ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS OF LOW BANDGAP ALTERNATING COPOLYMERS BASED ON FLUORENE-QUINOXALINE AND BENZOTHIADIAZOLE UNITS

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List of abbreviations

DMF: N,N-Dimethylformamide

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

δ: Chemical shift

J: Coupling constant

s: Singlet

d*:* Doublet

t: Triplet

brd: Broad doublet

brs: Broad singlet

m: Multiplet

dd: Doublet of doublets

ppm: Parts per million

NBS: *N*-Bromosuccinimide

PLED: Polymer light emitting diodes

PL: Photoluminescence

EL: Electroluminescence

PPP: Poly(*p*-phenylene)

PPV: Poly(*p*-phenylenevinylene)

PPE: Poly(*p*-phenyleneethylene)

TEAOH: Tetraethylammonium hydroxide

HAc: Acetic acid

DME: Dimethoxy ethane

M_n: number average molecular weight

M_w: weight average molecular weight

PFs: Polyfluorenes

BPO: Benzoylperoxide

Abstract

Donor/Acceptor-Copolymers, as so-called “low-band-gap” π-conjugated polymers, have been widely investigated and applied in different areas such as organic photovoltaics (OPVs), organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs). Due to the attractive features of those functional organic polymer materials such as light weight, flexibility and low cost of production they have attracted recent interest in research development.

In the course of this project, the synthesis of polyfluorene copolymers was attempted. Monomers based on quinoxaline, namely, 5,8-bis-(5-bromo-thiophen-2-yl-2,3-bis(4-octyloxyphenyl)quinoxaline was successfully synthesized. Two copolymers, namely, poly[5-(5-(9,9-bis-[2-(2-methoxy-ethoxy)-ethyl]-7-methyl-9H-fluoren-2-yl}-thiophen-2-yl)-8-(5-methyl-thiophen-2-yl)-2,3-bis-(4-octyloxyphenyl)-quinoxaline] and poly[5-(5-(7-(7-(9,9-bis-[2-(2-methoxy-ethoxy)-ethyl]-9H-fluoren-2-yl)-benzo[1,2,5]thiadiazol-4-yl)-9,9-bis-[2-(2-methoxy-ethoxy)-ethyl]-9H-fluoren-2-yl)-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-8-thiophen-2-yl-quinoxaline].
Were prepared with a palladium(0)-catalyzed Suzuki-coupling polymerization reaction and the polymers were characterized by NMR, Uv-Vis a

1. INTRODUCTION

Conjugated polymers have attracted considerable attention as a new class of electronic material, since the study of these systems has generated entirely new scientific concepts as well as potential for new technology[1].Conjugated polymers with low specific weight, processable, soluble, tunable and flexible mechanical properties are useful to obtain a unique and novel material with numerous exciting applications [1-4].

Organic polymers (conjugated polymers) have been widely employed in electronic device fabrication mainly for their insulating properties. Starting from 1997 the role of organic polymers and oligomers in the electronic industry has been continuously reconsidered in a new light as potential substituents of conventional inorganic conductors in a great variety of applications[1-5].Indeed, the pioneering work of Shirakawa, MacDiarmid, Heeger and coworkers allowed thin films of polyacetylene to be obtained[6], a new organic polymer discovered by Natta in 1958[7,8] which exhibited a relatively high electrical conductivity by "doping" with bromine or iodine[9].This fundamental discovery opened the way to the development of a wide range of organic polyconjugated materials, with different structural frameworks based upon aromatic, heteroaromatic, vinylic or acetylenic π-system (fig 1).

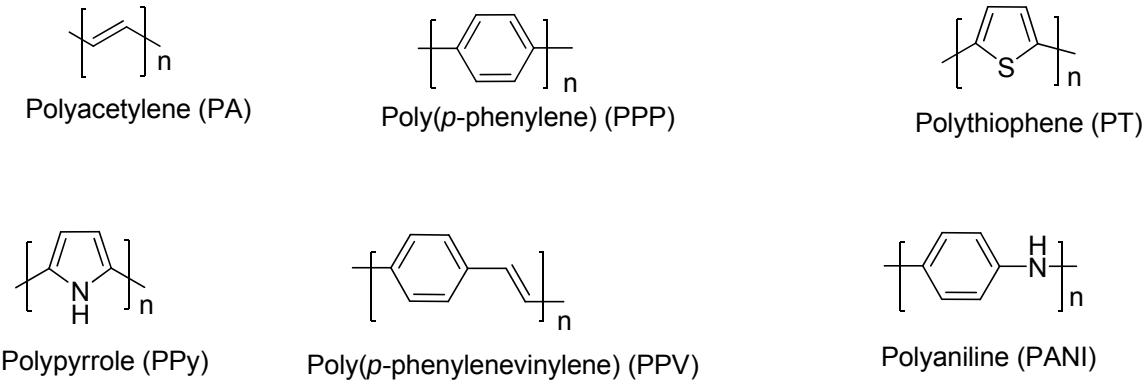


Fig 1: Structures of some conjugated polymers.

Among the great variety of applications developed during the last two decades, organic polymers (PPV, PPE and PPP) have been employed in the fabrication of electroluminescent devices[6] plastic lasers[7]and photovoltaic cells[8]. Furthermore, optical non-linearities of conjugated polymers offer potential applications in electrooptical and optical devices such as digital optical switch, light modulators and high density optical data storage devices[10-13]. New molecular architectures are continuously designed with the aim of improving the performance of electrical and electrooptical devices.

During the past years these conjugated polymers have given rise to an enormous amount of experimental and theoretical work devoted to (i) the analysis of their structure and properties using a whole arsenal of physical techniques, (ii) the development of synthesis methods allowing a better control of their structure and electronic properties, (iii) the synthesis of functional polymers in which the electronic properties are associated with specific properties afforded by covalently attached prosthetic groups[14,15] and (iv) the analysis of their multiple technological applications extending from bulk utilization such as antistatic coatings, energy storage to highly sophisticated electronic, photonic and bioelectronics devises[15,16] .

The world-wide demand for energy has grown dramatically over the last century with an increase in the industrialization of the world. The need for energy is likely to grow even more in the 21st century with the improvements in living standards across the planet. This high demand of energy brings into question the energy sources currently used and the depletion of natural resources[17]. Today, fossil fuels like coal, oil and natural gas are used for more than 60% of the world's electricity production. These fuels have a very negative impact on the environment and many researchers agree that the earth's climate is changing as a consequence of fossil fuel emissions. The earth's resources of oil, coal and natural gas usually referred to as non-renewable energy resources are limited

and will be depleted. Estimates suggest that within 20 years oil and natural gas production rates will start to decrease[17] with these prospects, new sources of energy must be implemented that do not rely on depleting resources. There are several examples of renewable and more environmentally friendly ways to produce electricity like bio fuels, hydroelectric power, wind power and solar energy[18].

Renewable energy, for instance the energy provided by the sun, can be used in solar collector system to heat water or by direct conversion into electric energy in photovoltaic devices. Current renewable energy systems cannot produce energy at the low cost that fossil fuel power plants can. For large scale implementation of renewable energy power plants, it is therefore necessary to develop systems that can compete on an economic level with fossil fuel.

1. LITERATURE REVIEW

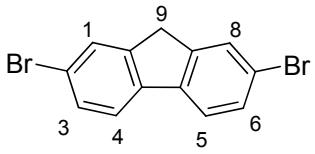
Recent application of alternating copolymers in light-emitting diodes (LEDs)[19], field-effect transistors (FETs)[20,21] and plastic solar cells[21] have attracted great attention. In polymer light-emitting diodes (PLEDs)[22], polyfluorenes are promising candidates as blue emitters due to their high photoluminescence quantum efficiencies (PLQEs) as a solid film[23], their excellent solubility, film forming ability, and the ease of controlling their properties through facile substitution in the 9,9-position of the fluorene unit[24]. For example the substituent at the 9,9-position decouple when they are placed at 90^0 angles to the π-conjugated system of the fluorene molecule this allows a fluorene compounds solubility and aggregation behavior to be improved without the influence of its electronic properties[25]. In addition, chemical modification on the main chain, side chain, and chain end of polyfluorenes allow elaborate tuning of emission color covering the whole visible range (blue, green, yellow, red and white)[26-28] and improvement of long-term operational stability[28,29] in organic electronic and photonics[20,21], exhibiting efficient polarized light emission[30], long lasting blue electroluminescence, impressive lasing gain[31], and promising performance in organic solar cells[31].

2.1. The fluorene monomer sub-unit

The ability to functionalize polyfluorene at the methylene bridge without distorting the conjugation between monomer units has been utilized as a method to improve the applications and properties of polyfluorenes. For example in unsubstituted fluorene, the protons at the sp^3 carbon in the methylene bridge (9-position) are susceptible towards oxidation reaction[32,33]. Such chemical reaction can be suppressed by double alkylation[33] or arylation[33] of fluorene, which has the additional advantage of enhancing the solubility in organic solvents[33].

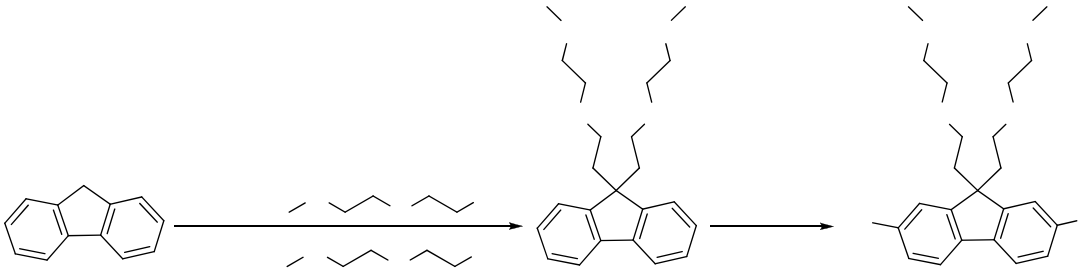
The 9,9-disubstituted fluorene monomer can be synthesized by using different types of reactions; the most commonly used reactions are nucleophilic

substitutions using an alkyllithium reagent (Scheme 1) and the phase transfer catalysis reaction (Scheme 2) [34].



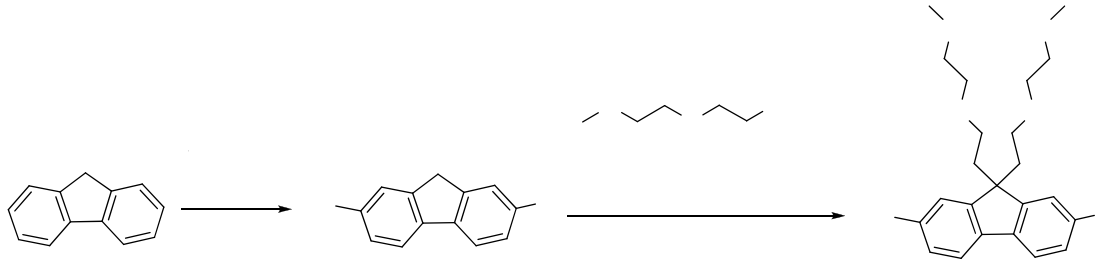
1

In nucleophilic substitution reaction using an alkyllithium reagent, 2,7-dibromofluorene cannot be used as a starting material, due to the relative competitive reaction of the halogens with the alkyllithium reagents than the proton on the benzylic carbon atom C9-H (Figure 1). Hence, this method can only use fluorene moiety as starting material and requires consequent bromination of the 9,9-disubstituted fluorene for the subsequent reactions.



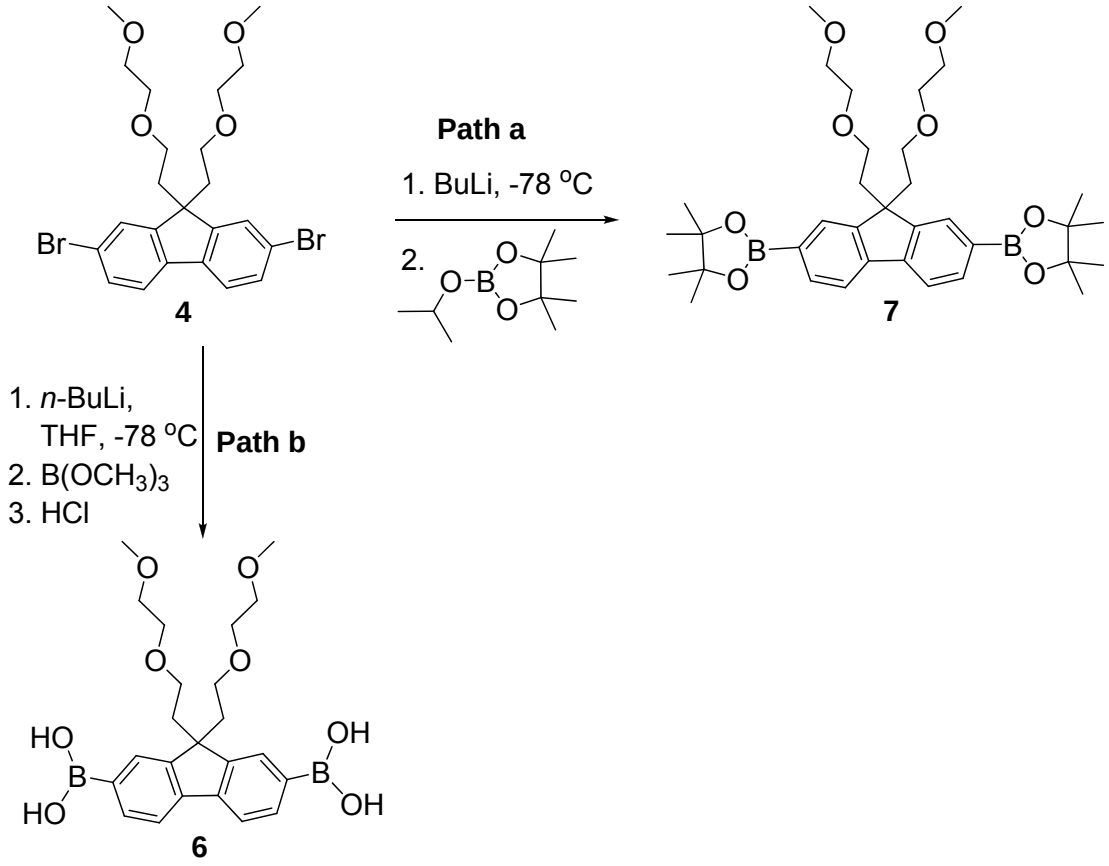
Scheme 1: Synthesis of 9,9-disubstituted fluorene monomer via nucleophilic substitution reaction.

An alternating pathway that has been used for the synthesis of 9,9-disustituted fluorenes is the phase transfer catalysis reaction . This reaction involves the use of two phase system composed of equal volumes of toluene and 50% (w/w) aqueous NaOH, and tetrabutylammonium bromide as a phase transfer catalyst (Scheme 2). The advantage of this reaction is that it can be implemented on 2,7-dihalogenated fluorene, and eliminates the risk of halogenating functional groups on the side chain[35].



Scheme 2: Synthesis of 9,9-disubstituted fluorene monomers using phase transfer catalysis.

The subsequent step, after the synthesis of 2,7-dibromo-9,9-dialkylfluorene, is preparation of the respective 2,7-diboronic acid and boronate ester for a consecutive Suzuki type copolymerization[36]. 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 gives the fluorene-2,7-diboronic acid (**6**) after an acid work up whereas treatment with pinacolborane gives compound **7**[21] as depicted in Scheme 3.



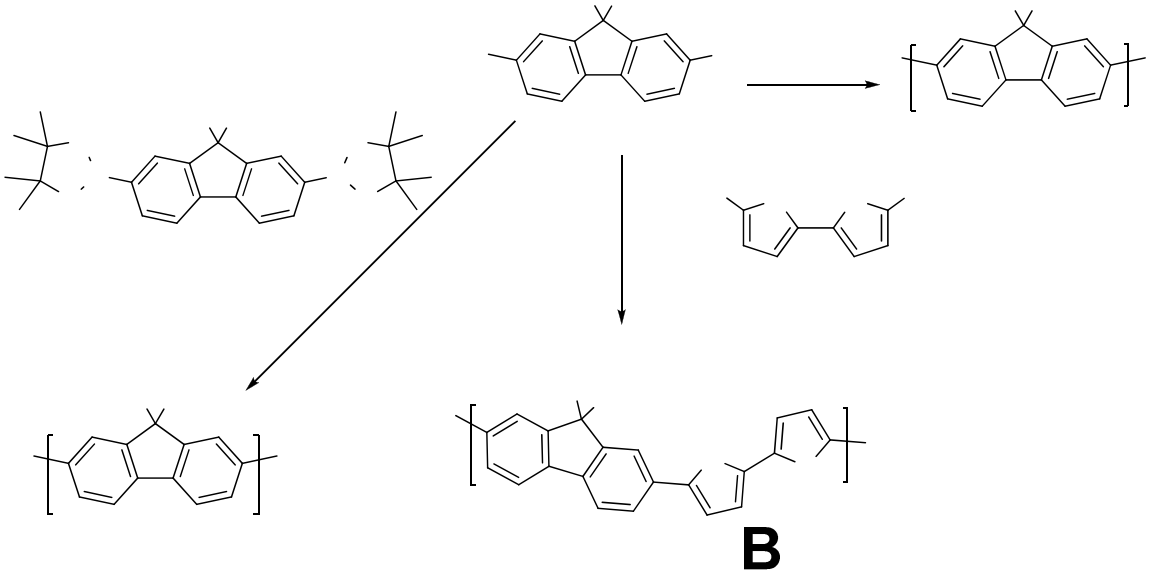
Scheme 3: Synthesis of boronate ester (path a) and boronic acid (path b) for Suzuki coupling reaction.

2.2. Synthesis of fluorene-based polymers

Through molecular design, fluorene-based conjugated oligomers can be tailored from crystalline to morphologically-stable amorphous materials. Oligofluorenes are quite attractive for the fabrication of blue-emitting devices because of their high photoluminescence quantum yields of up to 90% in the solid state. They also bring a number of unique strengths in the organic optoelectronics devices.

Fukuda and coworkers were the first to report fluorene-based polymers via oxidative polymerization of 9-alkyl and 9,9-dialkylfluorenes in the presence of ferric chloride[37]. A wide diversity of polyfluorenes is readily accessible with

versatile synthetic strategies supported by various cross-coupling reactions. The most prominent types of reactions used to prepare PFs are the Ni(0)-mediated Yamamoto and the Pd-catalyzed Suzuki condensations[32]. (Scheme 4)



Scheme 4: Synthesis of fluorene-based polymers using (A) Yamamoto, (B) Suzuki, and (C) Stille coupling reactions.

2.3. Optical and electronic properties of polyfluorenes.

Polyfluorenes absorb UV light (□-□* transition at about 380 nm) and emit blue light, with two photoluminescence maxima around 420-425 and 445 nm[32]. To improve 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[32]. Recently donor-acceptor conjugated copolymers based on fluorene with various acceptors were reported in the literature, including benzothiadiazole[38] and quinoxaline[39].

Due to the fact that the 9-position is not conjugated to the fluorene π-system and far away from the aryl coupled 2- and 7-positions, the influence of the alkyl side

chain architecture on the optical properties of polyfluorenes is negligible under dilute conditions. Strong influences have, however, been found on the aggregation behavior and in the solid state, which are reflected in distinct differences in the optical properties[32].

2.4. Applications of polyfluorenes.

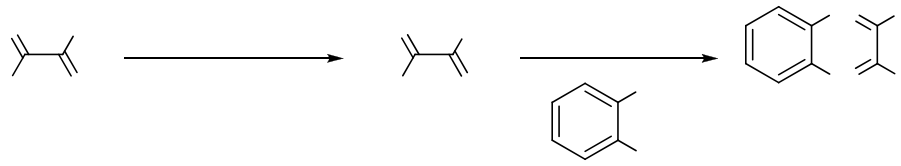
Fluorene-based conjugated polymers have received a lot of attention that can be attributed to the possibility that they could be used to develop all-plastic, full-color, light emitting diodes. An important driving force for this is the desire of building ultra thin films and flexible screens for electronic devices ranging from cell phones to computers and televisions. Except their manifold use in organic and polymer electronic, fluorene-based π-conjugated materials have recently found widespread applications as sensors, for instance as sensors for biologically interesting analytes[32].

2.5. The quinoxaline monomer sub-unit.

Quinoxaline derivatives are very important nitrogen-containing heterocyclic compounds. They have found applications in efficient electroluminescence materials[40] and in organic semiconductors[41]. The most common method of preparing quinoxaline-containing monomers involves the condensation of an aryl 1,2-diamine unit with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid[42].

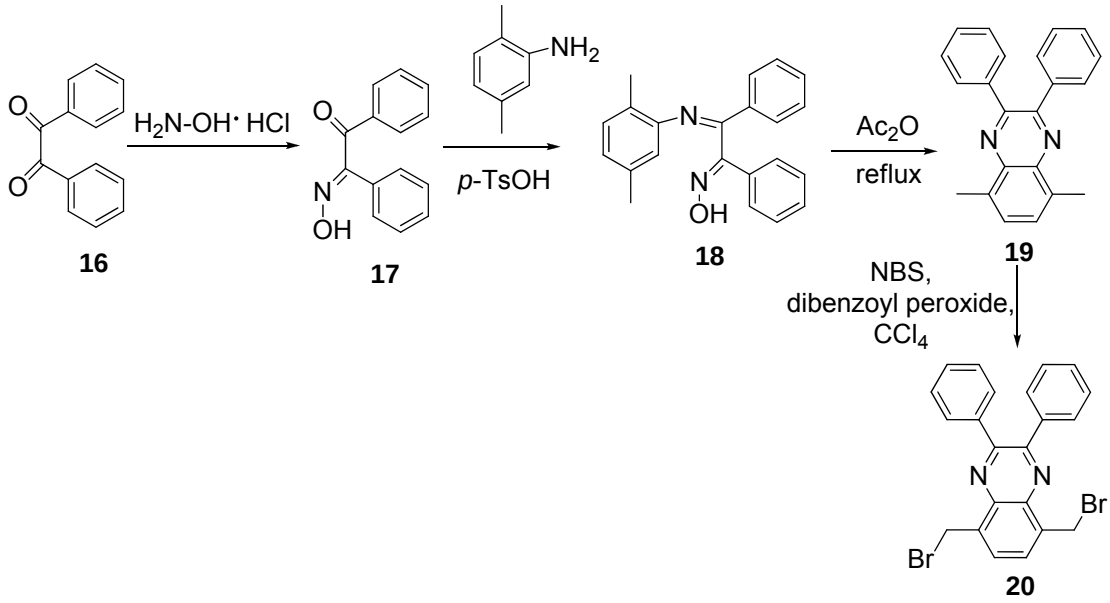
An interesting entry from oxalyl chloride to quinoxalines was made by Ji and Lee[43] (Scheme 5). They demonstrated the synthesis of quinoxaline by the condensation between 1,2-phenylenediamines and 1,2-diketo compounds, which

are available by the reactions of oxalyl chloride with mixed copper-magnesium reagents[43].



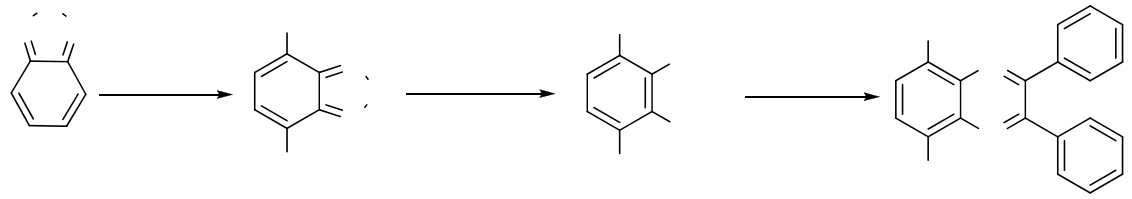
Scheme 5: Synthesis of quinoxaline derivative **15**.

There were reports on the synthesis of quinoxaline-based monomers via the iminooxime cyclization route and the benzothiadiazole route. The former route involves the oxidative cyclization of 2-(hydroxyimino)-1,2-diarylethanones to diarylquinoxalines. Scheme 6 depicts an application of this strategy towards the synthesis of **20**. Unfortunately, this method has problems of product purification and low yield[44,45]



Scheme 6: Synthesis of quinoxaline-based monomer **20** by the iminooxime cyclization route.

The benzothiazole route, on the other hand, is easier to carry out and gives higher yields of quinoxaline-based monomers. Scheme 7 depicts the synthesis of **24** starting from benzothiadiazole (**21**)[46].



Scheme 7: Synthesis of quinoxaline-based monomer **24** by the benzothiadiazole route.

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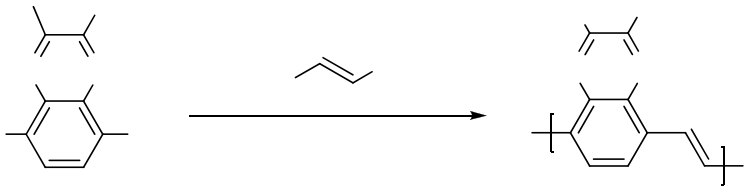
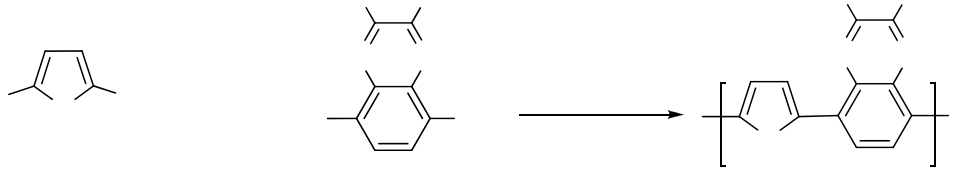
2.6. Synthesis of quinoxaline polymers.

In the last few years, there were reports on the synthesis of polymers having a quinoxaline unit. According to Takashi Fukuda and co-workers, poly-quinoxaline derivatives can be excellent electron ejecting materials (n-type) for photovoltaic devices because they have advantageous properties such as high electron affinity, good thermal stability and good processability[47,48] There are various methods such as the Stille[49] (Scheme 8) Sonogashira, Suzuki[41] and Heck cross coupling reactions[50] leading to the preparation of copolymers based on quinoxaline derivatives.



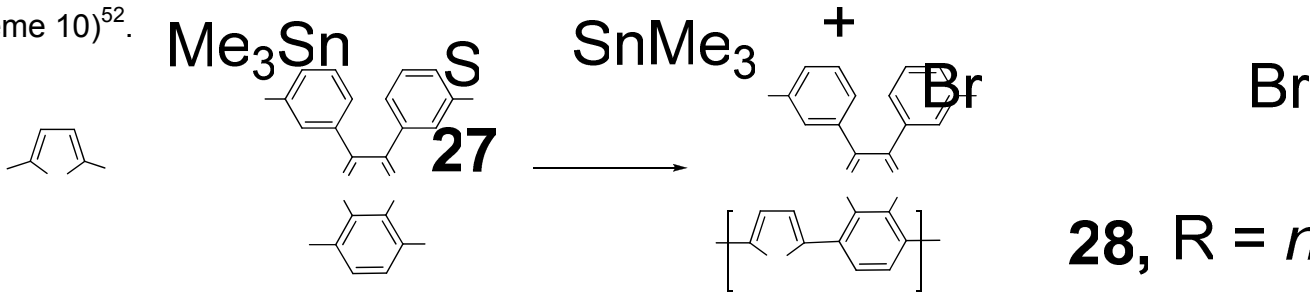
Scheme 8: Synthesis of poly[quinoxalinevinylene) **26** via Stille cross-coupling.

Lee and coworkers[51] prepared π-conjugated copolymers in high yield with thiophene as electron donating material and diheptylquinoxaline as strong electron withdrawing material via the Stille cross coupling reaction methodology (Scheme 9).



Scheme 9: Synthesis of quinoxaline-based copolymer using Stille cross-coupling reaction.

By changing the substituents on the quinoxaline unit, one can improve or manage the properties of the copolymers. The *n*-hexylquinoxaline copolymer **31** was obtained by organometallic polycondensation and the resulting copolymer had good solubility in common organic solvents such as $CHCl_3$, THF, and toluene (Scheme 10)[52].



Scheme 10: Synthesis of quinoxaline based copolymer **31**.

Quinoxaline acceptor units emerge especially suitable to alter the band-gap of polyfluorene copolymers allowing light emission from blue to yellow–orange[50,52]. In recent studies with a focus on stable blue light emission, random polyfluorene copolymers with quinoxaline units appeared to result in higher efficiencies than those comprised of alternating copolymers[53,54] This concept allows altering the

blue emission of pure polyfluorene to longer wavelengths and the copolymers reveal amorphous behavior and high thermal stabilities up to 430 ^{o}C[53,54]

3. OBJECTIVES OF THE WORK

The aim of this project work is to synthesize some conjugated, low bandgap, alternating quinoxaline and benzothiadiazole-based copolymers with 9,9-bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene sub-unit.

Co-polymerization will be achieved using palladium-catalyzed Suzuki-cross-coupling reaction. The intermediate compounds and the polymers will be characterized by spectroscopic techniques, including NMR, UV-Vis and CV.

4. RESULTS AND DISSCUSSION.

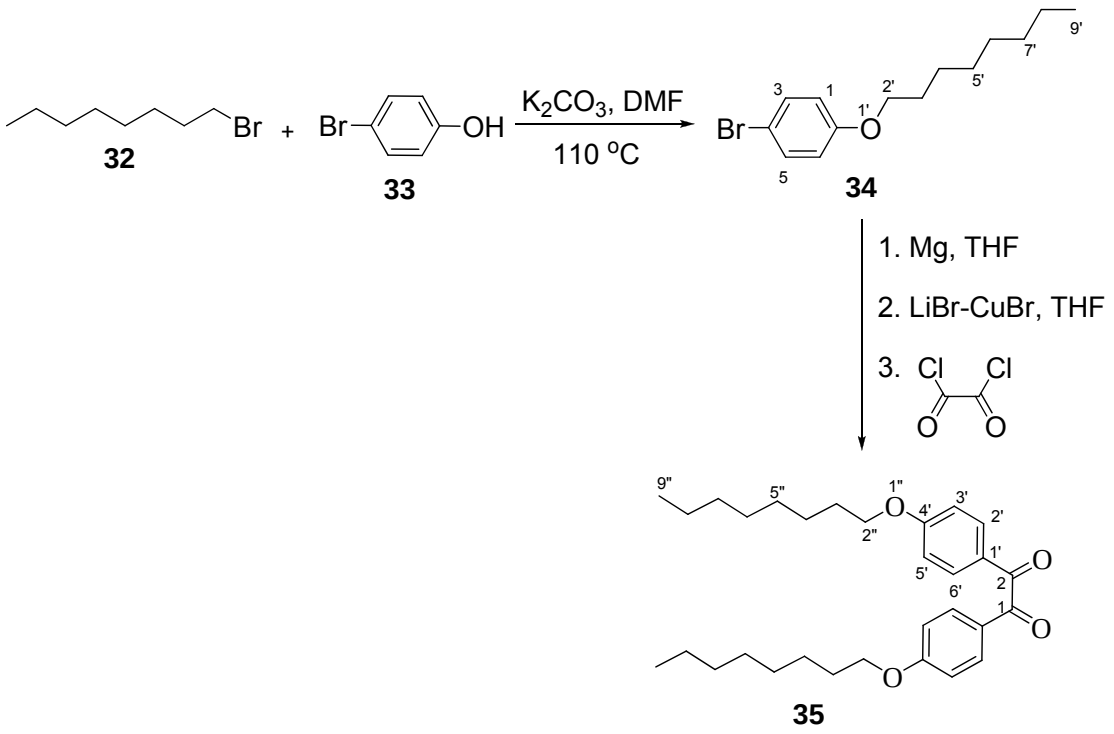
In the course of this project work, two copolymers based-on 9,9-bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene, quinoxaline and benzothiadiazole units were synthesized using the Suzuki coupling polymerization reaction. These were, poly[5-(5-(9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)thiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)-8-(thiophen-2-yl)quinoxaline] (**44**) and poly[5-(5-(7-(7-(9,9-bis[2-(2-methoxyethoxy)ethyl]-9*H*-fluoren-2-yl)-benzo[1,2,5]thiadiazol-4-yl)-9,9-bis-[2-(2-methoxyethoxy)ethyl]-9*H*-fluoren-2-yl)thiophen-2-yl)-2,3-bis(4-octyloxyphenyl)-8-thiophen-2-yl-quinoxaline] (**45**).

Attempted synthesis of a pyrazino[2,3-*g*]quinoxaline and a benzothiadiazole[3,4-g]quinoxaline were also made. The syntheses started by the preparation of the required monomers for the copolymerization reaction as discussed below.

4.1. Synthesis of quinoxaline-based monomers.

The synthetic route that led to the quinoxaline-based monomer **38** is shown in Scheme 12.

The synthesis of **38** commenced by the preparation of 1,2-dione **35** as depicted in Scheme 11. Thus, 4-bromophenol (**33**) was treated with 1-bromooctane in the presence of anhydrous potassium carbonate in DMF to give 1-bromo-4-octyloxybenzene (**34**). Compound **34** was converted to the corresponding Grignard reagent by treatment with Mg in THF and the Grignard reagent was added to a mixture of LiBr and CuBr. Oxalyl chloride was then added to this mixture to afford 1,2-bis-(4-octyloxyphenyl)ethane-1,2-dione (**35**). Compounds **34** and **35** were characterized based on their NMR spectra as described below.



Scheme 11: Synthesis of 1,2-bis-(4-octyloxy)phenyl)ethane-1,2-dione (**35**).

The ^{1}H-NMR spectrum of compound **34** (Table 1) showed two signals in the aromatic and four signals in the aliphatic region. The doublet peaks at δ 6.79 (J = 8.0 Hz) and δ 7.38 (J = 8.0 Hz) are attributed to the identical protons H-3 and H-5 and H-2 and H-6, respectively. The triplet at δ 3.93 is assigned to the H-2' which is on the carbon atom attached to the oxygen and the quintet at δ 1.79 is due to the methylene at C-3'. The multiplet between δ 1.50 – 1.30 is attributed to five methylene groups and the triplet at δ 0.92 is assigned to the terminal methyl group H-9' (Appendix 1).

The ^{13}C-NMR spectrum of compound **34** (Table 2) showed four resonances in the aromatic region and eight resonances in the aliphatic region. The quaternary carbon signals at δ 112.5 and 158.3 are assignable to C-1 and C-4, respectively. The carbon resonance at δ 132.2 is attributed to C-2 and C-6 and the signal at δ

116.3 is assigned to C-3 and C-5. The aliphatic carbon signals at δ 68.3, 31.8, 25.7, 31.8, 26.0, 31.9, 22.6 and 14.1, are due to C-2', C-3', C-4', C-5', C-6', C-7' C-8' and C-9', respectively. Thus, the data obtained from ^{1}H-NMR, ^{13}C-NMR and DEPT-135 agrees with the structure of compound **34**.

Table 1: ^{1}H-NMR (400.13, $CDCl_3$) data (δ_{ppm}) of compounds **34** and **35**.

34	**35**
7.38	7.94
(*d*, *J* = 8.0 Hz, 2H, H-2 and H-6)	(*d*, *J* = 8.0 Hz, 4H, H-2', H-6')
6.79	6.96
(*d*, *J* = 8.0 Hz, 2H, H-3 and H-5)	(*d*, *J* = 8.0 Hz, 4H, H-3', H-5')
3.93	4.04
(*t*, *J* = 6.8 Hz, 2H, H-2')	(*t*, 4H, H-2'')
1.79	1.82
(*q*, 2H, H-3')	(*q*, 4H, H-3'')
1.50-1.30	1.47-1.27
(*m*, 10H, H-4' to H-8')	(*m*, 20H, H-4"-H-8'')
0.92	0.95
(*t*, 3H, H-9')	(*t*, 6H, H-9'')

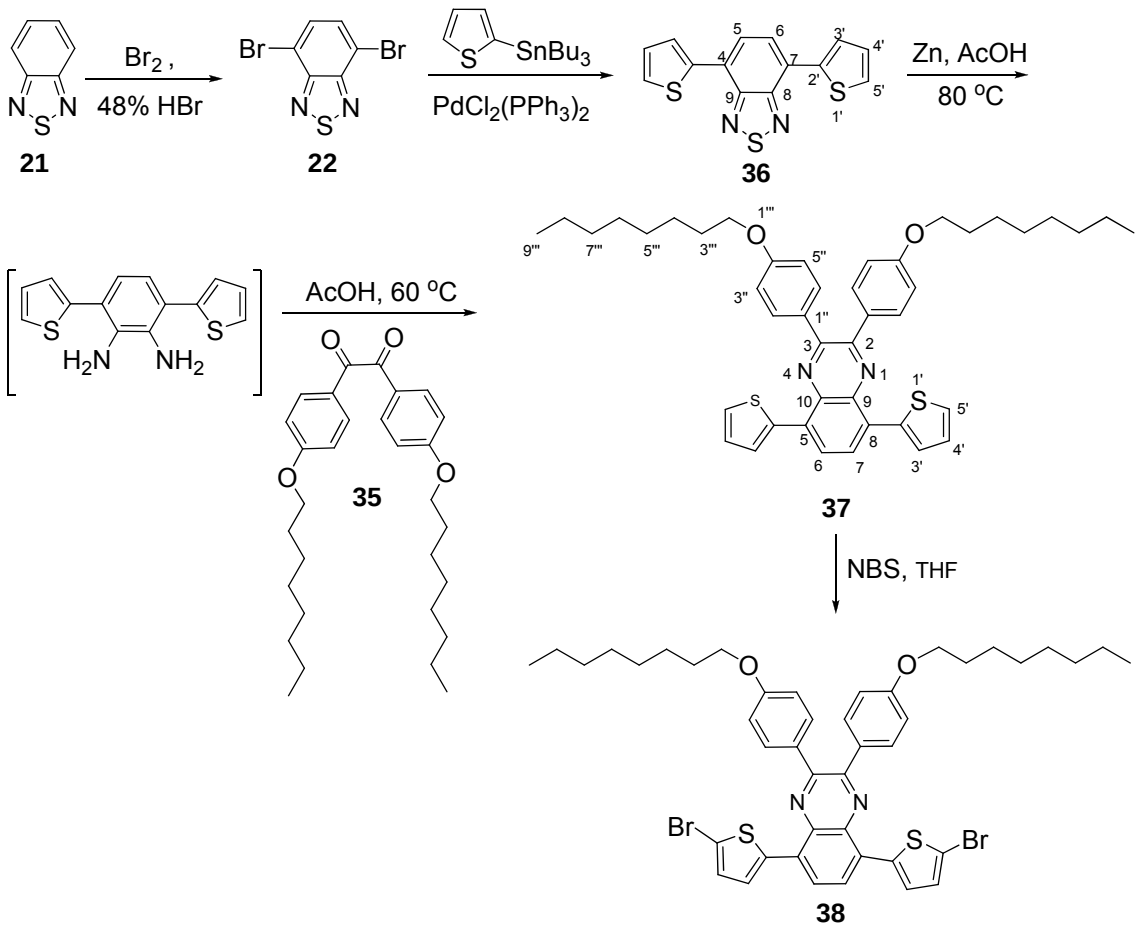
Likewise, the ^{1}H-NMR spectrum of compound **35** (Table 1) showed doublets at δ 6.96 (*J* = 8.0 Hz) and 7.94 (*J* = 8.0 Hz), which integrated for four protons each, due to H-3 and H-5 and H-2 and H-6, respectively, on both aromatic rings The triplet at δ 4.04, which integrates for four protons, is due to the methylene protons on the carbon atoms attached to the oxygen. The quintet at δ 1.82, which integrates for four protons, is assigned to CH_2 groups at C-3''. The unresolved multiplet between δ 1.27 - 1.47 is attributed to the remaining CH_2 groups on the side chains. Finally, triplet at δ 0.91 is due to H-9'' (Appendix 4).

Table 2: ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δ_{ppm}) of compound **34** and **35**.

34	**35**
158.3 (C-4)	193.6 (C-1, C-2)
132.2 (C-2,C-6)	164.5 (C-4')
116.3 (C-3,C-5)	132.4 (C-2', C-6')
112.5 (C-1)	126.1 (C-1')
68.3 (C-3',C-2')	114.7 (C-3', C-5')
31.9 (C-4')	68.5 (C-2'')
31.8 (C-5')	31.8 (C-7'')
26.0 (C-6')	29.0 (C-3'',C-6'', C-5'')
25.7 (C-7')	25.9 (C-6'')
22.6 (C-8')	22.6 (C-8'')
14.1 (C-9')	14.1 (C-9'')

The ^{13}C-NMR (Table 2) and DEPT-135 spectra of compound **35** confirmed the presence of three quaternary carbons, two methine, seven methylene and one methyl groups. The presence of two equivalent carbonyl groups was confirmed by the appearance of a signal at δ 193.6. The peak at δ 68.4 is due to the oxygenated methylene groups and the peak at δ 14.1 is due to the terminal methyl groups. The remaining signals at δ 31.8, 29.0, 25.9 and 22.6 are attributed to C-7'', C-3''- C-5'', C-6''and C-8'', respectively.

The synthetic route towards the quinoxaline segment **36** and the total synthesis of monomer **38** is depicted in Scheme 12. Thus, bromination of commercially available 2,1,3-benzothiadiazole (**21**) using Br_2 and 48% HBr gave 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**22**) in 81% yield as a greenish crystalline solid. Compound **22** was subjected to Stille coupling reaction with tributyl(thiophene-2-yl)stannane in the presence of bis-(triphenylphosphine)palladium(II) chloride as a catalyst to give compound **36**.



Scheme 12**:** Synthesis of quinoxaline-based monomer **38**.

The ^{1}H-NMR spectrum compound **22** showed only a singlet at δ 7.64 in agreement with the two chemically equivalent protons H-5 and H-6 in the molecule. The ^{13}C-NMR spectrum of compound **22** displayed only three carbon resonances among which two are due to quaternary carbon atoms. The quaternary carbon resonance at δ 114.5 is attributable to C-4 to which the bromine is attached. The carbon signal at 153.4 is due to the other quaternary 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.

Compound **36** was also characterized based on its NMR spectra prior to converting it to compound **38**. Thus, the ^{1}H-NMR spectrum (Table 3) of **36** showed four signals in the aromatic region. The singlet at δ 7.91 is due to the two

equivalent methine protons (H-5 and H-6) in the central aromatic ring. The thiophene ring protons appeared at δ 8.14 (*dd, J* = 1.2, 3.6 Hz, H-5'), 7.49 (*dd, J* = 1.2, 5.2 Hz) and 7.24 (*dd, J* = 3.6, 5.2 Hz, 2H H-4') (Appendix 7).

The ^{13}C-NMR spectrum (Table 4) of compound **36** displayed seven carbon resonances. Of these, three are quaternary carbon atoms and the remaining four are methine carbons. The quaternary carbon resonance at δ 152.7 is attributed to C-8 and C-9 to which the heteroatom nitrogen atoms are attached. The other quaternary carbon resonance at δ 128.1 is due to the two carbon atoms at C-4 and C-7 and the third quaternary carbon signal at δ 139.4 is due to C-2' on the thiophene rings. The methine carbon signal at δ 127.5 is due to C-5 and C-6 and the signals at δ 125.8, 126.7 and 126.0 are due to C-3', C-4', C-5, respectively.

Reduction of compound **36** by the action of zinc powder in acetic acid at 80 ^{o}C and subsequent condensation of the resulting diamine with 1,2-dione **35** gave compound **37** in 71.7% yield (Scheme 12). Compound **37** was brominated using *N*-bromosuccinimide under nitrogen atmosphere for 24 h to give a mixture of products which was further purified by silica gel column chromatography (toluene:hexane (1.5:3.5) solvent system) and pure quinoxaline monomer **38** was obtained in 78.95% yield. Compounds **37** and **38** were characterized based on their NMR data as described below.

The ^{1}H-NMR spectrum (Table 3) of compound **37** showed six signals in the aromatic region and five signals in the aliphatic region. The spectrum suggested that **37** is a symmetrical molecule. The triplet at δ 4.02 is due to the methylene protons (H-2''') on the carbon atoms attached to the oxygens. The unresolved multiplet at δ 1.34-1.49 is due to H-8''', H-7''', H-6''', H-5''', H-4''' and the triplet at δ 0.93 is due to the terminal methyl protons. The aromatic proton resonances appeared in the region between δ 6.9 and 8.12. The singlet at δ 8.12 is due to H-6 and H-7. The ABC pattern at δ 7.20 (*dd*), 7.53 (*dd*) and 7.87 (*dd*) is due to the thiophene ring protons H-4', H-5' and H-3', respectively. The remaining doublets

at δ 7.74 and 6.92 are due to due to H-2'', and H-3'', respectively, on the octyloxy-substituted aromatic rings (Appendix 9).

Table 3: ^{1}H -NMR (400.13, $CDCl_3$) data (δ_{ppm}) of compound **36**, **37** and **38**.

36	**37**	**38**
8.14	8.12	7.93
(*dd, J* = 1.2, 3.6 Hz, 2H, H-5')	(*s*, 2H, H-6, H-7)	(*s*, 2H, H-6, H-7)
7.91	7.87	7.66
(*s*, 2H, H-5, H-6)	(*d*, *J* = 4 Hz, 2H, H-5')	(*d*, *J* = 8 Hz, 4H, H-2'')
7.49	7.74	7.50
(*dd*, *J* = 1.2, 5.2 Hz, 2H, H-3')	(*d*, *J* = 8.4 Hz, 4H, H-2'')	(*d*, *J* = 4Hz, 2H, H-4')
7.24	7.53	7.10
(*dd, J* = 3.6, 5.2 Hz, 2H, H-4')	(*d*, *J* = 5.2 Hz, 2H, H-3')	(*d*, *J* = 4 Hz , 2H, H-3')
	7.20	6.93
	(*t*, *J* = 3.6, 4.4 Hz, 2H, H-4')	(*d*, *J* = 8 Hz, 4H, H-3'')
	6.92	4.04
	(*d*, *J* = 8.4 Hz, 4H, H-3'')	(*t*, 4H, H-2''')
	4.02	1.85
	(*t*, 4H, H-2''')	(*q*, 4H, H-3''')
	1.83	1.28-1.51
	(*q*, 4H, H-3''')	(*m*,20H, H-4'''-H-8''')
	1.34 – 1.49	0.94
	(*m*, H-7''', H-6''', H-5''', H-4''')	(*t*, 6H, H-9''')
	0.93	
	(*t*, 6H, H-9''')	

The ^{13}C-NMR spectrum (Table 4) of compound **37** displayed a total of twenty signals of which twelve appeared in the aromatic region and eight in the aliphatic region. The DEPT-135 spectrum revealed that there are one methyl, seven methylene, and six methine carbons. Thus, six of the twenty carbon atoms are

quaternary carbon atoms. The six quaternary carbon signals at δ 159.9, 131.0, 151.1, 136.8, 131.1, and 138.8 are attributable to C-4'', C-1'', C-2 and C-3, C-9 and C-10, C-5 and C-8, C-2', respectively. The six methine carbons signals at δ 114.2, 131.9, 128.7, 126.2, 128.6 and 126.5 are attributable to C-3'' and C-5", C-2'' and C-6", C-6 and C-7, C-3', C-4', and C-5', respectively. The aliphatic region carbon signals at δ 14.1, 22.6, 26.1, 29.1, 29.3, 31.0, 31.8, 68.1 are due to C-9''', C-8''', C-7''', C-6''', C-5''', C-4''', C-3''', C-2''', respectively.

The ^{1}H-NMR spectrum (Table 3) of compound **38** is in a good agreement with the incorporation of bromine atoms at position 5' of the thiophene moieties of compound **37**. Thus, the singlet peak at δ 7.93 attributed to H-6 and H-7, the four doublet signals at δ 7.66, 7.50, 7.10, and 6.93 is due to H-2'', H-4', H-3' and H-3'', respectively. The triplet at δ 4.04 is due to H-2''', quintet at δ 1.85 is due to C-3''', multiplet at δ 1.28-1.55 are due to H-8''' – H-4''' and triplet at δ 0.94 is due to H-9''' (Appendix 12).

The ^{13}C-NMR spectrum (Table 4) of **38** displayed twelve aromatic and eight aliphatic carbon resonances. Of the twelve aromatic carbons, seven are quaternary carbons whose resonances appeared at δ 160.0, 151.1, 138.8, 136.8, 131.1, 131.0, 126.2 and are attributed to C-4'', C-2', C-2 and C-3, C-9 and C-10, C-5 and C-8, C-1'', C-5', respectively. The peak at δ 128.7 is due to methine carbons C-6 and C-7 on the benzene ring of the quinoxaline core unit. The two methine carbon peaks at δ 114.2 and 131.9 are due to the equivalent C-3'' and C-5" and C-2''and C-6" on the benzene rings. The remaining methine peaks at δ 126.2 and 128.6 are assignable to C-3' and C-4' on the thiophene rings. The aliphatic carbon signal at δ 68.1 is due to C-2''' and the carbon peaks at δ 31.8, 29.3, 29.2, 29.1, 26.1, 22.7, 14.2 are attributable to C-3''', C-4''', C-5''', C-6''', C-7''', C-8''', C-9''', respectively.

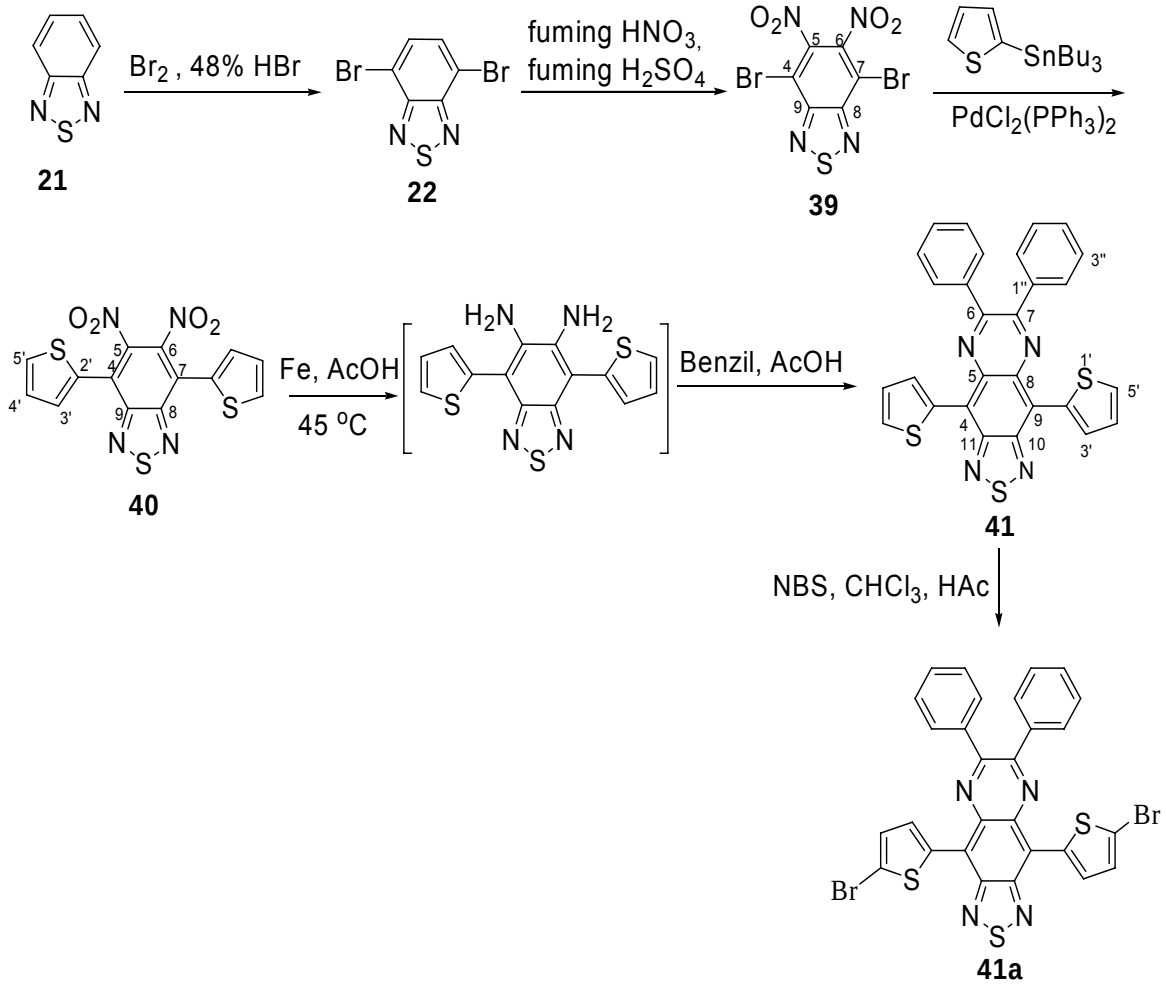
Table 4: ^{13}C-NMR (100.6, $CDCl_3$) data (δ_{ppm}) of compound **22**, **36**, **37** and **38**.

22	**36**	**37**	**38**
			[5]
114.3 (C-5, C-6)	152.7 (C-8, C-9)	159.9 (C-4'')	160.0 (C-4'')
153.4 (C-8, C-9)	128.1 (C-4, C-7)	151.1 (C-2, C-3)	151.1 (C-2')
132.7 (C-4, C-7)	127.5 (C-5, C-6)	138.8 (C-2')	138.8 (C-2, C-3)
	139.4 (C- 2')	136.8 (C-9, C-10)	136.8 (C-9, C-10)
	125.8 (C-3')	131.9 (C-2'')	131.9 (C-2'')
	126.7 (C-4')	131.1 (C-5, C-8)	131.1 (C-5, C-8)
	126.0 (C-5')	131.0(C-1'')	131.0 (C-1'')
		128.7 (C-6, C-7)	128.7 (C-4')
		128.6 (C-4')	128.6 (C-3')
		126.5 (C-5')	126.5 (C- 6, C-7)
		126.2 (C-3')	126.2 (C-5')
		114.2 (C-3'')	114.2 (C-3'')
		68.1 (C- 2''')	68.1 (C-2''')
		31.8 (C-3''')	31.8 (C-3''')
		31.0 (C-4''')	29.3 (C-4''')
		29.3 (C-5''')	29.2 (C-5''')
		29.1 (C- 6''')	29.1 (C-6''')
		26.1 (C-7''')	26.1 (C-7''')
		22.6 (C-8''')	22.7 (C- 8''')
		14.1 (C-9''')	14.2 (C-9''')

4.2 Synthesis of 6,7-diphenyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (41)

Scheme 13 shows the synthetic route towards compound **41**. Thus, compound **22** was prepared by bromination with bromine in 48% HBr. Treatment of **22** with a 1:1 (v/v) mixture of fuming nitric acid and fuming sulphuric acid afforded 4,7-

dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**39**) in 29% yield after recrystallization from ethanol and further purification by silica gel column chromatography (ethyl acetate:hexane (0.5:4.5) solvent system). The ^{1}H-NMR spectrum of **39** showed no proton signal. The ^{13}C-NMR (Table 6) together with the DEPT-135 spectrum proved that all carbon signals are due to quaternary carbon atoms. Thus, the peaks at δ 151.4, 144.7 and 110.3 are attributed to C-8 and C-9, C-5 and C-6, and C-4 and C-7, respectively.



Scheme 13: Synthesis of compound **41**.

Once pure compound **39** was obtained**,** it was subjected to Stille coupling reaction with tributyl(thiophene-2-yl)stannane in the presence bis-(triphenylphosphine)palladium(II) dichloride as a catalyst to give compound **40** in

72.7% yield. The ^{1}H-NMR spectrum of compound **40** was in good agreement with the incorporation of thiophene rings at the C-3 and C-6 of compound **39**. The doublet of doublets peaks at δ 7.77, 7.54 and 7.26 are attributed to H-5', H-3' and H-4', respectively.

Similairly, the ^{13}C-NMR spectrum of **40** (Table 6) was in good agreement with the assigned structure. The spectrum revealed a total of seven carbon signals of which four are due to quaternary carbons and the remaining three are due to methine carbons. The three methine carbon peaks at δ 131.5, 131.0, and 128.0 are assignable to the methine carbons C-4', C-5', C-3', respectively, of the thiophene rings. The four quaternary carbon peaks at δ 152.2, 129.6, 121.5, and 120.8 can be assigned to C-8 and C-9, C-5 and C-6, C-2', and C-4 and C-7, respectively.

Table 5: ^{1}H -NMR (400.13, $CDCl_3$) data (δ_{ppm}) of compound **40** and **41**.

40	**41**
7.77 (*dd*, *J* = 1.2, 5.2 Hz, 2H, H-5')	9.05 (*d*, *J* = 8.0 Hz, 2H, H-5')
7.54 (*dd*, *J* = 0.8, 3.6 Hz, 2H, H-3')	7.85 (*d*, *J* = 12.0 Hz, 4H, H-2'')
7.26 (*dd*, *J* = 3.6, 4.8 Hz, H-4')	7.72 (*d*, *J* = 8.0 Hz, 2H, H-3')
	7.45 (*m*, 6H, H-3'', H-4'')
	7.35 (*t*, *J* = 4 Hz, 2H, H-4')

Reduction of 5,6-dinitro-4,7-dithiophen-2-yl-benzo[*c*][1,2,5]thiadiazole (**40**) was effected using excess iron powder in acetic acid at 45 ^{o}C. The intermediate diamine was subsequently condensed with commercially available benzil to

afford compound **41**. The ^{1}H-NMR spectrum of compound **41** displayed five sets of signals in the aromatic region of which three are due to thiophene ring methine protons while the remaining signals are due to benzene ring methine protons. The doublets at δ 9.05 and 7.72 are attributed to H-3' and H-5', respectively The triplet at 7.35 is attributed to H-4', doublet at 7.85 is attributed to H-2'' and the multiplet at 7.45 is attributed to H-3'' and H-4''.

The ^{13}C-NMR spectrum of compound **41** has a total of twelve carbons signals, of these six quaternary carbons, six methine carbons. The quaternary carbon signals at 153.3, 130.6, 138.1, 151.9, 133.2, 135.9 is due to C-6, C-5, C-5, C-2', C-1'', C-4, respectively. The remaining methine carbons peak at δ 131.4, 128.3, 129.6, 129.3, 126.8, and 125.3 can be assigned to C-2'', C-3'', C-4'', C-3', C-5', and C-4'.

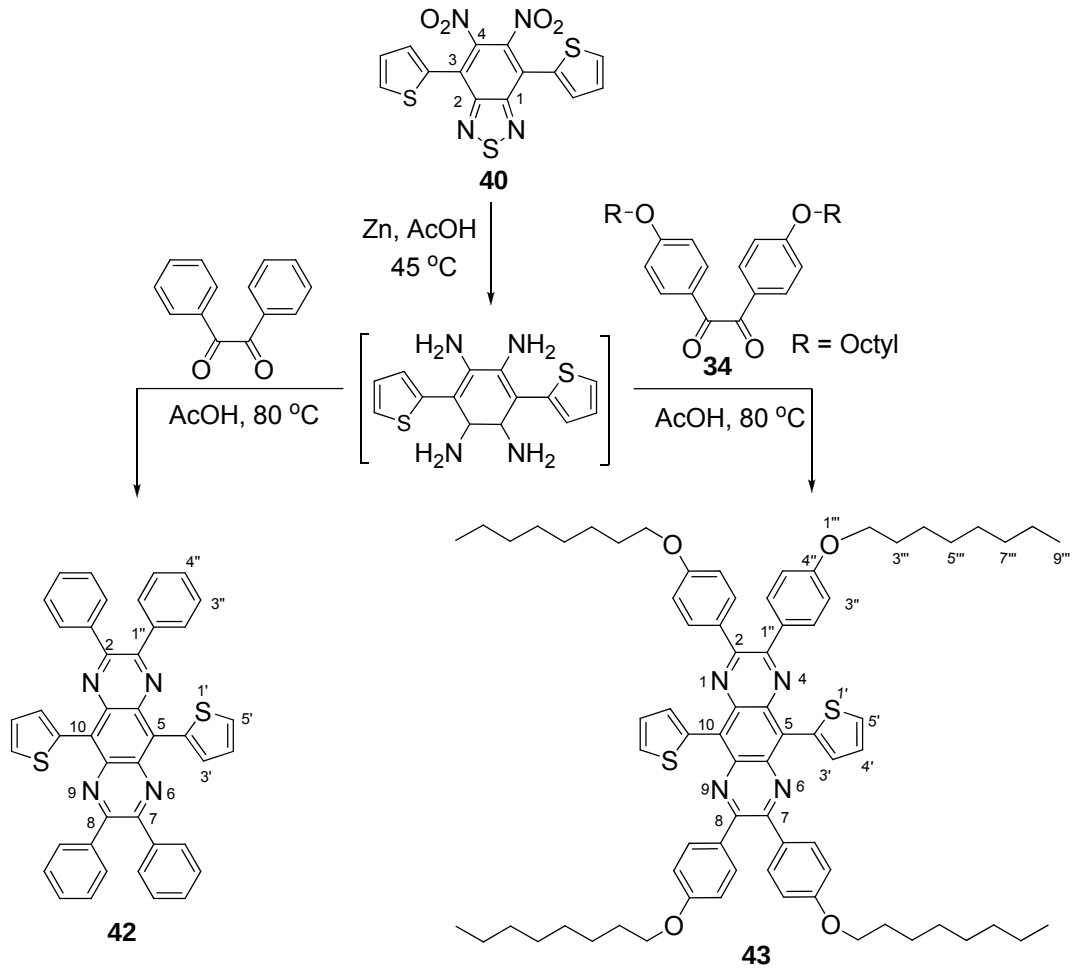
Table 6: ^{13}C-NMR (100.6, $CDCl_3$) data (δ_{ppm}) of compound **39, 40** and **41**.

39	**40**	**41**
151.4 (C-8, C-9)	152.2 (C-8, C-9)	153.3(C-10, C-11)
144.5 (C-4, C-7)	131.5 (C-4')	151.9(C-6, C-7)
110.3 (C-5, C-6)	131 (C-5')	138.1(C-5, C-8)
	129.6 (C-5, C-6)	135.9(C-2')
	128.0 (C-3')	133.2(C-1'')
	121.5 (C-2')	131.4(C-2'')
	120.8 (C-4, C-7)	130.6(C-4, C-9)
		129.6(C-4'')
		129.3(C-3')
		128.3(C-3'')
		126.8(C-5')
		125.3(C-4')

The bromination of compound **41** was attempted with *N*-bromosuccinimide in a 1:1 mixture of acetic acid and chloroform. The NMR spectral result showed a mixture of products. Attempt was made to separate the desired product using silica gel column chromatography. It was, however, not possible to separate the mixture.

4.3 Attempted synthesis of pyrazino[3,4-*g*]quinoxalines 42 and 43.

In the course of this project, attempt was made to synthesize pyrazino[3,4-g]quinoxalines **42** and **43**. Scheme 13 shows the general synthetic plan for the preparation of compounds **42** and **43**. Thus, compound **40** was reduced with zinc and acetic acid and the ensuing tetraamine was treated with the appropriate dicarbonyl compound as depicted in Scheme 14. In both cases, the yields of the products were very low and the products were not successfully separated. This is presumably because the formation of intermediate tetraamine was not either complete during the reduction or the tetraamine decomposed to a large extent after it was formed.

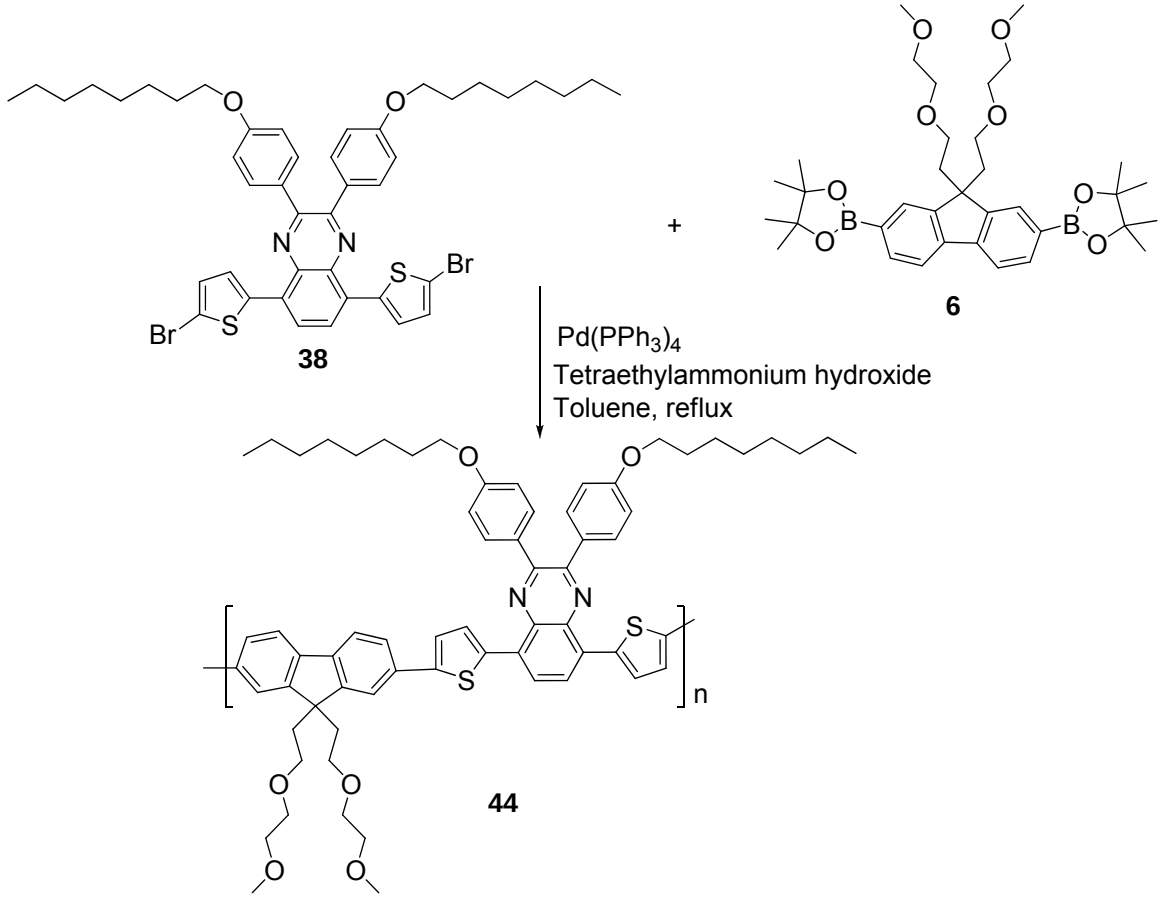


Scheme 14: Synthesis of pyrazino[2,3-*g*]quinoxalines **42** and **43**.

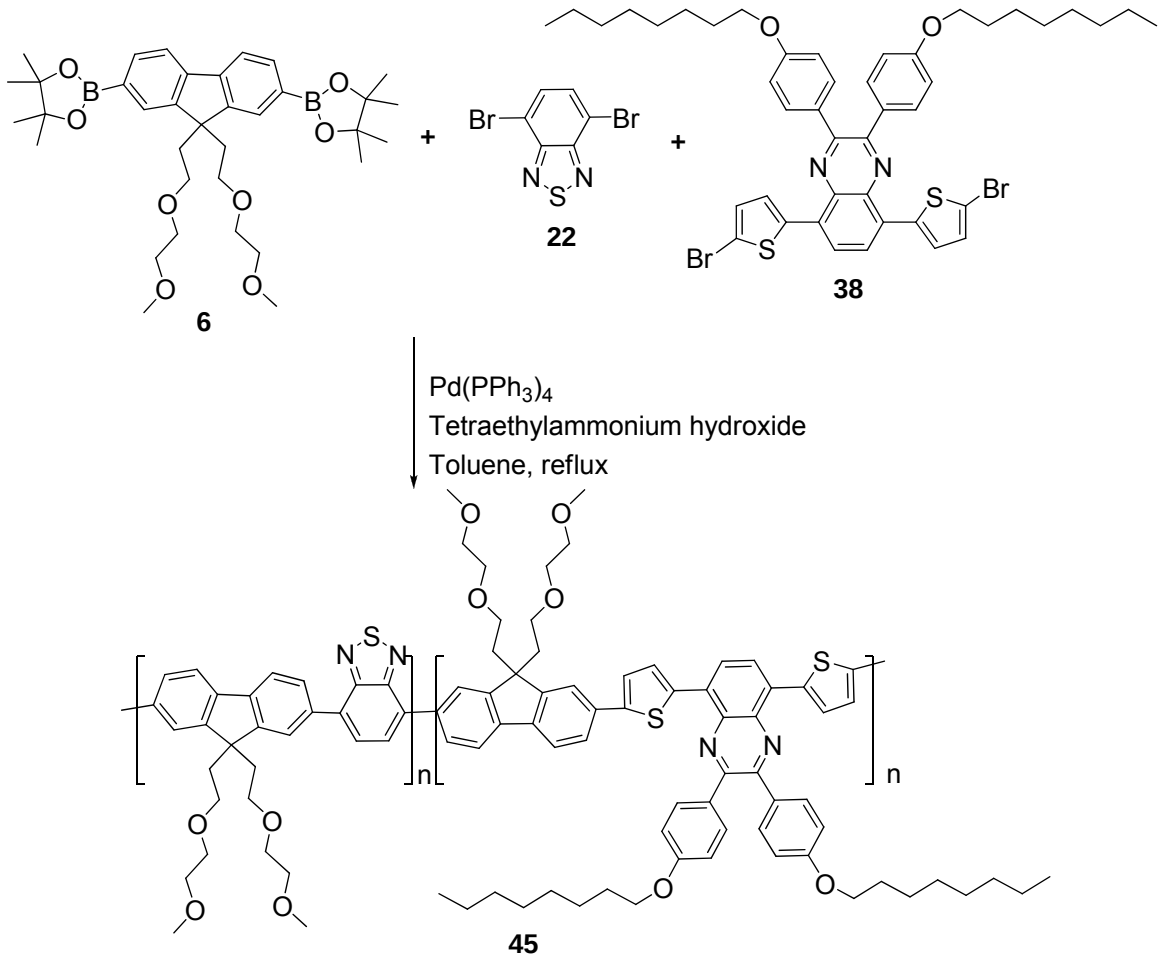
5. Synthesis of the copolymers.

The overall goal of the project work was to synthesize conjugated low bandgap alternating copolymers. Thus, monomer **39**, which was prepared according to the route described in Scheme 12, was subsequently subjected to two polymerization reactions as depicted in Schemes 15 and 16. The first polymerization reaction was performed with 9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**6**). The second polymerization reaction was done between **39** (25%), 9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**6**).(50%) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**22**) (25%). Both reactions were conducted

using a modified Suzuki coupling reaction with tetrakis(triphenylphosphine)palladium(0) as a catalyst and tetraethylammonium hydroxide as the base, instead of K_2CO_3 or $NaHCO_3$, which were used for the standard Suzuki polymerizations. The use of tetraethylammonium hydroxide is believed to reduce the reaction time to 2-4 hours compared to the 24 hours required for the standard Suzuki polymerization[55]. The low molecular weight oligomers and unreacted starting materials were separated by Soxhlet extraction with ether and the higher molecular weight materials were extracted with chloroform and precipitated from methanol as described in the Experimental section. Both **44** and **45** were obtained as red powders. The $CHCl_3$ solutions of both polymers had deep red colors.



Scheme 15: Synthesis of copolymer **44**.



Scheme 16: Synthesis of copolymer **45**.

5.1.Characterization of the polymers

In conjugated polymers, the bandgap determines which wavelength of light is absorbed and emitted by the material. Among the factors that influence the band-gap of a polymer are conjugation length, solid state ordering and the presence of electron withdrawing or donating moieties.

Optical properties

Figures 2 and 3 show the UV-Vis absorption spectra of polymers **44** and **45** measured in chloroform solutions and as thin films of the polymers on glass

plates, respectively. For polymer **44**, the absorption maxima (λ_{max}) were detected at 392 and 519 nm in solution and at 395 and 529 nm in thin film. In contrast, the absorption maxima appeared at 380 and 466 nm in solution and at 483 nm in film for polymer **45**.

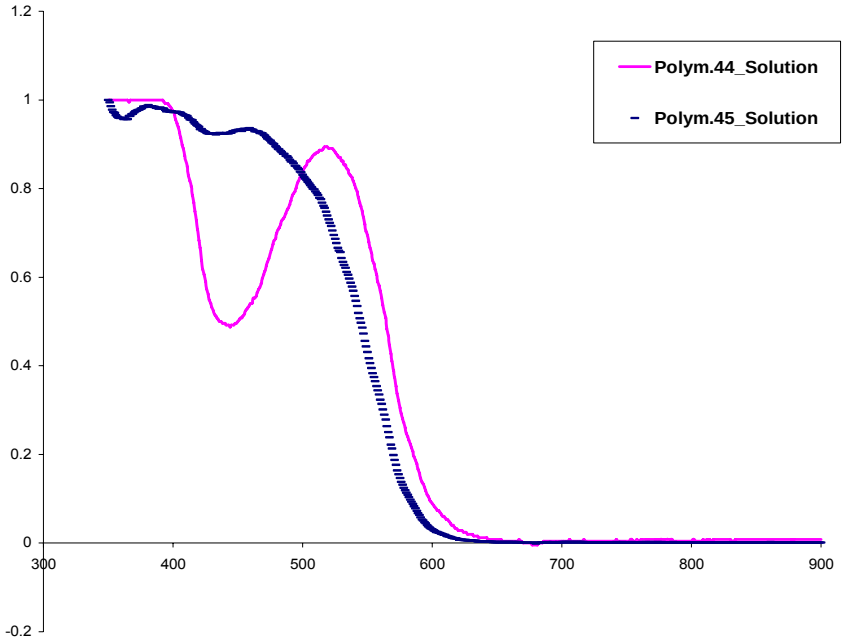


Figure 2: UV-Vis spectrum of polymer **44** and **45** in solution.

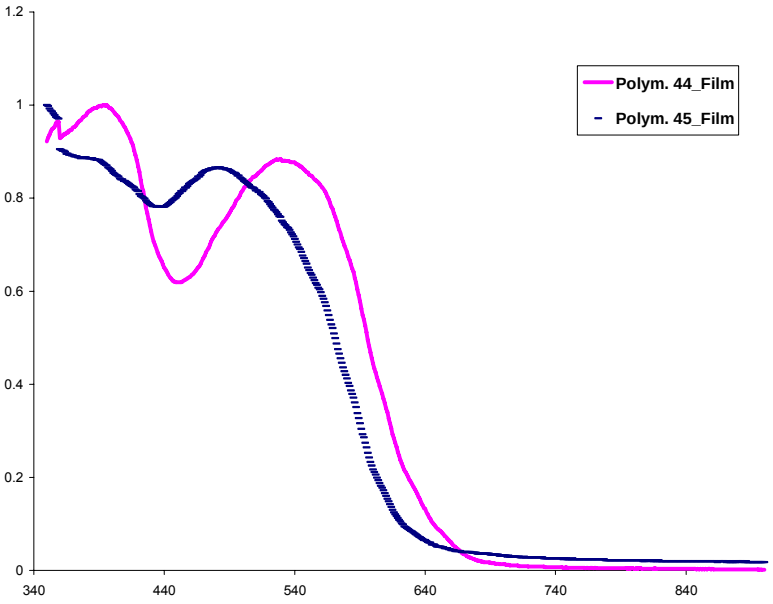


Figure 3: UV-Vis spectrum of polymer **44** and **45** in film.

Table 7: Optical data of the polymers in solution and in film.

	Solution			Film		
Polymer	$\lambda_{max(nm)}$	$\lambda_{onset(nm)}$	$E_{g\ (ev)}$	$\lambda_{max(nm)}$	λ_{onset}	$E_{g(ev)}$
44	392, 519	630	1.97	393, 529	679	1.83
45	380, 466	607	2.04	483	639	1.94

The λ_{max} at 466 nm in the UV-Vis spectrum of the $CHCl_3$ solution of polymer **45** was blue-shifted by 53 nm compared to that of polymer **44** (Table 7). This blue shift may be attributed to a less co-planar conformation and highly flexible chain of polymer **45**, which could have occurred by the inclusion of benzothiadiazole unit in the polymer chain. A blue-shift of 46 nm was observed between the long-wavelength absorption maxima of the thin films of the two polymers.

The absorption maxima of both polymers showed red-shifts in thin films, compared to the spectra recorded in $CHCl_3$ solutions. This is because of a higher concentration of interacting polymer chains - interchain interactions becomes dominating thereby enhancing the excited state energy transfer from fluorene units to respective acceptors. As a result an unstructured red-shifted emission appeared.[54]

The optical bandgaps (E_g) defined by the onset of the absorption spectra were determined for both polymers (Table 7). Thus, the onset of absorption was 630 nm for the absorption spectrum of **44** recorded in $CHCl_3$ solution and the calculated optical bandgap was 1.97 eV. A bandgap of 1.83 eV was calculated from the onset of the absorption spectrum of **44** recorded from thin film. The correspond+ding bandgap values for polymer **45** were 2.04 eV ($CHCl_3$ solution) and 1.94 eV (thin film). These findings demonstrated that the two polymers are rather low-bandgap polymers.

Electrochemical properties

Cyclic voltammetry is one of the most useful methods, which provides a great deal of useful information about the electrochemical behavior of conjugated polymers.

The electrochemical behaviors of polymers **44** and **45** were studied by cyclic voltammetry. Figures 4 and 5 show the cyclic voltammograms of **44** and **45**, respectively. The HOMO and LUMO levels were determined from the oxidation and reduction peaks. Thus, the HOMO and LUMO levels were -5.2 eV and -3.1 eV for polymer **44**. The corresponding values for polymer **45** were -5.3 eV and -3.2 eV, respectively. Although both polymers showed the same electrochemical bandgap (E_g = 2.1 eV), with the inclusion of an electron acceptor benzothiadiazole unit in polymer **45**, the LUMO level was slightly lower than that of polymer **45**. This implies that the electron affinity of polymer **45** is higher than that of polymer **44**. As a result polymer **45** may be used as an electron acceptor material in devices**.** The higher HOMO level of polymer **44** implies the polymer may be easily oxidized than polymer **45**.

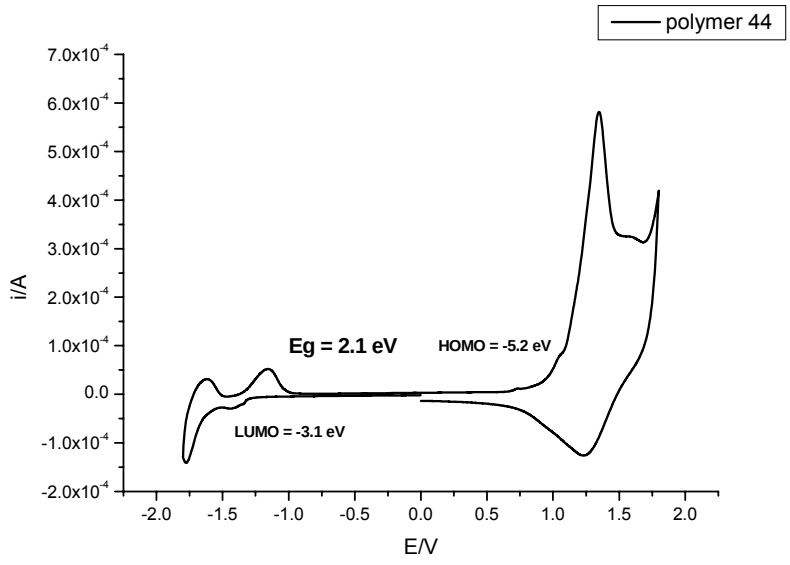


Figure 4: Cyclic voltammogram of polymer **44.**

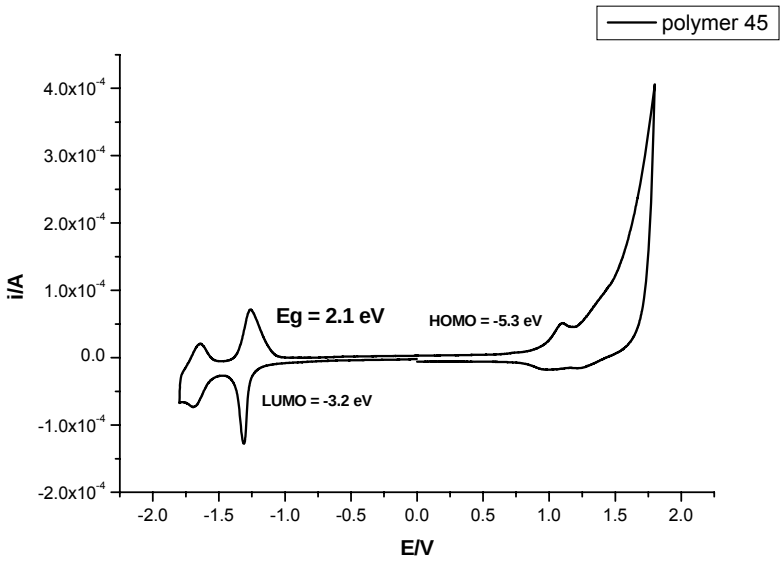


Figure 5: Cyclic voltammogram of polymer **45**.

6. CONCLUSION

In this project work, two low bandgap alternating polyfluorene copolymers were synthesized by the Suzuki coupling reaction using Pd(0) as a catalyst and tetraethylammonium hydroxide as a base. The donor-acceptor-donor segments were derived from quinoxaline **38** and benzothiadiazole units. The fluorene sub-unit contained 2-(2-methoxyethoxy)ethyl pendant groups at the C-9 position. Both polymers had good solubility in $CHCl_3$. The $CHCl_3$ solutions of both polymers had red color. Polymers **44** and **45** had low bandgaps. Thus, the optical bandgaps were determined from the UV-Vis spectra of both polymers in $CHCl_3$ solution as well as for the thin films of the polymers on glass. Similarly, the electrochemical bandgaps were estimated from the cyclic voltammograms of both polymers. It is worth nothing that introduction of benzothiadiazole units in polymer **45** showed a significant improvement over the absorption spectrum of **44** by having a better coverage of the visible region and by the disappearance of

the valley at *ca* 440 nm. Hence, polymer **45** can be a better candidate for solar cell application as it will have a better coverage of the solar irradiance in the region up to 600 nm.

7. EXPERIMENTAL

7.1. Materials and Methods

All of the compounds prepared in the course of the synthetic work were purified and characterized by NMR and UV-Vis techniques. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 400.13 and 100.6 MHz, respectively, in $CDCl_3$ and chemical shifts were reported in δ-ppm unit. The residual non-deuterated solvent signals were used as internal reference. The UV-Vis spectra were recorded in chloroform using T60 UV-Visible Spectrophotometer at room temperature. Cyclic voltammetric studies were performed on a BASi Epsilon Electrochemical Workstation using platinum electrodes at a scan rate of 100 mV.s-1 and a Ag/Ag^{+} (0.10 M of $AgNO_3$ in acetonitrile) reference electrode in a solution of 0.1 M of tetrabutylammonium tetrachloroborate (Bu_4NBCl_4) in acetonitrile..

7.2 Reagents

Bromine (BDH), potassium carbonate (Riedel-de Haen), sodium sulphate (Riedel-de Haen), *N*-bromosuccinimide (NBS) (Aldrich), 1-bromooctane (Aldrich), DMF (Aldrich), 2-(tributylstannyl)thiophene (Aldrich), 4-bromophenol (Aldrich), bis-(triphenylphosphine)palladium(II) dichloride(Aldrich), 2,1,3-benzothiadizole (Aldrich), dichloromethane (Aldrich), oxalyl chloride (Aldrich), hexane(Aldrich), acetone (Aldrich) were bought and used as received. Tetrahydrofuran (THF) was dried over Na-benzophenone under nitrogen atmosphere. Analytical grade methanol and chloroform were purchased from BDH. Analytical thin layer chromatography was performed on aluminum sheets precoated with 0.2 mm silica-gel 60 F_{254} (Merck). For open column chromatographic purification, glass columns packed with Silica gel 60 (230-400 mesh), were used.

7.3. Procedures.

7.3.1. Synthesis of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**22**).

In 1000 mL flask, a mixture of 2,1,3-benzothiadizole (19 g, 0.14 mol) and 48%HBr (76 mL) were heated at 110 ^{o}C with continuous stirring. Bromine (21 mL) was added to the mixture from a pressure equalizing dropping funnel. During refluxing, a white solid deposited on the walls of the flask. Additional HBr (66 mL) was added and the mixture was heated for 3 h. The mixture then was allowed to cool to room temperature and sufficient saturated solution of $NaHSO_3$ added to consume completely any excess Br_2. It was then filtered by suction, washed with 5% $Na_2S_2O_3$ and water. The product was recrystillized from isopropyl alcohol and dried in a vacuum oven to afford compound **22** (37.4 g, 91.0 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] 7.64 (*s*, H-5, H-6); ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] 114.3 (C-5, C-6), 153.4 (C-8, C-9), 132.7 (C-4, C-7).

7.3.2. Synthesis of 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (36).

4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (**22**) (10 g, 34 mmol) and $Pd(PPh_3)_2Cl_2$ (0.48 g, 0.68 mmol, 2mol%) were dissolved in THF (140 mL) by refluxing under nitrogen atmosphere. Tributyl(thiophene-2-yl)stannane (20.6 mL, 68 mmol) was then added dropwise from a dropping funnel over 70 min and the refluxing continued overnight. The completion of the reaction was checked by TLC (dichloromethane:pet-ether (1:4) solvent system). The mixture was then cooled to room temperature and the solvent was removed by rotary evaporatoration. The residue was taken up in petroleum ether and the resulting solid was collected by suction filtration to afford **36** (8.02 g, 78.5%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] 8.14 (*dd*, *J* = 1.2 , *J* = 3.6 Hz, 2H, H-5'), 7.91 (*s*, 2H, H-5, H-6), 7.49 (*dd*, *J* = 1.2, 3.6 Hz, 2H, H-3'), 7.24 (*dd, J* = 3.6, 5.2 Hz, 2H, H-4'); ^{13}C-NMR (100 MHz, $CDCl_3$): δ[ppm] 152.7 (C-8, C-9), 126.01 (C-4 ,C-7), 128.1 (C-5, C-6), 139.4 (C- 2'), 126.7 (C-3') 127.5 (C-4'), 125.8 (C-5').

7.3.3. Synthesis of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (39).

4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (**22**) (10 g, 34 mmol) was added in a small portions to a mixture of fuming HNO_3 (100 mL) and fuming H_2SO_4 (100 mL) at 0 ^{o}C. The reaction mixture was allowed warm to room temperature and after stirring for 96 h it was poured in to ice water (250 mL). The resulting greenish yellow slurry was filtered and the residue was recrystallized from ethanol and further purified by silica gel column chromatography (hexane:ethyl acetate (1:4) solvent system) to afford **39** (2.75 g, 21.1 %).

^{13}C-NMR (100 MHz, $CDCl_3$): δ[ppm] 151.4 (C-8, C-9), 144.7 (C-5, C-6), 110.3 (C-4, C-7).

7.3.4. Synthesis 1-bromo-4-octyloxybenzene (34).

To a mixture of *p*-bromophenol (10 g, 0.058 mol) and DMF (80 mL) in a three necked round-bottomed flask, of anhydrous K_2CO_3 (35 g, 0.253 mol) was added. The mixture was heated at 100 ^{o}C and 1-bromooctane (10 mL, 0.087 mol) was added from a pressure equalizing dropping funnel. After the addition was complete, the mixture was heated following the reaction progress of reaction by TLC (diethyl ether: hexane (3:2) solvent system). After 5 h, the mixture was cooled to room temperature and filtered. The filtrate was acidified with 2 M HCl and extracted with diethyl ether. The combined extract was washed with 1 M NaOH followed by brine solution and then dried over anhydrous Na_2SO_4.

Evaporation of the solvent under reduced pressure gave compound **34** (9.12 g, 55 %) as a yellowish oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] 7.38 (*d*, *J* = 8 Hz, 2H, H-2 and H-6)**,** 6.79 (*d*, *J* = 8 Hz, 2H, H-3 and H-5), 3.93 (*t*, *J* = 6.8 Hz, 2H, H-2'), 1.79 (*q*, 2H, H-3'), 1.50-1.30 (*m*, 10H, H-4' to H-8'), 0.92 (*t*, 3H, H-9'); ^{13}C-NMR (100 MHz, $CDCl_3$): δ[ppm] 158.3 (C-4), 132.2 (C-2,C-6), 116.3 (C-3,C-5), 112.5 (C-1), 68.3 (C-3',C-2'), 31.9 (C-4'), 31.8 (C-5'), 26.0 (C-6'), 25.7 (C-7'), 22.6 (C-8'), 14.1 (C-9').

7.3.5. Synthesis of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole (40).

A solution of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**39**) (2.71 g, 7.03 mmol) and 2-tributylstannylthiophene (6.54 g,17.52 mmol) in freshly distilled THF(35 mL) was degassed and put under nitrogen atmosphere. The mixture was heated to reflux and $Pd(PPh_3)_2Cl_2$(98.98 mg, 0.141 mmol) dissolved in freshly distilled THF(3.5 mL) was added via a siring. After 5 h an orange precipitate had formed and the heating was removed. When the mixture had cooled to room temperature, the precipitate was filtered off and washed with petroleum ether. Since the crude product contained trace of 2-tributylstannylthiophene, it was dissolved in boiling THF and precipitated by addition of petroleum ether. The precipitate was collected by filteration and washed with petroleum ether to give **40** (2.00 g, 72.72%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] 7.77 (*dd*, *J* = 1.2, 5.2 Hz, 2H, H-5'), 7.54 (*dd*, *J* = 0.8, 3.6 Hz, 2H, H-3'), 7.26 (*dd*, *J* = 3.6, 4.8 Hz, 2H, H-4'); ^{13}C-NMR (100 MHz, $CDCl_3$): δ[ppm] 152.2 (C-8, C-9), 131.5 (C-4'), 131 (C-5'), 129.6 (C-5, C-6), 128.0 (C-3'), 121.5 (C-2'),120.8 (C-4, C-7).

7.3.6. Synthesis of 1,2-bis- (4-octyloxyphenyl)ethane-1,2-dione (35).

A Grignard reagent was prepared by dropwise addition of 1-bromo-4-octylbenzene (**34**) (8.0 g, 0.03 mol) in THF (10 mL) to a suspension of magnesium (0.85 g, 0.03 mol) in THF (18 mL). In a separate flask, a solution of LiBr (5.17 g, 59.4 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 become homogenous and was then cooled to a temperature of −50 ^{o}C (immersion cooler). The Grignard reagent was added to LiBr/CuBr suspension. Oxalyl chloride (1.89 g, 14.88 mmol) was added and after 30 min the reaction was quenched with saturated NH_4Cl. The organic layer was separated, washed with saturated NH_4Cl, dried over anhydrous Na_2SO_4 and the solvent was removed to afford a pale yellow product (7.1g), which was further purified by silica gel column chromatography (pet ether:ethyl acetate (4.5:0.5) solvent system) to afford **35** (3.01 g, 22.99 %) as a pale yellow solid.

^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ[ppm] 7.94 (*d*, *J* = 8.0 Hz, 4H, H-2', H-6'), 6.96 (*d*, *J* = 8.0 Hz, 4H, H-3', H-5'), 4.04 (*t*, 4H, H-2'');, 1.82 (*q*, 4H, H-3''), 1.47-1.2 7(*m*, 20H, H-4''-H-8''), 0.95 (*t*, 6H, H-9''); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ[ppm] 193.6 (C-1, C-2), 164.5 (C-4'), 132.'4 (C-2', C-6'), 126.1 (C-1'), 114.7 (C-3', C-5'), 68.5 (C-2''), 31.8 (C-7''), 29.0 (C-3'' to C-5''), 25.9 (C-6''), 22.6 (C-8''), 14.1 (C-9'').

7.3.7. Synthesis of 2,3-bis-(4-octyloxyphenyl)-5,8-dithiophen-2-yl-quinoxaline (37).

A mixture of 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **(36)** (1.0 g, 3.33 mmol) and zinc dust (2.62 g, 39.94 mmol) in acetic acid (90 mL) was stirred at 80 ^{o}C under nitrogen for 5 h until the reaction mixture turned white. The insoluble material was separated by suction filtration. To the filtrate was added 1,2-bis-(4-octyloxyphenyl)ethane-1,2-dione (**35**) (1.55 g, 3.23 mmol) and the mixture was

heated at 60 ^{o}C under nitrogen following the reaction progress of reaction by TLC (pet ether:toluene 3:2 as solvent system). After 5 h, the reaction mixture was cooled to room temperature, the precipitate was collected by suction filtration and washed with acetic acid, methanol and water and was dried in a vacuum oven overnight to afford **37** (1.68 g, 71.1%).

Mp.101-104 ^{0}C ^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ[ppm] 8.12 (*s*, 2H, H-6, H-7), 7.87 (*d*, *J* = 4 Hz, 2H, H-5'), 7.74 (*d*, *J* = 8.4 Hz, 4H, H-2''), 7.53 (*d*, *J* = 5.2 Hz, 2H, H-3'), 7.20 (*t*, *J* = 3.6, 4.4 Hz, 2H, H-4'), 6.92 (*d*, *J* = 8.4 Hz, 4H, H-3''), 4.02 (*t*, 4H, H-2'''), 1.83(*q*, 4H, H-3'''), 1.34 – 1.49 (*m*, H-7''', H-6''', H-5''', H-4'''), 0.93 (*t*, 6H, H-9'''); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ[ppm] 159.9 (C-4''), 151.1 (C-2, C-3), 138.8 (C-2'), 136.8 (C-9, C-10), 131.9 (C-2''), 131.1 (C-5, C-8), 131.0(C-1''), 128.7 (C-6, C-7), 128.6 (C-4'), 126.5 (C-5'), 126.2 (C-3'), 114.2 (C-3''), 68.1 (C- 2'''), 31.8 (C-3'''), 31.0 (C-4'''), 29.3 (C-5'''), 29.1 (C- 6'''), 26.1 (C-7'''), 22.6 (C-8'''), 14.1 (C-9''')

7.3.8. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)- quinoxaline **(38).**

Compound **37** (1.24 g, 1.76 mmol) was dissolved in THF (47.13 mL) in a two-necked flask. NBS (627.84 mg, 3.53 mmol) was added and the mixture was stirred under nitrogen. The contents of the flask were protected from light by wrapping the flask with aluminum foil. After 80 min, The progress of the reaction was monitored by TLC. An additional amount of NBS (25 mg) was added and the mixture was stirred overnight. The reaction was quenched by adding water and was extracted with dichloromethane. The combined CH_2Cl_2 extract was washed with distilled water and brine, dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The resulting product was further purified by silica gel column chromatography (toluene:hexane (1.5:3.5) solvent system) to afford **38** (1.2 g, 78.95%).

Mp. 108-117 ^{0}C ^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ[ppm] 7.93 (*s*, 2H, H-6, H-7), 7.66 (*d*, *J* = 8 Hz, 4H, H-2''), 7.50 (*d*, *J* = 4Hz, 2H, H-4'), 7.10 (*d*, *J* = 4 Hz , 2H, H-3'), 6.93 (*d*, *J* = 8 Hz, 4H, H-3''), 4.04 (*t*, 4H, H-2'''), 1.85 (*q*, 4H, H-3'''), 1.28-1.51 (*m*,20H, H-4'''-H-8'''), 0.94 (*t*, 6H, H-9'''); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ[ppm] 160.0 (C-4''), 151.1 (C-2'), 138.8 (C-2, C-3), 136.8 (C-9, C-10), 131.9 (C-2''), 131.1 (C-5, C-8), 131.0 (C-1''), 128.7 (C-4'), 128.6 (C-3'), 126.5 (C- 6, C-7), 126.2 (C-5'), 114.2 (C-3''), 68.1 (C-2'''), 31.8 (C-3'''), 29.3 (C-4'''), 29.2 (C-5'''), 29.1 (C-6'''), 26.1 (C-7'''), 22.7 (C- 8'''), 14.2 (C-9''').

7.3.9. Synthesis of 6,7-diphenyl-4,9-dithiophen-2-yl[1,2,5]thiadiazole[3,4- *g*]quinoxaline (41).

To a mixture of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole **(40)** (850 mg, 2.175 mmol) and acetic acid (50 mL) was added iron powder (2.46 g, 43.93 mmol) and the mixture was heated at 45-50 ^{o}C. The progress of the reaction was monitored by TLC (dichloromethane:pet ether (1:1)) and after 3 h the starting material disappeared completely. Benzil (457.35 mg, 2.175 mmol) was added and the mixture was stirred overnight at room temperature. Acetic acid was removed by rotary evaporation and the residue was recrystallized from ethanol. This gave **41** (216 mg, 19.67%) as a dark blue-green powder.

^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ[ppm] 9.05 (*d*, *J* = 8 Hz, 2H, H-5'), 7.85 (*d*, *J* = 12 Hz, 4H, H-2''), 7.72 (*d*, *J* = 8 Hz, 2H, H-3'), 7.45 (*m*, 6H, H-3'', H-4''), 7.35 (*t*, *J* = 4 Hz, 2H, H-4'); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ[ppm] 153.3(C-10, C-11), 151.9(C-6, C-7), 138.1(C-5, C-8), 135.9(C-2'), 133.2(C-1''), 131.4(C-2''), 130.6(C-4, C-9), 129.6(C-4''), 129.3(C-3'), 128.3(C-3''), 126.8(C-5'), 125.3(C-4')

7.3.10. Synthesis of 9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (3).

Fluorene (8 g, 48.1 mmol) was dissolved in THF (120 mL) and cooled to −78 ^{o}C. 2.5 M *n*-BuLi (20 mL, 50 mmol) was added and the mixture was stirred for 30 min at the same temperature. 1-Chloro-2-(2-methoxyethoxy)ethane (6.8 g, 49.1 mmol) was then added and stirring continued for 1 h at −78 ^{o}C followed by stirring at room temperature for 30 min. The cooling bath was placed back and the reaction mixture was cooled to −78 ^{o}C. 2.5 M *n*-BuLi (24 mL, 60 mmol) was added and the mixture was stirred for 45 min. Then,1-chloro-2-(2-methoxyethoxy)ethane (7.2 g, 52 mmol) was added. After stirring at −78 ^{o}C for 30 min, the immersion cooler was turned off and the mixture was allowed to warm to room temperature gradually overnight. The mixture was quenched by adding water and the aqueous phase was extracted with diethyl ether. The combined organic phase was was washed with distilled water and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator and the oily crude product was passed through a column of silica gel using chloroform and chloroform-methanol (4.9:0.1) solvent systems and compound **3** was obtained in pure form (5.78 g, 32.4%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ[ppm]: 7.71 (*dd J* =1.2, 8Hz, 2H), 7.45 (*dd J* = 6.8, 1.2 Hz, 2H), 7.38 (*m*, 4H), 3.32 (*m*, 10H), 3.21 (*t*, 4H), 2.77 (*t*, 4H), 2.46 (*t*, 4H).

7.3.11. Synthesis of 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (4).

9,9-Bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene (**3**) (5.78 g, 15.6 mmol) was dissolved in DMF(80 mL) and bromine (80 mL, 73.75 mmol)) dissolved in DMF (5 mL) was added drop-by-drop from a pressure-equalizing dropping funnel over 30 min. Then it was stirred following the progress of reaction by TLC ($CHCl_3$:MeOH (4.9:0.1)). After 115 min, more bromine (1.2 mL) was added and stirring continued overnight. The reaction mixture was quenched with aqueous $Na_2S_2O_3.5H_2O$ solution (10%) and then extracted with diethyl ether. The ether extract was washed with distilled water, dried over anhydrous Na_2SO_4 and the solvent was removed to give an oily material (11.8 g). The crude product was

purified by passing through a column packed with silica gel and using $CHCl_3$ and $CHCl_3$:MeOH (4.9:0.1) solvent mixture. 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**4**) (8.0 g, 97%) was obtained in a pure form.

^{1}H NMR ($CDCl_3$, 400 MHz) δ[ppm]: 7.56 (*d, J* = 1.6 Hz, 2H), 7.52 (*s*, 2H), 7.49 (*d, J* = 1.6 Hz, 2H), 3.32 (*t*, 4H), 3.3 (*s*, 6H), 3.2 (*t*, 4H), 2.8 (*t*, 4H), 2.39 (*t*, 4H).

7.3.12. Synthesis of 2,2'-(9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6).

2,7-Dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**4**) (8.0 g, 16.01 mmol) was dissolved in dry THF (250 mL) under nitrogen atmosphere and cooled to −78 ^{o}C. 2.5 M *n*-BuLi (15.8 mL, 40 mmol) was added to the cooled mixture. Then, 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8 g, 32.02 mmol) was added and stirred for some time. Then the immersion cooler was turned off and the mixture was stirred overnight. The reaction mixture was quenched with water and extracted with diethyl ether. The organic phase was dried over anhydrous Na_2SO_4. Up on removal of the solvent, an oily material was obtained which almost solidified on standing. To the crude material, hot petroleum ether was added and the material was dissolved, and when cooled a white material precipitated. The white solid was collected by suction filtration, dried in a vacuum oven to afford the title compound (2.67 g, 28%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ[ppm]: 7.87 (s, 2H), 7.83 (*d, J* = 7.2 Hz, 2H), 7.73 (2 *d, J* = 7.6 Hz, 2H), 3.32 (t, 4H), 3.28 (*s*, 6H), 3.2 (*t*, 4H), 2.69 (*t*, 4H), 2.5 (*t*, 4H), 1.41 (*s*, 24H).

7.3.13. Synthesis of poly[5-(5-(9,9-bis-[2-(2-methoxyethoxy)ethyl]-9*H*-fluoren-2-yl)-thiophen-2-yl)-2,3-bis-(4-octyloxyphenyl)-8-thiophen-2-yl-quinoxaline] (44).

5,8-Bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline **(38)** (0.1 g, 0.12 mmol) was mixed with 2,2'-(9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**6**) (0.17 g, 0.12 mmol), tetrakis(triphenylphosphine)palladium(0) (13 mg) and toluene (10 mL) and was refluxed for 10 min under nitrogen atmosphere. 20% (w/w) Tetraethylammonium hydroxide in water (0.45 mL, 0.63 mmol) was added with a syringe and the mixture was refluxed for 3 h. Bromobenzene (0.158 mL, 1.69 mmol) was added and after 1 h phenylboronic acid (0.18 g, 1.5 mmol) was added. After 1 h of refluxing, the mixture was allowed to cool to room temperature and was precipitated by slowly adding the mixture in to methanol, filtered, washed with methanol and dried. The resulting solid was dissolved in chloroform, and was washed with ammonia and with water. The chloroform solution was concentrated to a small volume and the polymer was reprecipitated from methanol, filtered and dried. The dark-red colored solid was Soxhlet extracted first with diethyl ether and then with chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from methanol, filtered and dried to afford polymer **44** (117 mg).

7.3.14. Synthesis of poly[5-(5-(7-(7-(9,9-bis-[2-(2-methoxyethoxy)ethyl]-9H-fluoren-2-yl)benzo[1,2,5]thiadiazol-4-yl)-9,9-bis-[2-(2-methoxy-ethoxy)ethyl]-9*H*-fluoren-2-yl)-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-8-thiophen-2-yl-quinoxaline] (45).

2,2'-(9,9-Bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**6**) (144.65 mg, 0.23 mmol) was mixed with 5,8-Bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline **(38)** (100 mg, 0.12 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (**22**) **(**34.16 mg, 0.12 mmol), tetrakis(triphenylphosphine)palladium(0) (13 mg) and toluene (10 mL) and was refluxed for 10 min under nitrogen atmosphere. 20% (w/w) Tetraethylammonium hydroxide in water (0.35 mL, 0.49 mmol) was added with a

syringe and the mixture was refluxed for 3 h. Bromobenzene (0.1 mL, 0.96 mmol) was added and after 1 h phenylboronic acid (0.19 g, 1.55 mmol) was added. After 1 h of refluxing, the mixture was allowed to cool to room temperature and was precipitated by slowly adding the mixture in to methanol, filtered, washed with methanol and dried. The resulting solid was dissolved in chloroform, and was washed with ammonia and with water. The chloroform solution was concentrated to a small volume and the polymer was reprecipitated from methanol, filtered and dried. The red-colored solid was Soxhlet extracted first with diethyl ether and then with chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from methanol, filtered and dried to afford polymer **45** (122.7 mg).

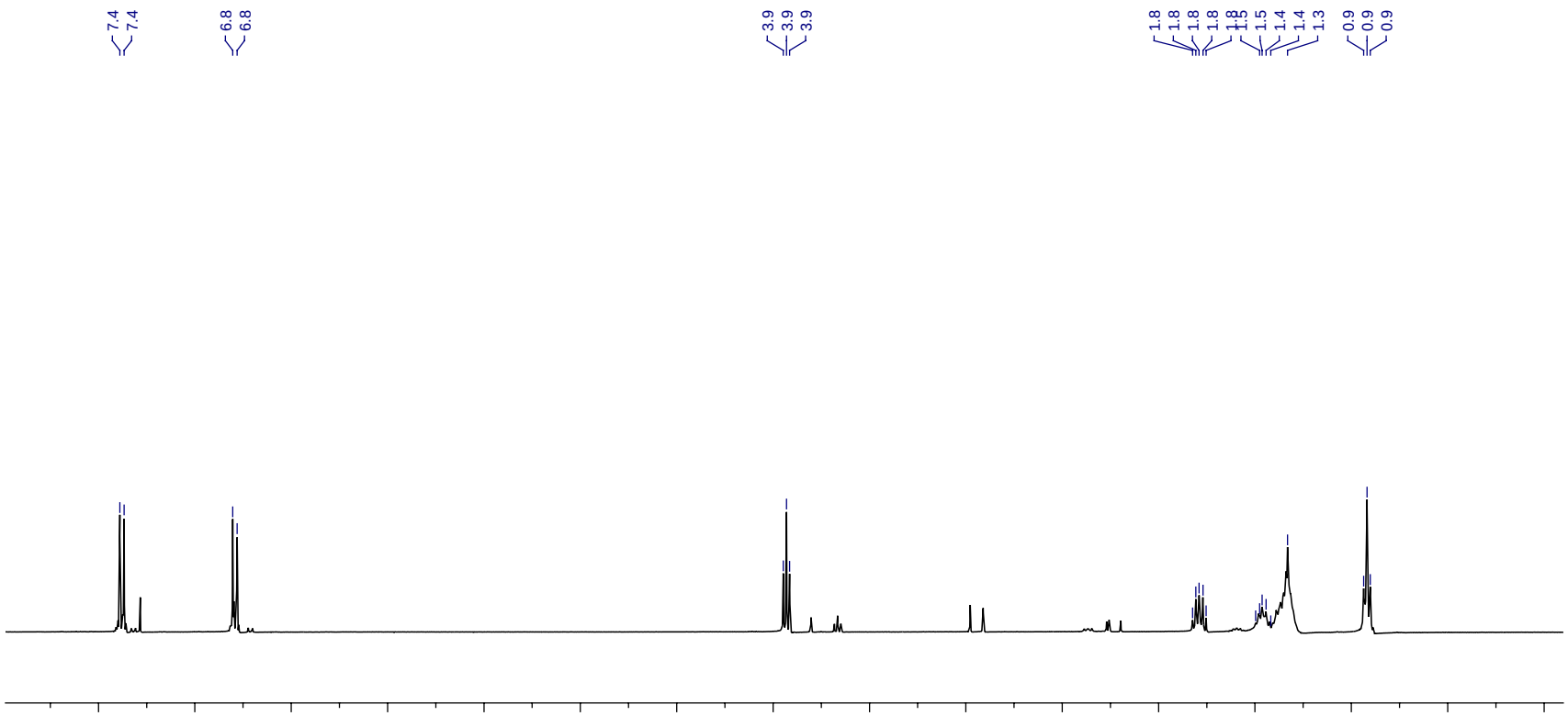
8. REFERENCES

1. Kraft, A.; Grimsdale, A.C.; Holmes, A.B. *Angew. Chem.* **1998***, 37*, 402*.*
2. Hide, F.; Diaz-Garcia, M.A.; Schwartz, B.J.; Heeger, A.J. *Acc. Chem. Res.* **1997***, 30,* 430*.*
3. Yu, G.; Gao, J.; Hummelen, J.C.; Wudl, F.; Heeger, A.J*. Science* **1995***, 270,* 1789*.*
4. Brédas, J.L.; Beljonne, D.; Coropceanu, V.; Cornil, J*. Chem. Rev.* **2004***, 104,* 4971*.*
5. Babudri, F.; Farinola, G.M.: Naso, F. *J. Mater. Chem.,* **2004***, 14,* 11.
6. Ito T.; Shirakawa H.; Ikeda S. *J. Polym. Sci. Polym. Chem..* **1974***, 12,* 11*.*
7. Natta, G.; Mazzanti, G.*;* Corradini, P. *Atti Accad. Naz. Lincei, Rend. Cl. Sci. Fis., Mat. Nat*. **1958**, *25*, 3.
8. Chiang, C.K.; Druy, M.A.; Gau, S.C.; Heeger, A.J.; Louis, E.J.; MacDiarmid, A.G.; Park, Y.W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978,** *100,* 1013*.*
9. Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. *J. Chem. Soc., Chem. Commun.,* **1977***,* 578*.*
10. Kraft, A.; Grimsclale, A.C.; Holmes, A.B. *Angew. Chem., Int. Ed.,* **1998***, 37,* 402*.*
11. Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000***, 10,* 1471.
12. Hide, F.; Diaz-Garcia, M.A.;Schwartz, B.J.;Heeger, A.J. *Acc. Chem. Res.,* **1997***, 30,* 430*.*
13. Gao, G.Y.; Hummelen, G.C.; Wudl, F.; Heeger, A.J. *Science,* **1995***, 270,* 1789.
14. Roncali, J. *Chem. Rev.* **1992***, 92,* 711*.*
15. Deronzier, A.; Moutet, J.C. *Acc. Chem. Res.* **1989***, 22,* 249*.*
16. Padinger, F.; Rittberger, R.S.; Sariciftci, N.S*. Adv. Func. Mater.* **2003***, 13,* 85*.*
17. United Nations Environment Programme (UNEP), *Global environment outlook (GEO year book 2004/5), Web site: www.unep.org/geo/yearbook*.

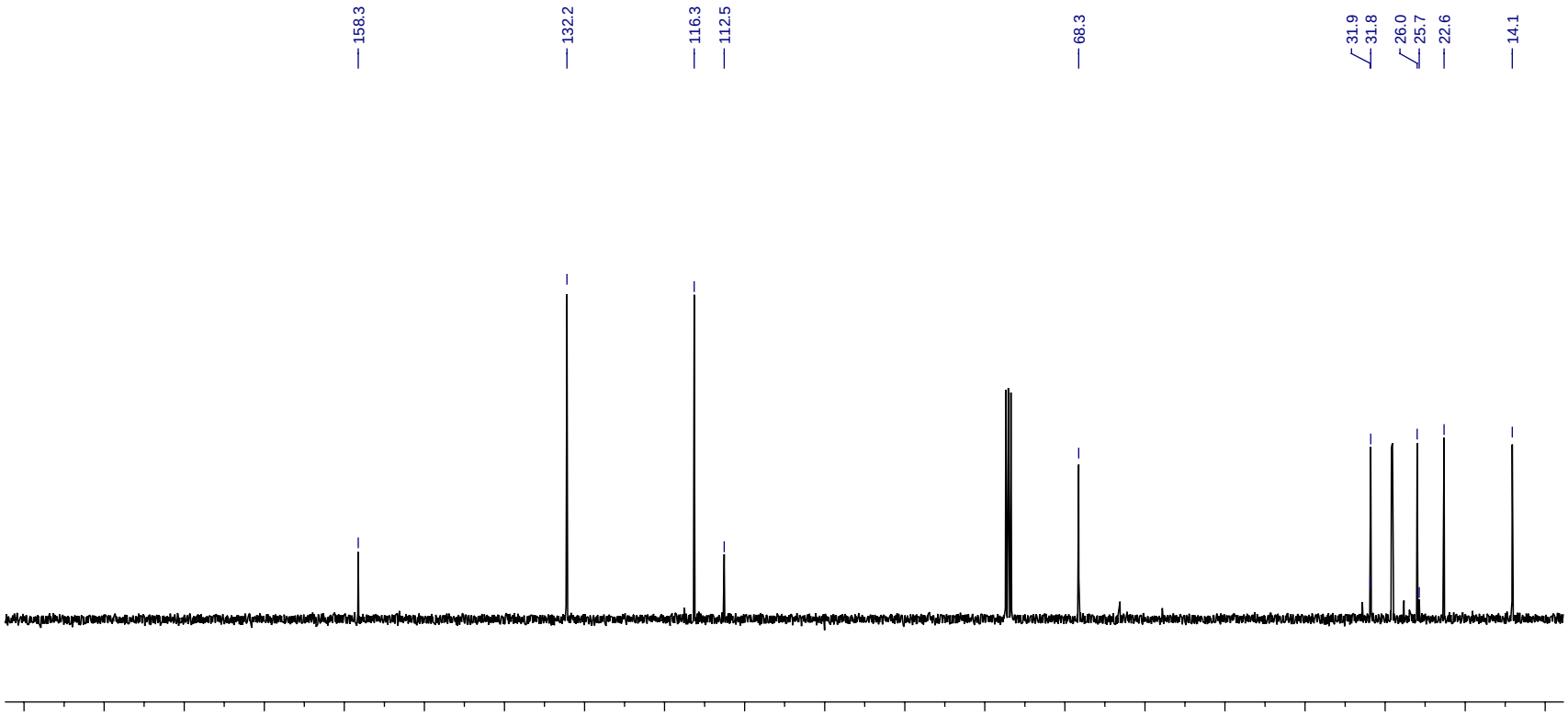
18. Intergovernmental Panel on Climate Change (IPCC), " *Third Assessment Report of Working Group I - Summary for policy makers", **2001**, Web page: http://www.ipcc.ch/*
19. Lee, S.K.; Hwang, D.-H; Jung, B.-J.; Cho, N.S.; Lee, J.; Lee, J.-D.; Shim, H.-K. *Adv. Func. Mater,* **2005***, 15,* 1647.
20. Tirapattur, S.; Belletê te, M.; Drolet, N.; Bouchard, J.; Ranger, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem B.,* **2002***, 106,* 8959.
21. Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C.H.; Su, Y.O.; Lee, G.-H.; Peng, S.-M. *J. Am .Chem. Soc.,* **2002***, 124,* 11576.
22. Bernius, M.T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater,* **2000***, 12,* 1737.
23. Leclerc, M. *J. Polym. Sci.Part A: Polym. Chem.* **2001***, 39,* 2867.
24. Leclerc, M.; Najari, A.; Beaupre, S. *Can. J. Chem.***2009***, 87,* 1201.
25. Scherf, U.; List, E.J.W. *Adv. Mater* **2002***, 14,* 477.
26. Knaapila, M.; Torkkeli, M.; Lyons, B.P.; Hunt, M.R.C.; Hase, T.P.A.; Seeck, O.H.; Bouncheoive, L.; Serimaa, R.; Monkman, A.P. *Phys. Rev.* **2006***, 74,* 214203.
27. Setayesh, S.; Grimsdale, A.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghadi, F.; List, E.; Leising, G. *J. Am. Chem. Soc.* **2001***, 123,* 946.
28. Beaupré, S.; Leclerc, M. *Adv. Funct. Mater.* **2002,** *12,* 192.
29. Lee, J.-I.; Hwang, D.-H.; Park, H.; Do, L.-M.; Chu, H.Y.; Zyung, T.; Miller, R.D. *Synth. Met.* **2000***, 111-112,* 195.
30. Cho, N.S.; Hwang, D.-H.; Lee, J.-I; Jung, B.-J; Shim, H.-K. *Macromolecules* **2002***, 35,* 1224.
31. Liu, B.; Niu, Y.-H.; Yu, W.-L; Cao, Y.; Huang, W. *Synth. Met.* **2002***, 129,* 129.
32. Abbel, R.; Schenning, A.P.H.J.; Meijer, E.W. *J. Polym. Sci. Part A: Polym. Chem.* **2009***, 47,* 4215 and references cited there in.
33. Grimsdale, A.G.; Mullen, K. *Adv. Polym. Sci., **2008**, 212,* 1.
34. Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996,** *118,* 7416.

35. Miteva, T.; Miesel, A.; Knoll, W.; Nothofer, H.G.; Scherf, U.; Muller, D.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater,* **2001***, 13,* 565.
36. Suzuki, A. *J. Organometallic Chem.,* **1999***, 576,* 147.
37. Inbasekaran, M.; Woo, E.; Wu, W.; Bernius, M.; Wujkowski, L. *Synth. Met.,* **2000***, 111-112,* 397 and references cited there in.
38. Lu J.; Tao Y.; Diaorio, M.; Li, Y.; Ding, T.; Day, M. *Macromolecules* **2004***, 37,* 2442.
39. Herguth, P.; Jiang, X.; Liu, M.; Jen, A. *Macromolecules* **2002***, 35,* 6094.
40. Stauart D.; James F.W.; Richard J.P.; Ian C.S.; Stephen T.; Emma, L.W. *J. Mater. Chem.,* **2001***, 11,* 2238.
41. Thomas, S.W.; Joly, G.D.; Swager, T.M.; *Chem Rev.,* **2007***, 107,* 1339.
Sun, Q.; Zhan, X.; Yang, C.; Liu, Y.; Li, Y.; Zhu, D. *Thin Solid Films* **2003***, 400,* 247.
43. Xekoukolotakis,N,P.; Hadjiantoniou, M.C.P.; Maroulis, A,J. *Tetrahedron. Lett.* **2000***, 41,* 10299.
44. Maroulis,A.J.; Domzaridou, K.C.; Hadjiantoniou-Maroulis, C.P. *Synthesis* **1998***, 12,* 1769.
45. Jonforsen, M. *Ph.D. dissertation,* Chalmers University of Technology **2002**.
46. Hegenrother, P.M. *J. Macromolecular Sci. Rev. Macromolecular Chem.,* **1971***, 1,* 1 and references cited there in.
47. Hegenrother, P.M. *Polym. Sci. Eng.* **1976***, 16,* 303.
48. Jonferson, M., Johansson, T., Spijuth, L., Inganäs, O.,Andersso, M. R., *Synthetic Metals* ***2002****, 131(1-3),* 53.
49. Kulkarni, A.P.; Jenekhe, S.A. *Macromolecules* **2003***, 36,* 5287.
50. Lee, B. L.; Yamamoto, T. *Macromolecules* **1999***, 32,* 1375.
51. Yamamoto, T.; Lee, B. L.; Kokubo, H.; Kishida, H.; Hirota, K.; Bayashi, T. W.; Okamoto, H. *Macromol*. *Rapid Commun.,* **2003***, 24,* 440.
52. Tsami, A.; Yang, X-H.; Heidernoff, R.; Balk, L.J.; Neher, D.; Holder, E. *J. Polym. Sci. Part A: Polym. Chem.* **2007***, 45,* 4773.
53. Wu, W-C.; Liu, C-L.; Chen, W-C. *Polymer* **2006***, 47,* 527 and references cited there in.

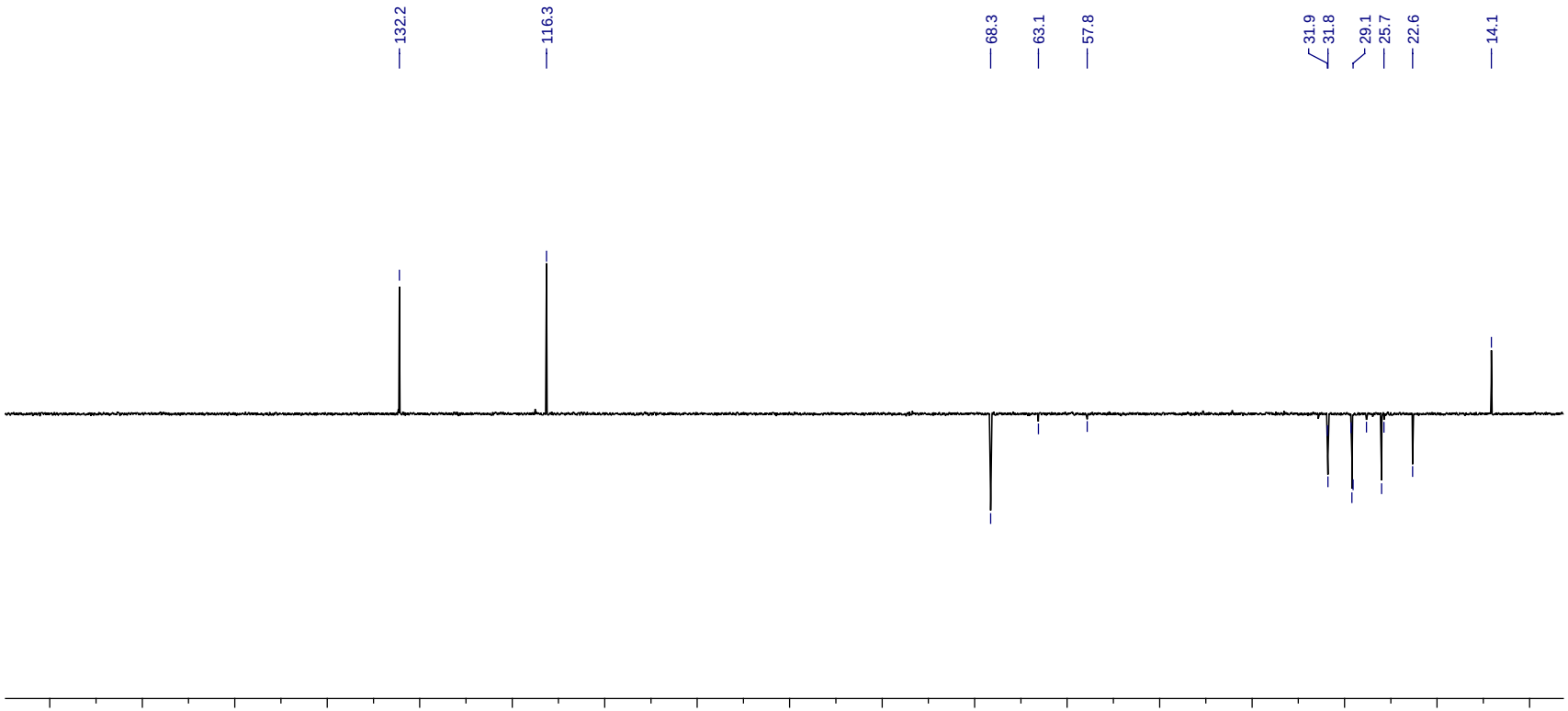
54. Ranger, M.; Rondeau, D.; Leclerc, M., *Macromolecules,* **1997***, 30,* 7686.



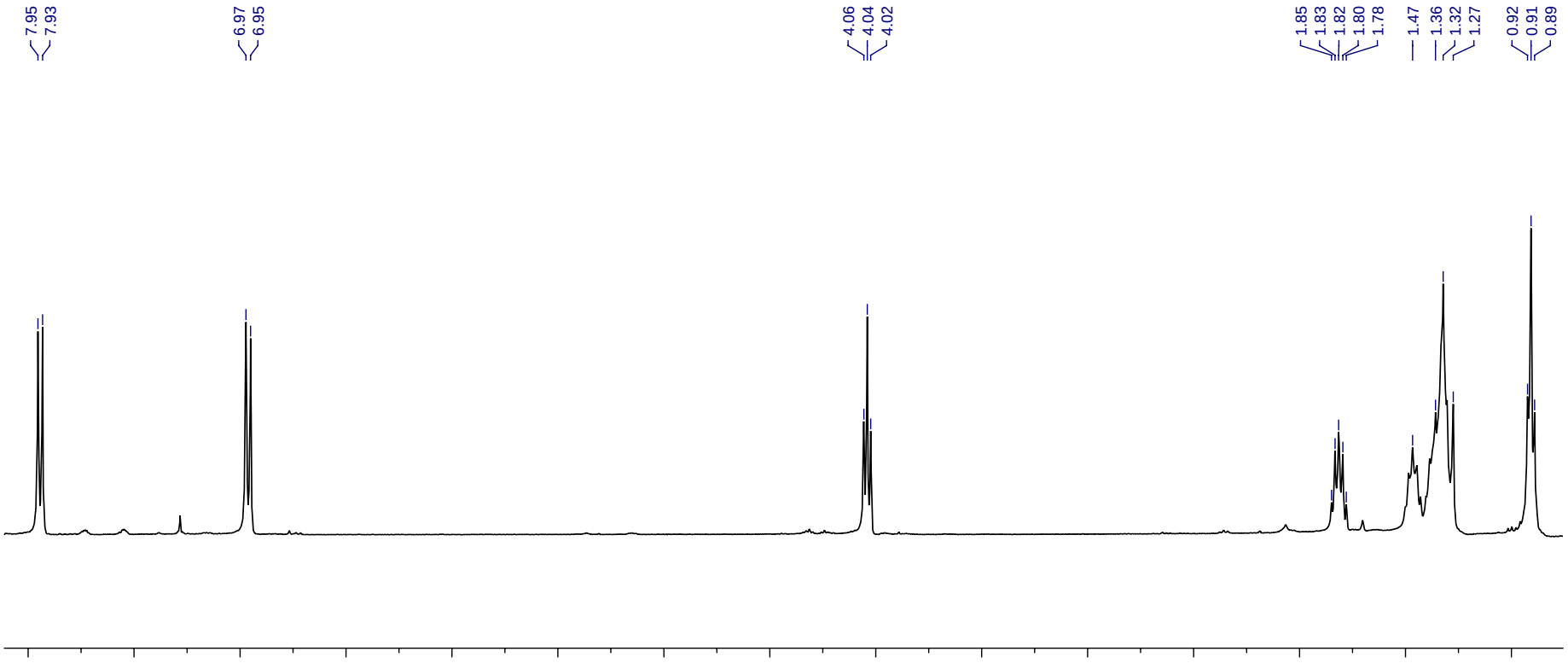
Appendix 1: ^{1}H-NMR spectrum of 1-bromo-4-octyloxybenzene (**34**).



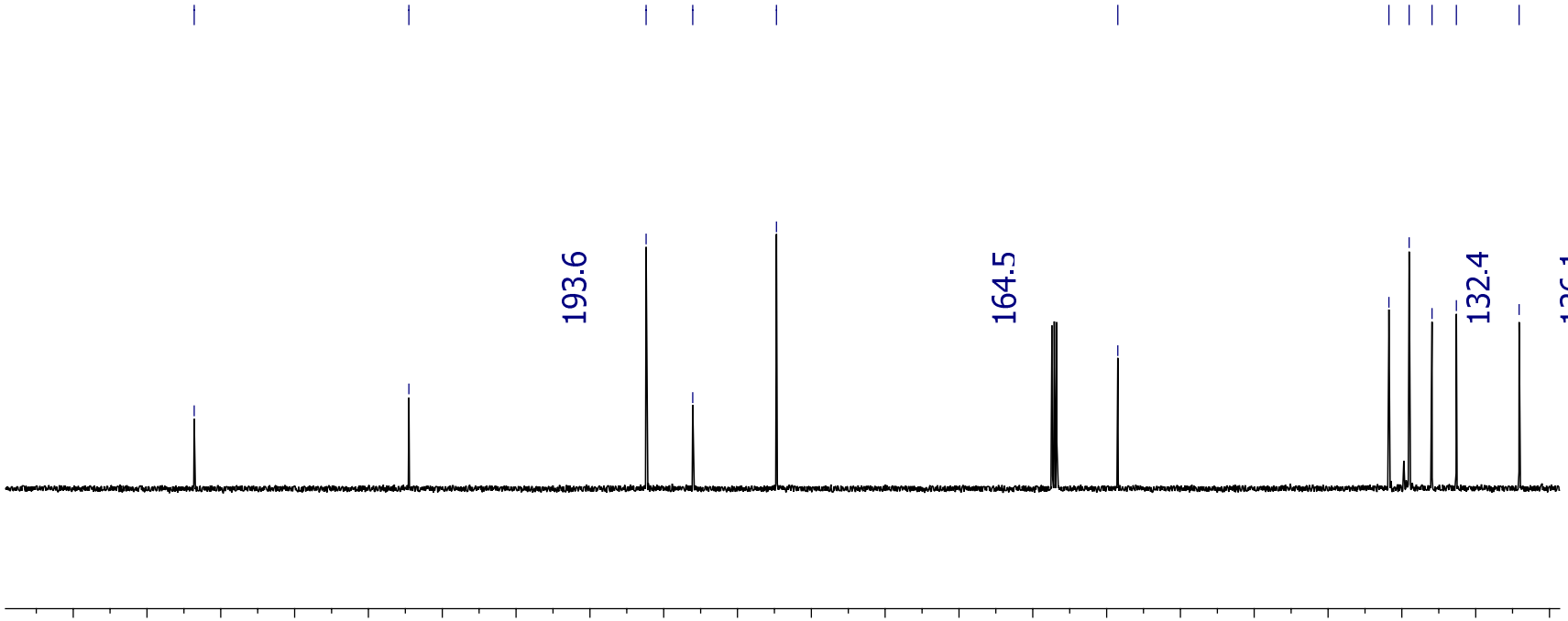
Appendix 2: ^{13}C-NMR spectrum of 1-bromo-4-octyloxybenzene (**34**).



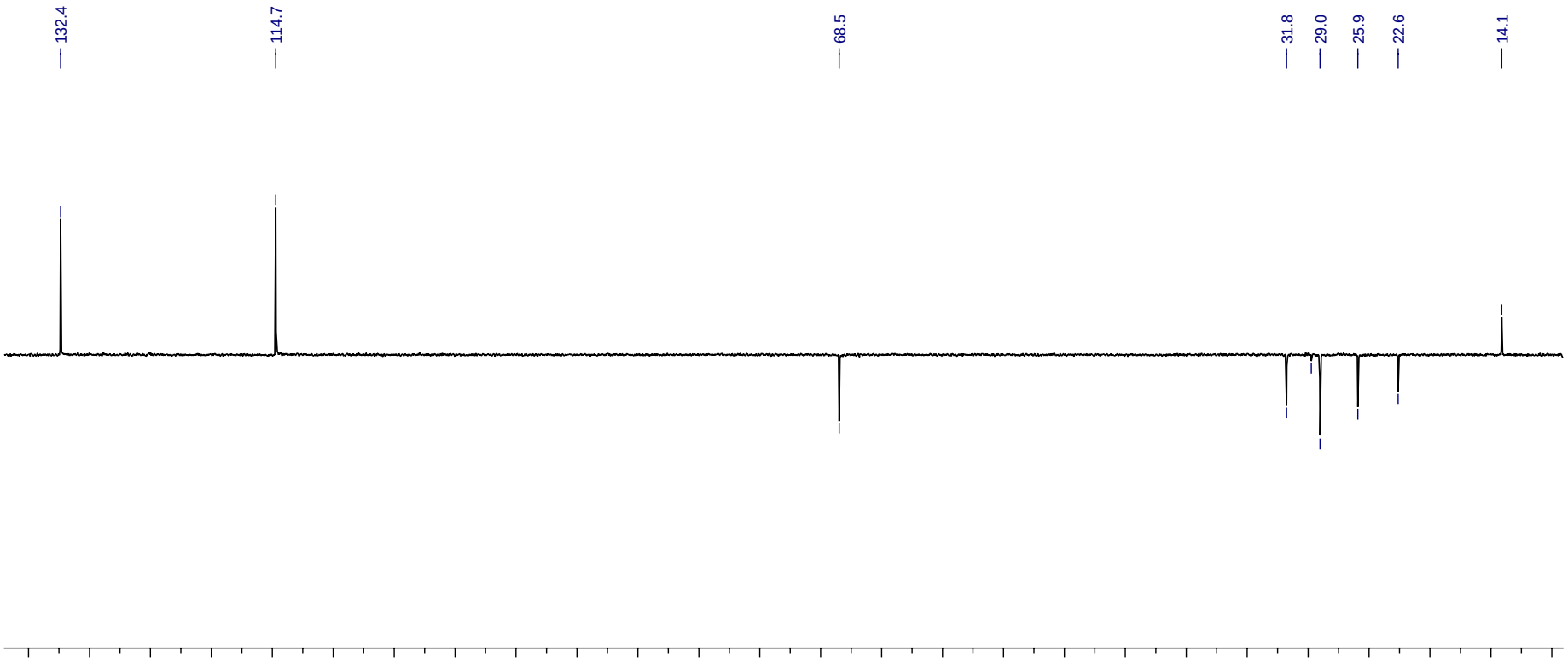
Appendix 3: Dept-135 spectrum of 1-bromo-4-octyloxybenzene (**34**).



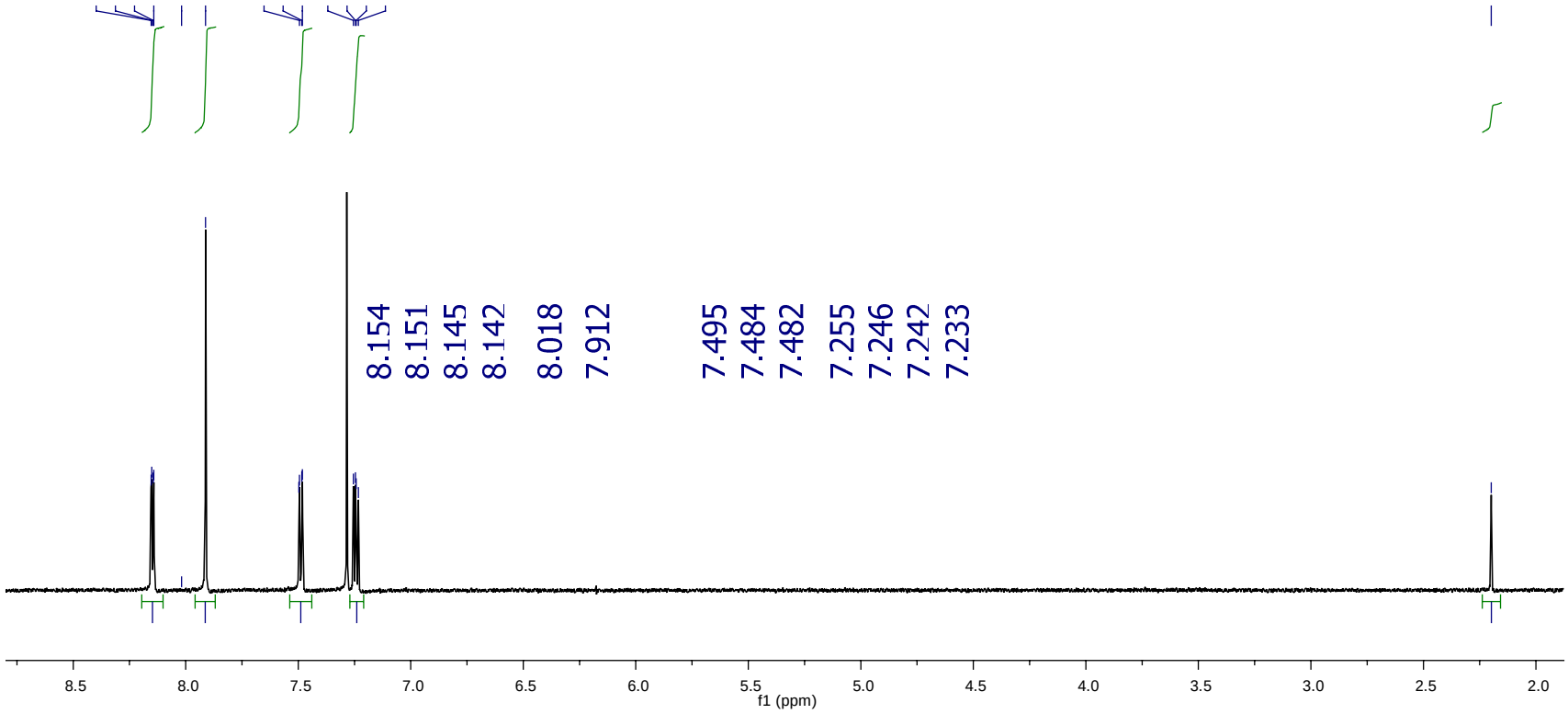
Appendix 4: ^{1}H-NMR spectrum of 1,2-bis-(4-octyloxyphenyl)ethane-1,2-dione (**35**).



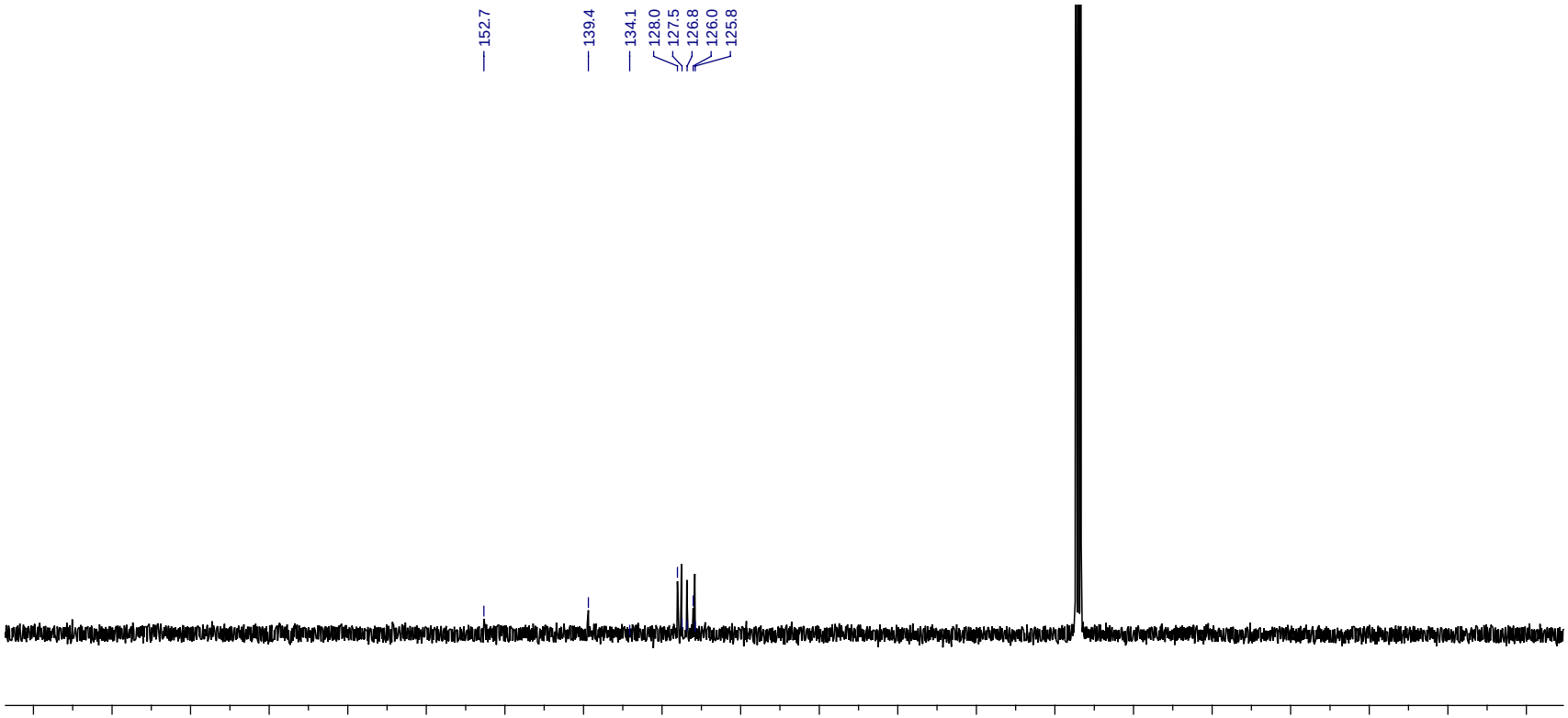
Appendix 5: ^{13}C-NMR spectrum of 1,2-bis-(4-octyloxyphenyl)ethane-1,2-dione (**35**).



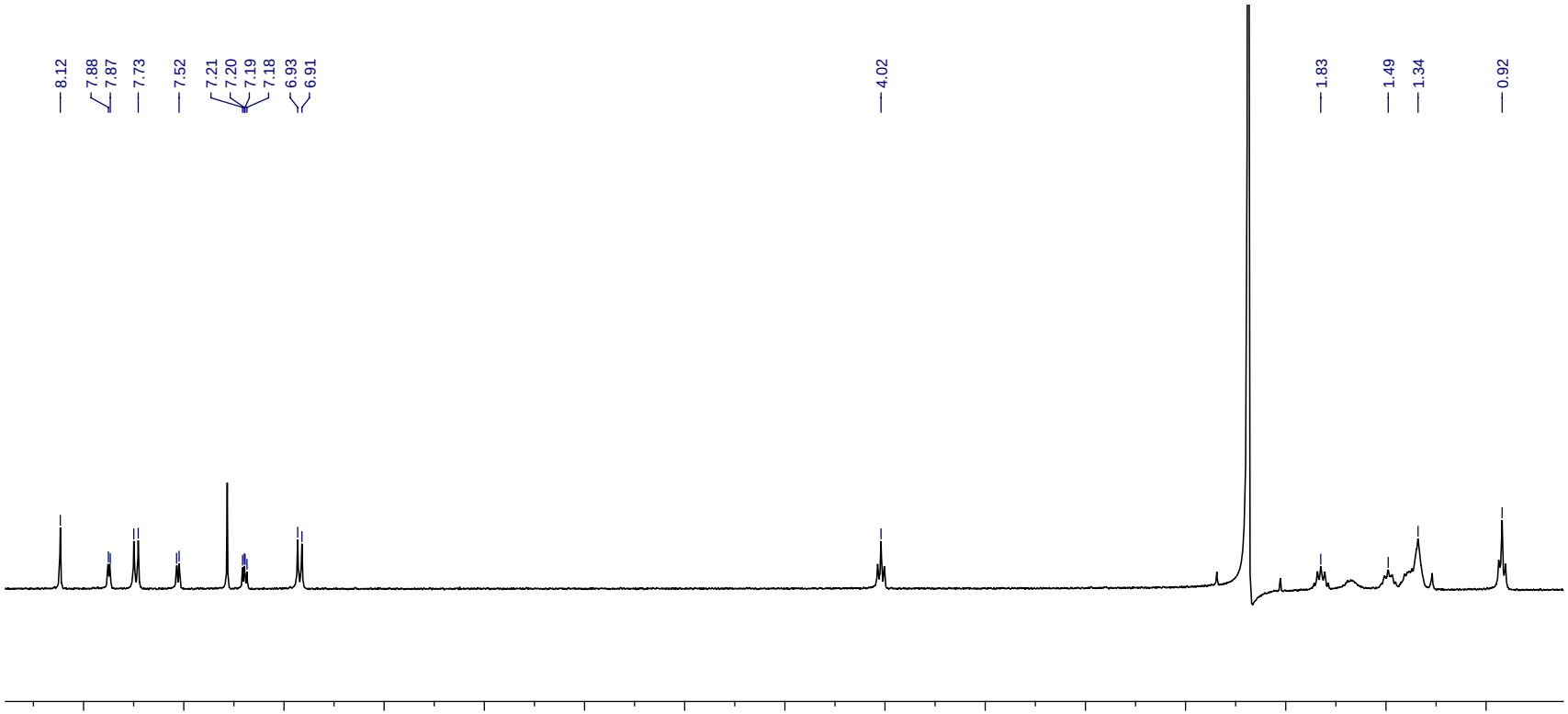
Appendix 6: Dept-135 NMR spectrum of 1,2-bis-(4-octyloxyphenyl)ethane-1,2-dione (**35**)



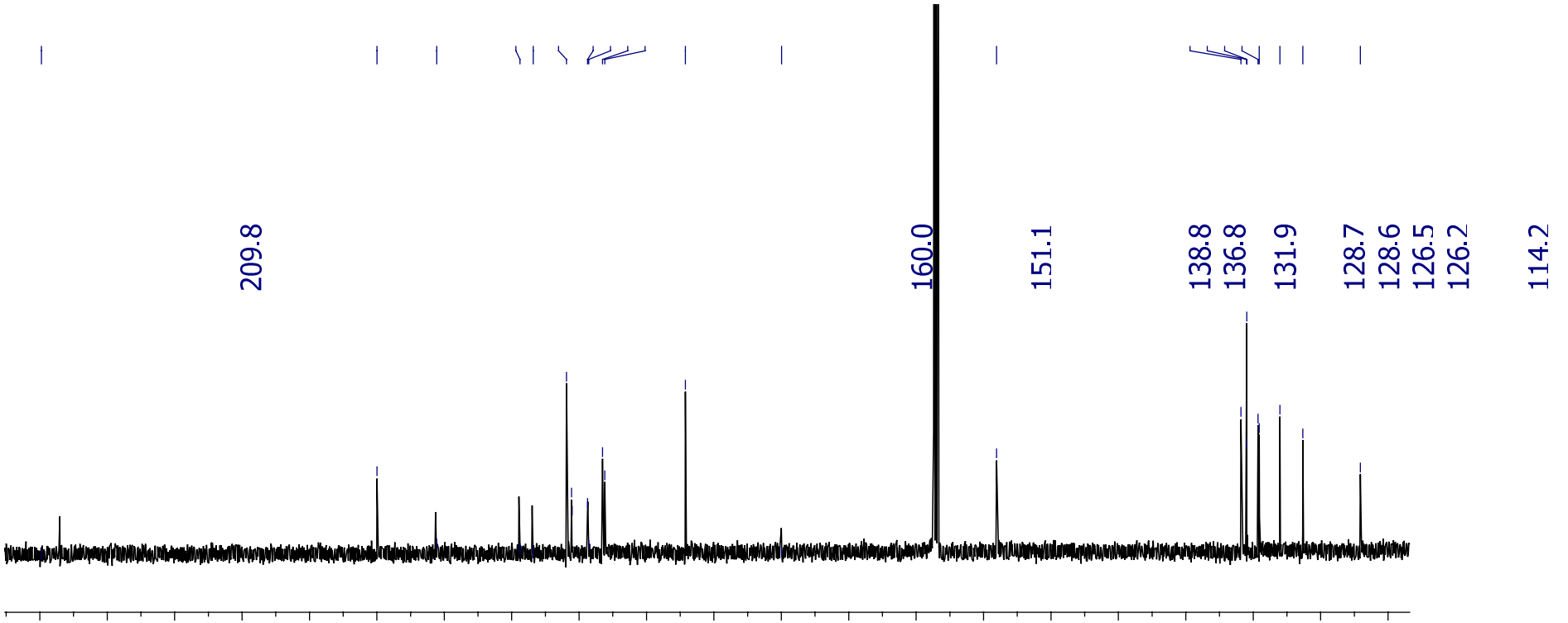
Appendix 7: ^{1}H NMR spectrum of 4,7-dithiophen-2-yl-benzo[*c*][1,2,5]thiadiazole (**36**).



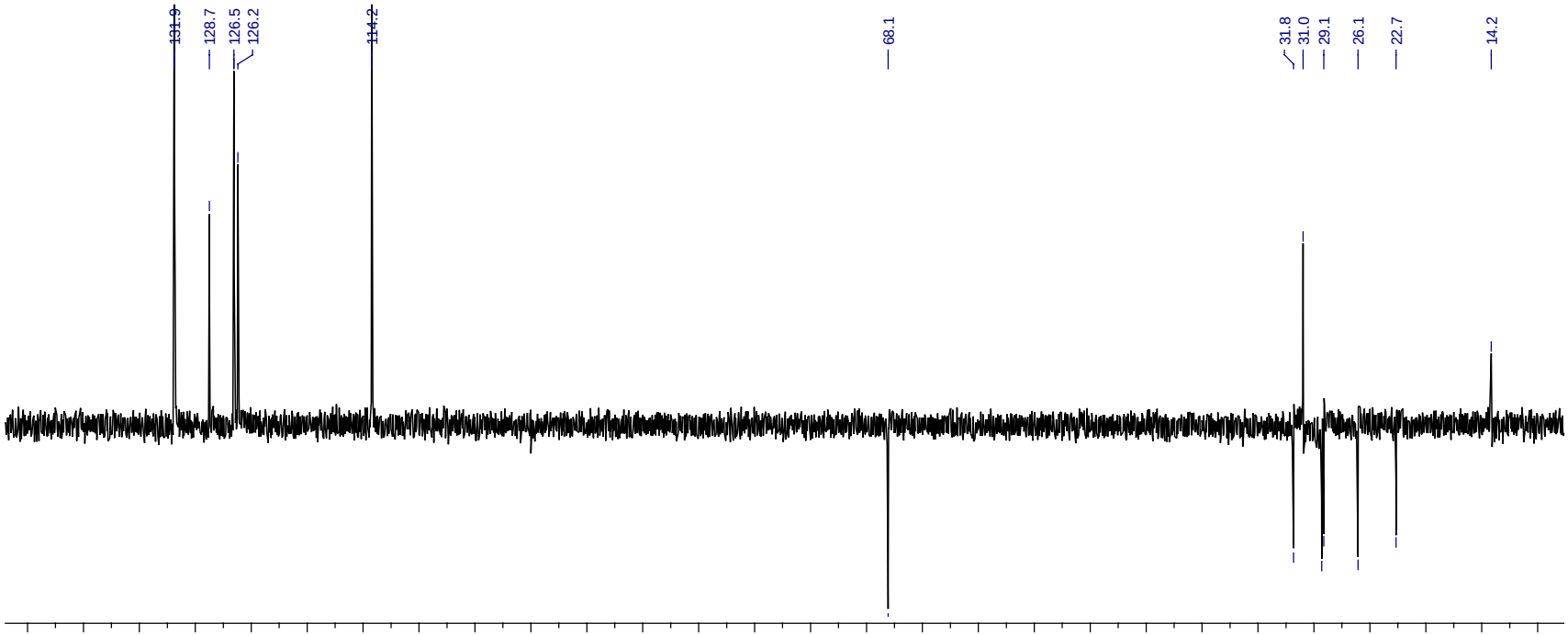
Appendix 8: ^{13}C- NMR spectrum of 4,7-di-thiophen-2-yl-benzo[*c*][1,2,5]thiadiazole(**36**).



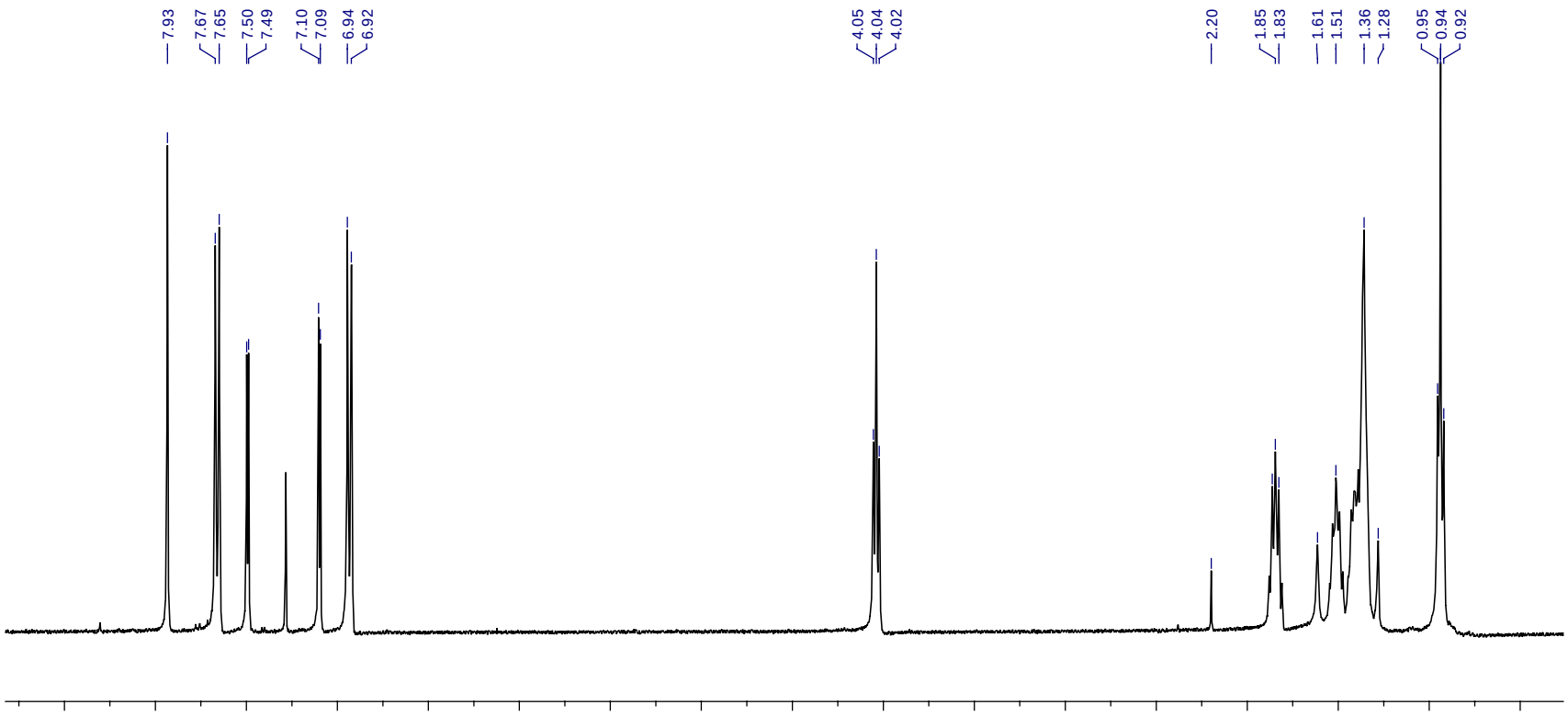
Appendix 9: ^{1}H-NMR spectrum of 2,3-bis-(4-octyloxyphenyl)-5,8-di(thiophene-2-yl)quinoxaline (**37**).



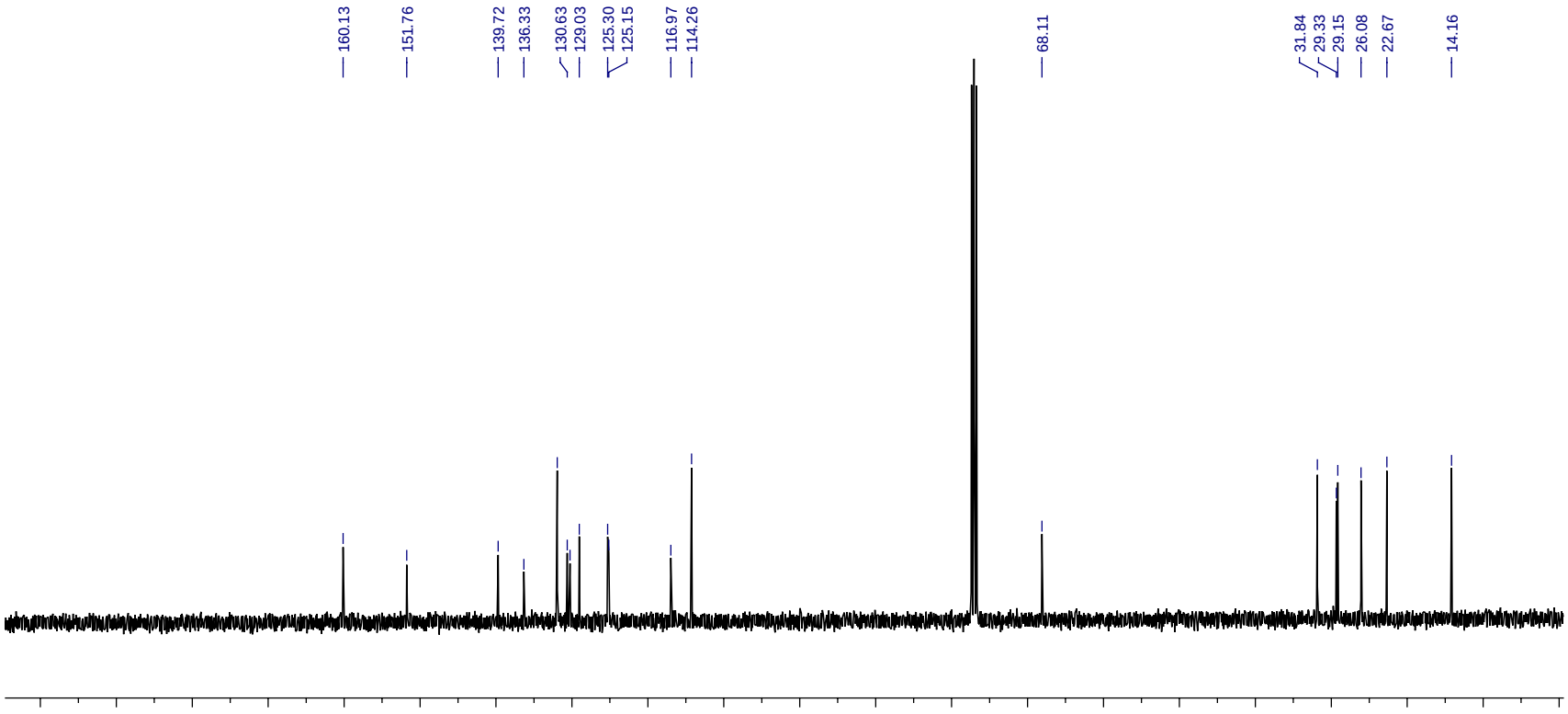
Appendix 10: ^{13}C-NMR spectrum of 2,3-bis-(4-octyloxyphenyl)-5,8-di(thiophene-2-yl)quinoxaline (**37**).



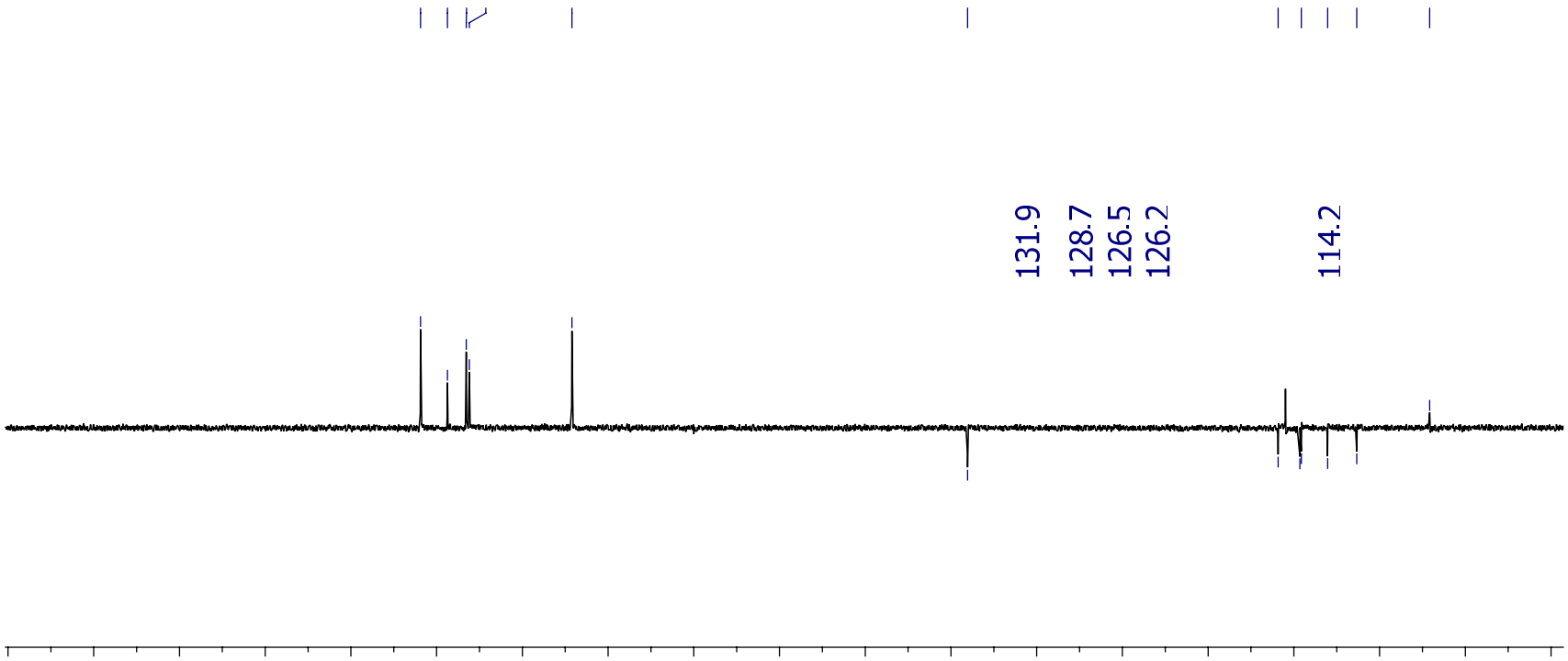
Appendix 11: DEPT-135 spectrum of 2,3-bis-(4-octyloxyphenyl)-5,8-di(thiophene-2-yl)quinoxaline (**37**).



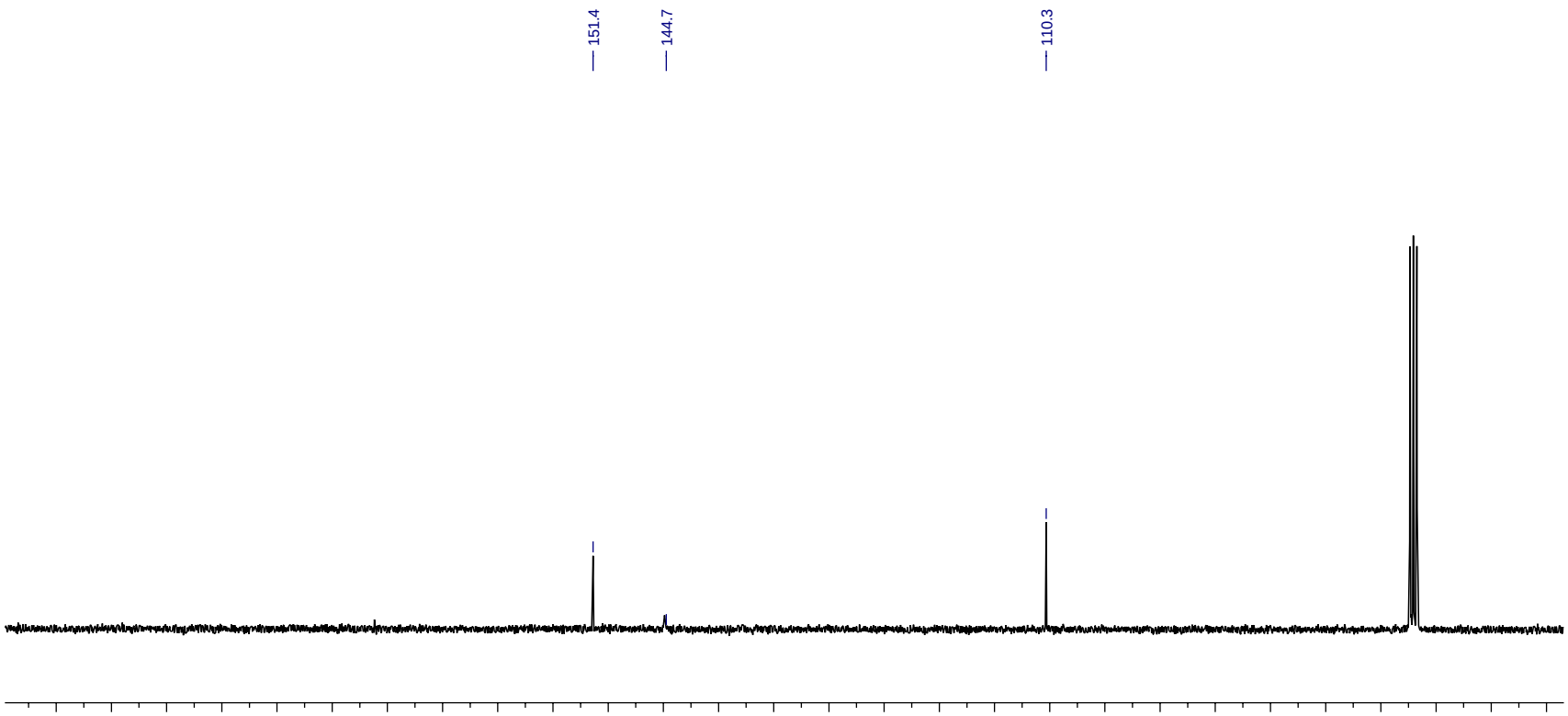
Appendix 12: ^{1}H-NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (**38**).



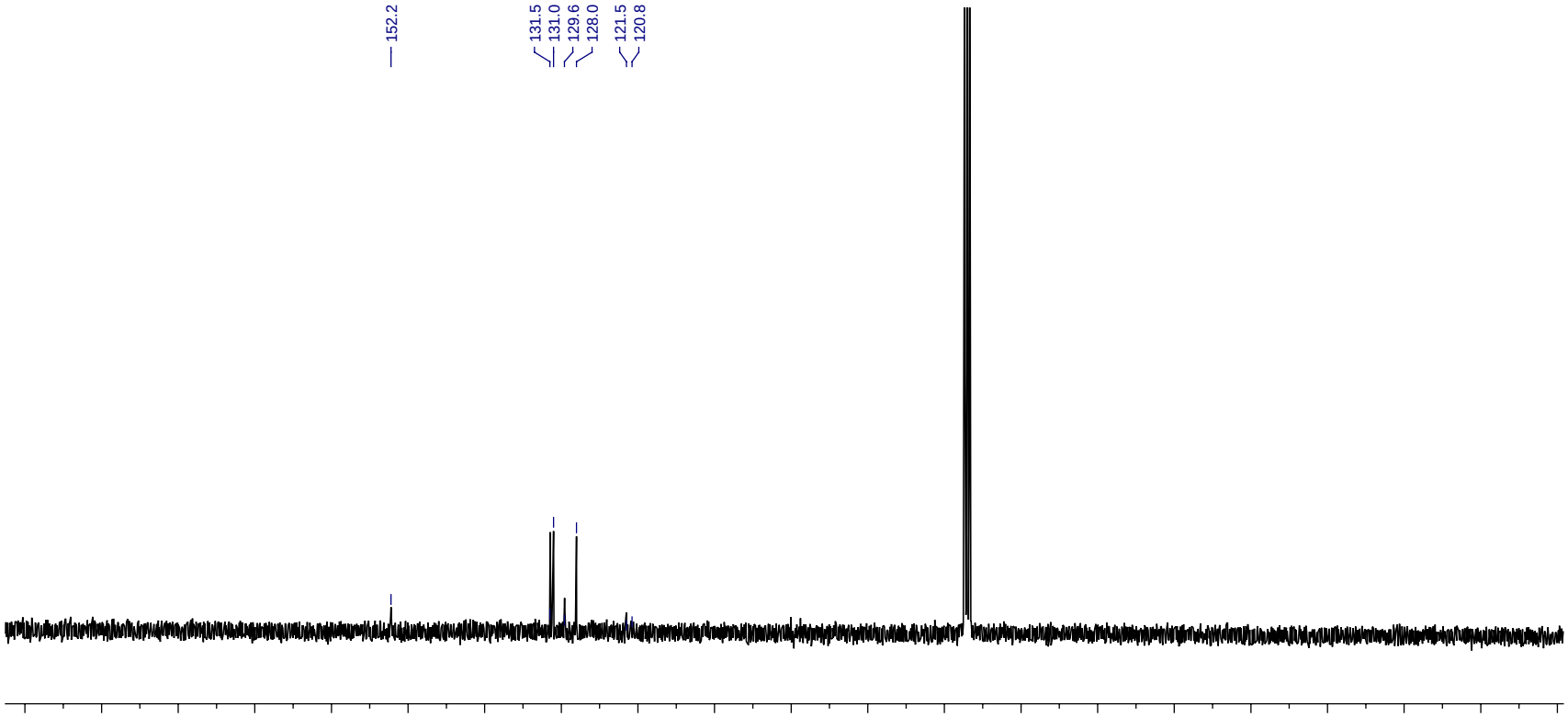
Appendix 13: ^{13}C-NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (**38**).



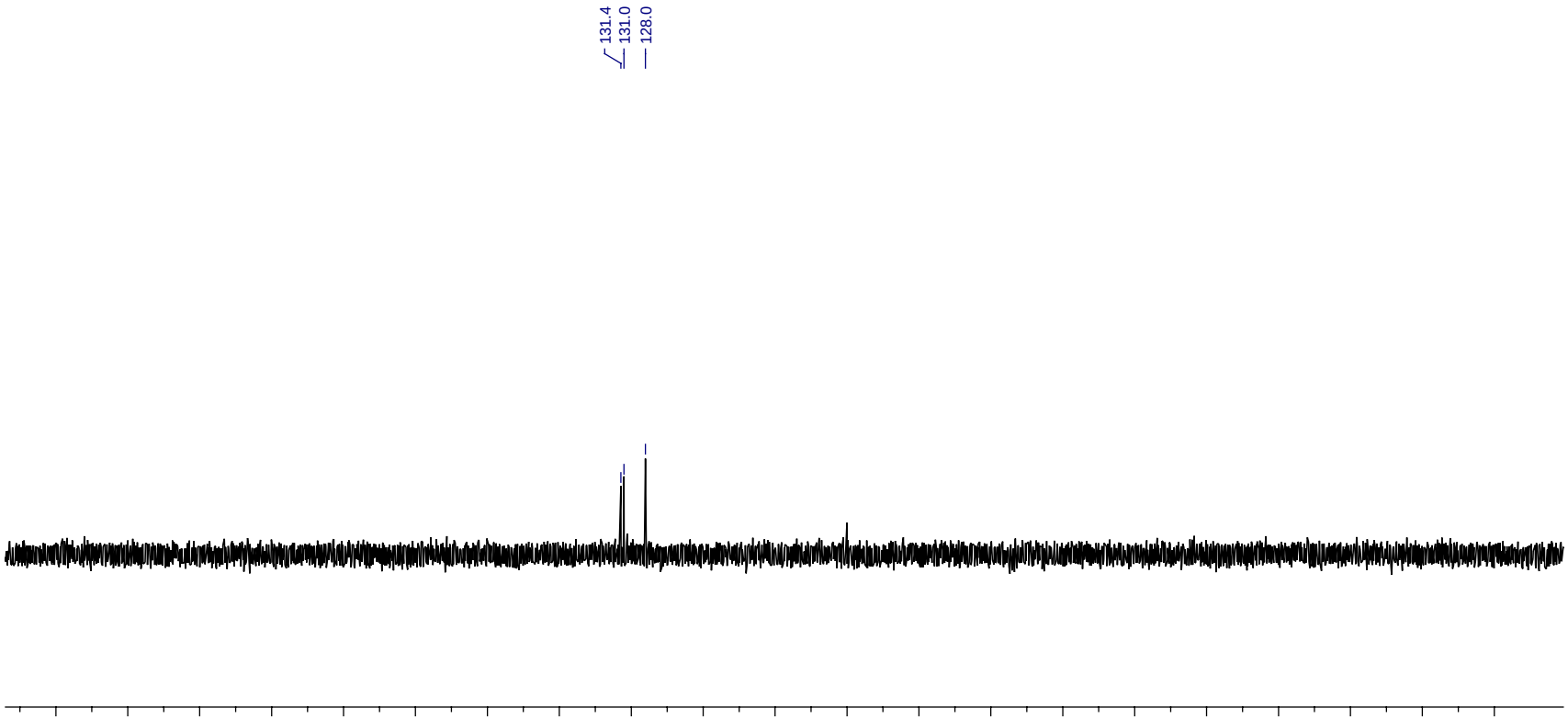
Appendix 14: DEPT-135 spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (**38**).



Appendix 15: ^{13}C-NMR spectrum of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**39**).



Appendix 16: ^{13}C-NMR spectrum of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**40**).



Appendix 17: Dept-135 NMR spectrum of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**40**).