ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

SYNTHESIS OF PYRAZINOQUINOXALINE AND THIADIAZOLOQUINOXALINE-CONTAINING 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

ADVISOR: WENDIMAGEGN MAMMO (Prof.)

GIZACHEW MULUGETA

JULY, 2008

ADDIS ABABA UNIVERSITY SCHOOL OF GRADUATE STUDIES DEPARTMENT OF CHEMISTRY.

SYNTHESIS OF PYRAZINOQUINOXALINE AND THIADIAZOLOQUINOXALINE CONTAINING MONOMERS

By: GIZACHEW MULUGETA

JULY 10, 2008

Examining Committee

Name	**Signature**
Dr. Ashebir Fisseha (Chairman).	_____
Prof. Ermias Dagne	_____
Dr. Gizachew Alemayehu	_____
Prof. Wendimagegn Mammo (Advisor)	_____

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 material used for this MSc. project have been duly acknowledged.

Name: **Gizachew Mulugeta**

Signature: _____

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

Name: Wendimagegn Mammo

Signature: _____

Date and place of submission: Department of Chemistry

Addis Ababa University

July, 2008

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my research supervisor, prof. Wendimagegn Mammo.

I would also like to thank Yoseph Atilaw and Medanit Mamo for running spectra of most of the compounds.

I would like to express my sincere appreciation and heart-felt thanks to my parents and friends, especially Gizaw Debebe, for their unreserved moral and financial support.

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

Table of Contents

List of Tables

List of Figures

List of Schemes

List of abbreviations

HOMO: Highest occupied molecular orbital

LUMO: Lowest unoccupied molecular orbital

DMF: Dimethyl formamide

NBS: N-Bromosuccinamide

DME: Dimethoxy ethane

HAc: Acetic acid

THF: Tetrahydrofuran

LED: Light emitting diodes

OPV: organic photovoltaic cells

s: singlet

d: doublet

t: triplet

q: quartet

p: pentet

dd: doublet of doublet

ddd: doublet of doublet of doublet

ABSTRACT

A thiadiazoloquinoxline-containing monomer, 8-(7-octyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxalin-6-yl)octanoic acid (**74**), was designed and synthesized starting from benzothiadiazole and oleic acid. An attempt was also made to synthesize a pyrazine-containing monomer, 8,8'-(3,7-dioctyl-5,10-di(thiophen-2-yl)pyrazino[2,3-g]quinoxaline-2,8-diyl)dioctanoic acid (**73**). The syntheses of the above donor-acceptor based monomers involved the preparation of 9,10-diketostearic acid via the oxidation of oleic acid using potassium permanganate as oxidant and condensation of this with 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine and 3,6-di(thiophen-2-yl)benzene-1,2,4,5-tetraamine, respectively. In the course of this work, attempts were made to synthesize 1,2-diketones via the benzoin condensation of substituted benzaldehydes and the Sonogashira reaction of arylbromides and 1-octyne. All intermediate compounds and products were characterized by spectroscopic methods including NMR, FT-IR and UV-VIS.

1. INTRODUCTION

The word polymer is the combination of the Greek words *poly* and *meros* which mean *many* and *parts*, respectively. Thus, a polymer is a molecule consisting of many parts. There have been several different suggestions made on how a polymer should be defined but the generally accepted conception is that a polymer is a large molecule containing small, repeating units (*meros*). The small molecules which are fused, or polymerized, in the formation of a polymer are called monomers, meaning *one part*. Polymers can be both man-made (synthetic polymers) and naturally occurring (biopolymers).

Among the naturally occurring polymers are cellulose, protein, fat, natural rubber, etc., while polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), nylon, polymethylmethacrylate and some specialized polymers such as the conducting polymers are among the synthetic ones. In 1909, Leo Hendric Backland published the first man made polymer called Bakelite [1]. For most of their history, polymers have been considered as electrical insulators. It was the discovery in 1977 by the groups of Heeger [2], Shirakawa [3], and MacDiarmid [4] that doped polyacetylene could achieve metallic conductivity which initiated intense research. The above researchers were later honored with Nobel prize in chemistry in 2000 [5]. From this earlier work, it was not till the late 1990s that highly purified and soluble conjugated polymers became widely available. While initial research was conducted mostly on improving the conductivity of conjugated polymers by chemical doping, serious interest also grew in intrinsically semi conducting and highly soluble polymers. From then on, the application of conjugated polymers for wide range semiconductor devices such as light emitting diodes (LEDs) [6, 7], solar cells, and thin film transistors (TFTs) [8] was systematically investigated. Some of the conjugated polymers are listed here below **Figure 1**.

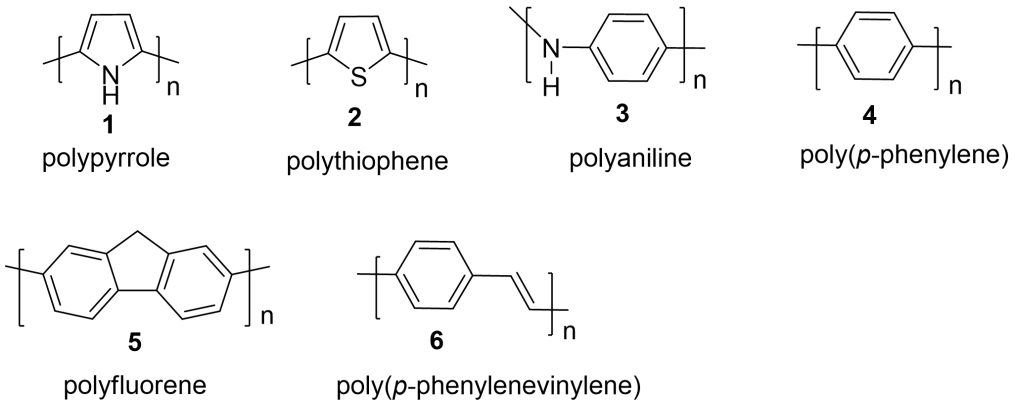


Figure 1. Some aromatic conjugated polymers.

Ultimately, conjugated polymers should combine the physical properties of polymers such as low specific weight, processibility, solubility, tunable mechanical properties, and flexibility with those of semiconductors to obtain unique and novel materials with numerous exciting applications. Besides their attractive material properties, the power of conjugated polymers is to be found in the ease to manipulate their chemical structure.

The band-gap of a material is defined as the energy difference between *the highest occupied molecular orbital* (HOMO) and *the lowest unoccupied molecular orbital* (LUMO). The HOMO, also known as the valence band, is the molecular orbital of the highest energy that, in the ground state, contains electrons. Subsequently, the LUMO, or conduction band, is the molecular orbital of lowest energy, which is not occupied in the ground state. Conjugated polymers are semiconductors which have an intermediate band gap between conductors and insulators that they can not transport charges in their ground state, but an electron can fairly easily be excited into the conduction band where the charge can be transported.

Since π-conjugated polymers allow virtually endless manipulation of their chemical structure, control of the band gap of these semiconductors is a research issue of ongoing interest. This “band gap engineering” may give the polymer its desired electrical and optical properties, and reduction of the band gap is expected to afford an intrinsically conducting polymer [9, 10, 11].

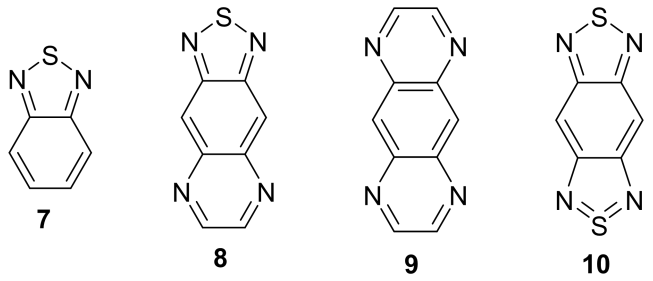


Figure 2.Structure of [2,1,3]-benzothiadiazole (**7**), thiadiazoloquinoxaline (**8**), pyrazinoquinoxaline (**9**), and benzobis(thiadiazole) (**10**).

[2,1,3]-Benzothiadiazole (**7**) has been employed as a starting material in the synthesis of alternating donor-acceptor based low band-gap copolymers [12]. It has been used as an acceptor unit, mainly with thiophene, pyrole, and fluorene which serve as electron donating blocks. One possibility of increasing the electron-withdrawing power of [2,1,3]-benzothiadiazole is by fusion of pyrazine or thiadiazole ring onto the vacant site of the phenyl ring to obtain thiadiazoloquinoxaline (**8**), pyrazinoquinoxaline (**9**), and benzobis(thiadiazole) (**10**). Donor-acceptor conjugated polymers containing thiadiazole or pyrazine-based acceptor units give vanishingly small band-gap values; this justifies considering them as very promising subunits and remained a growing area of interest for chemists making the synthetic organic metal.

2. LITERATURE REVIEW

One way of controlling the band gap of a conjugated polymer is by incorporating alternating donor (D) and acceptor (A) moieties in the polymer main-chain. This causes a partial charge-separation along the polymer backbone, which gives the polymer a lower band-gap. Several monomers and polymers in this category have been synthesized and evaluated. Some of these are shown in **Figure 3**.

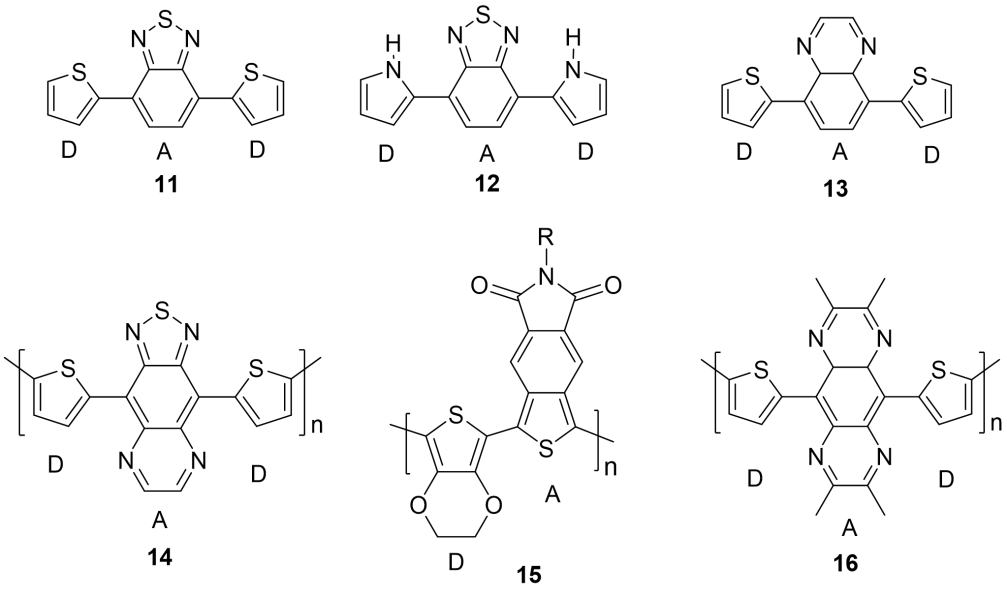


Figure 3. Donor-acceptor monomers (top) and polymers (bottom).

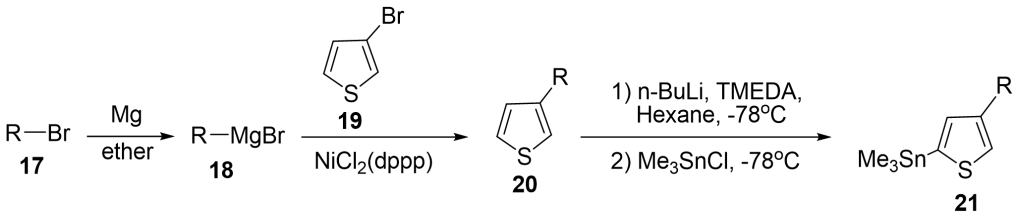
2.1. Thiophene, Benzothiadiazole and Benzobis-(thiadiazole)-Containing Monomeric Sub-Unit

2.1.1. Synthesis of Monomers

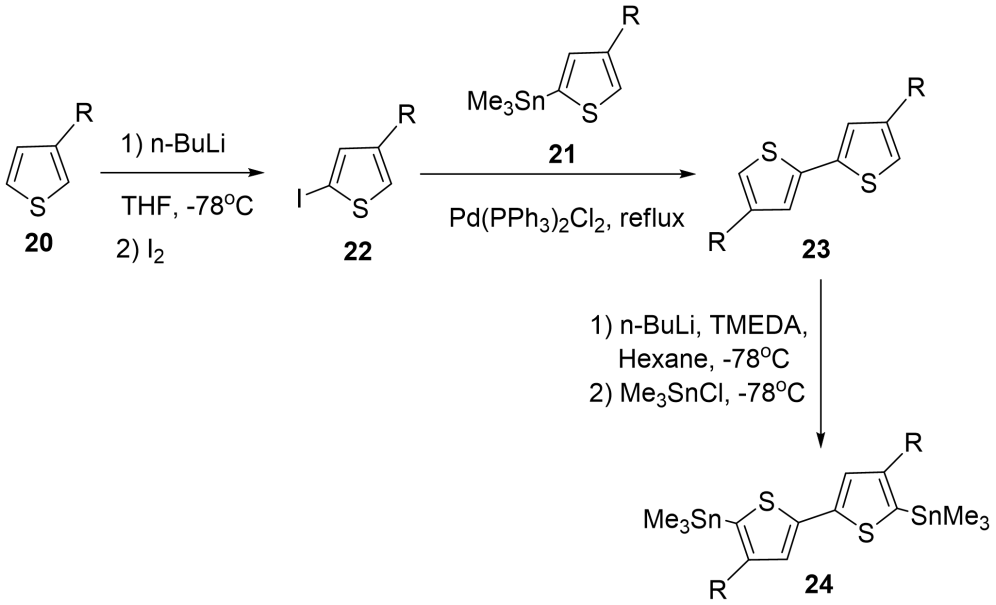
The synthesis of 4-alkyl-2-(trimethylstannyl)thiophene (**21**) begins with a Grignard reaction [13] of alkyl bromide (**17**) to give alkylmagnesium bromide (**18**). Addition of **18** to 3-bromothiophene (**19**) in the presence of nickel catalyst gives 3-alkylthiophene (**20**) (Kumanda reaction) [14] as depicted in **Scheme 1**. Lithiation of **20** with n-BuLi and TMEDA followed by reaction with trimethylstannyl chloride will give 4-alkyl-2-(trimethylstannyl)thiophene (**21**).

The synthesis of 4,4'-bis(alkyl)-2,2'-dithiophene (**23**) was carried out by Stille coupling [15] reaction between 4-alkyl-2-(trimethylstannyl)thiophene (**21**) and 2-iodo-4-alkylthiophene (**22**), which was made in one-pot by addition of I_2 to the aryllithium derived from 3-alkylthiophene (**20**). The dilithiation of 4,4'-bis(alkyl)-2,2'-dithiophene (**23**) was successfully carried out using n-BuLi and three equivalent

of TMEDA, and addition of trimethyltin chloride gave 4,4'-bis(alkyl)-5,5'-bis(trimethylstannyl)-2,2'-dithiophene (**24**) (**Scheme 2).**



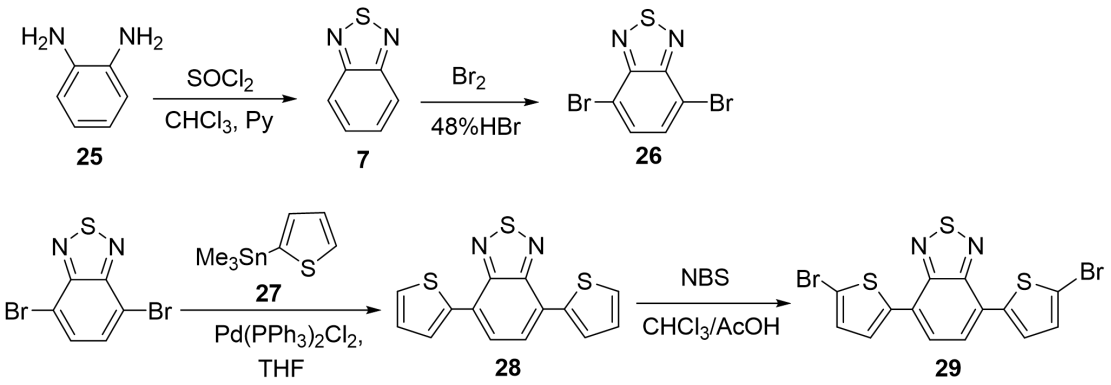
Scheme 1. Synthesis of 4-alkyl-2-(trimethylstannyl)thiophene (**21**)



Scheme 2. Synthesis of 4,4'-bis(alkyl)-5,5'-bis(trimethylstannyl)-2,2'-dithiophene (**24**).

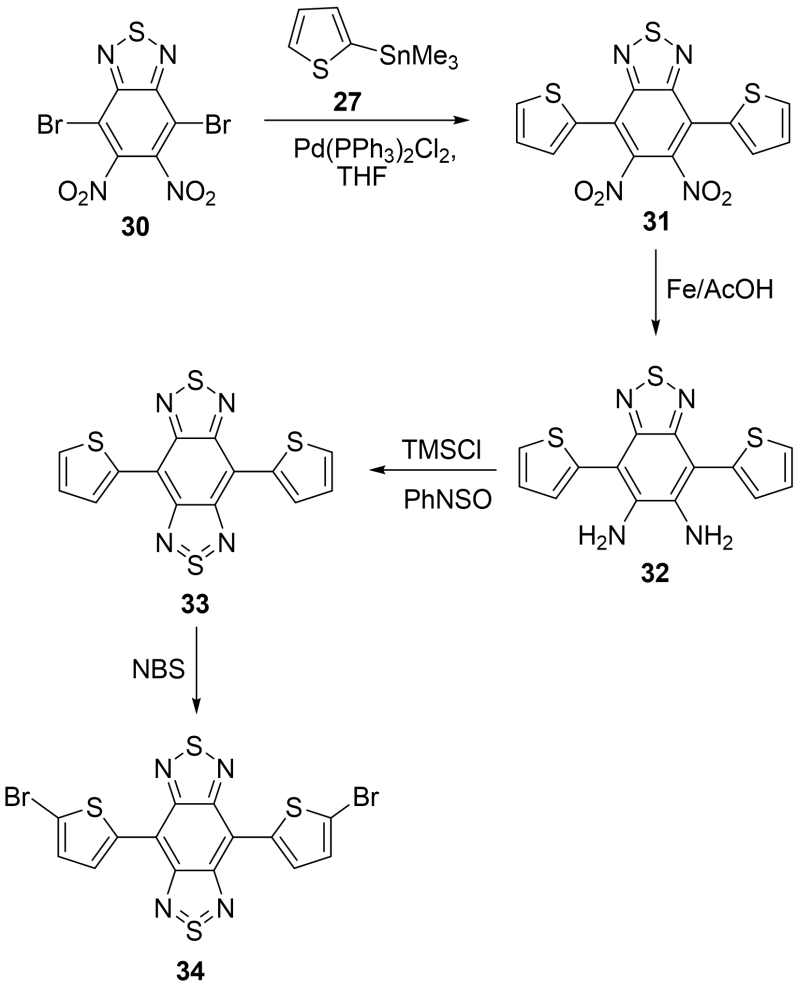
The synthesis of 4,7-dibromobenzo-[2,1,3]-thiadiazole (**26**) and 4,7-di(5-bromothiophene-2-yl)benzo-[2,1,3]-thiadiazole (**29**) have been accomplished according to **Scheme 3**. Treatement of *o*-phenylenediamine (**25**) with thionylchloride in $CHCl_3$ gave [2,1,3]-benzothiadiazole (**7**) which was subsequently brominated using Br_2 and 48%HBr to afford 4,7-dibromobenzo-[2,1,3]-thiadiazole (**26**). The Stille cross-coupling reaction [15] between 4,7-dibromobonzo-[2,1,3]-thiadiazole (**26**) and 2-(trimethylstannyl)thiophene (**27**) in the presence of catalytic amount of $Pd(PPh_3)_2Cl_2$ resulted in 4,7-di(thiophene-2-yl)benzo-[2,1,3]-thiadiazole (**28**) which

was then brominated using NBS in chloroform and acetic acid (1:1) to afforded **29** [16].



Scheme 3. Synthesis of 4,7-dibromobenzo-[2,1,3]-thiadiazole(**26**) and 4,7-di(5-bromothiophene-2-yl)benzo-[2,1,3]-thiadiazole(**29**).

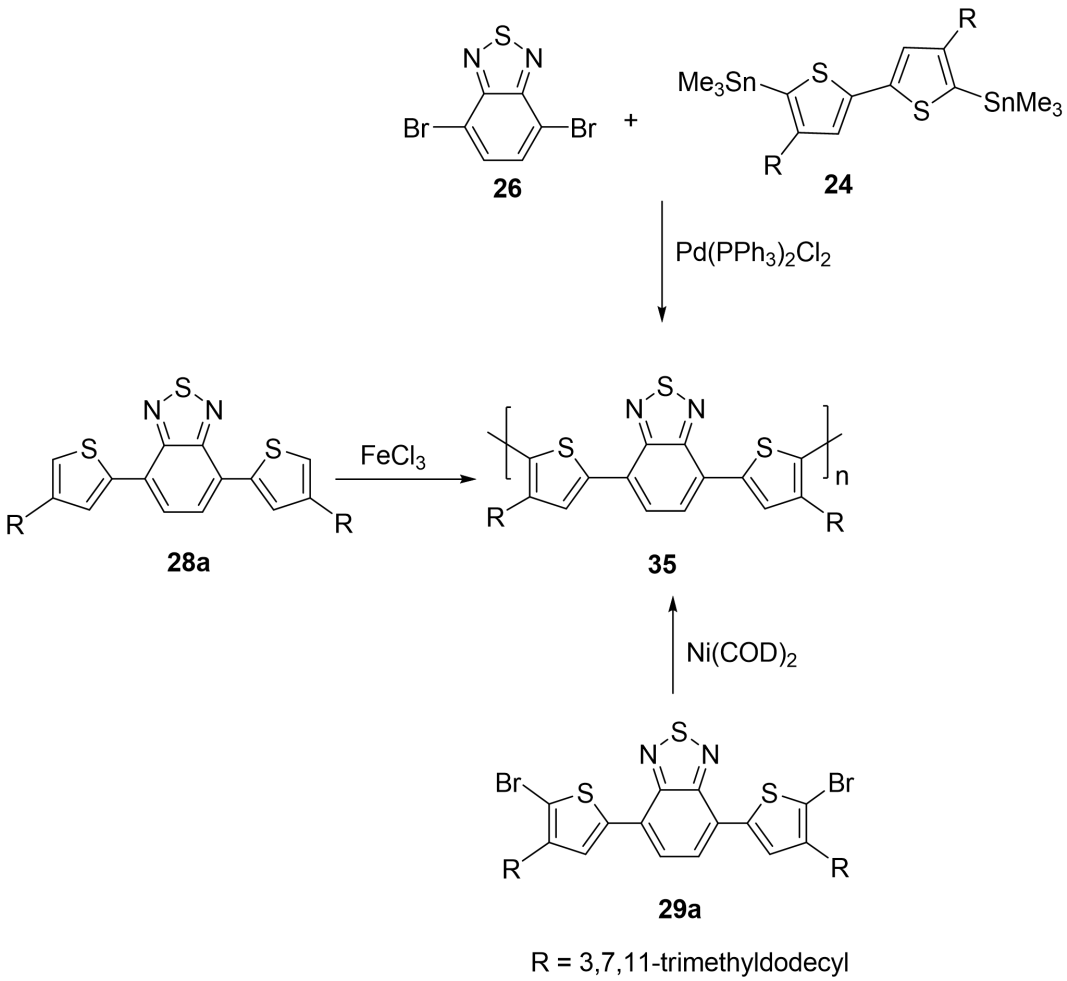
4,7-Di(5-bromothiophene-2-yl)-benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (**34**) was synthesized from 4,8-dithen-2-yl-benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (**33**) and NBS in chloroform and acetic acid [16,17]. The synthetic route towards compound **34** is depicted in **Scheme 4**. Stille cross-coupling reaction between 4,7-dibromo-5,6-dinitrobenzo-[2,1,3]thiadiazole (**30**) and 2-(trimethylstannyl)thiophene (**27**) in the presence of catalytic amount of $Pd(PPh_3)_2Cl_2$ gave 4,7-di(thiophene)-5,6-dinitrobenzo-[2,1,3]thiadiazole (**31**). Reduction of compound **31** using Fe in acetic acid afforded diamine **32** which subsequently reacted with thionylaniline to give compound **33**.



Scheme 4. Synthesis of 4,7-di(5-bromothiophene-2-yl)benzo[1,2-c;4,5-c']thiadiazole (**34**).

2.1.2. Synthesis of Copolymers Based on Thiophene, Benzothiadiazole and Benzobis(thiadiazole)

The synthesis of the copolymers has been carried out by three different methods. 1) Stille cross-coupling polymerization of di-stannyl derivatives of thiophene or dithiophene and di-bromoderivatives of benzothiadiazole (benzo-bis(thiadiazole) can also be used) with a palladium catalyst [18], 2) Oxidative ferric chloride polymerization of the monomer with a $FeCl_3$ catalyst [18], and 3) Polymerization of the di-brominated monomers with $Ni(COD)_2$ as a catalyst in a Yamamoto coupling [19] as shown in **Scheme 5**.



Scheme 5. Synthesis of copolymers based on thiophene and benzothiadiazol by Stille, Ferric chloride or Yamamoto polymerization.

The copolymers based on thiophene and benzothiadiazole are examples of electron donor-acceptor alternating copolymers. Thiophene is the electron donor unit and here benzothiadiazole is the electron acceptor unit. Benzo-bis(thiadiazole) can also be used in place of benzothiadiazole. The structures of different copolymers are shown in **Figure 4**, where R represents either alkyl or alkoxy chains to achieve a soluble polymer [18, 20].

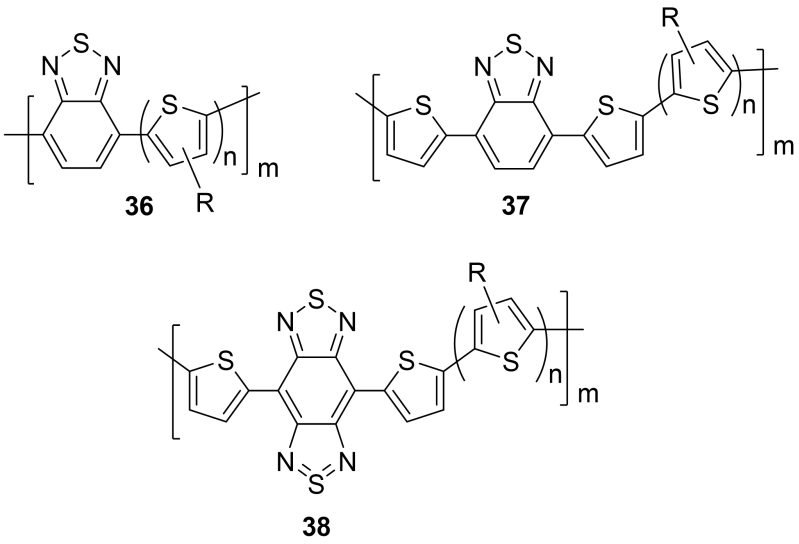


Figure 4. Structure of copolymers of thiophene and benzothiadiazole/benzo- bisthiadiazole. R = 3,7,11-trimethyl-dodecyl for **36**, **37** and **38**: n = 1, 2; R = hexyl for **36**, **37**, and **38**: n = 2; and R = 2-ethylhexyl for **36** and **38**: n = 1; R = alkoxy for **36**: n=2.

For the copolymer based on thiophene and benzothiadiazole, results have shown that the number of thiophenes between the benzothiadiazole units affects the band gap of the copolymer. Thus, it was possible to tune the band gap of the copolymer with the number of thiophene units between the benzothiadiazole units from 2.1 eV, for one thiophene unit, to 1.65 eV, for four thiophenes [18]. This is ascribed to an optimization of the donor properties of the oligothiophene donor segment with respect to the acceptor unit and for this reason there is an optimal length of the oligothiophene segment for a given acceptor unit such as benzothiadiazole. Increasing the number of thiophenes beyond the optimum will gradually approach the band gap of polythiophene.

The low band gaps of these types of copolymers, based on either benzothiadiazole or benzo-bis(thiadiazole), are ascribed to the strong quinoid form of the polymer as shown in **Figure 5**. This contributes to the low band gap due to the more stable 1,2,5-thiadiazole which is formed [16]. Further, the polymer shows a planar geometry,

which results in non-steric repulsion between the two hetrocycles. The polymer has a high electron affinity due to the sulphur atoms in the thiadiazole rings and the short intermolecular contact between S and N results in strong interchain interactions. It was found out that the benzo-bis(thiadiazole) unit showed the highest electron-accepting ability among thienopyrazine, pyrazino-quinoxaline and benzothiadiazole and that this also resulted in the lowest band gap [17].

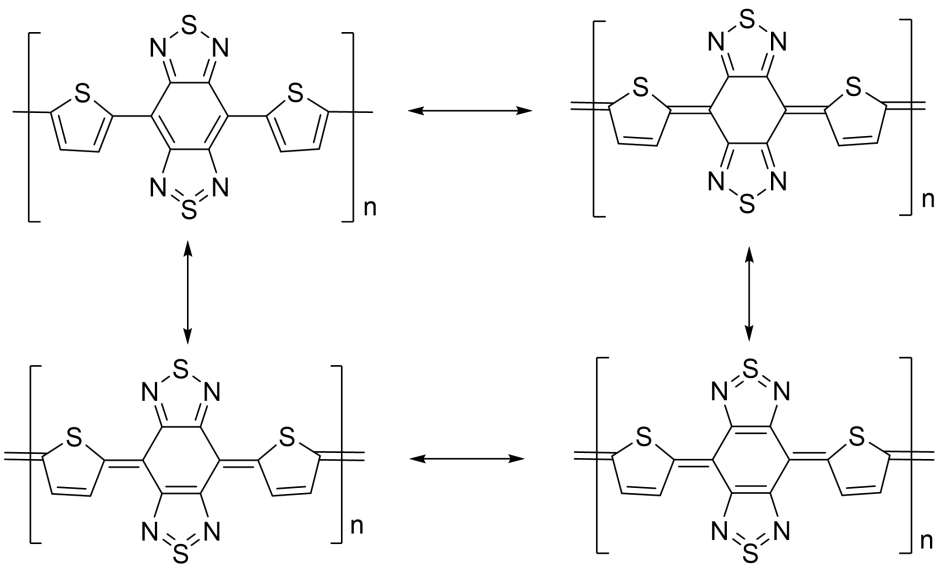


Figure 5. Resonance structures in benzo-bis(thiadiazole).

The use of side-chains is essential to make the polymer soluble enough for applications in OPVs by, for instance, spin coating [18, 20]. However, the side chains often introduce steric hindrance affecting the coplanarity of the polymer and hence, the band gap of the polymer increases. Further, the side chains can affect the regularity of the structure when applied in different positions in the polymer [20]. This can be seen for the copolymers with R = H, where the band gap was found to be 1.1 eV for the copolymer based on di-thiophene and benzothiadiazole and below 0.5 eV for the copolymer based on di-thiophene and benzo-bis(thiadiazole) [17].

The substitution in different positions on the thiophene ring also shows a large effect on the band gap [21]. It was shown for dodecyl side chains that having the side chain close to the benzothiadiazole ring in position 3 of the thiophene, compared to the 4 position, causes the band gap to increase due to steric hinderance, which causes the

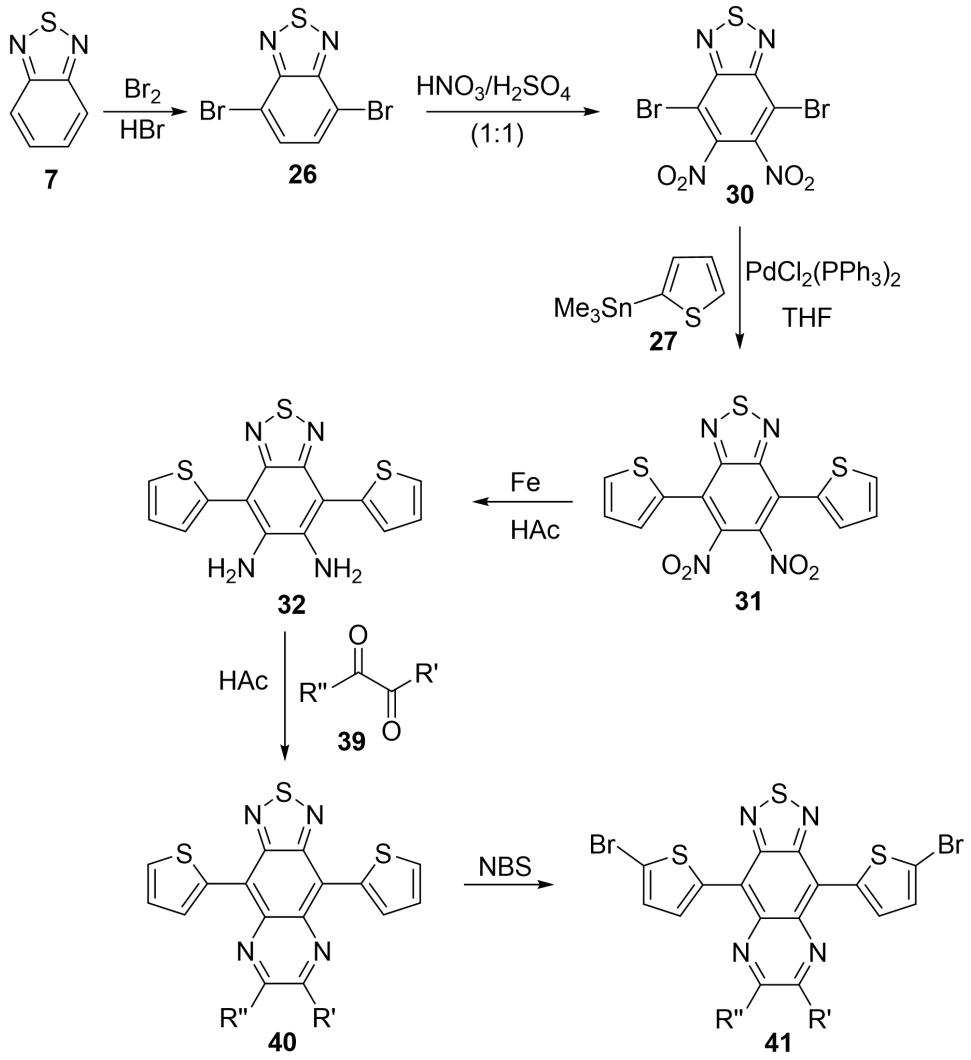
planarity to break [21]. However, for the polymer with the alkyl chain in 4 position, the band gap was increased when the alkyl chain was added compared to the insoluble analog with no side chains from 1.1 to 1.96 eV.

2.2. Thiadiazoloquinoxaline, Thiophene, and Fluorene-Containing Low Band-Gap Monomeric Segment

2.2.1. Synthesis of Low Band-gap Monomeric Sub-unit

The general schematic route for the synthesis of thiadiazoloquinoxaline-containing monomeric sub-unit is as depicted in **Scheme 6**.

4,7-Dibromobenzo-[2,1,3]thiadiazole (**26**) was synthesized by refluxing benzo-[2,1,3]thiadiazole (**7**) in concentrated HBr (aq) with an excess of bromine. Compound **26** was nitrated using a 1:1 (vol/vol) mixture of fuming HNO_3 and fuming H_2SO_4 to give dibromo-dinitrobenzothiadiazole (**30**) which was then treated with 2-(tributylstannyl)thiophene (**27**) in the presence of catalytic amount of $PdCl_2(PPh_3)_2$ and gave 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[1,2,5]thiadiazole (**31**). Compound **31** was then readily reduced to its corresponding diamine (**32**) by heating it at 80ºC for 4 h in acetic acid with a large excess of fine iron powder.



Scheme 6. Synthesis of 6,7-di(alkyl/phenyl)-4-9-bis-(5-bromothiophen-2-yl)-[1,2,5]-thiadiazole[3,4-g]quinoxalines (**41**).

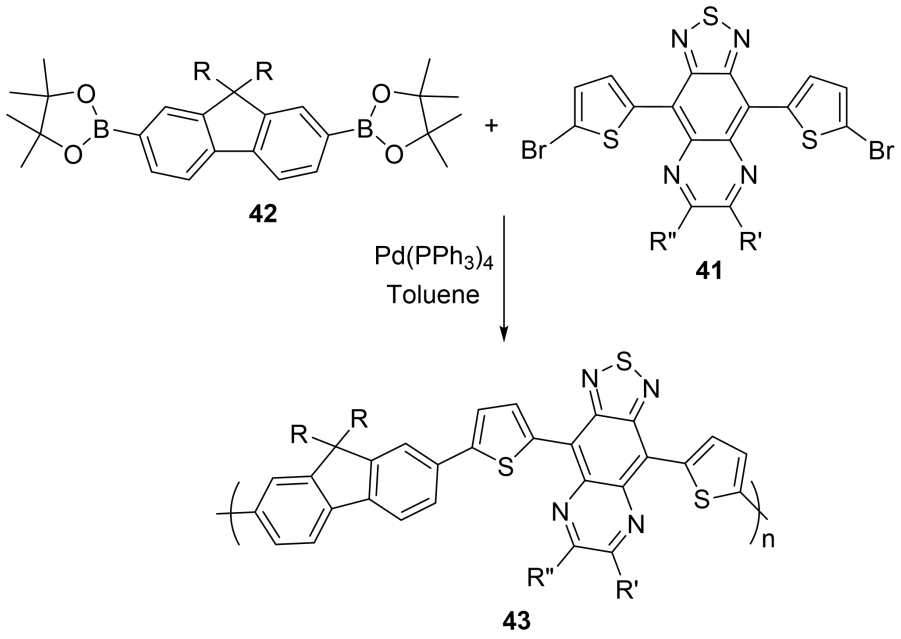
The diamine (**32**) was then condensed with the desired 1,2-diketone (**39**) and subsequently dibrominated with n-bromosuccinimide in a 1:1 mixture of acetic acid and chloroform.

2.2.2. Copolymerization of Thiadiazoloquinoxaline, Thiophene and Fluorene

The homopolymers of polyfluorene have large band gaps (3.65 eV) and have been used as a blue light emitters in light emitting diodes [22]. However, the light emitted, and hence the band gap of polyfluorene, could be tuned with addition of different electron donating or electron accepting units in the backbone of the polymer [16]. Within the past few years the focus on fluorene units incorporated in alternating donor-acceptor polymers have therefore increased tremendously.

The monomeric sub-unit of fluorene, for the consecutive Suzuki-type of copolymerization with dihaloaryls, was synthesized in the form of either fluorene-2,7-diboronic acid or diboronate ester [23]. The respective diboronic acid or diboronate ester of fluorene can be prepared through metal-halogen exchange of either the dialkylated 2,7-dibromofluorene or 2,7-dibromofluorene derivatives with n-BuLi, and then subsequent treatment with tributylborate or pinacol borane, respectively [24, 25, 26].

The copolymers were synthesized by a Suzuki polymerization [27, 28] reaction between 2,7-diboronate fluorene (**42**) and 6,7-di(alkyl/phenyl)-4,9-bis-(5-bromo-thiophen-2-yl)-[1,2,5]thiadiazolo-[3,4-g]quinoxalines (**41**), in the presence of catalytic amount of $Pd(PPh_3)_4$ in toluene. The alternating donor-acceptor copolymers APFOGreen1, APFOGreen3, APFOGreen4 [29, 30] (**Scheme 7**) were synthesized following this strategy.



Scheme 7. Synthesis of Copolymers APFOGreen1, 3, 4.

2.3. Electron-Acceptors with Multiply-Fused Pyrazine and Thiadiazole Rings

The electron-withdrawing power of quinoxaline or 2,1,3-benzothiadiazole may be further increased by fusion of another pyrazine or thiadiazole ring onto the vacant sites of the phenyl ring to yield pyrazinoquinoxaline (**9**), thiadiazole (**8**) and benzobis(thiadiazole) (**10**) [31] (**Figure 5**).

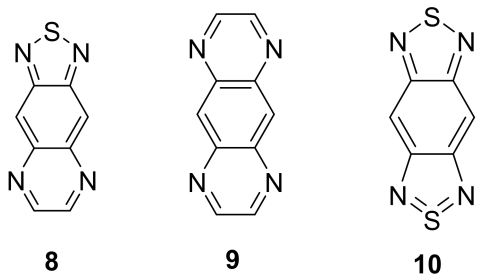
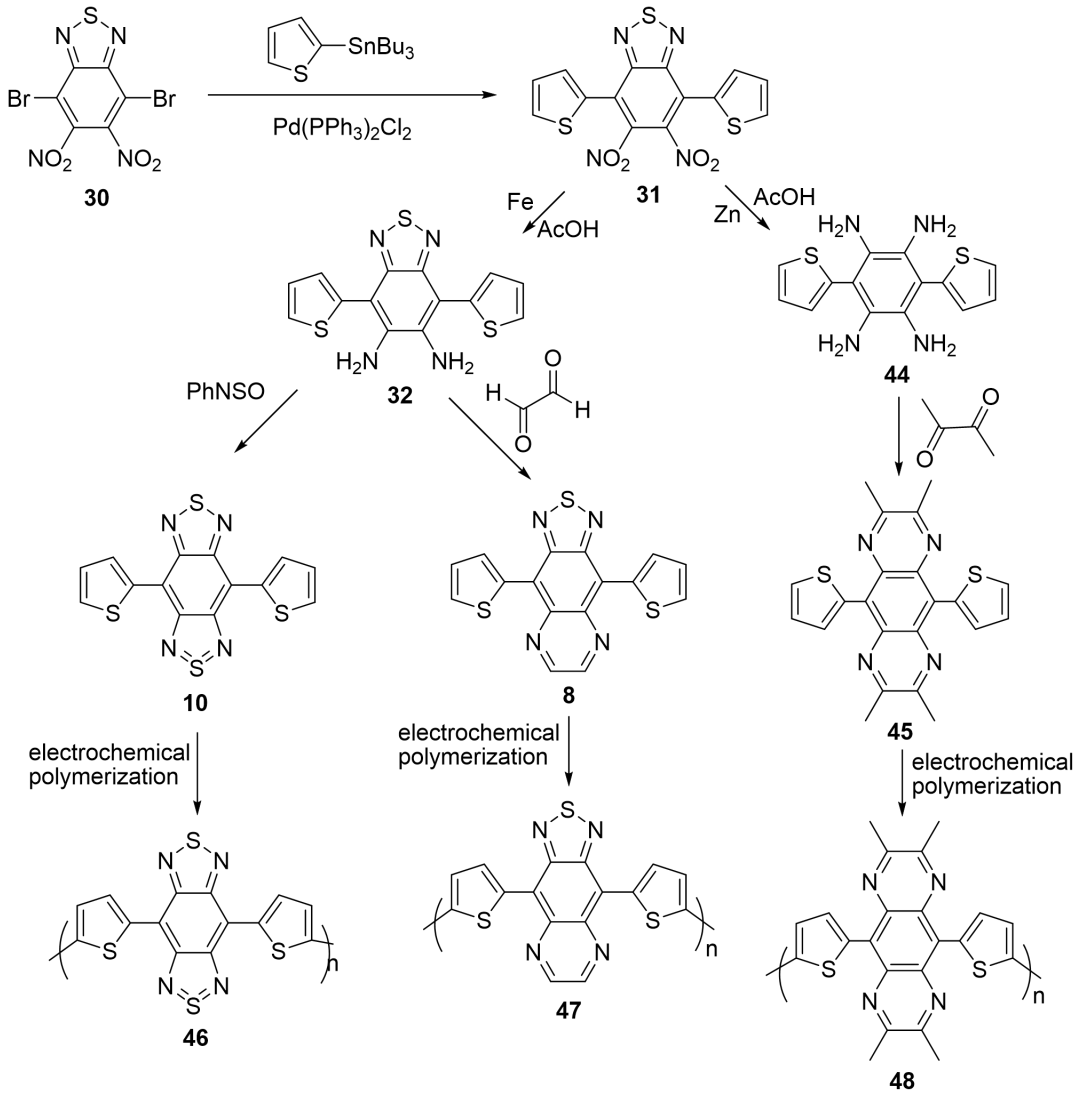


Figure 6. Structure of pyrazinoquinoxaline (**9**), thiadiazole (**8**), and benzo-bisthiadiazole (**10**).

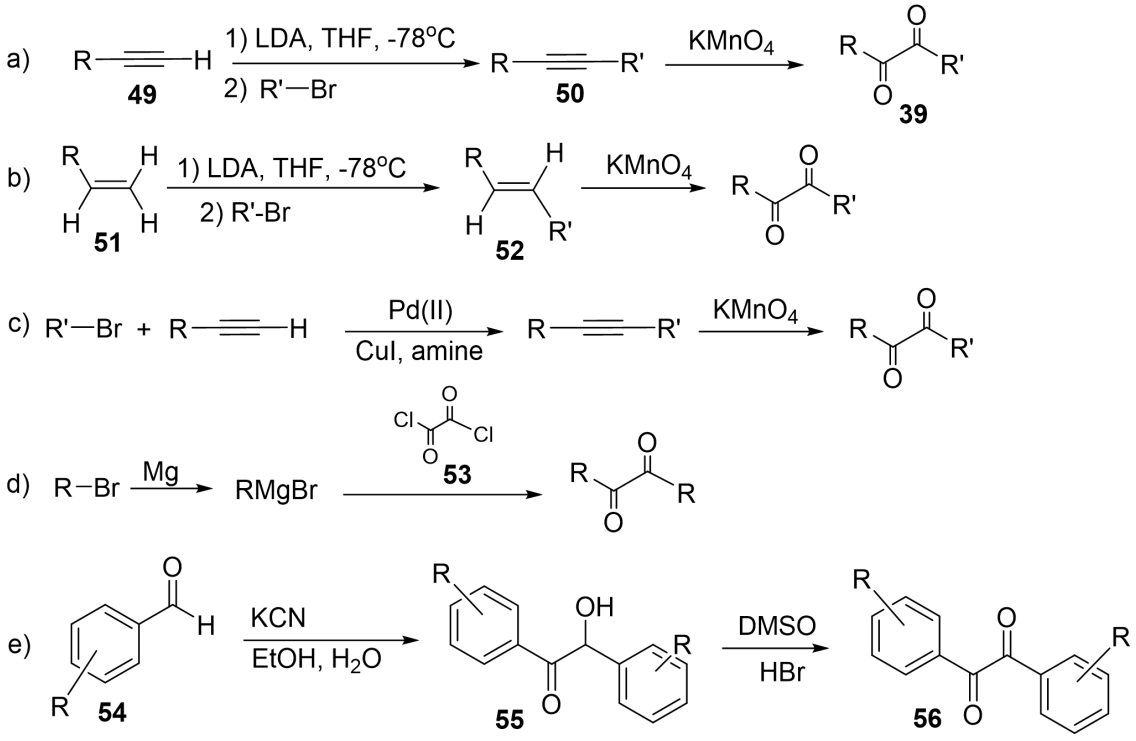
The synthesis of monomers containing quinoxaline units is outlined in **Scheme 8**. Starting from 5,6-dinitro-4,7-dibromobenzo-[2,1,3]-thiadiazole (**30**) (prepared by nitration of 4,7-dibromobenzo-2,1,3-thiadiazole [32]), a Stille coupling with 2-(trimethystannyl)thiophene furnished the dinitro intermediate **31**. Reduction of this compound could be carried out either with iron powder to yield diamine **32**, or with zinc powder to yield tetra-amine **44**. The diamine **32** could be reacted with either thionylaniline to yield benzobisthiadiazole-containing co-trimer **10**, or with glyoxal to yield the thiadiazoloquinoxaline-containing co-trimer **8**. Finally, tetra-amine **44** was reacted twice with diacetyl to yield the pyrazinoquinoxaline-containing co-trimer **45**. The corresponding polymers were prepared electrochemically from their monomers and showed band gaps of 0.5, 0.7 and 0.9 eV, respectively [16, 17].



Scheme 8. Synthesis of polymers containing benzo-bis(thiadiazole) (**46**), thiadiazoloquinoxaline (**47**) and pyrazinoquinoxaline (**48**) sub-units.

2.4. Synthesis of 1,2-Diketones

Numerous alternative ways for the synthesis of 1,2-diones are reported in the literature. One alternative way makes use of an alkyne rather than an alkene to synthesize the corresponding 1,2-dione by oxidizing it with potassium permanganate [34]. The desired alkyne can be synthesized by lithiation of a terminal alkyne and reacting it with alkylbromide (**Scheme 9 a** and**.b**) or using Pd-catalyzed coupling of terminal alkynes with aryl or alkenyl halides which was described for the first time by Sonogashira *et al.* [35] (**Scheme 9.c**). The other alternative way towards 1,2-diones makes use of the Grignard reaction [13]. An alkyl halide can be converted to its corresponding Grignard reagent using iodine-activated magnesium and reacted with oxalyl chloride to give a symmetrical 1,2-dione [35] **(Scheme 9.d**). Aromatic aldehydes, when treated with alkali metal cyanide, usually in aqueous solution, undergo condensation to the α-hydroxyketone or benzoin [37]. Oxidation of the α-hydroxyketone with concentrated nitric acid or 48% HBr and DMSO yields the diketone. (**Scheme 9.e**).



Scheme 9. Synthesis of 1,2-diketones.

3. OBJECTIVES OF THE WORK

The aim of this M.Sc project is to synthesize pyrazinoquinoxaline- and thiadiazoloquinoxaline-containing monomers, which can be used to synthesize alternating donor-acceptor-donor copolymers. It involves the synthesis of 1,2-diketones via oxidation of alkenes and alkyne using potassium permanganate and benzoin condensation of substituted benzaldehydes as shown in **Scheme 10, 11,** and **12** and synthesis of thiadiazoloquinoxaline and pyrazinoquinoxaline sub-units as shown in **Scheme 13**. The intermediate compounds will be characterized by spectroscopic methods including NMR, FT-IR and UV-VIS.

4. RESULTS AND DISCUSSION

The synthesis of 8-(7-octyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxalin-6-yl)octanoic acid (**74**) and 8,8'-(3,7-dioctyl-5-10-di(thiophen-2-yl)pyrazino[2,3-g]quinoxaline-2,8-diyl)dioctanoic acid (**73**) have been attempted by condensation reactions of a diamine and a tetra-amine with 1,2-diketone, respectively. The synthesis of these donor-acceptor based monomeric sub-units began with the preparation of 1,2-diketones as shown in **Scheme 10**, **11** and **12** and the 1,2-diketones were subsequently condensed with the amines as shown in **Scheme 13**.

4.1. Attempted synthesis of 1,2-diketones

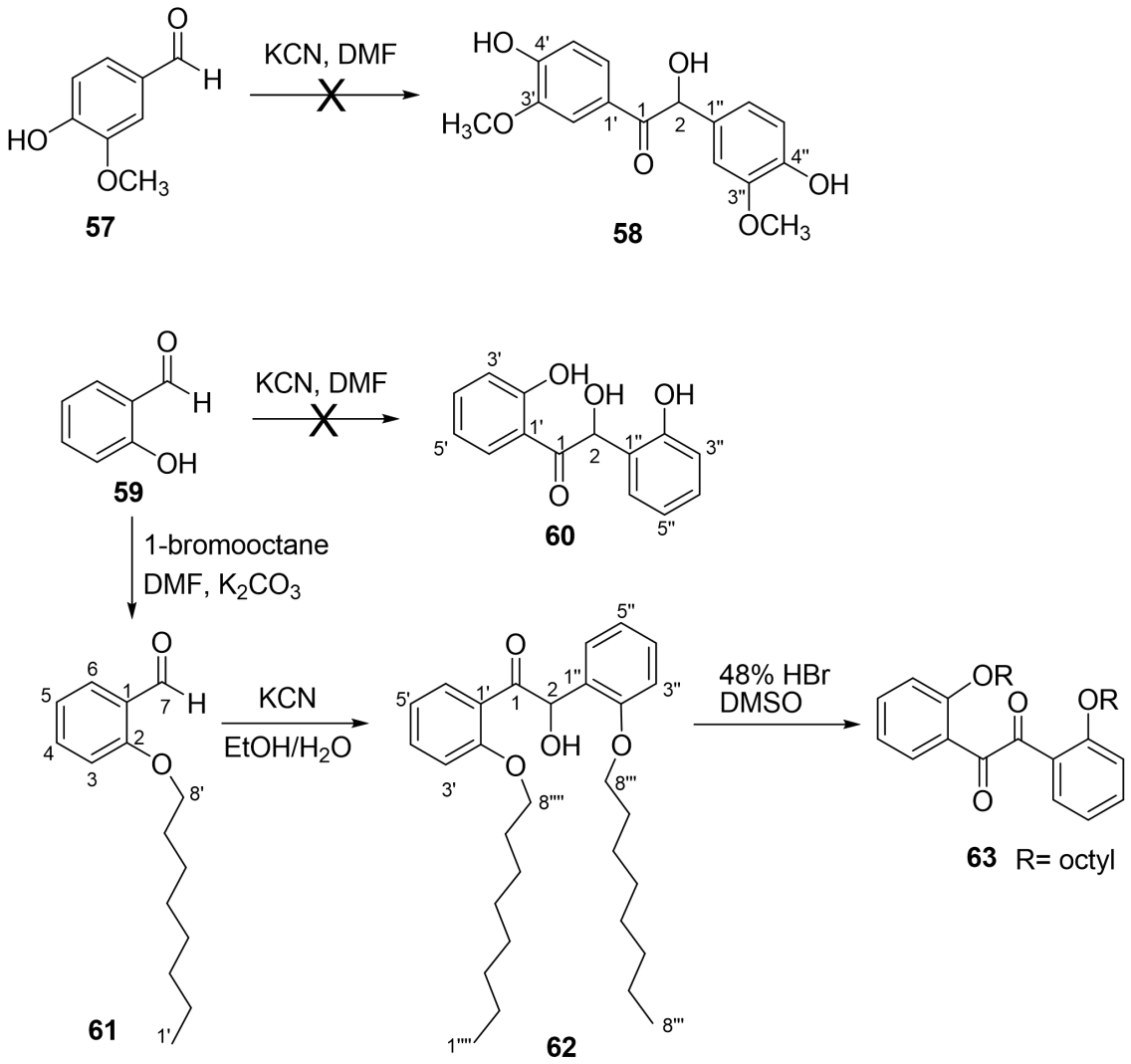
Schemes 10, 11 and **12** show the syntheses of 1,2-diketones attempted in the course of this work. Two general routes were followed to prepare the 1,2-diketones. These are 1) oxidation of an alkyne and an alkene with potassium permanganate ($KMnO_4$), and 2) through the benzoin condensation.

4.1.1. Attempted Synthesis of 1,2-Diketones through Benzoin Condensation

An attempt was made to prepare α-hydroxyketone **58** intermediate by the benzoin condensation of 4-hydroxy-3-methoxybenzaldehyde (**57**) with KCN in DMF (**Scheme 10**). The mixture was heated at 80ºC for 6 h and was cooled to room temperature. A brownish oil separated up on addition of water which did not crystallize on standing. The TLC (silica gel: hexane/ethyl acetate (4:1)) of the resulting oil showed that much of the starting material remained unchanged.

The starting material was recovered and was dissolved in ethanol instead of DMF and aqueous KCN was added. TLC (silica gel: hexane/ethyl acetate (4:1)) of the resulting oil showed that much of the starting material remained unreacted. The mixture was acidified and extracted with CH_2Cl_2. The resulting brownish oil was taken up in different solvent system combinations (hexane/diethyl ether (4:1),

hexane/dichloromethane (3:2), hexane/ethyl acetate (4:1), ethanol) and kept in the refrigerator but the desired intermediate was not obtained. The failure of the reaction is probably due to the reversibility of the reaction that once the equilibrium is set in it may not be pushed to the product side.



Scheme 10.**.** Attempted synthesis of 1,2-diketones through benzoin condensation.

An attempt was made to synthesize 2-hydroxy-1,2-bis(2-hydroxyphenyl)ethanone (**60)** by suspending *o*-hydroxybenzaldehyde (**59**) in DMF and then adding KCN (**Scheme 10**). After heating the reaction mixture at 80ºC for 6 h, TLC (silica gel: hexane/chloroform (1:1)) showed no significant amount of product formation. The reddish oil that was obtained after working up the reaction mixture was then purified using column chromatography (silica gel: hexane/chloroform (1:1) as eluent. Fractions 15-30 afforded a compound whose ^{1}H-NMR spectrum showed signals at δ 11.30,

11.85, 12.40, 12.60 and 13.25 suggesting that the compound has acidic hydrogens. The acids are formed probably due to oxidation of the intermediate cyanide in aqueous acidic solution during work up. No further attempt was made to identify the kind of acids formed.

2-Hydroxybenzaldehyde (**59**) was alkylated with 1-bromooctane and K_2CO_3 in DMF to give 2-(octyloxy)benzaldehyde (**61**) in 64.93% yield as a yellowish oil. **Table 1** shows the ^{1}N-NMR spectral data of **61**. Thus, the doublet of doublets at δ 7.83 integrating for one proton is assignable to H-6. The proton resonance at δ 7.53 is due to H-4. The doublet of doublets at δ 6.88 is assignable to the two methine protons H-3 and H-5. The sharp downfield singlet at δ 10.53 is due to aldehydic proton H-7. The triplet at δ 3.80 is assignable to the methylene protons H-8'. The pentet at δ 1.85 is due to H-7' and the unresolved multiplet in the range δ 1.20-1.50, that integrates for a total of ten protons, is due to methylene protons H-2'-H-6' of octyl side chain. The triplet at δ 0.90 is due to methyl protons H-1'.

The ^{13}C-NMR spectrum of compound **61** showed six carbon resonances in the aromatic region, one carbon resonance in the carbonyl region and eight resonances in the alkyl region. The methine carbon resonance at δ 189.8 is assignable to the aldehydic carbonyl carbon. The quaternary carbon resonances at δ 161.6 and 124.9 are due to the aromatic C-2 and C-1 carbons, respectively. The carbon resonances at δ 135.9, 128.1, 120.4 and 112.5 are due to the aromatic methine carbons C-4, C-6, C-5 and C-3, respectively. The carbon resonance at δ 68.5 is assignable to C-8' the methylene carbon adjacent to oxygen (**Table 3**).

2-Hydroxy-1,2-bis(2-(octyloxy)phenyl)ethanone (**62**) was synthesized by dissolving compound **61** in ethanol and adding aqueous KCN and heating the reaction mixture for 4 h. The resulting reddish oily product was separated by column chromatography (silica gel: hexane/diethyl acetate (4:1), then methanol) and compound **62** was obtained in 25.64% yield.

The ^{1}H-NMR spectrum of compound **62** showed a one-proton doublet at δ 8.04 (J = 7.5 Hz), attributable to H-6'. The multiplet at δ 7.44 is assignable to H-4'. The proton resonance at δ 7.22 which is multiplet is due to the two aromatic methine protons H-

4'' and H-6''. The doublets of doublet at a proton resonance value of δ 6.99 (*J*=1.7 and 8.1 HZ) is due to the aromatic methine protons H-3' and H-5'. The multiplet at δ 6.90 is due to H-3'' and H-5''.The sharp singlet at δ 5.40 is due to –OH proton. The four-proton multiplet at δ 4.13 is assignable for the methylene protons H-8''' and H-8''''**.** The multiplet at δ 1.83-1.28 that integrates for a total of twenty-four protons corresponds to the methylene protons H-2'''-H-7''' and H-2''''-H-7''''. The singlet at δ 0.88 that integrate for six protons is assignable for the methyl protons. (**Table 1**).

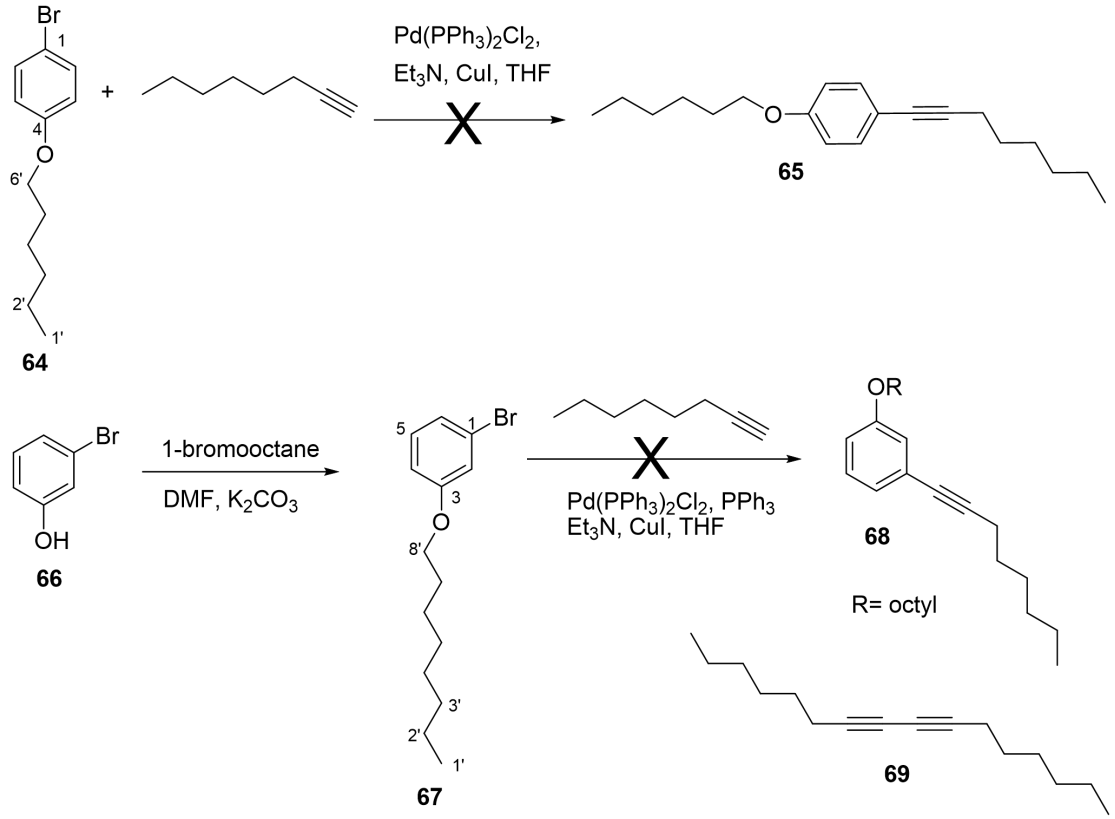
The ^{13}C-NMR spectrum of compound **62** showed five quaternary, nine methine carbon, twelve methylene carbon and one methyl carbon resonances. The signal at δ 176.1 is attributable to the carbonyl carbon C-1. The quaternary carbon signals at δ 157.9 and 155.5 are assignable to C-2' and C-2'', respectively. The remaining quaternary carbon resonances at δ 128.0 and 128.0 are due to C-1' and C-1''. The aromatic methine carbon signals at δ 134.5, 133.1, 129.1, 129.1, 121.5, 121.2, 112.9 and 11.7 are assignable to C-4', C-6'', C-4'', C-5'', C-5', C-3' and C-3'', respectively. The carbon resonance at δ 67.98 is attributable to the only aliphatic methine carbon C-2 which is attached to the – OH. The carbon resonances at δ 68.85 and 68.96 are due to the aliphatic methylene carbons C-8''' and C-8'''' of octyl side chain that are adjacent to the oxygen. The other resonances of the octyl side chain appear in the range 14.13-31.83 (**Table 4**).

1,2-Bis(2-(octyloxy)phenyl)ethane-1,2-dione (**63**) was synthesized by the reaction of compound **62** with DMSO and 48% HBr. Compound **63** was obtained in 4.00% yield. Compound **63** was soluble in D_2O for ^{1}H-NMR and ^{13}C-NMR characterization, but no resonance was seen. Hence compound **63** was characterized only using FT-IR and UV-VIS spectroscopic means. The electronic spectrum of compound **63** in water solution showed two bands at 283 nm and 319 nm which can be assigned for π – π* transition of the conjugated aromatic ring and n - π* transition of the carbonyl, respectively (Appendix). The FT-IR spectrum of compound **63** showed aromatic mode of vibration at 1458 cm^{-1} and C=O stretching at 1601 cm^{-1}. The C-H stretching and bending of methylene appeared at 2927 and 1248 cm^{-1}, respectively. The methyl C-H stretching and bending appeared at 2856 and 1384 cm^{-1}, respectively. C-H out-of-plane bending of o-disubstituted benzene at 754 cm^{-1} (Appendix 13).

4.1.2. Attempted coupling reaction of 4-(hexyloxy)-1-bromobenzene (**64**) and 3-(octyloxy)-1-bromobenzene (**67**) with 1-octyne

Attempt were made to synthesize an arylalkynes through Sonogashira coupling reaction between arylbromides and 1-octyne in the presence of $Pd(PPh_3)_2Cl_2$ catalyst as shown in **Scheme 11**.

The first attempt made was by stirring at room temperature the mixture of 4-(hexyloxy)-1-bromobenzene (**64**), $Pd(PPh_3)_2Cl_2$ and CuI in THF under nitrogen. Et_3N and 1-octyne were added as last components after a few minutes of stirring. TLC of the reaction mixture (silica gel: hexane/ dichloromethane (1:1)) showed no product formation after two days. The volatile component was then removed under reduced pressure and attempt was made to purify the residue by column chromatography. But the ^{1}H-NMR and ^{13}C-NMR spectra clearly showed that no product was formed. This may be due to the low reactivity of the aryl bromide in this coupling reaction as has already been reported in the literature [38]. The other reason for the failure of the reaction may be because oxygen was not completely excluded from the reaction mixture. There are literature reports that Sonogashira reactions fail to work properly in the presence of oxygen [38].



Scheme 11. Attempted coupling reactions of 4-(hexyloxy)-1-bromobenzene (**64**) and 3-(octyloxy)-1-bromobenzene (**67**) with 1-octyne.

3-(Octyloxy)-1-bromobenzene (**67**) was synthesized from 3-bromophenol by reaction with 1-bromooctane and K_2CO_3 in DMF. Compound **67** was purified by distillation under reduced pressure and was obtained as light-yellow oil.

The ^{1}H-NMR spectrum of compound **67** showed a one-proton triplet at δ 7.16 (J = 8.3 Hz) which is attributed to H-5. The doublet of doublet at δ 7.10 corresponds to the two methine protons H-2 and H-6. The signal at δ 6.86 (*ddd*, J = 1.8, 4.3 Hz, 1H) is assignable to H-4. The triplet at δ 3.95 is due to the two methylene protons H-8'. The proton resonance at δ 1.81, which is a pentet, is due to the H-7' methylene protons. The multiplet at δ 1.35, which integrated for a total of ten protons, is due to a group of methylene protons, H-2'-H-6'. The triplet at δ 0.95 corresponds to the methyl protons H-1 (**Table 2**).

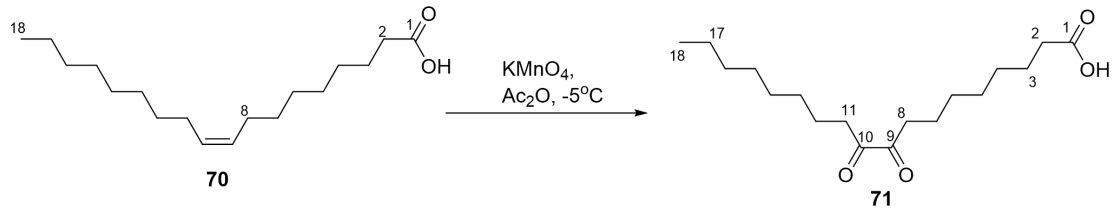
The ^{13}C-NMR spectrum of compound **67** showed six carbon resonances in the aromatic region of which two are due to quaternary carbon atoms. The quaternary

carbon resonance at δ 160.0 corresponds to the carbon attached to the oxygen, C-3. The remaining quaternary carbon resonance at δ 122.8 belongs to the carbon atom attached to the bromine, C-1. The carbon signals at δ 130.5, 123.6, 117.8, and 113.6 are assignable to the aromatic methine carbons C-5, C-6, C-2, and C-4, respectively. The eight aliphatic carbon resonances appear in the range between δ 14.2 and 68.3 (**Table 3**).

An attempt was made to synthesize compound **68** via Sonogashira coupling [35] reaction between compound **67** and 1- octyne in the presence of $Pd(PPh_3)Cl_2$, PPh_3, Et_3N and CuI in dry THF at room temperature. The progress of the reaction was monitered by TLC (silica gel: cyclohexane) and after three days the reaction mixture was concentrated under reduced pressure and the residue was then purified using column chromatography. However, characterization of the resulting fractions using ^{1}H-NMR and ^{13}C-NMR showed that the desired product was not obtained. Instead diyne **69** was formed, presumably through oxidative homocoupling of 1-octyne [38].

4.1.3. Synthesis of 9,10-diketostearic acid (**71**)

Oxidation of oleic acid by $KMnO_4$ at –5ºC in acetic anhydride gave 9,10-diketostearic acid (**71**) as a yellow crystalline solid, after crystallization from ethanol. (**Scheme 12**).



Scheme 12. Synthesis of 9, 10-diketostearic acid (**71**).

In this synthetic method, a very small percentage yield of the product was obtained, which mainly was due to the inefficiency of the oxidation reaction. In order to hydrolyze and remove the remaining acetic anhydride from the product, the reaction mixture was treated with pyridine and left to stir overnight. The pyridine was then removed by treating the resulting solution with 1M HCl.

The ^{1}H-NMR spectrum of **71** showed a four-proton triplet at δ 2.74 due to the H-8 and H-11 protons on either side of the α-diketone sub unit. The triplet signal at δ 2.36 is due to H-2. The three-proton triplet at δ 0.88 corresponds to the protons on the terminal carbon atom of the long alkyl chain. The remaining twenty-two protons appeared as a multiplet signal at δ 1.33.

The ^{13}C-NMR and DEPT-135 spectra were used to confirm the structure of compound **71**. The presence of two ketone carbonyl groups was evident from the carbon resonance at δ 200.0 and 200.1. The acid carbonyl carbon atom showed a signal at δ 180.0. The remaining methylene carbon atom resonances appeared in the range δ 22.9-36.1, while the terminal methyl carbon appeared at δ 14.1 (**Table 4**).

The FT-IR spectrum of 9, 10-diketostearic acid showed asymmetric CO_2 stretching band of the carboxylic acid group at ca. 3200 cm^{-1}, and an O-H out-of-plane bending vibration at 918 cm^{-1} due to the carboxylic acid functionality. The CH_3 group also showed asymmetric C-H bending vibrations at 1459 and 1373 cm^{-1}. The asymmetric C-H stretching vibration of the CH_2 groups appeared at 2918 and 2848 cm^{-1}.

Table 1. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δ ppm) of compounds **61** and **62**.

61	**62**
10.53 (1H, *s*, H-7) 7.83 (2H, *dd*, *J* = 1.8 Hz, H-1, H-3) 7.53 (2H, *dt*, *J* = 3.1, 6.1 Hz, H-4, H-5) 6.99 (1H, *dd*, *J* = 7.9Hz, H-6) 4.07 (2H, *t*, *J* = 6.4 Hz, H-8') 1.49 (2H, *p*, H-7') 1.30 (10H, *m*, H-2'-H-6') 0.90 (3H, *t*, H-1')	8.04 (1H, *d*, *J* = 75 Hz, H-6') 7.44 (1H, m, H-4') 7.22 (2H, *m*, H-4'', H-6'') 6.99 (2H, *dd*, *J* = 8.1 Hz, H-3', H-5') 6.90 (2H, *m*, H-3'', H-5'') 5.40 *(*1H, *s*, -OH) 4.13 (4H, *m*, H-8''', H-8'''') 1.28 (24H, *m*, H-2'''-H-7''', H-2''''-7'''') 0.88 (6H, *s*, H-1''', H-1'''')

Table 2. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δ ppm) of compounds **67** and **71**.

67	**71**
7.16 (1H, t, J = 8.3 Hz, H-5) 7.10 (2H, dd, J = 1.8, 4.3 Hz, H-2, H-6) 6.86 (1H, ddd, J = 1.8, 4.3 Hz, H-4) 3.95 (2H, t, J = 6.5, 13.1, H-8') 1.81 (2H, p, H-7') 1.35 (10H, m, H-2'-H-6') 0'95 (3H, t, H-1')	7.28 (1H, bs, H-OOC) 2.74 (4H, t, J = 7.5 Hz, H-8, H-11) 2.36 (2H, t, J = 7.3, H-2) 1.60-1.33 (22H, m, H-3-H-7, H-12-H-17) 0.88 (3H, t, J = 7.2, H-18)

Table 3. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data **(**δ ppm) for compounds **61** and **67**.

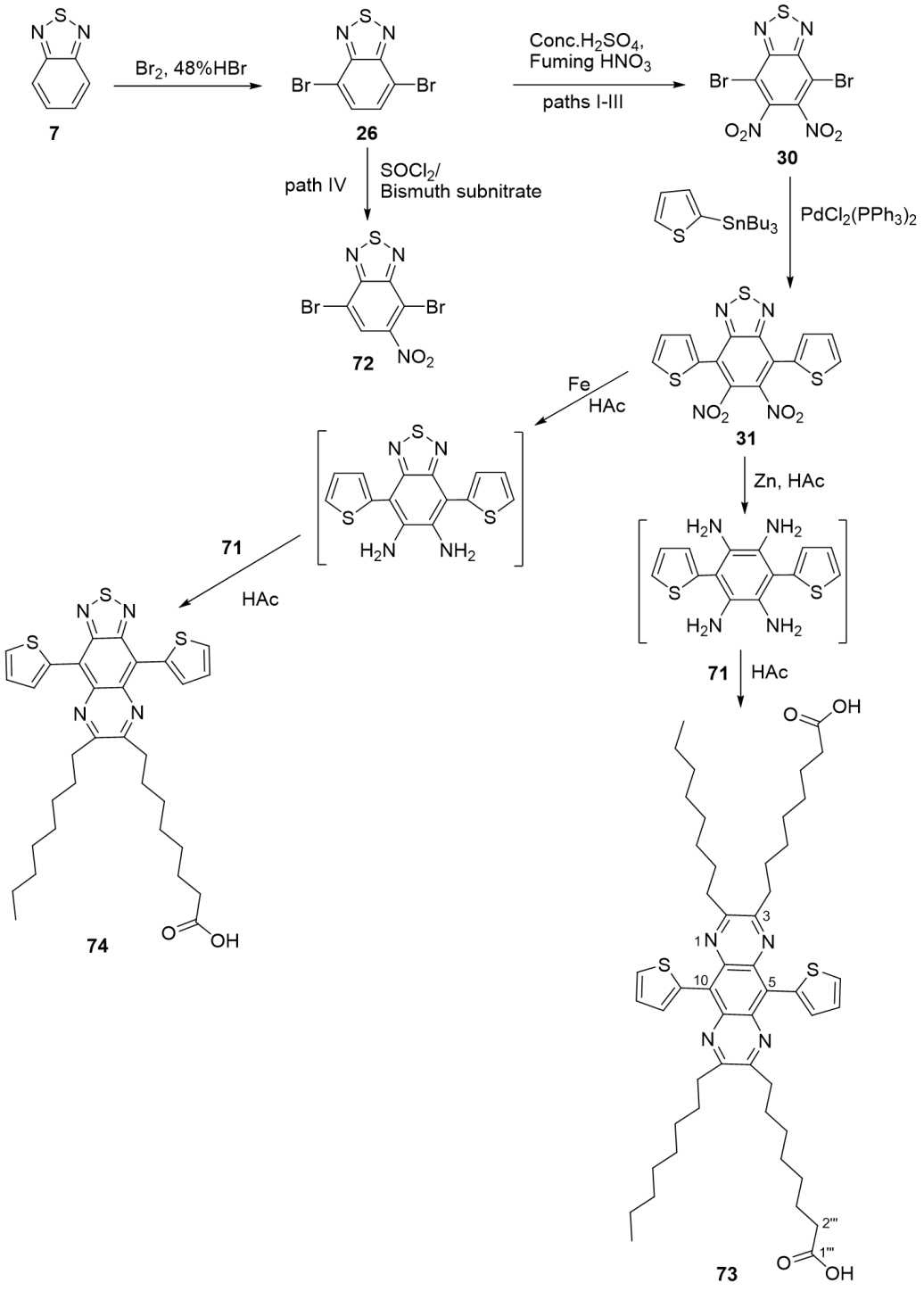
C	**61**	**67**
1	124.9	122.8
2	161.6	117.8
3	120.4	160.0
4	135.9	113.6
5	120.4	130.5
6	128.1	123.6
7	189.8	-
1'	14.1	68.3
2'	22.6	29.3
3'	31.9	26.1
4'	29.1	29.3
5'	29.2	29.2
6'	26.1	31.9
7'	29.3	22.7
8'	68.5	14.1

Table 4: ^{13}C-NMR (100.6 MHz, $CDCl_3$ data (δ ppm) for compounds **62** and **71**

C	62	C	71
1	176.1	1	180.0
2	67.9	2	33.9
1’	128.0	3	24.6
2’	157.9	4	29.3
3’	112.9	5	29.2
4’	134.5	6	29.1
5’	121.1	7	23.0
6’	129.1	8	36.1
1’’	128.0	9	200.0
2’’	155.3	10	200.1
3’’	111.7	11	36.0
4’’	129.1	12	22.9
5’’	121.4	13	28.8
6’’	133.1	14	28.9
1’’’	14.1	15	28.3
2’’’	22.8	16	31.8
3’’’	25.9	17	22.9
4’’’	29.1	18	14.1
5’’’	29.2		
6’’’	29.4		
7’’’	31.8		
8’’’	68.6		
1’’’’	14.1		
2’’’’	22.8		
3’’’’	26.1		
4’’’’	28.9		
5’’’’	29.2		
6’’’’	29.3		
7’’’’	31.8		
8’’’’	68.9		

4.2. Synthesis of Pyrazinoquinoxaline (**73**) and Thiadiazoloquinoxaline (**74**)

In the course of this work, efforts were made to synthesize compounds **73** and **74**. Scheme 13 depicts the routes followed towards the synthesis of **73** and **74**.

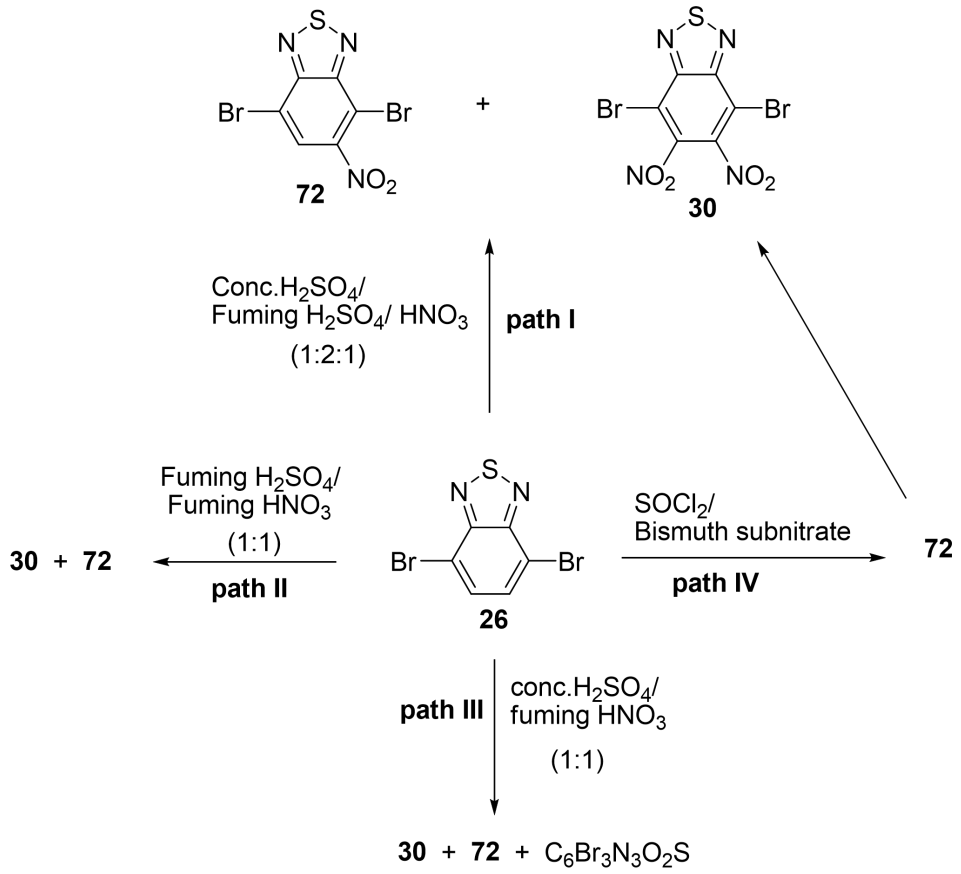


Scheme 13. Attempted synthesis of thiadiazoloquinoxaline (**74**) and pyrazinoquinoxaline (**73**).

Bromination of 2,1,3-benzothiadiazole (**7**), using Br_2 and 48% HBr gave 4,7-dibromobenzo-[2,1,3]thiadiazole (**26**) in 91% yield as light yellow solid, which melted

at 188-190ºC. The ^{1}H-NMR spectrum of this compound showed only one singlet at δ 7.80 in agreement with the two chemically equivalent aromatic methine protons H-5 and H-6 (**Table 5**). The ^{13}C-NMR spectrum of compound **26** displayed only three carbon resonances among which two are quaternary carbon resonances. The quaternary carbon resonance at δ 113.9 is attributable to C-4 and C-7 to which the bromines are attached. The other quaternary carbon resonance at δ 152.9 is due to the two carbon atoms connected to the thiadiazole moiety at C-8 and C-9. The only methine carbon signal at δ 132.4 is due to C-5 and C-6 (**Table 6**). The FT-IR spectrum of **26** showed the C-Br stretching band at 586 cm^{-1} and aromatic mode at 1476 cm^{-1}. Compound **26** was synthesized according to the procedure of Edwlmann, M.J *et al*. [39] The ^{1}H-NMR and ^{13}C-NMR data discussed above agree very well with those reported in the literature [40].

Different attempts were made to nitrate 4,7-dibromobenzo-[2,1,3]thiadiazole (**26**) as shown in **Scheme 14.** The first attempt made was by stirring compound **26** in a mixture of concentrated H_2SO_4, fuming H_2SO_4 and fuming HNO_3 (**Scheme 14** Path **I**). Monitoring the progress of the reaction by TLC (silica gel: hexane/ethyl acetate (4:1)) showed that the starting material had disappeared shortly after the reaction started but there were two spots, which were presumably due to the mononitro (**72**) and dinitro (**30**) compounds. Extending the reaction time to three days did not push the mono side product into the dinitro product. Further extending the reaction time to one week decreased the amount of the mono-nitrated compound but did not completely disappear completely.



Scheme 14. Syntheisis of 4,7-dibromo-5,6-dinotrobenzo-[2,1,3]thiadiazole (**30**).

The second attempt made to synthesize 4,7-dibromo-5,6-dinitrobenzo-2,1,3-thiadizole (**30**) (**Scheme 14** Path **II**) was by swirling 4,7-dibromobenzo-2,1,3-thiadiazole (**26**) in a mixture of fuming H_2SO_4 and fuming HNO_3 (1:1 vol/vol) for 10 minutes and stirring the mixture at room temperature for two days. This method also gave a product mixture consisting of the mono and dinitro products.

The third trial was using a mixture of concentrated H_2SO_4 and fuming HNO_3 in 1:1 volume ratio. Unlike the above two trials this method (**Scheme 14** Path **III**) resulted in the formation of a third product as detected by TLC (silica gel: cyclohexane/benzene (1:1)). This presumably, was due to the formation of tribromo derivative, $C_6Br_3N_3O_2S$, which might be formed due to the bromine cation produced by partial oxidative decomposition of 4,7-dibromobenzo-2,1,3-thiadiazole (**26**) under the influence of fuming nitric acid. This phenomena had been observed by Uno *et al.* in their attempted nitration of 4,7-dibromo-[2,1,3]-benzothiadiazole using a mixture of concentrated H_2SO_4 and fuming HNO_3 [33, 40].

A fourth attempt was made to synthesize compound **72** using bismuth subnitrate and thionyl chloride (**Scheme 14** path **IV**) [41] and then to further nitrate the mono-nitro product using the mixture of concentrated H_2SO_4 and fuming HNO_3. The intial reaction of compound **26** with bismuth subnitrate and thionyl chloride gave compound **72** as a light yellow solid. ^{1}H-NMR spectrum of compound **72** showed only one signal at δ 8.29 which is assignable to the only aromatic methine proton. The ^{13}C-NMR and DEPT spectra of compound **72** showed six carbon resonances of which the signals at δ 153.0, 152.8, 149.9, 114.8 and 109.2 are due to quaternary carbons and the resonance at δ 127.5 was due to the only methine carbon C-6. Compound **72** was then nitrated using a mixture of concentrated H_2SO4, fuming H_2SO4 and fuming HNO_3 by stirring at room temperature for one hour. The ^{1}H-NMR and ^{13}C-NMR spectra of the resulting compound showed a singlet proton resonance at δ 8.29 and six carbon resonances in the aromatic region of which five are quaternary carbons. This indicated that the mono-nitro compound was not converted completely to the dinitro compound and that more reaction time was needed to push the reaction to completion.

The mixtures of mono-and di-nitro compounds obtained from the above reactions were combined and chromatographed on silica gel using hexane/chloroform (2:1) as eluent. Compound **30** was obtained in a pure form as a light yellow solid and was characterized by using ^{1}H-NMR and ^{13}C-NMR.

The ^{1}H-NMR spectrum of compound **30** showed no proton resonance. The ^{13}C-NMR spectrum of compound **30** displayed only two carbon signals which are due to quaternary carbon atoms. One quaternary carbon resonance was not observed. The carbon resonance at δ 151.37 corresponds to the two carbons attached to the thiadiazole ring at C-8 and C-9. The carbon resonance at δ 110.28 is attributable to the two carbons attached to the bromine, C-4 and C-7. The signal for the carbon attached to the nitro group was not observed in the carbon spectrum (**Table 6**). The FT-IR spectrum of compound **30** showed bands at 583, 1460 and 1448 cm^{-1} due to C-Br, C=N and C=C groups, respectively. The bands at 1545 and 1376 cm^{-1} correspond to the NO_2 groups. The ^{1}H-NMR and ^{13}C-NMR data discussed above for compound **30** agree very well with those reported in the literature [33].

The Stille cross-coupling reaction between 2-(tributhylstannyl)thiophene and 4,7-dibromo-5,6-dinitrobenzo-[2,1,3]thiadiazole (**30**) in the presence of $Pd(PPh_3)_2Cl_2$ catalyst (2 mol%) in dry THF gave 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**31**) in 62% yield as reddish solid.

The ^{1}H-NMR spectrum of compound **31** showed doublet signal at δ 7.77 which correspond to the two chemically equivalent protons H-5' and H-5''. The two-proton doublet at δ 7.54 is assignable to H-3' and H-3''. The doublet of doublet resonance at δ 7.27 belongs to H-4' and H-4'' (**Table 5**).

The ^{13}C-NMR spectrum of compound **31** showed six carbon resonances of which three are quaternary carbons and three are methine carbon signals. The signal due to the carbons attached to the nitro group was not observed. The quaternary carbon resonance at δ 152.2 is assignable to the two equivalent carbons attached to the thiadiazole ring, C-8 and C-9. The carbon resonance at δ 129.6 corresponds to the two equivalent quaternary carbons C-4 and C-7 attached to the thiophene rings. The other quaternary carbon resonance at δ 121.5 is attributed to the chemically equivalent carbons C-2' and C-2'' of the thiophene rings. The carbon resonances at the δ 131.4, 131.0 and 127.9 are due to the methine carbons C-5' and C-5'', C-3' and C-3'' and C-4' and C-4'', respectively (**Table 6**).

Compound **31** was reduced using iron powder in HAc by stirring the reaction mixture at 60ºC for 40 minutes. The mixture was then filtered while still hot and the 1,2-diketone compound **72** was added to the filtrate and the mixture was heated at 60ºC for 6 h. Compound **74** was obtained in 51% yield as a purple solid . The ^{1}H-NMR spectrum of compound **74** showed a doublet at δ 8.93, which is assignable to the two equivalent methine protons, H-5' and H-5'' on the thiophene ring. The resonance at δ 7.62 is assignable to H-3' and H-3'', and the signal at δ 7.28 was due to H-4' and H-4''. The singlet at δ 4.25 is due to acidic protons on the side chain. The other aliphatic proton resonances on the pendant side chain were unresolved and appeared in the range δ 3.05 to 0.93.

The ^{13}C-NMR spectrum of compound **74** showed three methine carbon resonances in the aromatic region at δ 132.7, 130.5 and 125.5 which correspond to the equivalent

thiophene methine carbons, C-4' and C-4'', C-3' and C-3'' and C-5' and C-5'', respectively. Comparison of the DEPT and ^{13}C-NMR spectra of compound **74** clearly showed that the resonances at δ 177.5, 156.9, 145.8, 135.8 and 122.5 are due to quaternary carbons. The signal at δ 177.5 was assignable to the carbonyl carbon of the carboxylic acid on the side chain. The signal at δ 156.9 is due to the equivalent pyrazine quaternary carbons, C-6 and C-7 that are attached to the pendant side chain. The resonance at δ 145.8 and 135.8 were due to C-8 and the equivalent carbons C-2' and C-2'' of thiophene, respectively. The quaternary carbon resonance due to the carbon attached to the thiophene ring was not observed. The quaternary carbon signal at δ 122.5 is due to the carbons attached to the thiadiazole ring. The resonance at δ 35.4 is assignable to the methylene carbon adjacent to the carbonyl carbon of the pyrazine side chain. The other aliphatic carbons of the side chain appear in the range δ 31.9 to 14.2 (**Table 7**).

The FT-IR spectrum of compound **74** showed –COOH stretching at 3423 cm^{-1} and C=N stretching at 1460 cm^{-1}. The carbonyl carbon stretching of the carboxylic acid appeared at 1712 cm^{-1}. Aromatic mode of vibration appeared at 1419 cm^{-1}. The C-H stretching of methylene and methyl were seen at 2919 and 2848 cm^{-1}, respectively.

The UV-Vis spectrum of compound **74** in chloroform showed absorption maxima at 293, 382, and 483 nm. The peak at 293 nm corresponds to the π- π* transition of the conjugated aromatic system. The maxima at 382 and 483 nm can be ascribed to n- π* transitions from the lone pairs of sulphur of thiophene and nitrogen of pyrazine rings, respectively (Appendix 16).

An attempt was made to reduce compound **31** to the tetra-amine intermediate using zinc in acetic acid, and then to condense with the 1,2-diketone compound, 9,10-diketostearate (**72**) *in situ*, to synthesize compound **73**. The ^{1}H-NMR and ^{13}C-NMR of compound **73** in $CDCl_3$ showed very weak signals and it was difficult to characterize the compound obtained based on its NMR spectra.

The FT-IR spectrum of compound **73** showed aromatic mode of vibrations at 1597 and 1460 cm^{-1} and C=N stretching of imine at 1546cm^{-1}. O-H and C=O stretching of the carboxylic acid appeared at 3421 and 1712 cm^{-1}, respectively. The C-H stretching of

methylene and methyl appeared at 2922 and 2849 and bending mode of vibration was observed at 698 cm^{-1}, respectively. The UV-Vis spectrum of compound **73** showed almost identical absorption maxima with that of compound **74**. The electronic transition at 295 nm corresponds to the π- π* of the conjugated aromatic system. The transitions at 384 and 483 nm are due to n- π* transition from the lone pair of sulphur of thiophene and nitrogen of pyrazine rings, respectively (Appendix 15).

Table 5. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δ ppm) of compounds **26** and **31**.

26	**31**
7.76	7.77
(2H, s, H-5, H-6)	(2H, *d*, *J*=4.7 Hz, H-5', H-5'')
	7.54
	(2H, *d*, *J*=2.6 Hz, H-3', H-3'')
	7.27
	(2H, *dd*, *J*=4.3, 8.2 Hz, H-4', H-4''

Table 6. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δppm) for compounds **26**, **30**, **31**.

C	**26**	**30**	**31**
1	-	-	-
2	-	-	-
3	-	-	-
4	113.9	110.3	129.6
5	132.4	a	a
6	132.4	a	a
7	113.9	110.3	129.6
8	152.9	151.4	152.2
9	152.9	151.4	152.2
1’	-	-	-
2’	-	-	131.4
3’	-	-	131.0
4’	-	-	127.9
5’	-	-	129.6
1’’	-	-	-
2’’	-	-	131.4
3’’	-	-	131.0
4’’	-	-	127.9
5’’	-	-	129.6

a= resonance not observed

Table 7. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δppm) for compound **74.**

C	74	C	74
1	-	1’	-
2	-	2’	135.8
3	-	3’	130.5
4	--	4’	132.7
5	145.8	5’	125.5
6	156.3	1’’	-
7	156.8	2’’	135.8
8	145.8	3’’	130.5
9	-	4’’	132.7
10	122.4	5’’	125.5
11	122.4	1’’’	177.5
12	145.8	2’’’-7’’’/1’’’’-8’’’’	14.1-31.9

5. CONCLUSION

In the course of this project work, a thiadiazoloquinoxline-containing monomer, 8-(7-octyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxalin-6-yl)octanoic acid (**74**)**,** was designed and synthesized starting from benzothiadiazole and oleic acid. The synthesis involved bromination of benzothiadiazole followed by nitration and Stille coupling reaction with 2-(tributylstannyl)thiophene to afford 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**31**). This compound was reduced and subsequently condensed with 9,10-diketostearic acid, which was prepared from oleic acid by oxidation with $KMnO_4$, to afford compound **74**. Similarly, an attempt was also made to synthesize a pyrazine-containing monomer, 8,8'-(3,7-dioctyl-5,10-di(thiophen-2-yl)pyrazino[2,3-g]quinoxaline-2,8-diyl)dioctanoic acid (**73**). Attempts were also made to synthesize 1,2-diketones via the benzoin condensation of substituted benzaldehydes and the Sonogashira reaction of arylbromides and 1-octyne. The above quinoxaline-containing monomers can be polymerized to give low band-gap homopolymers. It is also possible to prepare copolymers with appropriate donor segments, like fluorene-containing units, to prepare materials with potential application in organic photovoltaic cells.

6. EXPERIMENTAL

6.1. Materials and methods

All of the compounds prepared in the course of the synthetic work were characterized by UV-Vis, FT-IR and NMR techniques. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer at 400.13 and 100.6 MHz, respectively, in $CDCl_3$, D_2O (for compound **63**), and DMSO-d_6 (for compound **74**) and are reported in δ units. The solvent signal was used as internal standard. The UV-Vis spectra of compound **63**, **73** and **74** were recorded in H_2O (for compound **63**) and chloroform using SPECTRONIC GENESYS 2PC spectrophotometer with 1 cm cell at room temperature. Infrared spectra were obtained using a PERKIN ELMER BX infrared spectrophotometer. FT-IR spectra of the crystalline solid compounds were obtained as KBr pellets. Melting points were measured using a Mettler FP85HT cell, and FP90 processor and are uncorrected.

6.2. Reagents

Bromine (BDH), benzothiadiaizole (Aldrich), 3-bromothiophene (Alderich), 4-bromothiophene (Aldrich), 2-(tributylstannyl)thiophene (Aldrich), bis(triphenylposphine)palladium(II) chloride (Aldrich), 4-hydroxy-3-methoxybenzalldeyde (Fulka), 2-hydroxybenzaldeyde (Fulka), potassium cyanide(BDH), N,N-dimethylforamide (Aldrich), dimethylsulphoxide (BDH), 1-octyne (Aldrich), triphenylphosphine (Aldrich), potassium permanganate, oleic acid (Aldrich), 48% HBr (BDH), n-octyl bromide (Aldrich) were bought and used as received. Tetrahydrofuran (THF) was dried over Na-benzophenone under nitrogen. Triethylamine was dried over NaOH. Analytical grade benzene was purchased from BDH and used without further purification. All solvents used for column chromatography and extraction were distilled before use. Silica gel 60 (43-63 μm) was used as a stationary phase for column chromatography. 0.25 mm Silica gel pre-coated plates were used for thin layer chromatography.

6.3. Procedures

6.3.1. ATTEMPTED BENZOIN CONDENSATION OF 4-HYDROXY-3- METHOXYBENZALDEHYDE (**58**)

4-Hydroxy-3-methoxybenzaldehyde (vanillin) (15.23 g, 0.10 mol) was dissolved in DMF (30 mL) and to this was added KCN (0.78 g, 0.012 mol) and the mixture was heated at 80ºC for 6 h. The mixture was cooled to room temperature and water (30 mL) was added and the mixture was stirred overnight. A brownish oil separated which did not crystalize upon standing. The mixture was acidified with 2 M HCl and was extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. TLC (silica gel: hexane/ diethyl ether (4:1)) of the resulting oil showed that much of the starting material remained unchanged. The oil was taken up in hexane/diethyl ether (4:1) and kept in refrigerator but did not give any crystals. No attempt was made to separate the mixture by chromatography.

6.3.2. ATTEMPTED BENZOIN CONDENSATION OF 2-HYDROXYBENZALDEHYDE (**60**)

2-Hydroxybenzaldehde (6.10 g, 0.05 mol) was added into DMF (15 mL) and to this was added KCN (0.39 g, 6.00 mmol) and the mixture was heated at 80 ºC. TLC of the reaction mixture showed no progress of the reaction. The mixture was cooled into room temperature and water (15 ml) was added and allowed to stir for overnight. The mixture was then acidified using 2 M HCl and extracted with CH_2Cl_2. The organic phase was then washed with brine and dried over Na_2SO_4 and the solvent was removed. A reddish oily product obtained which was purified using column chromatography (silica gel:hexane/chloroform (1:1)) as eluent. But characterization using NMR showed that the compound contains acid and no attempt was made to identify the kind of acids formed.

6.3.3. SYNTHESIS OF 2-(OCTYLOXY)BENZALDEHYDE (**61**)

2-Hydroxybenzaldehyde (94.99 g, 0.04 mol), K_2CO_3 (23 g, 0.16 mol) and DMF (50 mL) where placed in a 250 mL two necked round-bottomed flask equipped with a pressure-equalizing dropping funnel and a condenser. The mixture was heated to 100ºC and 1-bromooctane (8.39 g, 0.04 mol) was added drop-wise and the mixture was heated for 5 h. The mixture was then filtered while still hot and the residue was washed with DMF. The filtrate was acidified with 2 M HCl and extracted with diethyl ether. The diethyl ether extract was washed with 2 M HCl, aq. NaOH and brine and dried over Na_2SO_4 and the solvent was removed under reduced pressureL to affored compound 61 as a light yellow oily product (6.22 g, 64.93%).

^{1}H-NMR (400.13 MHz, CDCl3): δ[ppm] 10.53 (s, 1H, H-7), 7.83 (2H, *dd*, *J*=1.8, 7.7 Hz, H-1, H-3), 7.53 (2H, *dt*, *J*=3.1, 6.1 Hz, H-4, H-5), 6.99 (1H, *dd*, *J*=7.9, 12.8 Hz, H-6), 4.07 (2H, *t*, *J*=6.4 Hz, H-8'), 1.49 (2H, *p*, H-7'), 1.30 (10H, *m*, H-2'-H-6'), 0.90 (3H, t, H-1'); ^{13}C-NMR (100.6 MHz, CDCl3): δ[ppm]: 189.80 (C-7), 161.58(C-2), 135.86(C-4), 128.14(C-6),124.94(C-1), 120.41 (C-5),120.42 (C-3), 68.54 (C-8'), 31.78 (C-3'), 29.29 (C-7'), 29.20 (C-5'), 29.09 (C-4'), 22.63 (C-2'), 14.06 (C-1').

6.3.4. Synthesis of 2-hydroxy-1, 2-bis(2-(octyloxy)phenyl) ethanone(**62**)

2-(Octyloxy)benzaldehyde (5.85 gm, 0.03 mol) was dissolved in ethanol (16.25 ml) and to it was added a solution of KCN (1.70 gm, 0.01 mol) in water (5 ml) and the mixture was heated at 80ºC for 4 h. Then, the mixture was allowed to cool to room temperature and acidified with 2 M HCl and then poured onto water (32.5 ml) and extracted with CH_2Cl_2. The CH_2Cl_2 extract was concentrated under reduced pressure and purified using column chromatography (silica gel: hexane/diethyl ether (4:1), then methanol) as eluent. Compound 62 was obtained as reddish oil (3.00 g, 25.64%).

^{1}H-NMR (400.13 MHz, $CDCl_3$): δ [ppm]: 8.04 (1H, *d*, *J*=7.5, H-6'), 7.44 (1H, *m*, H-4'), 7.22 (2H, *m*, H-4'', H-6''), 6.99 (2H, *dd*, *J*=8.1, H-3', H-5''), 6.90 (2H, *m*, H-3'', H-5''), 5.40 (1H, *s*, -OH), 4.13 (4H, *m*, H-8''', H-8''''), 1.28 (24H, *m*, H-2'''-H-7''', H-2''''-H-7''''), 0.88 (6H, *s*, H-1''', H-1''''). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ [ppm]:176.05 (C-1), 157.88 (C-2'), 155.33 (C-2''), 134.53 (C-4'), 133.13 (C-6''), 129.11 (C-4''), 129.05 (C-6'), 128.01 9C-1''), 128.00 (C-1'), 121.45 (C-5''), 112.87 (C-3'), 111.74 (C-3''), 68.96 (C-8''''), 68.85 (C-8'''), 67.98 (C-2), 31.83 (C-7''''), 31.76 (C-7'''), 29.35 (C-6'''), 29.27 (C-6''''), 29.23 (C-5'''), 29.15 (C-4'''), 29.15 (C-5''''), 28.84 (C-4''''), 26.10 (C-3''''), 25.87 (C-3'''), 22.85 (C-2''''), 22.84 (C-2'''), 14.13 (C-1''').

6.3.5. Attempted synthesis of 1, 2-bis(2-(octyloxy)phenyl)ethane-1, 2-dione (**63**)

Compound **63** (3.00 g, 6.41 mmol) was dissolved in DMSO (6.86 mL) and to this was added drop-wise 48% HBr (3.43 mL) from a pressure-equalizing dropping funnel over 10 minutes. The mixture was heated at 50 ºC for 4 h and the temperature was raised to 90 ºC and heating continued for 2 h. The mixture was then cooled to room temperature and poured onto ice cold-water. The oily product was then extracted using CH_2Cl_2 and the solvent was removed under reduced pressure. Recrystalization from ethanol afforded white solid (0.12 g) which was not characterized using ^{1}H-NMR and ^{13}C-NMR.

FT-IR (KBr) ν_{max} [cm^{-1}]:2927, 2856, 1601, 1458,1248. UV-Vis (nm): 283, 319.

6.3.6. Synthesis of 3-(octyloxy)bromobenzene (**67**)

To a mixture of 3-bromophenol (10 g, 5.77 mmol) and DMF (80 mL)in a three necked round-bottomed flask, an anhydrous potassium carbonate was added (35 g). The mixture was heated at 100 ºC and 1-bromooctane (11.04 g , 60 mmol) was added. The mixture was heated under nitrogen atmosphere for 5 h and the mixture was filtered while still hot. The filtrate was cooled, acidified with 2M HCl and extracted with diethyl ether and the extract was washed with 1M NaOH followed by brine solution,

then dried over an anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by vacuum distillation at 0.21 torr and 94 ºC.

^{1}H-NMR (400.13 MHz, $CDCl_3$), δ[ppm]: 7.16 (1H, *t*, *J*=8.3, 16.4 Hz, H-5), 7.10 (2H, *dd*, *J*=1.8, 4.3 Hz, H-2, H-6), 6.86 (1H, *ddd*, *J*=1.8, 4.3 Hz, H-4), 3.95 (2H, *t*, *J*=6.5, 13.1, H-8'), 1.81 (2H, *p*, H-7'), 1.35 (10H, *m*, H-2'-H-6'), 0.95 (3H, *t*, H-1'). ^{13}C-NMR (100.6 MHz, $CDCl_3$),δ[ppm]: 160.02 (C-3), 130.47 (C-5), 123.55 (C-6), 122.82 (C-2), 117.76 (C-2), 113.56 (C-4), 68.28 (C-1'), 31.88 (C-6'), 29.33 (C-2'), 29.29 (C-4'), 29.21 (C-5'), 22.72 (C-7'), 14.15 (C-8').

6.3.7. ATTEMPTED SYNTHESIS OF 1-(OCT-1-YNYL)-3-(OCTYLOXY)BENZENE (**68**)

A mixture of 1.43 gm (5.00mmol) of octyloxy-*m*-bromobenzene (**6**), 175 mg (0.25 mmol) of $Pd(PPh_3)_2Cl_2$, 33 mg (0.13 mmol) of PPh_3, (0.83 gm,7.5 mmol) of 1-octyne, (1.01 gm, 7.5 mmol) of dried triethylamine in 20 ml of dry THF was stirred for 20 minutes at room temperature. CuI (12 mg, 0.06 mmol) was then added and the mixture was stirred at room temperature. The solvent was then removed under reduced pressure and the residue was dissolved in pentane and filtered through celite. The resulting oily product was then purified using column chromatography (silica gel: cyclohexane). Characterization of the resulting fractions showed that diynes are formed and the desired product was not obtained.

6.3.8. SYNTHESIS OF 9, 10-DIKETOSTEARIC ACID (**8**)

Oleic acid (11.1 g, 36 mmol) was stirred in acetic anhydride (100 mL) under nitrogen atmosphere overnight. The resulting clear solution was cooled to -5 ºC using an ice-salt bath and $KMnO_4$ (25.10 g, 160.00 mmol) was added over 10 minutes keeping the temperature below -5 ºC. Stirring was continued for another 90 minutes during which time the flask temperature rose to the maximum of 7 ºC. Then a 2:1 ethyl acetate:hexane mixture (150) cooled to -10 ºC using acetone cooling bath was added to the reaction vessel. Additional cooled aqueous extracting solution 1:1 mixture of 20% sodium metabisulfite and saturated NaCl was directely added to the reaction vessel.

After a few minutes of stirring and adding ice to the reaction mixture, the resulting dark liquid was placed in a separatory funnel and the aqueous phase was drawn off as soon as it separated. The purple organic phase was further washed with more amounts of cooled 1:1 aqueous sodium metabissulfite and saturated NaCl solution until the organic solution become yellow. The organic phase was washed with water several times, dried with anhydrous Na_2SO_4 and the solvent was removed. The resulting oil was dissolved in pyridine (25 mL) and to it was added water (12.5 mL) with stirring in ice-water bath and the solution was stirred overnight at room temperature. To the resulting solution, ether (200 mL) was added and the organic phase was washed with 1 M HCl until the aqueous extract remained acidic. The remaining yellow ether solution was dried over anhydrous Na_2SO_4 and the solvent was removed to give 13.69% yellow crystalline solid product after recrystallization from ethanol.

Mp.84-86 ºC; FT-IR (KBr) νmax [cm^{-1}]: 2956,2919,2848, 1713, 1459, 918, 901,713; ^{1}H-NMR ($CDCl_3$, 400.13 MHz), δ [ppm]: 7.20 (1H, *br s*, H-OOC), 2.74(4H, *t,* H-8, H-11), 2.36(2H, *t*, *J*=7.3, H-2), 1.60-1.33(22H, m, H-3-H-7, and H-12, H-17), 0.88 (3H, *t*, H-18); ^{13}C-NMR ($CDCl_3$,100.6 MHz), δ [ppm]: 200.04 (C-9, C-10), 180.02 (C-1), 36.11 (C-8), 36.02 (C-11), 33.99 (C-2) 31.82 (C-16), 29.32 (C-4), 29.14 (C-5), 29.12 (C-6), 28.83 (C-13), 28.32 (C-15), 24.58 (C-3).

6.2.9. Synthesis of 4, 7-Dibromobenzo-[2,1,3]thiadiazole(**26**)

Benzothiadiazole (10.03 g, 75.65 mmol) was suspended in 48% HBr (150 mL) in a 500 mL two-necked round bottomed flask equipped with a reflux condenser and a pressure-equalizing dropping funnel. To this was added drop-wise a solution of bromine (11.34 mL, 221.06 mmol) in 48% HBr (100) over 2 hours. The mixture was heated for two hours at 130ºC. The temperature was lowered to 70 ºC and the mixture was stirred for overnight. The temperature was raised to 130 ºC and heated for two hours and then cooled to room temperature and treated with 5% $Na_2S_2O_3$ solution and then filtered. The orange residue was washed with water and dried. It was then washed with cold ether (-25 ºC) once and dried in a vaccum oven at 50 ºC overnight to affored 19.67 gm of a light yellow solid in 91% yield.

Mp. 188-190 ºC; FT-IR (KBr) ν_{max} [cm^{-1}]: 3046, 1654, 1587, 1498, 1476, 1310, 1272, 1184, 936, 875, 843, 825, 586, 488; ^{1}H-NMR ($CDCl_3$, 400.13 MHz), δ [ppm]: 7.76 (2H, *s*, H-5, H-6); ^{13}C-NMR ($CDCl_3$,100.6 MHz), δ [ppm]: 152.97 (C-8, C-9), 132,39 (C-6, C-7), 113.92 (C-4, C-7).

6.3.10. Synthesis of 4,7-Dibromo-5,6-Dinitrobenzo-[2, 1, 3]thiadiazole (**30**)

The nitrating mixture was prepared by adding fuming H_2SO_4 (17.1 mL) onto an ice-cold concentrated H_2SO_4 (11 mL) followed by addition of fuming HNO_3 (9.75 mL). To this was added 4,7-dibromobenzo-[2,1,3]thiadiazole (7.5 g, 25.5 mmol) in small portions keeping the internal temperature below 10 ºC ice-bath. An equal using amount of the nitrating mixture was added to wash the starting material from the wall of the flask. The mixture was allowed to stirr at room temperature for a week and was poured onto ice-cold water. The precipitate was collected by filtration and was washed with water and dried and purified using column chromatography (silica gel: hexane/chloroform (2:1)). Compound **30** was obtained as a white solid (0.93 g, 14.14%).

Mp. 202-204ºC; FT-IR (KBr) νmax [cm^{-1}]: 2958, 2927, 1728, 1545, 1448, 1460, 1344, 1266, 1123, 885, 749. ^{13}C-NMR ($CDCl_3$, 100.6 MHz), δ [ppm]: 151.38 (C-8, C-9), 110.29 (C-4, C-7).

6.3.11. Synthesis of 4, 7-di(dithieno-dinitro-benzothiadiazole) (**31**).

4,7-dibromo-5,6-dinitrobenzo-[2,1,3]thiadiazole (1.49 g,3.80 mmol), 2-tributylstannyl thiophene (3.38 g, 8.99 mmol), $Pd(PPh_3)_2Cl_2$ (57.55 mg) and THF (36.00 mL) were mixed and heated under reflux for 5 h. The mixture was cooled and filtered and was then washed with petroleum ether and dried to afford a red solid (0.88 g, 62.00% yield).

Mp. 148-150ºC; FT-IR (KBr) ν_{max} [cm^{-1}]: 3107, 1543, 1461, 1421, 1381, 1357, 1229, 1064,899, 863, 827, 717,625, 510; ^{1}H-NMR ($CDCl_3$, 400.13 MHz), δ [ppm]: 7.77 (2H,

d, *J*=4.7, H-5', H-5''), 7.54 (2H, *d*, *J*=2.6, H-3', H-3''), 7.27 (2H, *dd*, *J*=4.3, 8.2, H-4', H-4''); ^{13}C-NMR ($CDCl_3$, 100.6 MHz), δ [ppm]: 152.24 (C-8, C-9), 129.57 (C-4, C-7).

6.3.12. Synthesis of 8,8'-(3,7-dioctyl-5,10-di(thiophen-2-yl)pyrazino[2,3-g]quinoxaline-2,8-diyl)dioctanoic acid (**73**).

5,6-Dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**31**) **(**100 mg, 0.27 mmol), zinc dust (498 mg) was dissolved in 10 mL of glacial acetic acid and two drops of water was added and the mixture was stirred at 60ºC for 40 minutes. Then, the mixture was filtered while still hot and 9,10-diketostearic acid (0.32 g, 0.54 mmol) was added to the filtrate and the mixture was stirred at 40ºC for 4 h. Then, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was then taken in chloroform and the chloroform insoluble portion was filtered and washed with methanol two times and dried to afford a red solid in 51% yield. However, the compound was not fully characterized due to its poor solubility.

Mp.148-150 ºC, FT-IR (KBr) ν_{max} [cm^{-1}]: 3421, 2922, 2849, 1712, 1597, 1460, 698, Uv-Vis (nm): 483, 384, 295.

6.3.13. Synthesis of 6-(octanoic acid)-7-(octyl)-4, 9-dithien-2-yl-[1, 2, 5]thiadiazolo-[3, 4-g]quinoxaline (**74)**

To the mixture of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**31**) (100 g, 0.26 mmol) and acetic acid (5 mL) was added iron powder (0.18 gm, 3.072 mmol) and the mixture was stirred at 50ºC for three hours. Then, the mixture was filtered while still hot and 9,10-diketostearic acid (0.08 g, 0.26 mmol) was added to the filtrate and then the mixture was stirred at 40ºC for 4 h. Then, the mixture was cooled to room temperature and the solvent was removed under reduced pressure to afford a purple solid after drying in vacuum oven.

Mp.85-87 ºC, ^{1}H-NMR ($CDCl_3$, 400.13 MHz), δ [ppm]: 8.93 (2H, *dd*, *J*=4.1 Hz,H-5', H-5''), 7.62 (2H, *dd, J*=4.7 Hz, H-3', H-3''), 7.28 (2H, *dd*, *J*=4.1 Hz, H-4', H-4''), ^{13}C-NMR ($CDCl_3$, 100.6 MHz), δ [ppm]: 177.51, 156.93, 156.81, 145.81, 122.47,

135.83, 132.71, 130.54, 125.48, 14.19-31.98, FT-IR (KBr) ν_{max} [cm^{-1}]: 3423, 2919, 2848, 1712, 1460, 1419, UV-Vis (nm): 483, 382, 293.

6.3.14. Attempted mononitration of 4,7-dibromobenzo-[2,1,3]thiadiazole using bismuth subnitrate and thionyl chloride (**72**)

In a 250 mL two-necked round bottomed flask fitted with a condenser was charged with dibromobenzoothiadiazole (0.74 gm, 2.5 mmol), dry CH_2Cl_2 (50 mL) and thionyl chloride (1.20 g, 10 mmol). The mixture was stirred and bismuth sub nitrate (2.20 g, 1.25 mol) was added. After vigorous stirring at room temperature for three hours, the mixture was filtered to remove the inorganic materials. The filtrate was washed with dilute HCl and water and it was then evacuated *in vacuo* to give a yellow solid in 42.35%.

Mp. 170-172 ºC, ^{1}H-NMR ($CDCl_3$, 400.13 MHz), δ [ppm]: (1H, *s*, H-6), ^{13}C-NMR ($CDCl_3$, 100.6 MHz), δ [ppm]: 153.0152.8, 149.9, 127.5, 114.8, 109.2.

7. REFERENCES

1. Baekeland, L.H. *J. Ind. Eng. Chem*. **1909**, 1, 149.
2. Heeger, A.J. *Angew. Chem. Int. ed*. **2001**, 40, 2591.
3. Shirakawa, H. *Angew. Chem. Int. ed*. **2001**, 40, 2575.
4. MacDiarmid, A.G. *Angew. Chem. Int. ed*. **2001**, 40, 2581.
5. Shirakawa, H.; MacDiarmid, A.; and Heeger, A. *Chem. Commun.* **2003**, 1.
6. Braun; Heeger, A.J. *App. Phys. Lett.*, **1991,** 58, 1982.
7. Burroughes, J.H; Bragley, D.D.C.; Brown, A.R, *Nature*, **1990**, 347,539541.
8. Sirringhaus, H.; Brown , P. J.; Friend ,R; Nielson, M.M, Bechgaard, K; Langeveld-Voss, B.M.M.; Spiering, A.J.H.; Janssen, R.A.J.; Meeijer, E.W.; Herwig, p.; deLeeuw, D.M. *Nature*, **1999**, 401, 685.
9. Jonforsen, M.; Johannes, T.; Inganas, O.; Anderson, R.M. *Macromolecules*. **2002**, 35,1638.
10. Roncali, J. *Chem. Rev*.; **1997**, 97,173.
11. Higgins, S. *J. Chem. Soc. Rev*., **1997**, 26, 247.
12. Bauerce, P. *Adv. Mater*., **1993**, 5, 879.
13. Lasperas, M.; Rubalcaba, A.; Quiroga, M.L. *Tetrahedron* **1980**, 36, 3403.
14. Van Pharm, C. *Synth. Commun*. **1986**, 16, 689.
15. Stille, J.K. *Angew. Chem., Int. Ed*. **1986**, 25, 508.
16. Hou, Q.; Xu, Y.; Yang, W.; Yuan, M.; Peng, J.; Cao, Y. *J. Mater. Chem*.**2002**, 10, 2887.
17. Kanikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc*. **1995**, 117, 6791.
18. Kanikomi, M.; Tanaka, S.; Yamashita, Y. *Chem. Mater*. **1996**, 8, 570.
19. Bundgard, E.; Krebs, E.C. *Macromolecules*., **2006**, 39, 2823.
20. Wienk, M.M; Struijk, M.P.; janssens, R.A. *J. Chem. Phys. Lett*. **2006**, 422, 488.
21. Jayakannan, M.; Hal, V.; Jansson, R.A.J. *J. Polym. Sci. A Pol. Chem*.,**2002**,40, 2360.
22. Tirapattur, S.; Beletete, M.; Drolet, N.; leclerc, M.; Durocher, G. *J. Phys. Chem B*., **2002**, 106, 8959.
23. Xia, C.; Advincula, R. C. *Macromolecules*., **2001**, 34, 5853.

24. Jayakannan, M.; Hal, V.; Jansson, R.A.J. *J. Polym. Sci. A Pol. Chem*., **2002**, 40, 251.

25.. Setayesh, H.; Grimsdale, A.C.; Weil, T.; Enkelmann, V.; Mullen, K.; Mehadadi, F.; List, E.J.W.; Leising, G. *J. Am. Chem. Soc*., **2001**, 123, 946.

26. Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules*., **1997**, 30, 7686.

27. Suzuki, M.; J.C., L.; Saegusa, T. *Macromolecules*., **1990**. 191,191.

28. Bernius, M; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater*., **2002**, 12, 1737.

29. Svenson, M.; Zhang, F.; Veenstra, S.C.; Verhees, W.J.H,; Hummelen, J.C.; Kroon, J.M.; Inganas, O.; Anderson, M.R. *Adv. Mater*., **2003**, 15, 988.

30. Wang, X.; Perzon, E.; Oswald, F.; Langa, F.; Admassie, S.; Anderson, M.R.; Inganas, O. *Adv. Funct. Mater*., **2005**, 15, 1665.

31. Zhang, F.; Persons, E.; Mammo, W.; Anderson, M.R.; Inganas, O. *Adv. Funct. Mater*., **2005**, 15, 745.

32. Yamashita, Y.; Ono, K.; Tomura, M.; Tanaka, S. *Tetrahedron* **1997**, 53, 10169.

33. Uno, T.; Tanaka, K.; Tornoeda, M. *Chem. Pharm. Bull*., **1980**, 28, 1909.

34. Jensen, H.P.; Sharpless, K.B. *J. Org. Chem*., **1974**, 39, 2314.

35. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tet. Lett*. **1975**, 4467.

36. Kenning, D.D.; Mitchell, K.A.; Calhoun, T.R.; Runfar, R.M.; Satter, D.J.; Rasmussem, S.C. *J. Org. Chem.*, **2002**, 67, 9073.

37. White,M.J.; Leeper, F.J. *J. Org. Chem*., **2001**, 66, 5124.

38. Thorand, S.; Krause, N. *J. Org. Chem*. **1998**, 8551.

39. Austin, W.B.; Bilow, N.; Kelleghan, W.J.; Lau, K.S.Y., *J. Org. Chem*. **1981**, 46, 2280.

40. Eldmann, M. J.; Raimundo, J.M.; Ulesch, N.F.; Diederich, F. *Helvetica. Chemica. Acta.,* **2002**, 85, 2195.

41. Pesin, V.G.; Sergeev, V.A. *Chem. Abstr*., **1968**, 68, 105110.

42. Muathen, H.A. *Molecules*., **2003**, 8, 593.

8. APPENDICES

Appendix 1. ^{1}H-NMR spectrum of 2-hydroxy-1, 2-bis 92-hydroxyphenyl) ethan-1-none(60).

Appendix 2. ^{1}H-NMR spectrum of 2-(octyloxy)benzaldehyde (**61**).

Appendix 3. ^{13}C-NMR spectrum of of 2-(octyloxy)benzaldehyde (**61**).

Appendix 4. DEPT-135 spectrum of 2-(octyloxy)benzaldehyde (**61**).

Appendix 5. ^{1}H-NMR spectrum of 2-hydroxy-1, 2-bis (2-(octyloxy)phenyl)ethanone (**62**).

Appendix 6. ^{13}C-NMR spectrum of 2-hydroxy-1, 2-bis (2-(octyloxy)phenyl)ethanone (**62**).

Appendix 7. DEPT-135 spectrum of 2-hydroxy-1, 2-bis (2-(octyloxy)phenyl)ethanone (**62**).

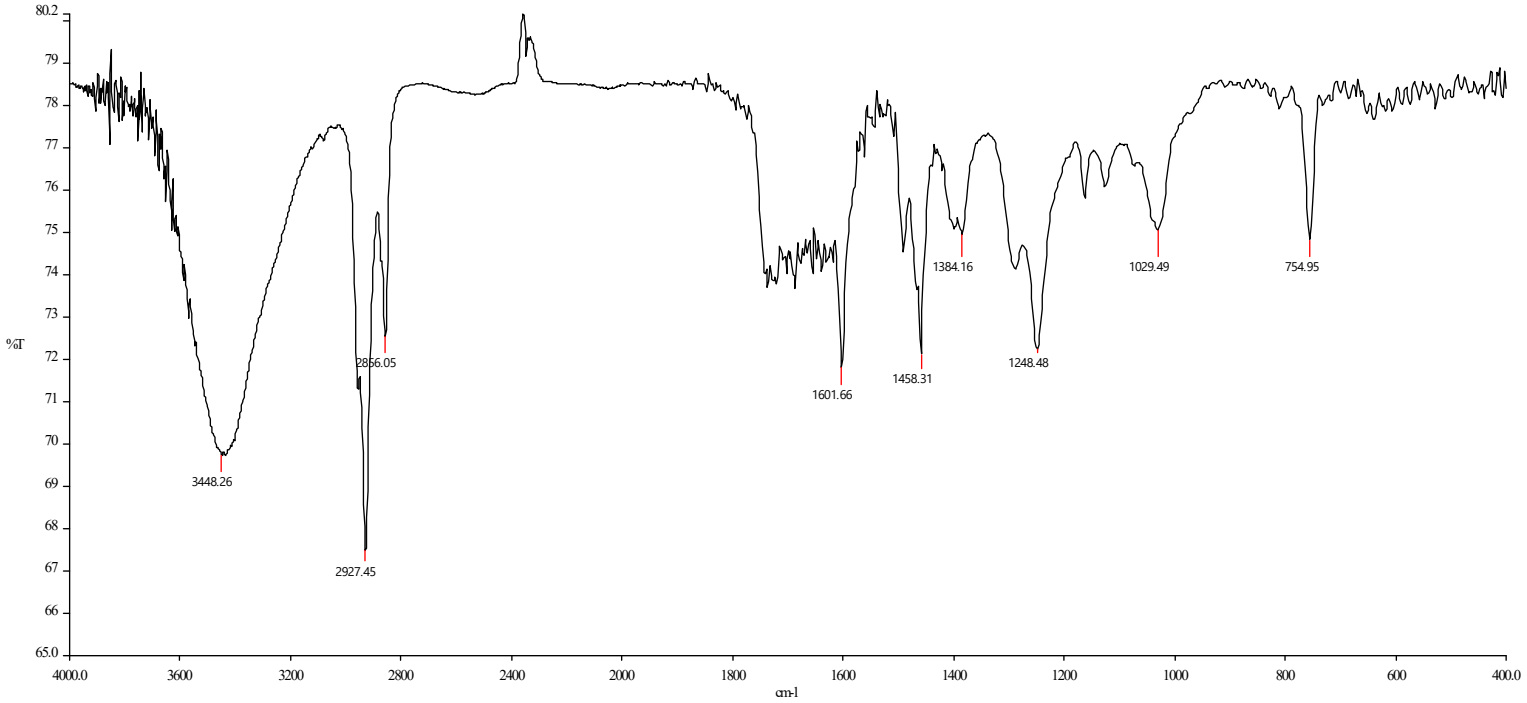
Appendix 8. ^{1}H-NMR spectrum of compound **68***. * mixture of **67** and **69**

Appendix 9. ^{13}C-NMR spectrum of **68*.** * mixture of **67** and **69**

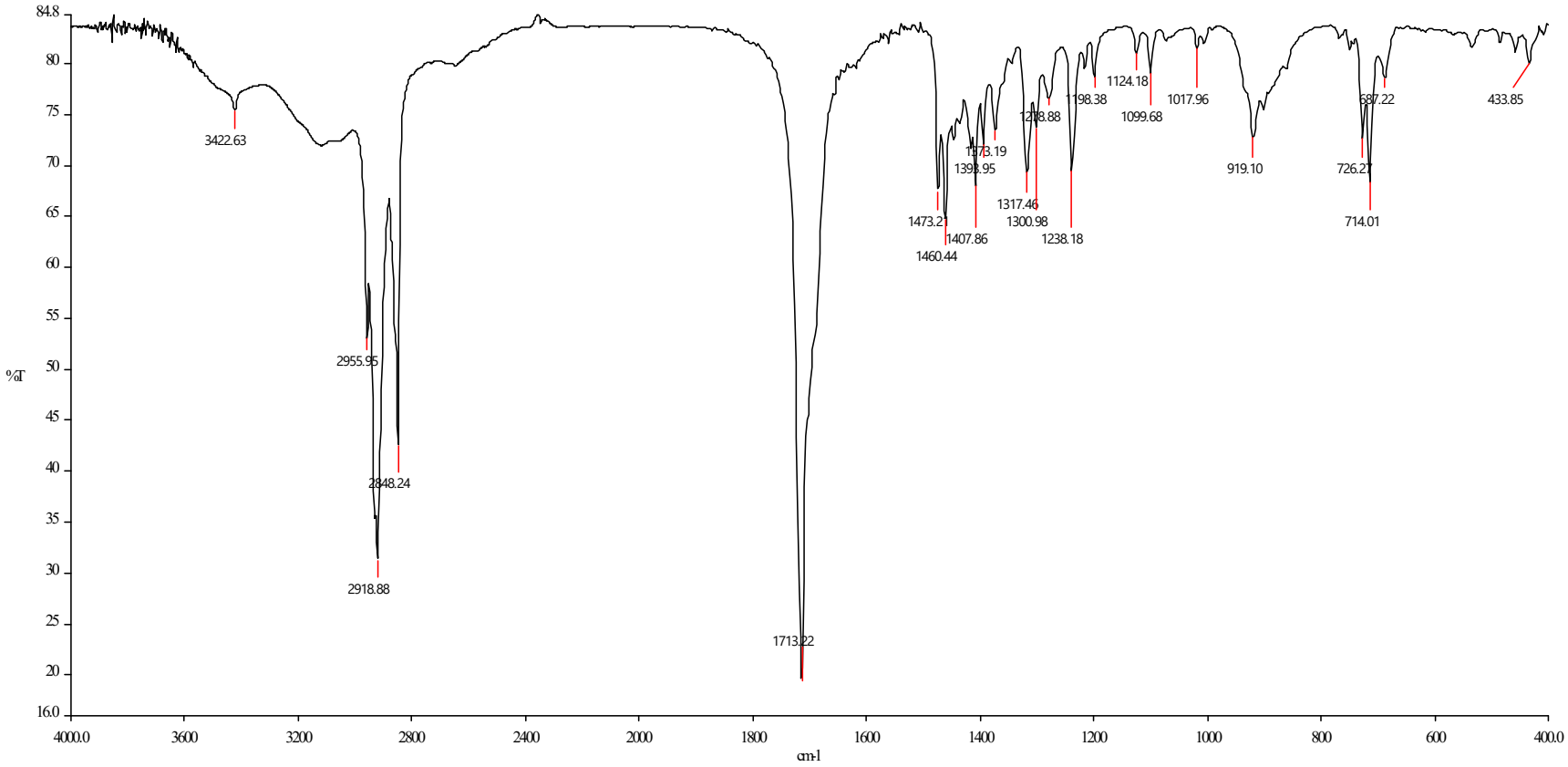
Appendix 10. DEPT-135 spectrum of **68***   ***mixture of **67** and **69**

Appendix 11. ^{1}H-NMR spectrum of 4, 7-dibromo-5, 6-dinitrobenzo-[2, 1, 3]thiadiazole (**30**).

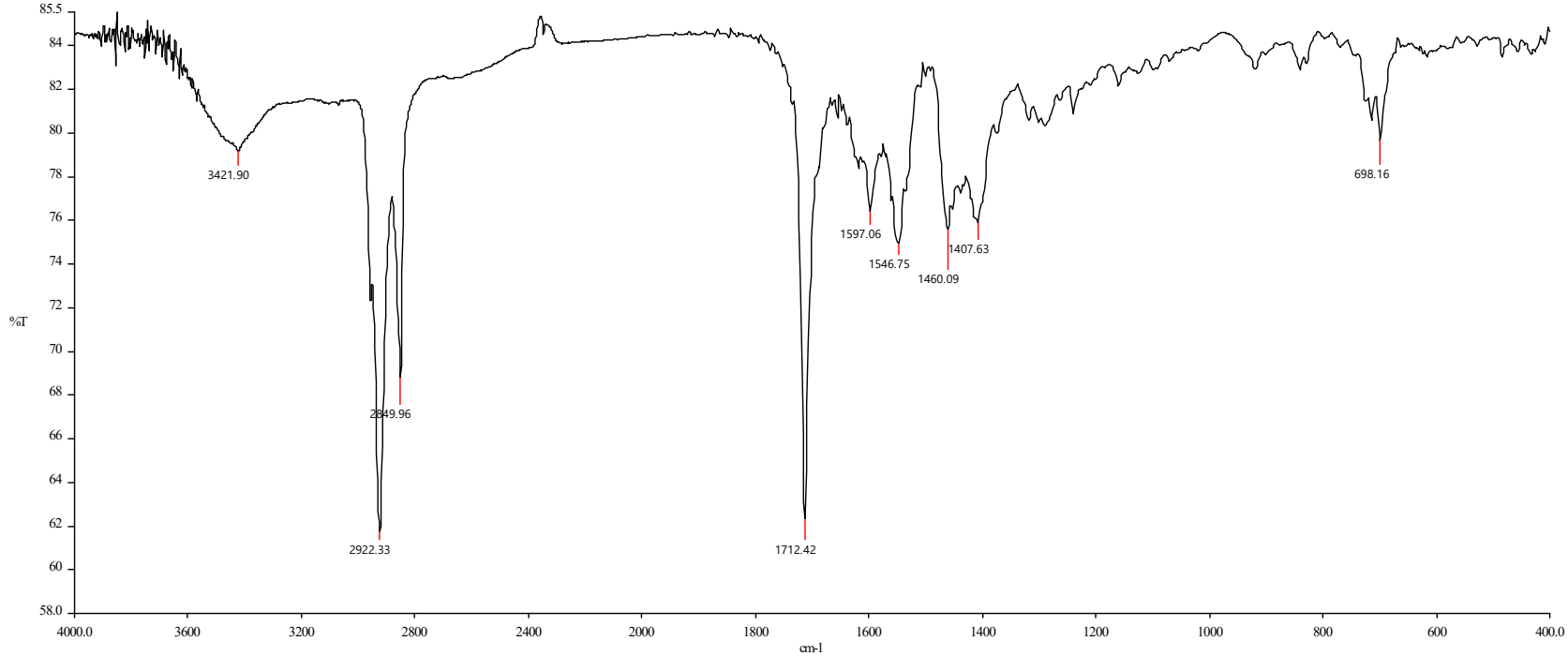
Appendix 12. ^{13}C-NMR and DEPT-135 spectra of 4, 7-dibromo-5, 6-dinitrobenzo-[2, 1, 3]thiadiazole (**30)**



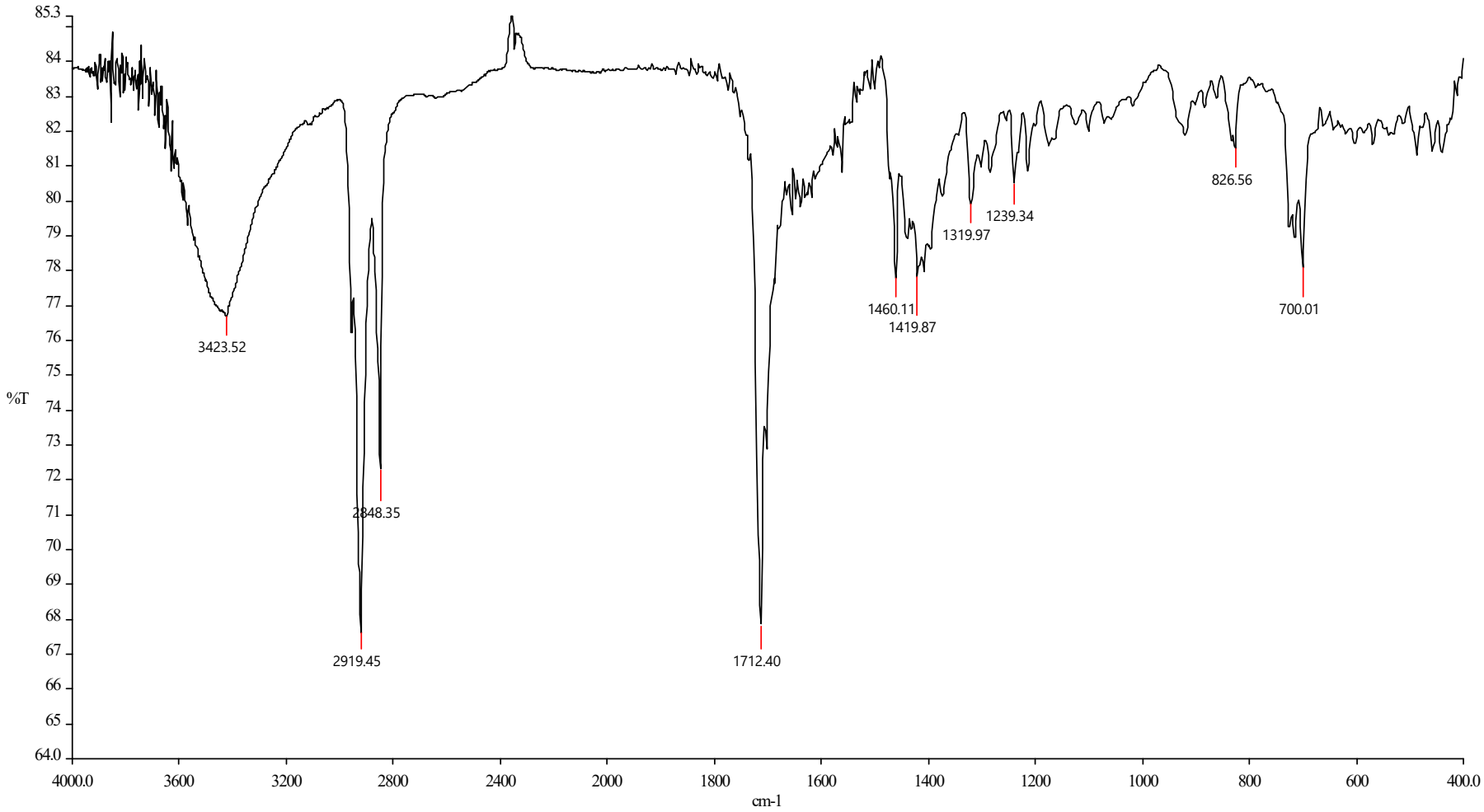
Appendix 13. FT-IR (KBr) λ_{max} (cm^{-1}) spectrum of **63.**



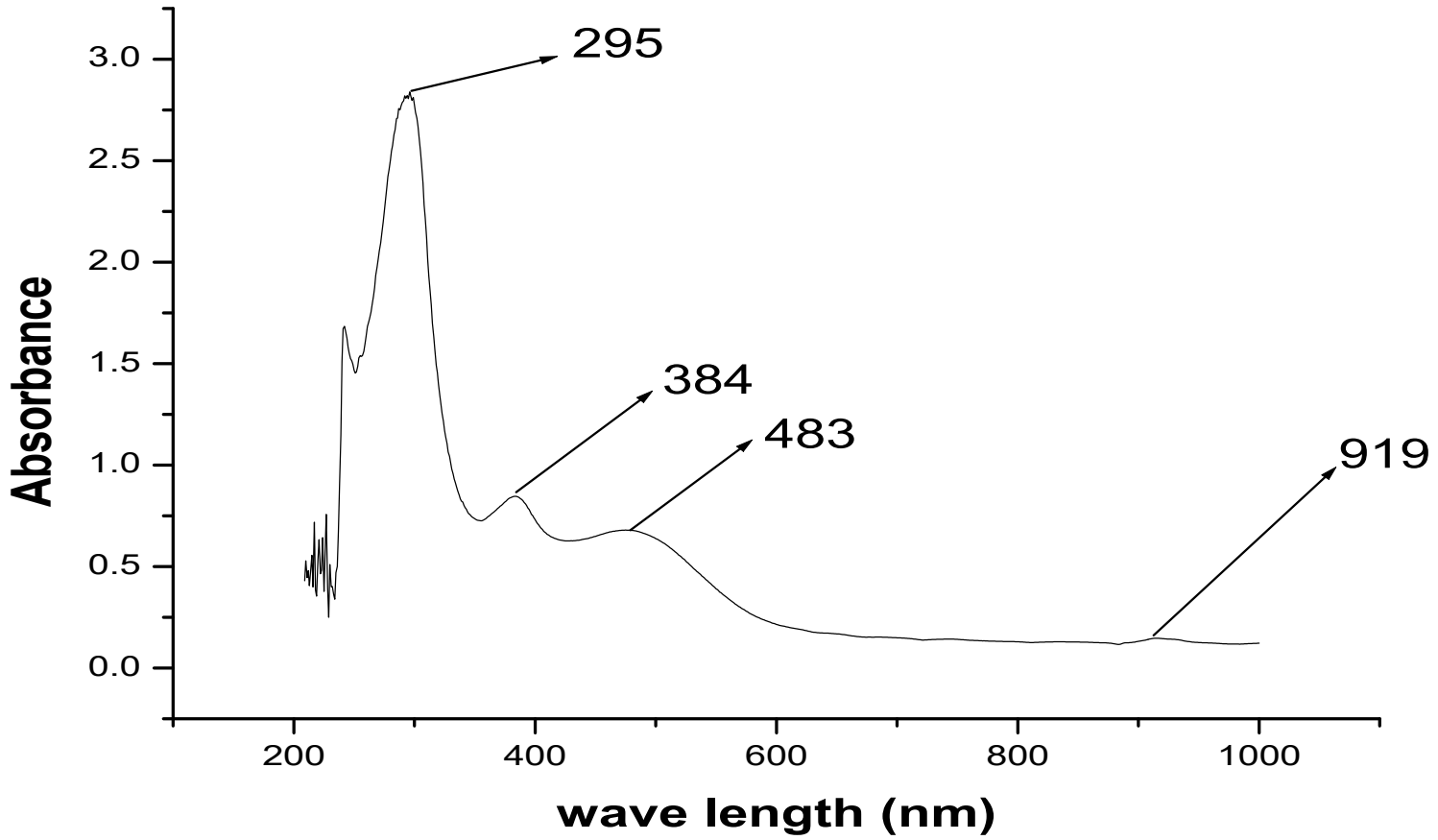
Appendix 14. FT-IR (KBr) λ_{max} (cm^{-1}) spectrum of **71.**



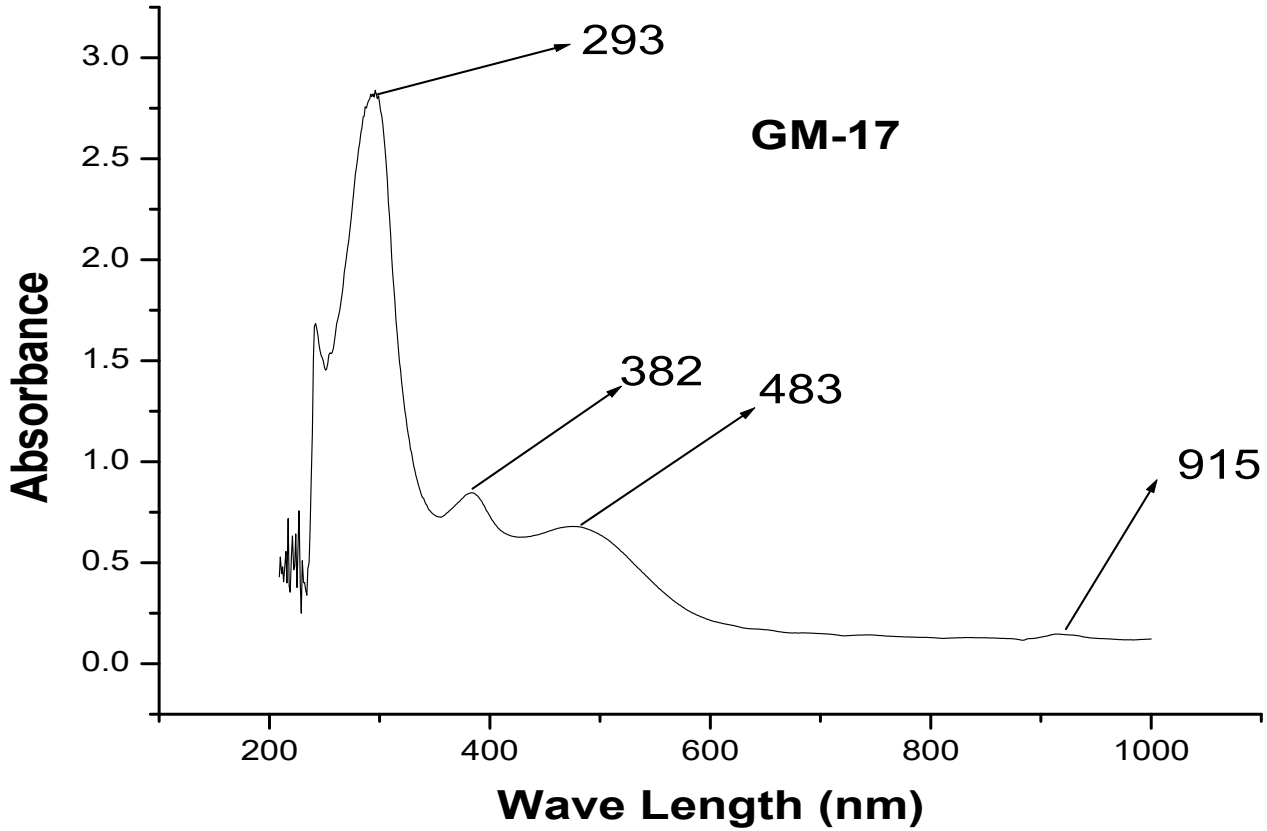
Appendix 15. FT-IR (KBr) λ_{max} (cm^{-1}) spectrum of **73.**



Appendix 16. FT-IR (KBr) λ_{max} (cm^{-1}) spectrum of **74.**



Appendix 17. UV-Vis spectrumof compound **73.**



Appendix 18**.** UV-Vis spectrumof compound **74.**