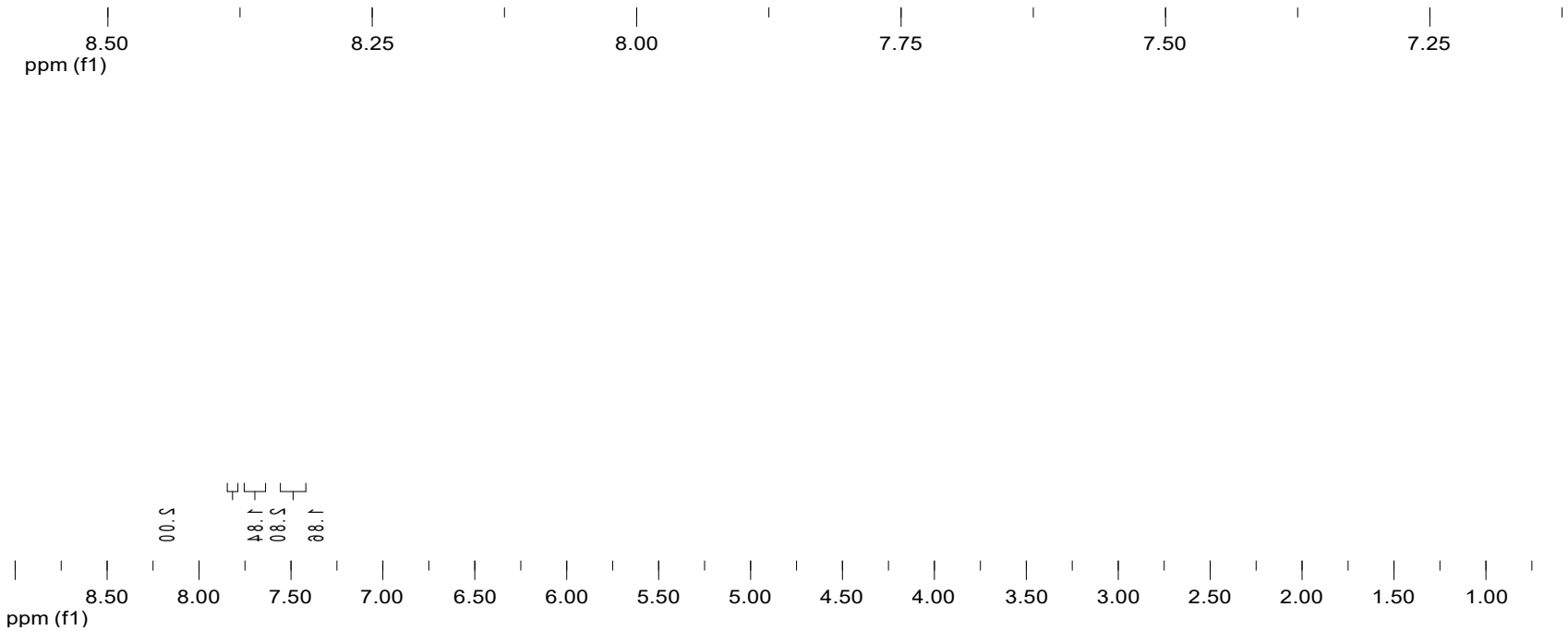
Appendix 4. ^{1}H-NMR spectrum of 1-bromo-4-hexyloxybenzene **(42)**.



Appendix 5 ^{13}C-NMR spectrum of 1-bromo-4-hexyloxybenzene **(42)**.

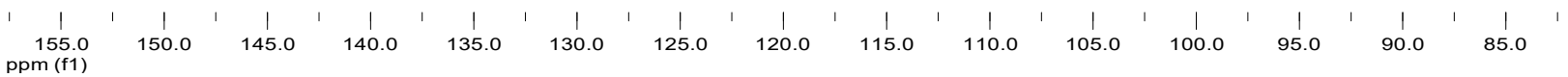


Appendix 6. DEPT-135 spectrum of 1-bromo-4-hexyloxybenzene **(42)**.

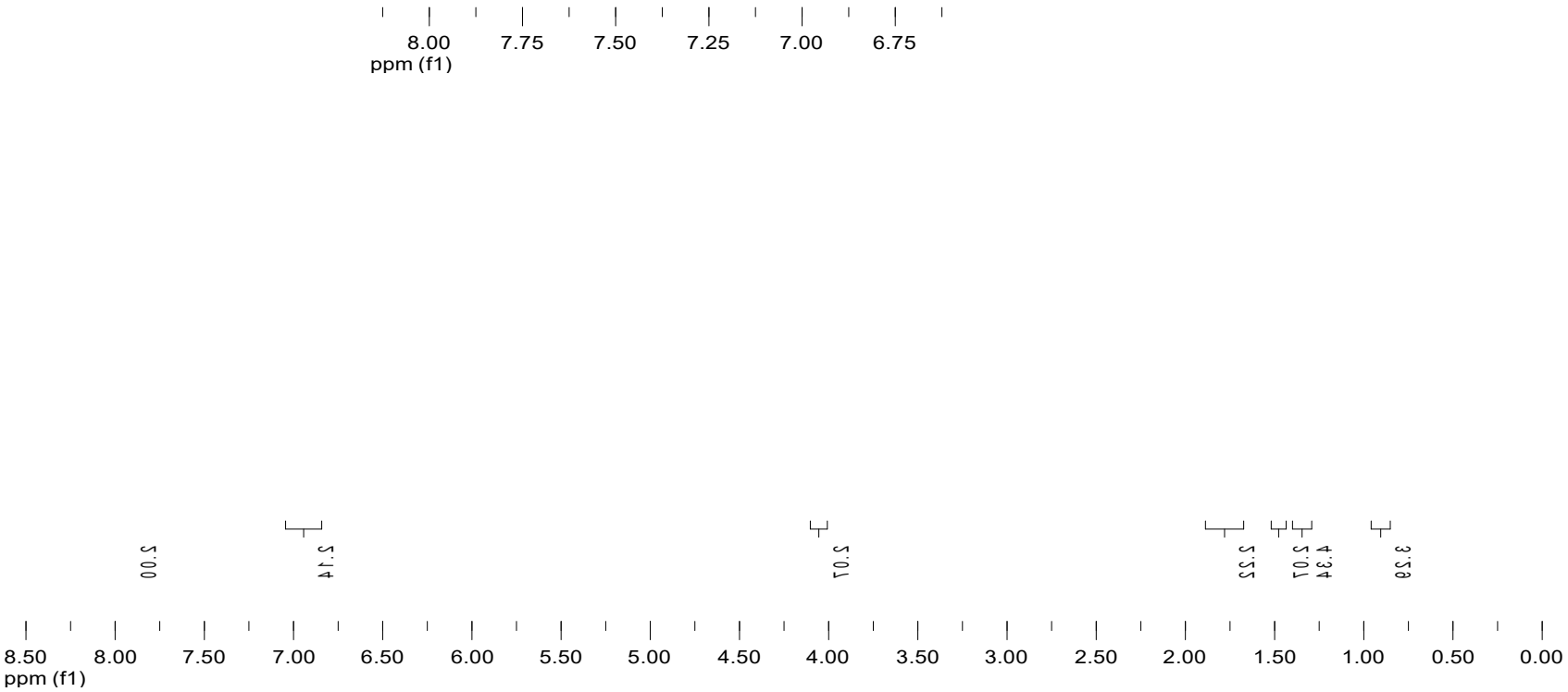


Appendix 7. ^{1}H-NMR spectrum of 2-phenyl-1*H*-benzo[d]imidazole **(47)**.

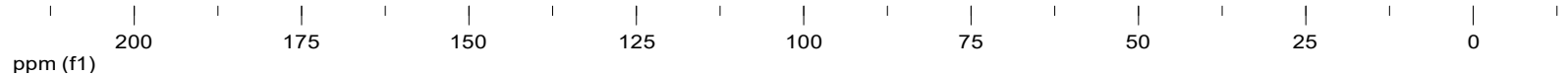
Appendix 8.[13]C-NMR spectrum of 2-phenyl-1*H*-benzo[d]imidazole **(47)**.



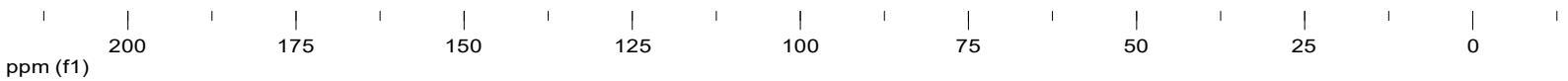
Appendix 9. DEPT-135 spectrum of 2-phenyl-1*H*-benzo[d]imidazole **(47)**.



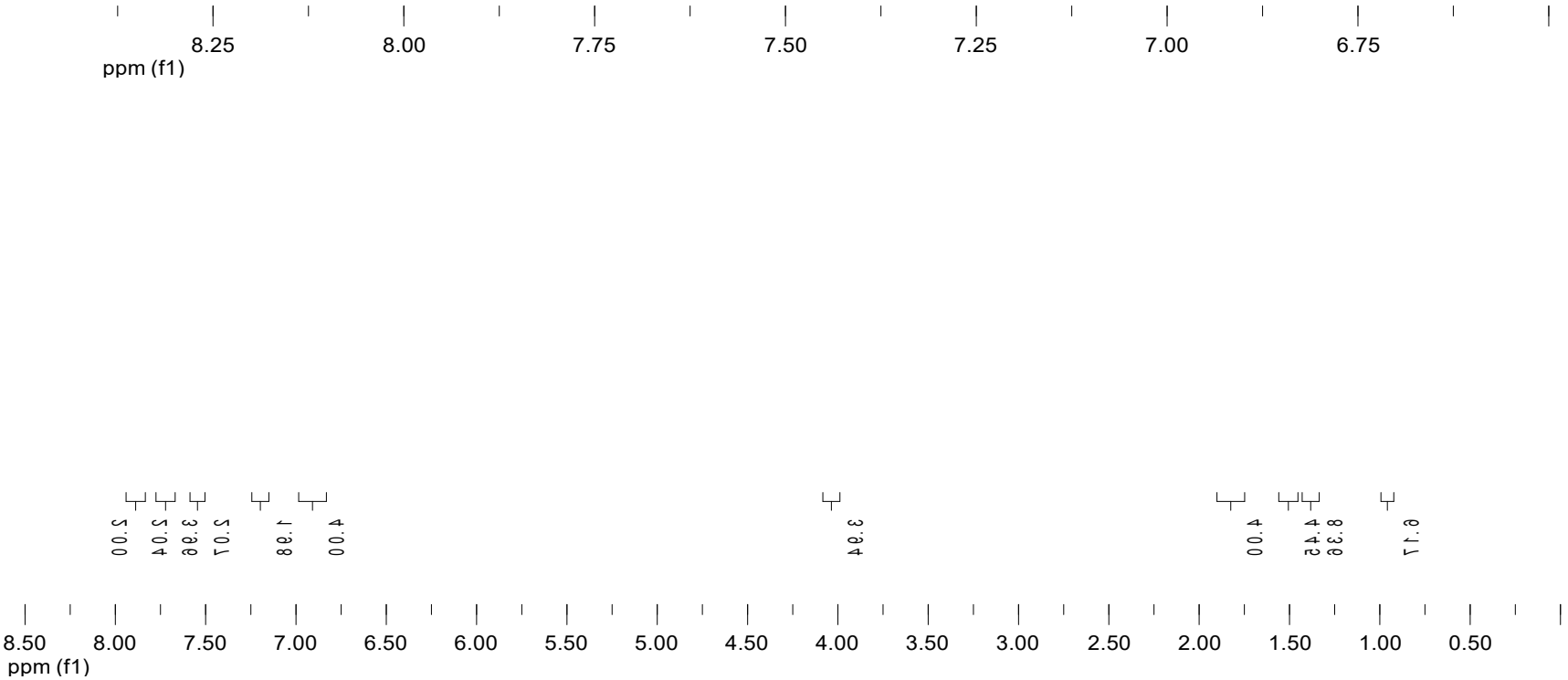
Appendix 10. ^{1}H-NMR spectrum of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione **(43)**.



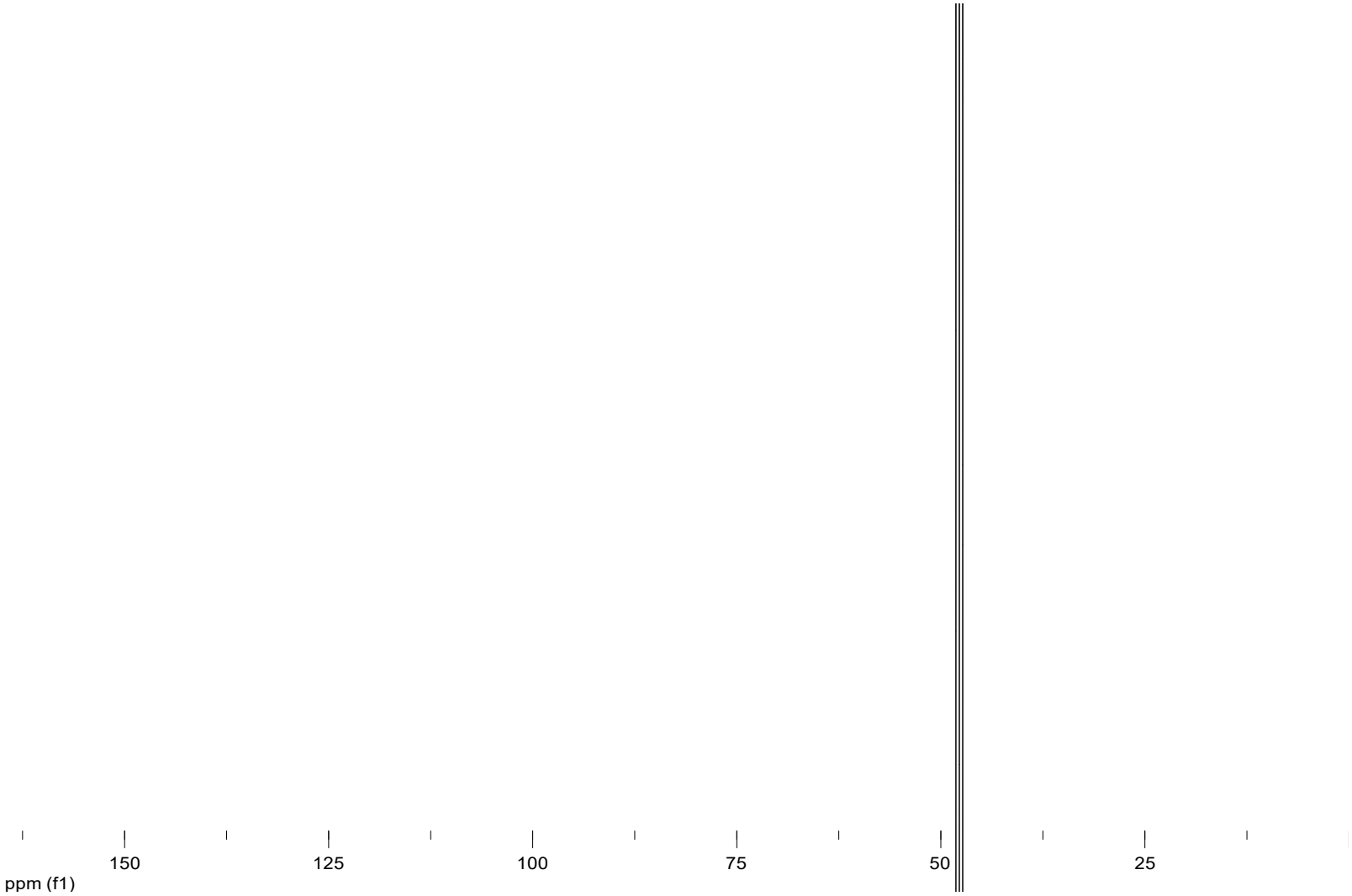
Appendix 11. ^{13}C-NMR spectrum of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione **(43)**.



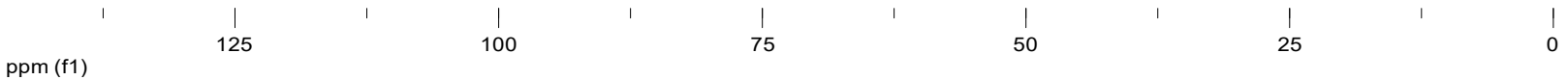
Appendix 12. DEPT-135 spectrum of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione **(43)**.



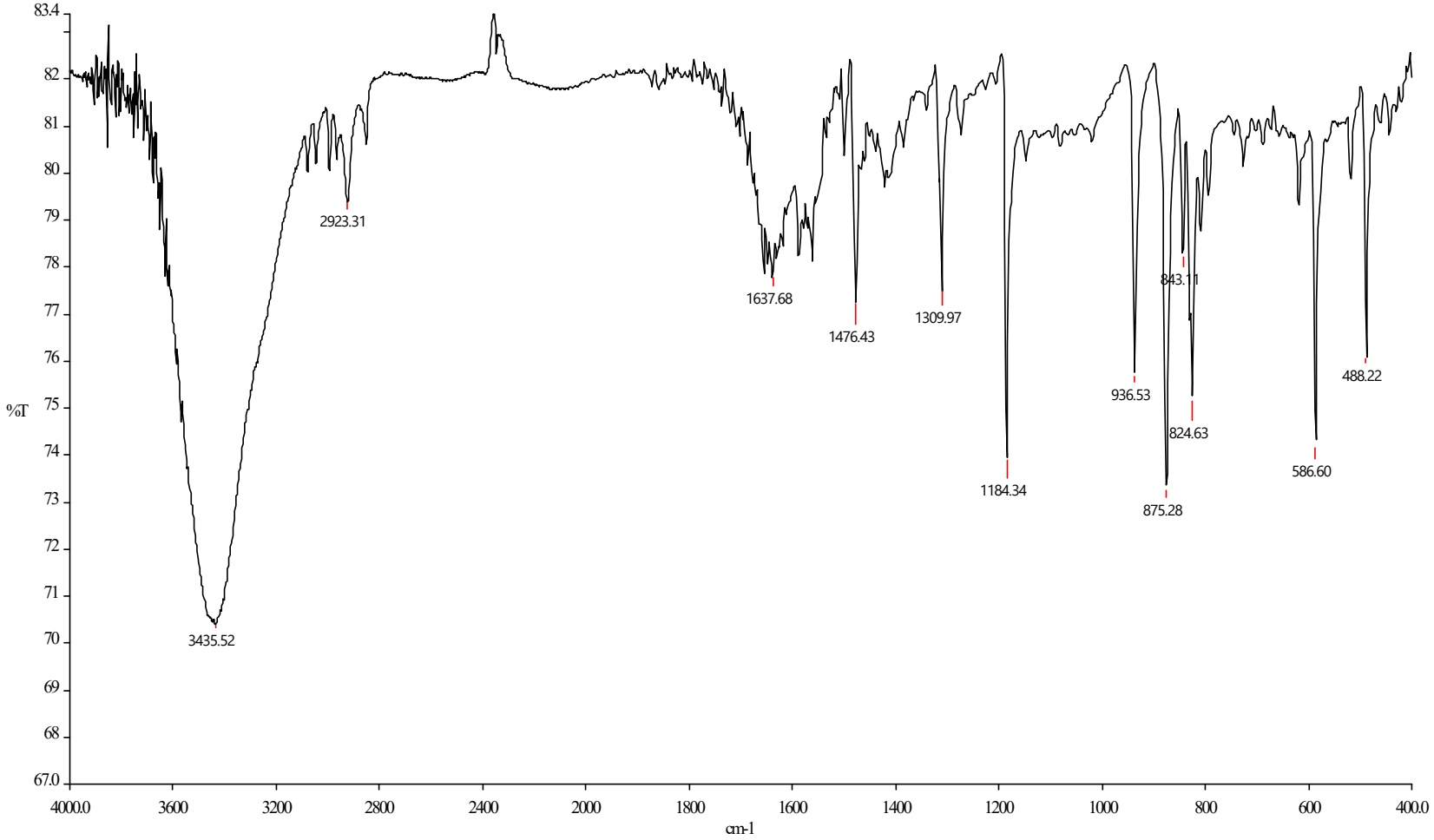
Appendix 13. ^{1}H-NMR spectrum of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**.



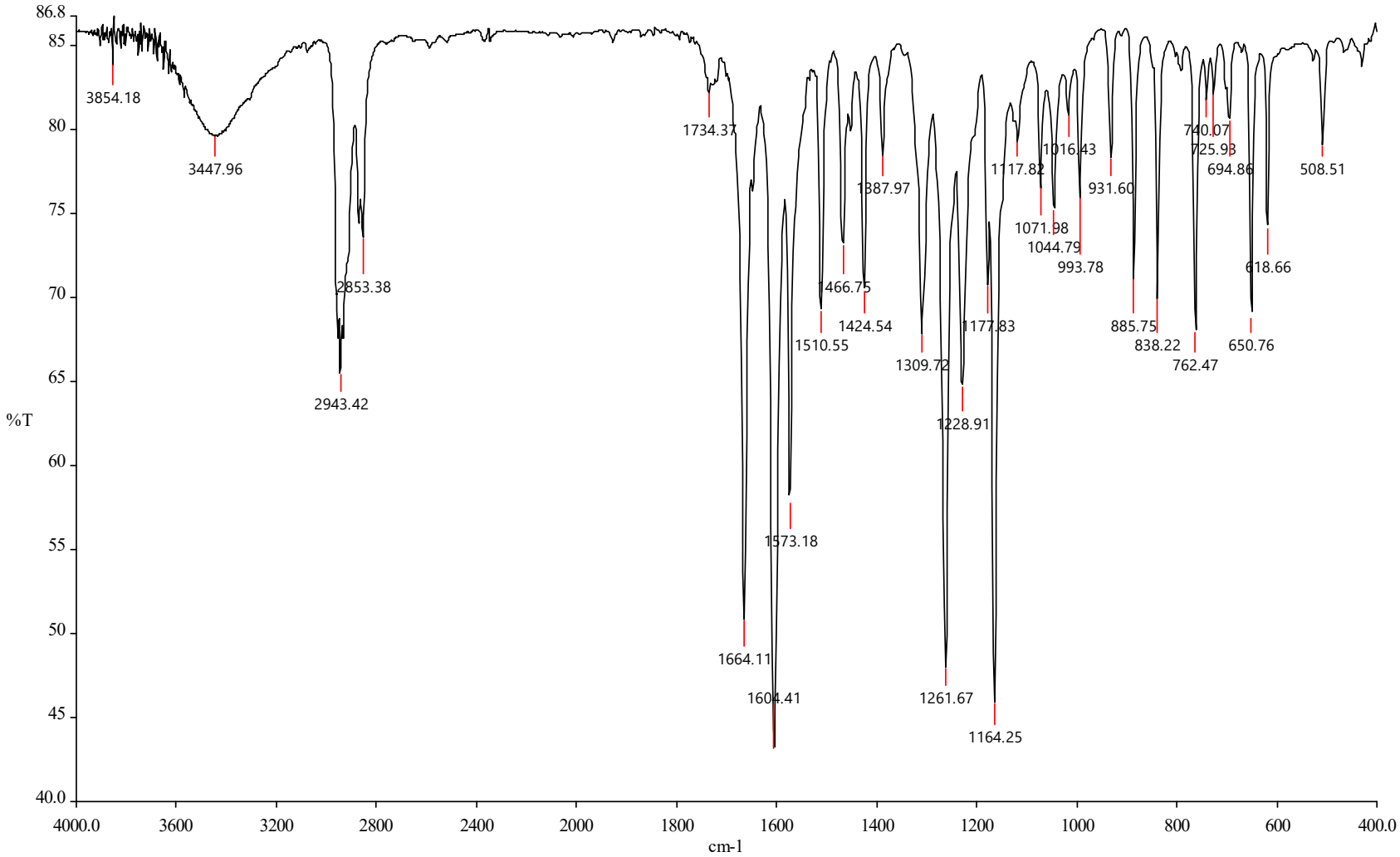
Appendix 14. ^{13}C-NMR spectrum of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**.



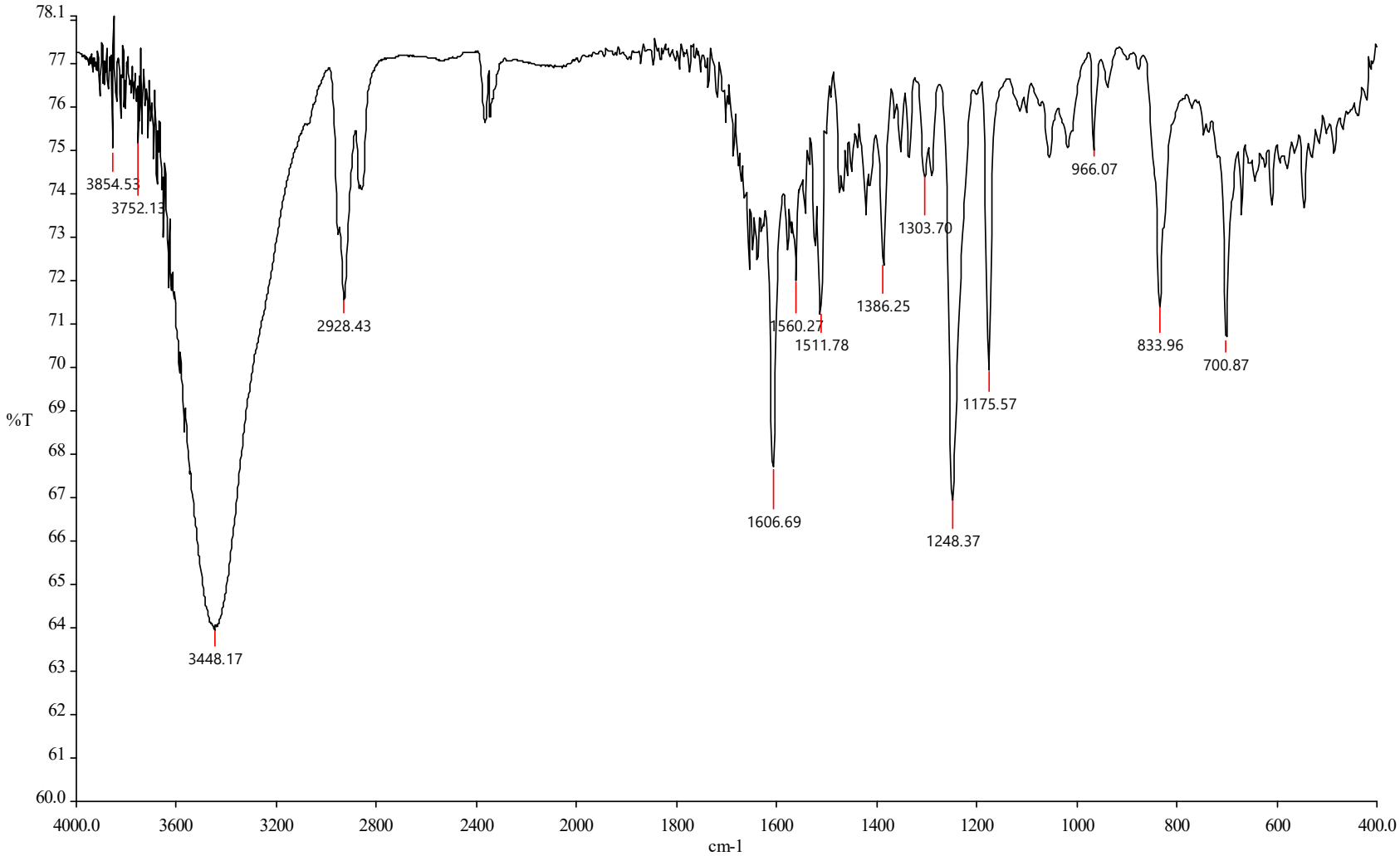
Appendix 15. DEPT-135 spectrum of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**.



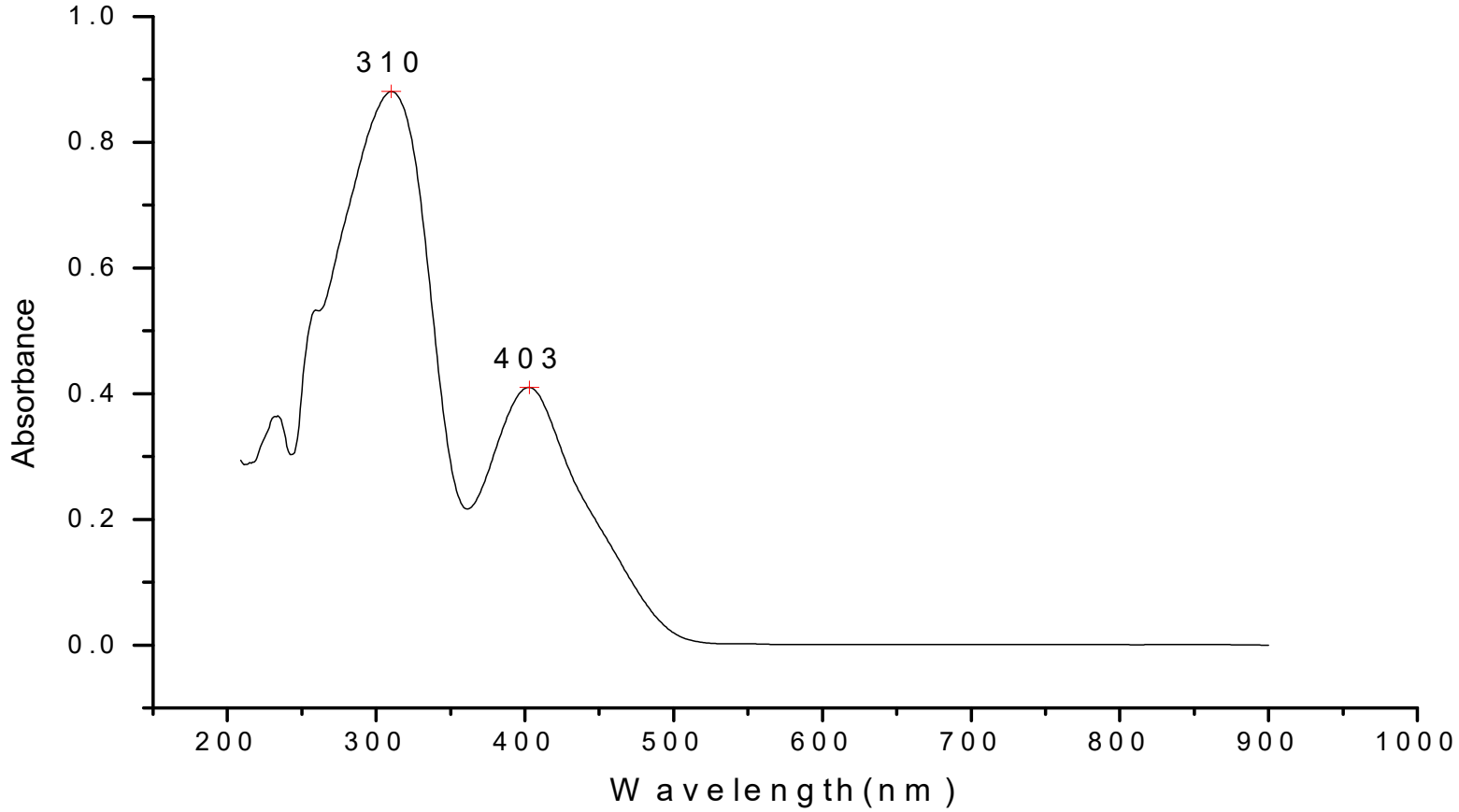
Appendix 16. FT-IR spectrum of 4,7-dibromobenzo(2,1,3)thiadiazole **(17)**.



Appendix 17. FT-IR spectrum of 1,2-bis(4-(hexyloxy)phenyl)ethane-1,2-dione **(43)**.



Appendix 18. FT-IR spectrum of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**.



Appendix 19. UV-Vis spectrum of 2,3-bis(4-(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline **(44)**.