ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS OF THIOPHENE-BASED CONJUGATED POLYMERS

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 (Ph.D)

BY
ADDISU GETACHEW

JULY 12, 2007

July 16, 2007

To: The Chairman,
Department of Chemistry

From: Wendimagegn Mammo

Subject: Addisu Getachew MSc. Project

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

Thank you.

_____.

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ADDISU GETACHEW

DEPARTMENT OF CHEMISTRY

SCIENCE FACULTY

JULY 12, 2007

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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.

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

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Above all, I would like to acknowledge the Department of Chemistry, AAU, for giving me the opportunity to work on this MSc. Project.

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List of abbreviation

EDTA: Ethylenediaminetetracetic acid
h: hour(s)

HOMO: Highest Occupied Molecular Orbital

^{o}C: degree Celsius

%: percentage

dd: doublets of doublet

d: doublet

DEPT: Distortionless enhancement by polarization transfer

DME: Dimethoxy ethane

DMF: Dimethyl formamide

DMSO: Dimethyl sulfoxide

dppf: diphenylphosphinoferrocene

dppp: bis-diphenylphosphinopropane

IR: Infrared

J: coupling constants

LUMO: Lowest Unoccupied Molecular Orbital

m: multiplet

NBS: *N*-Bromosuccinamide

NMR: Nuclear Magnetic Resonance

PATs: Poly(3-alkyl)thiophenes

PLEDs: Polymer light emitting diodes

Pyr: Pyridine

s: singlet

t: triplet

THF: Tetrahydrofuran

1. Introduction

Polymers are macromolecules built up by the linking of large number of much smaller molecules. The smaller molecules that combine with each other to form polymer molecule are termed monomers, and the reactions by which they combine are termed polymerization [1].

Polymers can be synthetic and natural. Synthetic polymers are usually considered to be good insulators and the insulating properties of polymers are used in many applications of plastics, such as encapsulating of electrical materials and cases for batteries. On the other hand, natural polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life [2].

Organic polymers, which have a framework of alternating single and double carbon-carbon bonds, are termed conjugated polymers. Although the chemical structure of these materials is represented as alternating single and double bonds, in reality, the electrons that constitute the л-bonds are delocalized over the entire molecule. The simplest molecule one can imagine is polyacetylene (Figure 1), a linear hydrocarbon chain consisting of alternating single and double bonds.

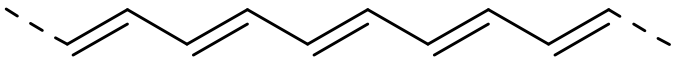


Figure1. Structure of polyacetylene.

Most polymers act as an electrical insulator and originally, it was believed that all polymers were insulators, but the use of polymers will undoubtedly move from primarily passive materials such as coating or insulating containers, to active materials with useful optical, electrical, energy storage and mechanical properties. Indeed, this development has already begun with the discovery and study of conducting polymers. MacDiarmid, Shirakawa and Heeger [3] brought the unique properties of conjugated polymers to the fore in 1977 when they discovered that chemically doping of these materials resulted in increasing in electrical conductivity over several

orders of magnitude. Since then, electrically conducting materials based on conjugated polymers have been applied in diverse items.

Thiophene (C_4H_4S), a five-membered heterocyclic aromatic ring and colorless liquid at room temperature, was a target compound as a potential precursor for polymer synthesis. Indeed, in the field of conjugated polymers, polythiophenes (thiophene-based polymers and oligomers) have received significant attention for their unique electrical properties, ability to exhibit environmental stabilities, the ease of derivatization and ability to be polymerized by a variety of chemical and electrochemical methods[4,5,6] . Other polymers such as polypyrrole [6], polyaniline [8] and poly(*p*-phenylene) [9] (Figure 2) were prepared but all these polymers do not still have good stability.

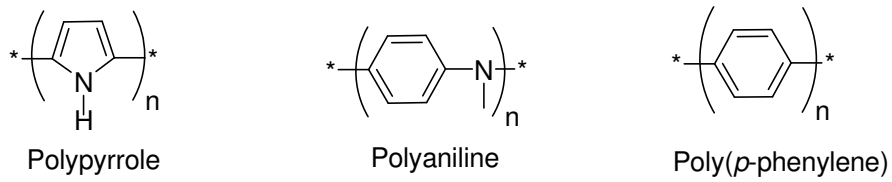


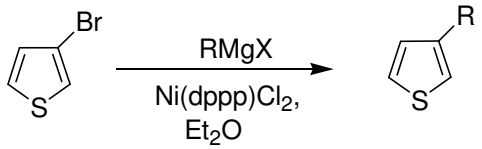
Figure2. Structures of some conjugated polymers.

2. Background

2.1 Synthesis of substituted thiophenes

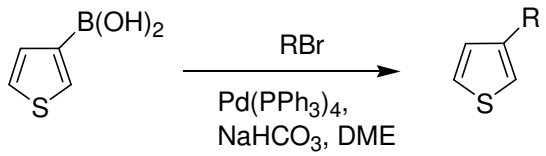
While unsubstituted polythiophenes are insoluble and infusible, alkyl chain derivatization at the 3-postion induces solubility and fusibility making them true thermoplastics. The addition of side chains on to the aromatic back bone does not only allow an easy processing of the polymeric materials but can also modify the electronic properties of the resulting polymer [10]. A variety of substituted thiophenes were used as starting materials to produce processable polymers. The syntheses of derivatives of thiophene (monomers) were achieved by well-known routes. Grignard coupling is a general, versatile method of alkylation and arylation of heterocyclic compounds in the presence of catalytic amount of $[NiCl_2(dppp)]$, where dppp = $Ph_2P(CH_2)_3PPh_2$.

3-bromo-, 2,5-dibromo-, and 3,4-dibromothiophenes react with alkyl and aryl Grignard reagents at room temperature or at a reflux temperature to give the cross-coupling products[11] as shown in Scheme 1.



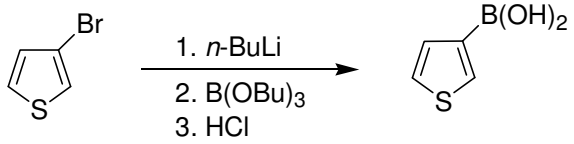
Scheme 1. Grignard coupling reaction to give 3-substituted thiophenes.

The boronic acid derivatives of thiophene serve as thiophene-group donors during the coupling reactions with alkyl or aryl halides in the presence of low-valent palladium(0) as a catalyst [12] to yield alkyl or aryl thiophenes (Scheme 2).



Scheme 2. Suzuki coupling reaction to give substituted thiophene.

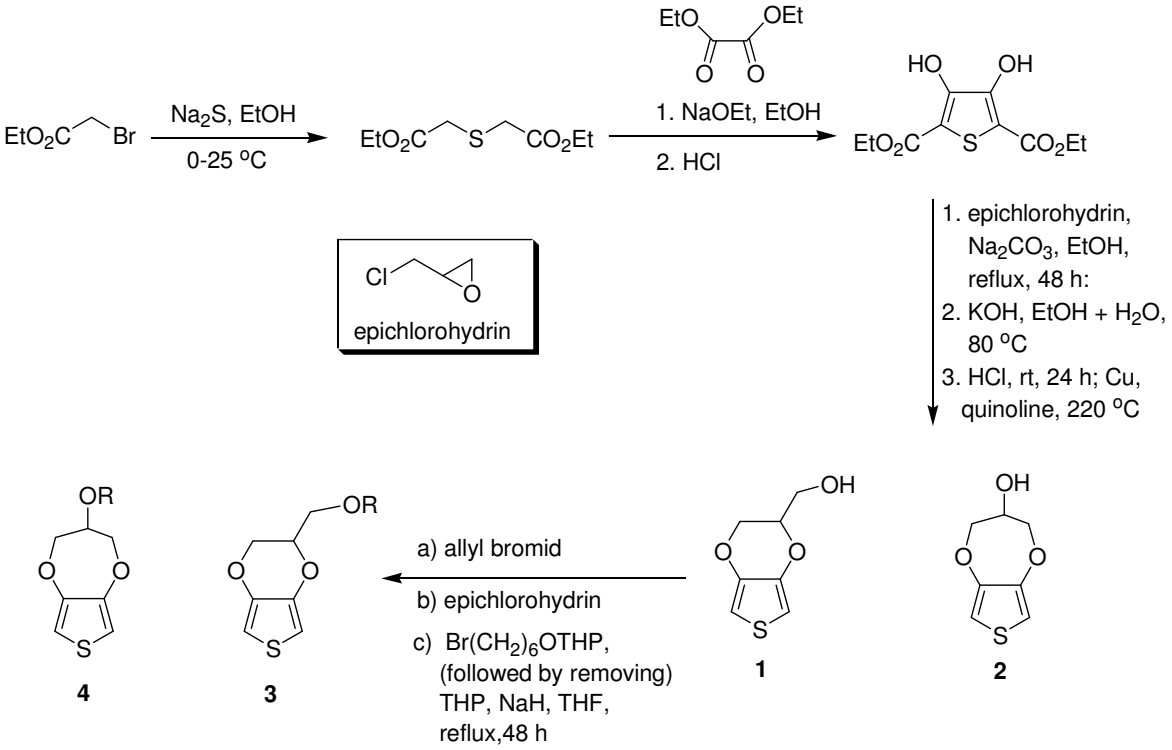
The boronic acid can easily be prepared from 3-bromothiophene by treating it first with *n*-BuLi and tributyl borate followed by hydrolysis of the intermediate boronate ester with hydrochloric acid [13] (Scheme 3).



Scheme 3. Synthesis of 3-thiophene boronic acid.

On the basis of electronic effects alone, the energy of polythiophenes decreases with alkyl substitution and is further diminished with alkoxy functionalization [14, 15]. However, lowering of the band-gap energy (the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) by di-substitution with

electron-donating pendants is limited by the accentuated steric effects of the substituents on adjacent thiophene rings which forces them out of coplanarity with a consequent of reduction of conjugation and electrical conductivity [14-17]. An approach towards minimizing steric effects of di-substituted thiophene, whilst retaining the favorable electronic effects, was derived, which involved tying the 3,4-substituents back in to the ring [18]. In this approach, ethylenedioxythiophene and 1,3-propylenedioxythiophene incorporating reactive pendant ω-moieties of hydroxyl, allylic and epoxy groups were synthesized[19] (Scheme 4).



R= a, b and c

Scheme 4. Synthesis of ethylenedioxy- and 1,3-propylenedioxythiophenes.

2.2. Polymerization of substituted thiophenes.

Since the first synthesis in 1986[20, 21], poly(3-alkyl)thiophenes (PATs) have attracted interest owing to the significant improvement in solubility resulting from the grafting of flexible hydrocarbon chains on to the polythiophene backbone. This processability and the prospect of

industrial applications have triggered a strong renewal of interest in chemical synthesis. Thus, polymerization of 3-alkylthiophenes using $FeCl_3$ as oxidant acquired a growing importance and became a well-know method to polymerize thiophenes [22, 24]. However, this synthetic method used to make PATs generate a large number of defects due to the random coupling at the 2,5-positions on the thiophene ring. Since the thiophene ring is a five-membered ring that is polymerized through the 2- and 5-positions, substitution introduces directionality in the polymer and every time a monomer is incorporated in the growing polymer chain, it can add with the head (2-position) or the tail (5-positoin) first. This gives three possible couplings (Figure 3). These are:

- 2,5', or head-tail (HT), coupling
- 2,2', or head-head (HH), coupling
- 5,5', or tail-tail (TT), coupling

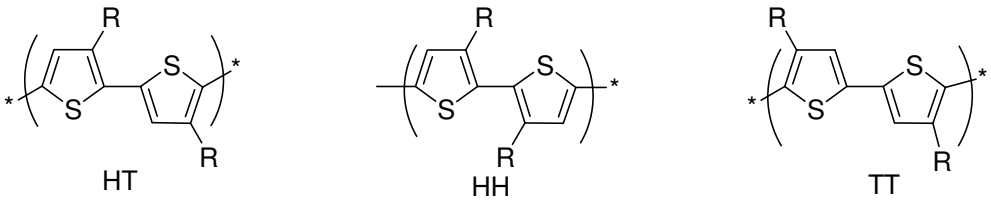
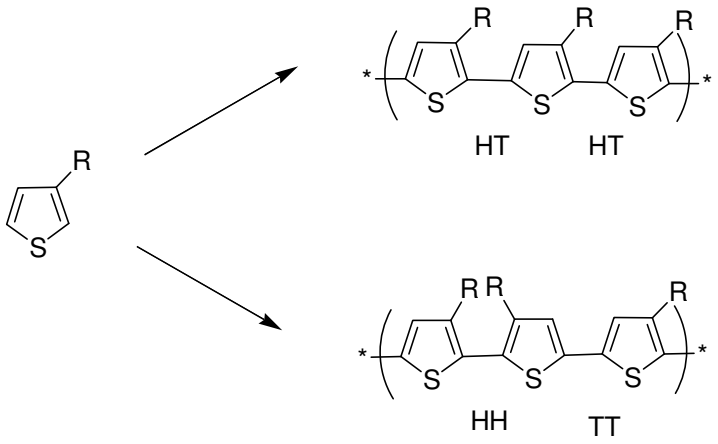


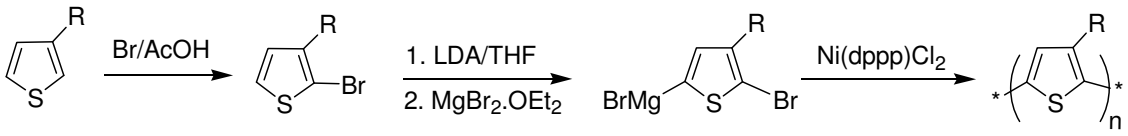
Figure 3. Structure of substituted derivatives of polythiophene in HH, HT and TT couplings [23].

A structurally homogenous head-to-tail (HT) arrangement would therefore improve the material's electronic and optical properties, since any defect in the ideal HT induces a severe repulsion between substituents and thus a distortion of the conjugated chain with a loss of effective conjugation (Scheme 5).



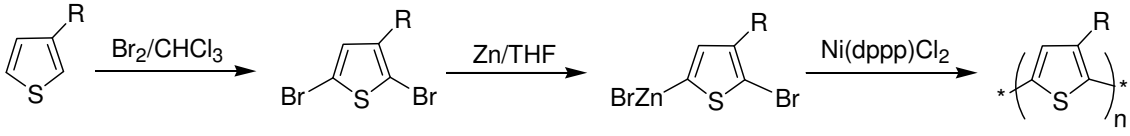
Scheme 5. Defects in head-to-tail that results in distortion.

In order to circumvent this obstacle, new regiospecific chemical syntheses have been proposed. These methods are based on the selective formation of an organometallic group at a selected α-position of the thiophene ring. Thus McCullough *et al*. have developed a synthesis based on the lithiation of 2-bromo-3-alkylthiophenes at the 5-position followed by metal exchange to obtain the Grignard compound, which is then polymerized by cross- coupling using $Ni(dppp)Cl_2$ as catalyst [26] (Scheme 6).



Scheme 6. Regioselective synthesis of PATs (McCullough *et al*. method).

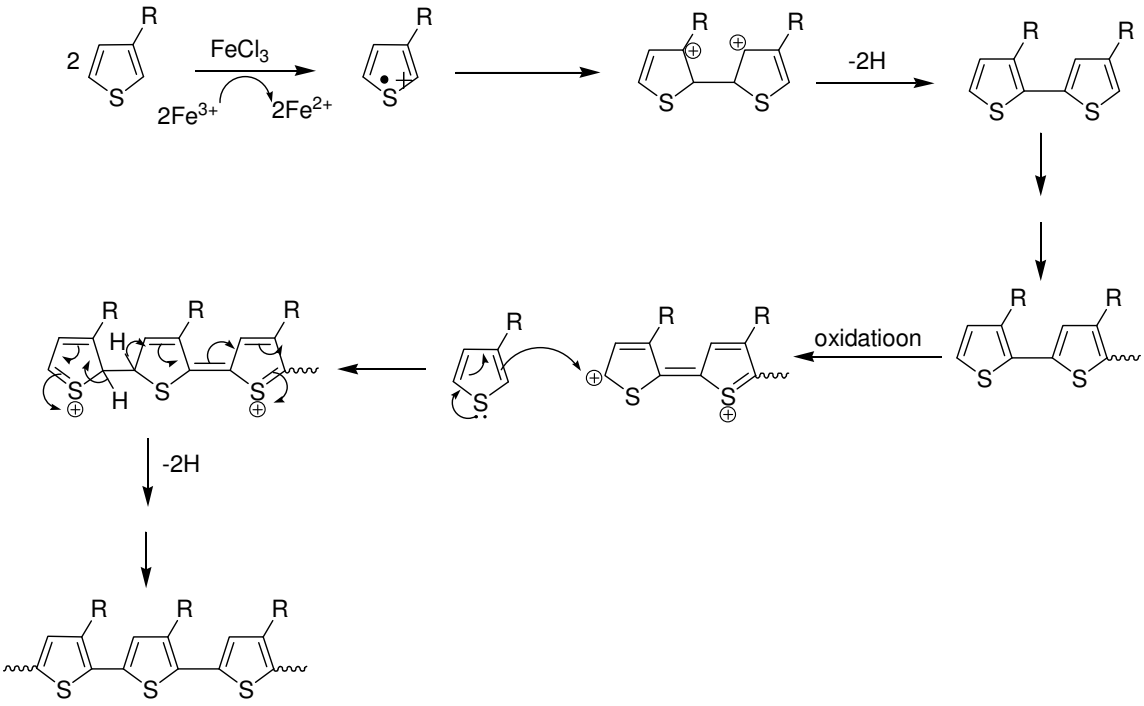
Another approach reported by Rieke *et al.* involves the regiospecific formation of an organozinc compound by the reaction of dibromo-3-alkylthiophenes with highly reactive zinc, and subsequent nickel-catalyzed polymerization [27] (Scheme 7).



Scheme 7. Regioselective synthesis of PATs (Rieke *et al.* method).

Polythiophenes can also be synthesized electrochemically, by applying potential across a solution of the monomer to be polymerized. Generally, polythiophenes can be obtained either electrochemically or chemically, using oxidants or cross coupling catalysts. The chemical method offers two advantages compared with electrochemical synthesis of polythiophenes: a greater selection of monomers, and, using the proper catalyst, the ability to synthesize perfectly regioregular substituted polythiophenes.

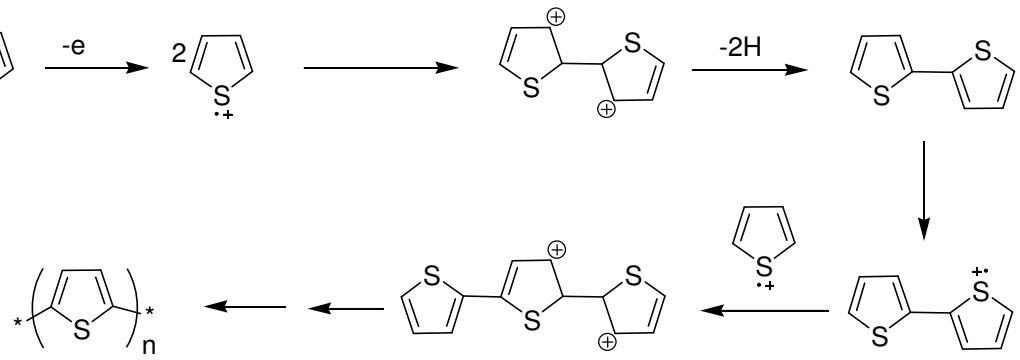
The mechanism of propagation for regioselective polymerization by the ferric chloride method is believed to proceed as shown in Scheme 8.



Scheme 8. Polymerization mechanism of 3-substituted thiophene with $FeCl_3$ as oxidant.

The propagation is believed to be initiated by a thiophene radical cation. But because polymer chain cannot be neutral under the strong oxidizing conditions, as soon as oligomers are formed, the propagation is formed by carbocation [28].

In an electrochemical polymerization, a potential is applied across a solution containing thiophene and an electrolyte, producing a conductive polythiophene film on the anode [29]. Electrochemical polymerization is convenient, since the polymer does not need to be isolated and purified, but it produces structures with varying degrees of structural irregularities, such as cross-linking. The mechanism of the reaction is shown in Scheme 9.



Scheme 9. Electrochemical polymerization mechanism of thiophene.

As shown in Scheme 9, oxidation of monomers produces a radical cation which can then be coupled with a second cation to form a di-cation dimer. The process repeats and hence the polymer chain grows.

2.3. Conductivity studies of polythiophenes

Uncharged polythiophenes have very low conductivity. When the π-system in the polymer is partially oxidized or reduced, the conductivity increases by several orders of magnitude. This process is usually referred to as *p*-doping or *n*-doping of the polymer, respectively. A fully doped polythiophene has approximately one positive charge on every fourth thiophene ring along the polymer backbone [30, 31] (Figure 4).

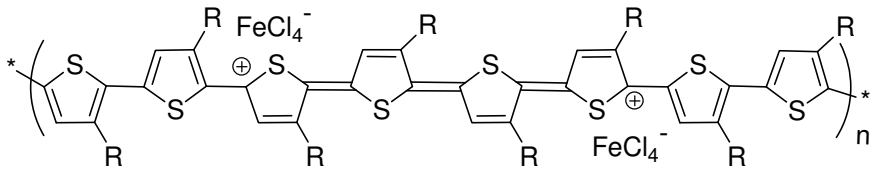


Figure 4. Fully doped poly thiophene containing bipolaron [30].

Treating the polymer with an oxidizing agent, usually iodine, bromine or ferric chloride normally does the *p*-doping. Iodine and bromine produce high conductivities [32] but are unstable and slowly evaporate from the materials [33]. *n*-Doping is so much less common because the earths atmosphere is oxygen-rich, which creates an oxidizing environment. An electron-rich *n*-doped polymer will react immediately with elemental oxygen to a de-doped (re-oxidized to the neutral state) polymer. For some samples of poly(3-dodeyclthiophene) doped with iodine, the conductivity can approach 1000 S/ cm [32]. Poly(3-octylthiophene), prepared by the $FeCl_3$ method and doped by $FeCl_3$ or iodine, has a conductivity of approximately 20-30 S/ cm [34].

2.4. Application of polythiophenes

Since the first report in 1990 of polymer light emitting diodes using PPV (poly(*p*-phenylenevinylene)) as the light emitting material [35], considerable effort has been directed towards the preparation of materials with improved properties such as wide tunability of emission wavelength and high photoluminescence and electroluminescence efficiency. The color of the emission is directly dependent on the extent of conjugation along the π-system. Short conjugation gives blue-shifted emission and long conjugation gives red-shifted emission from the polymer. Polymer light emitting diodes (PLEDs) prepared from poly(3-(4'-octylphenyl)thiophene (**5**), poly(3-(4''-octylphenyl)-2,2'-bithiophene) (**6**), and poly(3-cyclohexylthiophene) (**7**) showed electroluminescence from blue to near-infrared [36].

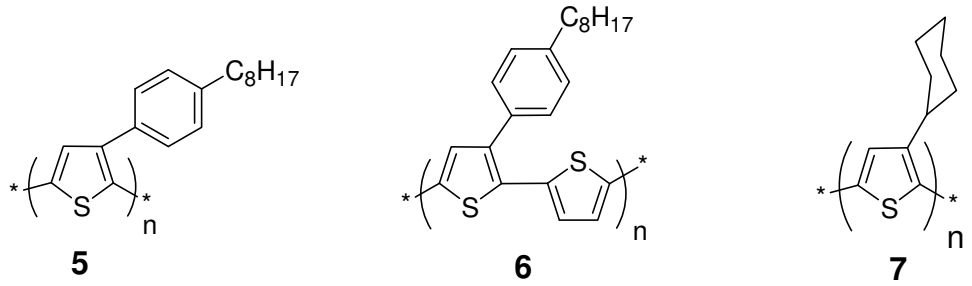


Figure 5. Some electroluminescent substituted polythiophenes.

Phenyl-substituted polythiophenes containing oxygenated side chains may be capable of solvating ions and thus serve to transport ions. Such polymers may find applications in light emitting electrochemical cells. Some of such kinds of polymers are poly[3-(2',5'-bis(1'',4'',7''-trioxaoctyl)phenyl)thiophene] (**8**) and poly[3-(2'',5''-bis(1''',4''',7'''trioxa-octyl)phenyl)-2,2'-bithiophene] (**9**) [37].

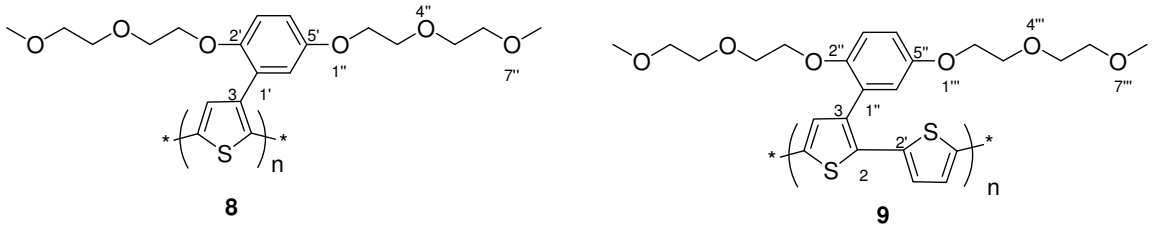


Figure 6. Some substituted polythiophenes containing oxygenated side chains.

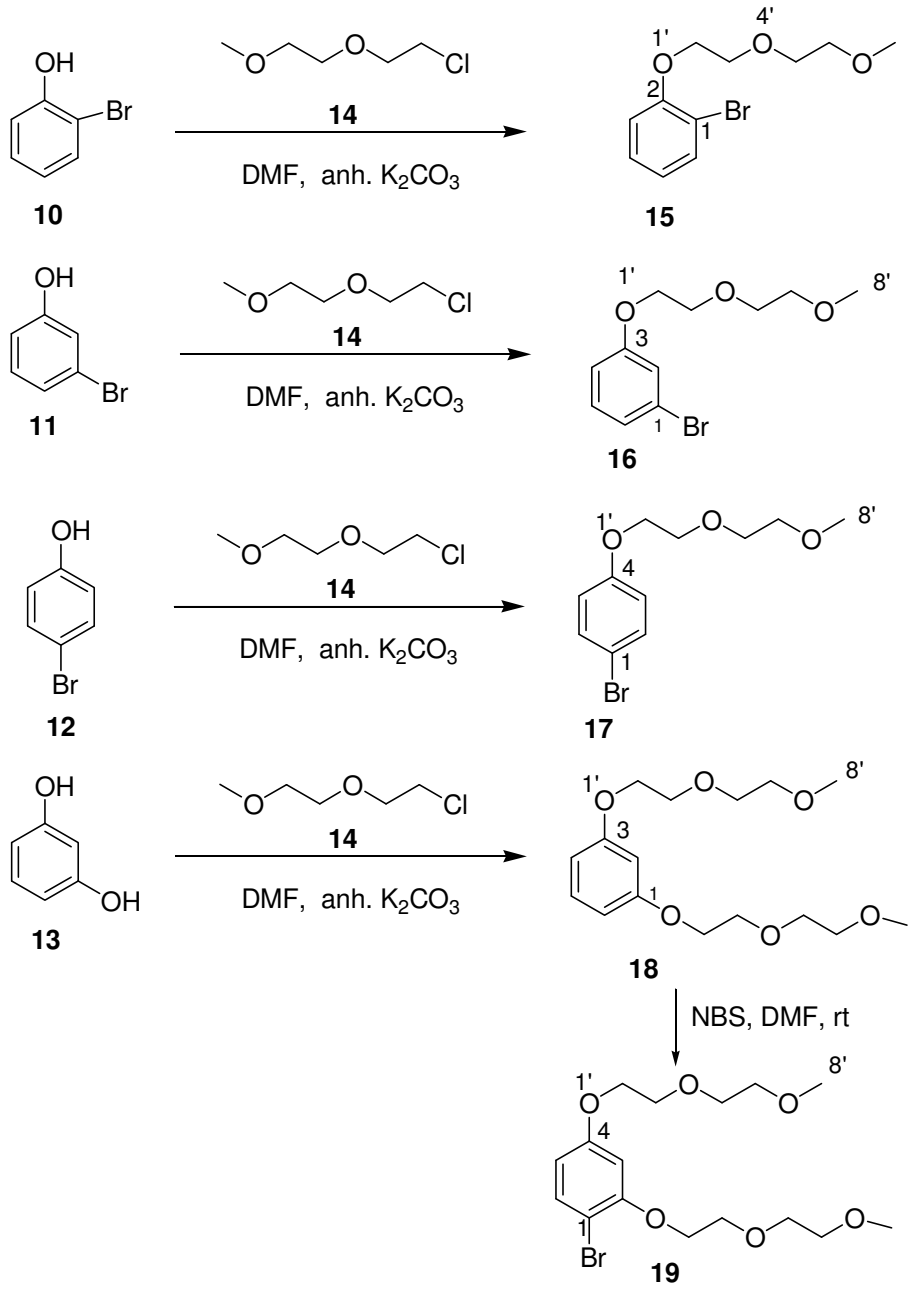
The conjugated polythiophene backbone is capable of transporting electrons while the 1,4,7-trioxaoctyl side chains are capable of solvating ions and thus serves to transport ions.

3. Objective

The objective of this MSc. project is to synthesize substituted 3-phenylthiophenes and to subsequently polymerize these monomers to the corresponding polymers by oxidative polymerization using ferric chloride or copper(II) perchlorate hexahydrate. The synthesis of the monomers will be carried out starting from a variety of compounds such as 2-bromophenol, 3-bromophenol, 4-bromophenol, 1,4-dibromobenzene and resorcinol. 2-bromophenol, 3-bromophenol, 4-bromophenol will be *o*-alkylated with appropriate alkylating agents and the resulting bromides will be coupled with 3-thiopheneboronic acid to afford substituted monomers. Grignard coupling of 1,4-dibromobenzene with octylbromide will give the alkylated product which will be coupled with 3-thiophene boronic acid. Resorcinol will be *o*-alkylated, brominated and coupled with 3-thiophene boronic acid. The 3-phenylthiophenes will be functionalized at the 2-position and another thiophene unit will be incorporated by employing the Suzuki or Stille coupling. The 3-phenylthiophenes and bithiophenes will be polymerized using $FeCl_3$ or copper(II) perchlorate hexahydrate. The intermediate compounds will be characterized by ^{1}H-NMR, C^{13}, UV-Vis and IR spectroscopy.

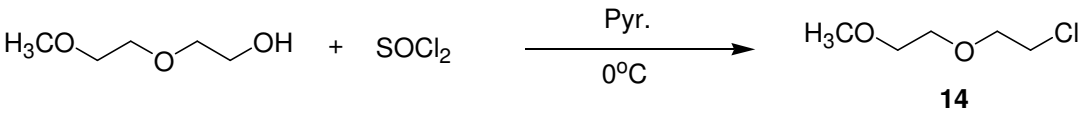
4. Results and Discussion

In the course of this project, a number of thiophene-based monomers were synthesized. Some of these monomers were subjected to polymerization by the oxidative polymerization technique using $FeCl_3$ and copper(II) perchlorate hexahydrate. The attempt to build the monomer units for the polymerization reactions started with 2-bromophenol (**10**), 3-bromophenol (**11**), 4-bromophenol (**12**), resorcinol (**13**) and 1,4-dibromobenzene (**21**) as starting materials. The first stage involved alkylation of **10**, **11**, **12**, **13** with 1-chloro-2-(2-methoxyethoxy)ethane in the presence of anhydrous K_2CO_3, which resulted in the formation of compounds **15**-**18** as shown in Scheme 10. Compound **18** was further brominated with NBS to yield compound **19**.



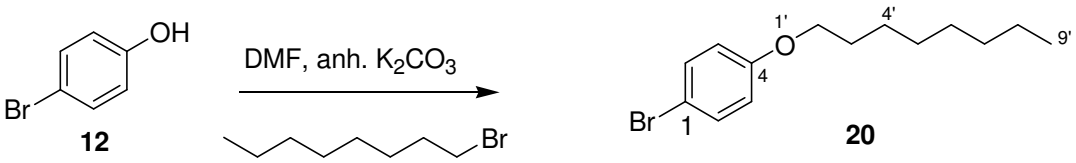
Scheme 10. Synthesis of alkoxy substituted bromobenzenes.

1-Chloro-2-(2-methoxyethoxy)ethane (**14**), which was used in the alkylation of the phenolic compounds shown in Scheme 10, was synthesized by treating 2(2-methoxyethoxy)ethanol with thionylchloride ($SOCl_2$) and pyridine according to Scheme 11. After the reaction was complete, diethyl ether was added to the product mixture to precipitate pyridinium chloride. Unreacted thionylchloride was removed by careful addition of water in to the ether solution.



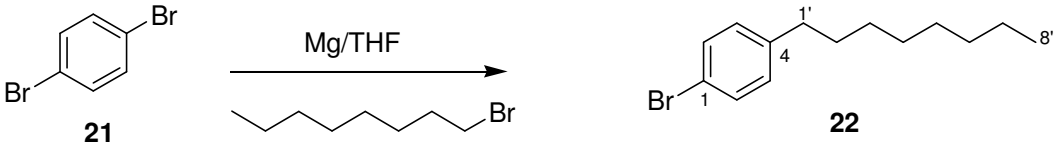
Scheme 11. Synthesis of 1-chloro-2-(2-methoxyethoxy)ethane (**14**)..

A similar alkylation of 4-bromophenol (**12**) with *n*-octylbromide in the presence of K_2CO_3 afforded compound **20** (Scheme 12).



Scheme 12. Synthesis of 1-bromo-4-octyloxybenzene (**20**).

1,4-Dibromobenzene (**21**) was also converted to 1-bromo-4-octylbenzene (**22**) by first treating it with magnesium in ether to form the corresponding Grignard reagent followed by alkylation with *n*-octylbromide as shown in Scheme 13.



Scheme 13. Synthesis of 1-bromo-4-octylbenzene (**22**).

The alkoxy bromobenzene compounds (compounds **15**, **16**, and **19)** were found to be liquids while compound **17** solidified up on cooling. These compounds were characterized by their ^{1}H- and C^{13}-NMR spectral data (Table 1). Since all four compounds have the same side chain containing a methoxy group, and methylene protons flanked between oxygen atoms, resonances appeared between δ 3.2 - 4.7 owing to these protons as indicated in Table 1.

Table 1. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **15**-**19**.

15	**16**	**17**	**18**	**19**
7.25 (dd, *J* = 8, 1.6 Hz, 1H, H-6) 7.14 (*dt*, *J* = 7.8, 1.6 Hz, 1H, -4) 6.82 (*dd*, *J* = 8, 1.2 Hz, 1H, H-5) 6.72 (*dt*, *J* = 7.8, 1.2 Hz, 1H, H-3) 4.07 (*t*, *J* = 4.8 Hz, 2H, H-2') 3.80 (*t*, *J* = 4.8 Hz, 2H, H-3') 3.67 (*t*, *J* = 4.2 Hz, 2H, H-5') 3.28 (*s*, 3H, H-8') 3.47 (*t*, *J* = 4.2 Hz, 2H, H-6')	7.03-7.11 (*m*, 3H, H-2, H-5, H-6) 6.84 (*m*, 1H, H-4) 4.07 (*t*, *J* = 4.8 Hz, 2H, H-2') 3.81 (*t*, *J* = 4.8 Hz, 2H, H-3') 3.67 (*t*, *J* = 4 Hz, 2H, H-5') 3.53 (*t*, *J* = 4 Hz, 2H, H-6') 3.36 (*s*, 3H, H-8')	7.20 (*d*, *J* = 8.8 Hz, 2H, H-2, H-6) 6.65 (*d*, *J* = 8.8 Hz, 2H, H-3, H-5) 3.92 (*t*, *J* = 4.8 Hz, 2H, H-2') 3.67 (*t*, *J* = 4.8 Hz, 2H, H-3') 3.54 (*t*, *J* = 4.4 Hz, 2H, H-5') 3.41 (*t*, *J* = 4.4 Hz, 2H, H-6') 3.23 (*s*, 3H, H-8')	7.10 (*dd*, *J* = 6.8, 2.8 Hz, 1H, H-5) 6.48 (*d*, 2H, H-4, H-6) 6.45 (*d*, *J* = 2.8 Hz, 1H, H-2) 4.03 (*t*, *J* = 4.8 Hz, 4H, H-2') 3.76 (*t*, *J* = 4.8 Hz, 4H, H-3') 3.63 (*t*, *J* = 4Hz, 4H, H -5') 3.50 (*t*, *J* = 4 Hz, 4H, H-6') 3.32 (*s*, 6H, H-8')	7.24 (*d*, *J* = 8.8 Hz, 1H,H-6) 6.27 (*dd, J* = 8.8, 2.4 Hz, 1H, H-5) 6.43 (*d, J* = 2.4 Hz, 1H, H-3) 3.88-3.82 (*m*, 4H, H-2') 3.62-3.56 (*m*, 4H, H-3') 3.51-3.43 (*m*, 4H, H-5') 3.31-3.30 (*m*, 4H, H-6') 3.12 (*s*, 6H, H-8')

The ^{1}H-NMR spectrum of compound **15** revealed four aromatic proton resonances at δ 6.72 (*dt*) , 6.82 (*dd,*), 7.14 (*dt*) and 7.25 (*dd*) in agreement with a 1,2-disubstituted benzene ring. On the contrary, in the ^{1}H-NMR spectrum of compound **16**, a one-proton signal appeared at δ 6.84 (*dd*) and an unresolved multiplet appeared between δ 7.03-7.11, integrating for three protons, corresponding to the 1,3-disubstituted benzene ring protons. The aromatic proton resonances of compound **17** appeared as clean doublets at δ 7.20 (2H) and 6.65 (2H) as expected for a 1,4-disubstituted aromatic system .

The C^{13}-NMR spectra of compound **15**-**17** and **19** (Table 3) showed six carbon resonances in the aromatic region, of which two are quaternary. The remaining five carbon resonances appeared between δ 72.7 and 59.3 and are due to the carbon atoms on the 1',4',7'-trioxaoctyl side chain. Thus, both the ^{1}H- and C^{13}-NMR spectral data agreed with the structures of compounds **15 – 17** and **19.**

The pure *p*-octyloxybromobenzene (**20**) and *p*-octylbromobenzene (**22**) were also liquids but **20** was yellowish in color and **22** was colorless liquid after distillation under reduced pressure. The structures of these compounds were confirmed by their ^{1}H-NMR and C^{13}-NMR spectra. Thus, in the ^{1}H-NMR spectrum of compound **20**, two doublets appeared at δ 7.38 (H-2 and H-6) and δ 6.80 (H-3 and H-5), which integrated for two protons each and are characteristic of a 1, 4-disubstituted benzene. The proton resonance at δ 3.93 (*t*) was assigned for the C-2' methylene protons. The quintet signal at δ 1.71 was assigned to H-3'. The remaining methylene proton resonances appeared as an unresolved signal at δ 1.30- 1.10 and the signal due to the methyl protons appeared at δ 0.9 as a distorted triplet. Similarly, the doublets characteristics of *p*-substituted benzene were observed in the ^{1}H-NMR spectrum of compound **22**. Thus, the doublet at δ 7.31 is assignable to H-2 and H-6 and the doublet at δ 6.96 is attributed to H-3 and H-5. The benzylic methyl protons gave a signal at δ 2.49 (*t*) and the C-2' methylene protons resonated at, δ 1.54 (*q*). The remaining methylene protons gave an unresolved signal centered at δ 1.27. The triplet at δ 0.9 (*t*) is assigned to the methyl protons (Table 2). In the C^{13}-NMR spectrum of compounds **20** and **22**, six-carbon signals were observed in the aromatic region of which two are due to quaternary carbons as determined by the DEPT-135 spectra. The C^{13} signal of C-4 in

compound **20** appeared down field compared to the C-4 resonance of compound **22** owing to the attachment of an electron withdrawing oxygen atom to C-4 of compound **20** (Table 3).

Table 2. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **20** and **22**.

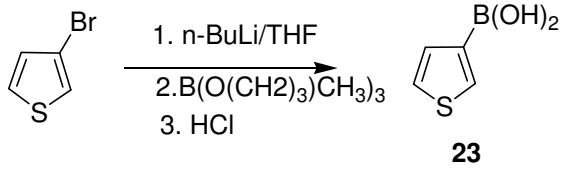
20	**22**
7.38	7.31
(*d*, *J* = 9.2 Hz, 2H, H-2)	(*d*, *J* = 8.4 Hz, 2H, H-2, H-6)
6.80	6.96
(*d*, *J* = 9.2 Hz, 2H, H-3)	(*d*, *J* = 8.4 Hz, 2H, H-3, H-5)
3.93	2.49
(*t*, *J* = 6.8 Hz, 2H, H-2')	(*t*, *J* = 4 Hz, 2H, H-1')
1.71	1.57
(q, 2H, H-3')	(*q*, 2H, H-2')
1.30-1.10	1.27
(*m*, 10H, H-4', H-5', H-6', H-7', H-8')	(*m*, 10H, H-3', H-4', H-5', H-6', H-7')
0.9	0.9
(*t*, 3H, H-9')	(*t*, 3H, H-8')

After successful syntheses and characterization of compounds **15**-**17**, **19**, **20** and **22**, the next step was to couple these compounds with 3-substituted thiophene. The coupling reactions were conducted in two ways: the first involved the synthesis of 3-thiopheneboronic acid (**23**) and coupling of this with the aryl bromides using the Suzuki reaction[12]. Thus compounds **15, 16, 17**, and **19** were made to react with 3-thiopheneboronic acid by employing tetrakis(triphenylphosphine)Pd(0) as catalyst as depicted in Scheme 15.

Table 3 . C^{13}-NMR (100.6 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **15**-**20**, and **22**.

C	15	16	17	18	19	20	22
1	112.0	123.9	112.7	159.8	102.1	112.5	119.4
2	155.2	117.9	132.0	101.5	155.4	132.1	131.3
3	113.5	159.5	116.3	159.8	101.2	116.3	130.2
4	128.4	113.5	157.8	106.8	159.9	158.3	141.8
5	122.0	130.5	116.3	129.6	106.9	116.3	130.2
6	133.2	122.7	132.0	106.8	132.5	132.1	131.3
1’	------	-----	------	------	------	------	35.5
2’	69.0	67.6	67.5	67.2	67.3	68.2	32.1
3’	69.4	69.5	69.4	69.4	69.0	31.8	31.5
4’	------	-----	-----	-----	-----	29.4	29.6
5’	70.9	70.7	70.5	70.4	70.3	29.2	29.5
6’	71.9	71.9	71.8	71.8	71.5	26.0	29.4
7’	-----	-----	-----	-----	-----	22.7	22.9
8’	58.8	59.0	58.8	58.6	58.1	14.1	14.3

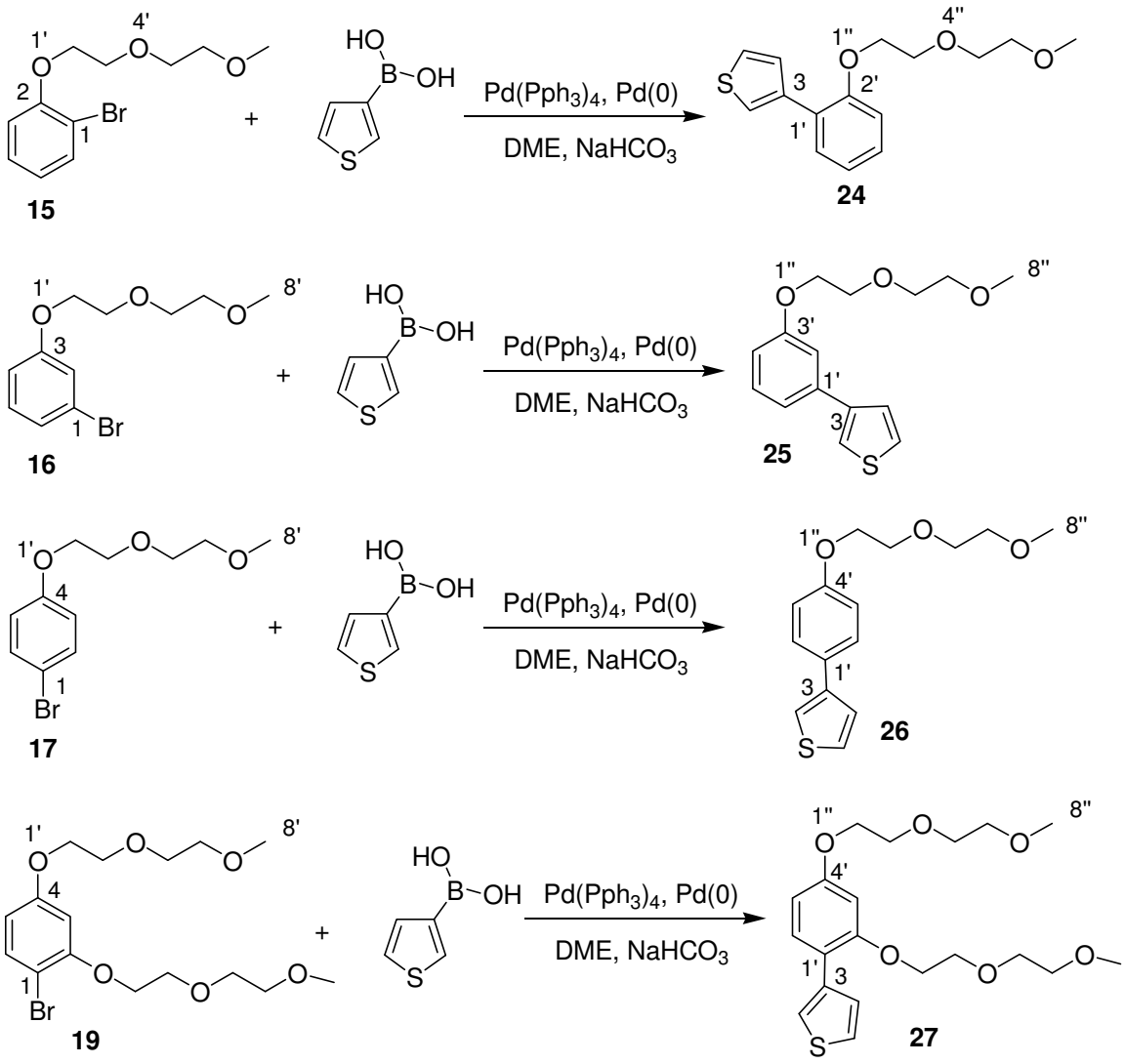
3-thiophenboronic acid (**23**) was synthesized from 3-bromothiphene (Sheme 14) in good yield by the reaction with *n*-butyllithium and tributyl borate at -78 ^{o}C under inert atmosphere followed by hydrolysis with dilute hydrochloric acid. The resulting white solid was used with out storing for a long time as it could decompose on standing



23

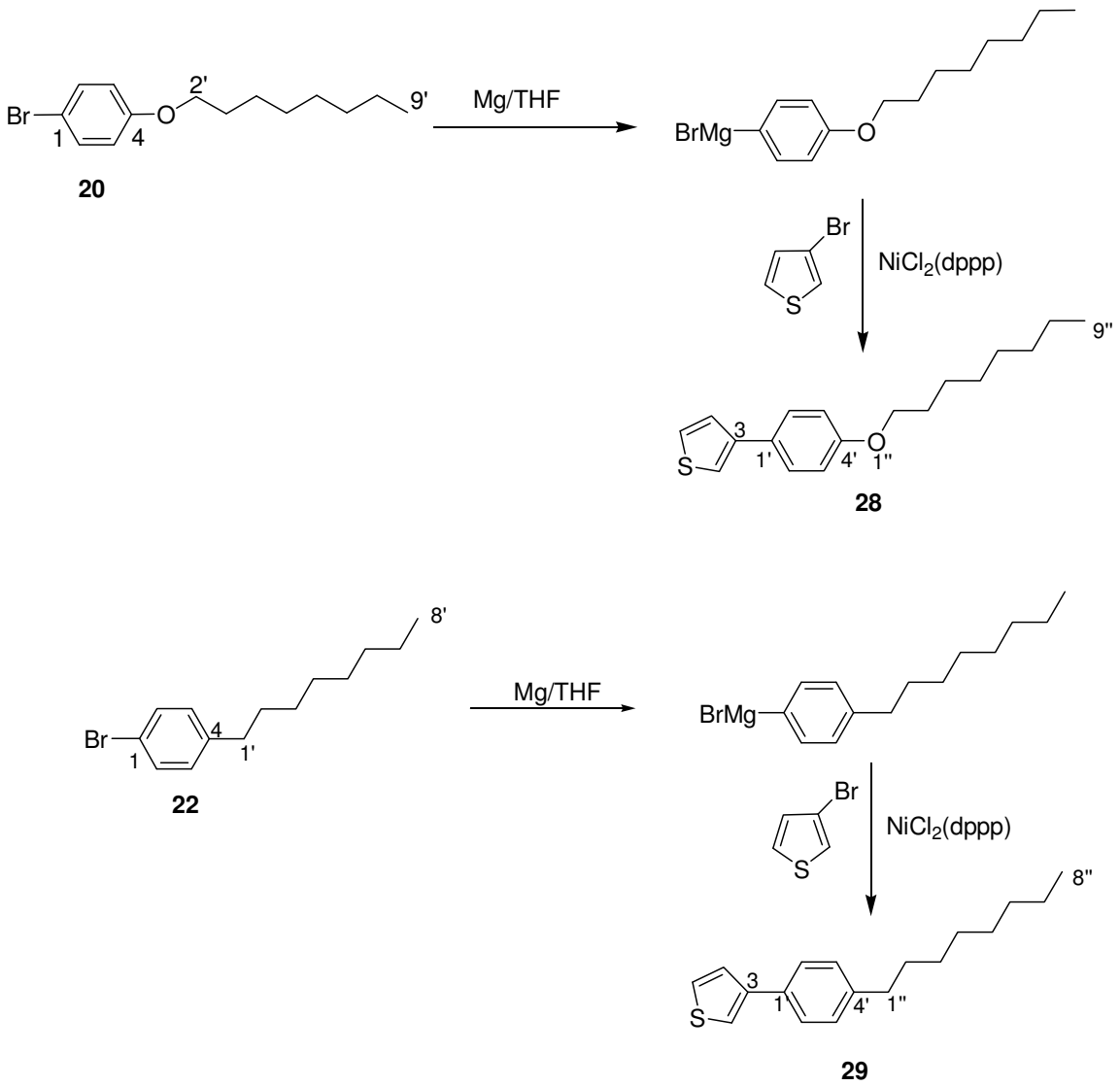
Scheme 14. Synthesis of 3-thiopheneboronic acid.

Tetrakis(triphenylphosphine)Pd(0) was prepared from palladium chloride and triphenylphosphine for use in Suzuki reactions (Experimental section).



Scheme 15. Synthesis of phenyl-substituted thiophenes by Suzuki coupling reaction.

Compounds **28** and **29** were synthesized from compounds **20** and **22,** respectively by reaction with 3-bromothiophene following the Grignard route as shown in Scheme 16.



Scheme 16. Synthesis of phenyl-substituted thiophenes **28** and **29** by Grignard reaction.

The products obtained from both the Suzuki and Grignard coupling reactions turned out to be mixtures, which needed purification by silica gel column chromatography. Compounds **26**, **28**, **29** were obtained in pure form while compounds **24**, **25** and **27** remained impure after column chromatography as revealed by the ^{1}H- and C^{13}-NMR spectra of the products. Compound **26** was obtained as white crystalline solid after passing it through a short column of silica gel using CH_2Cl_2 as a solvent and recrystallization from methanol.

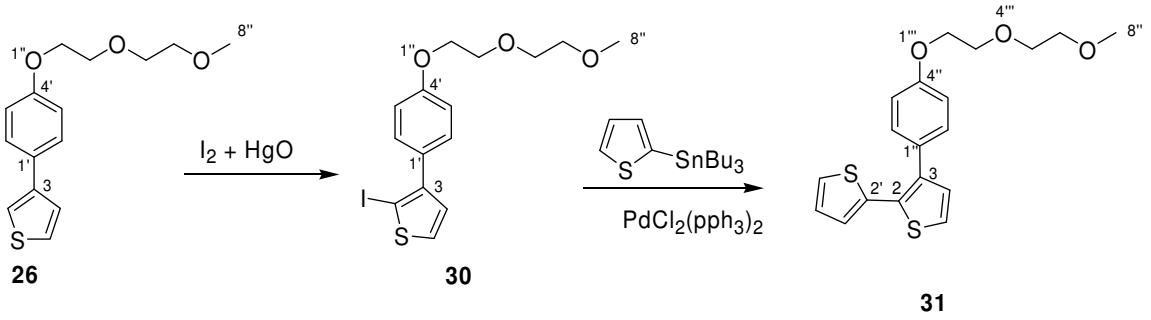
The ^{1}H-NMR spectra (Tables 5 and 4) of compounds **26**, **28**, **29** showed similar patterns because their substitution patterns are similar in both the thiophene and phenyl rings. The aromatic and

thiophene ring proton resonances appeared in the region between δ 7.56- δ 6.95. The *para*-disubstituted phenyl ring protons appeared as doublets (J = 8 - 9 Hz) integrating for two protons each while the thiophene ring protons appeared as unresolved multiplets. In the ^{1}H-NMR spectrum of compound **28** the oxygenated aliphatic proton resonances appeared at δ 3.43 (*s*, 3H), 3.61 (*t,* 2H), 3.76 (*t*, 2H), 3.90 (*t*, 2H) and 4.19 (*t*, 2H) in agreement with the presence of a 1,4,7-trioxaoctylside chain. The aliphatic protons in compound **29** gave signals between δ 0.93 and 4.01. The triplet at δ 4.01 is due to the methylene protons at the C-2". On the other hand, the aliphatic proton resonances in compound **29** appeared in the range between 0.94 and 2.67. The ^{13}C-NMR spectra (Table 6) of compounds **26**, **28** and **29** showed ten carbon resonances in the aromatic region due to the phenyl and thiophene ring carbon atoms. The signals due to C-2' and C-6' appear together since these two carbon atoms are equivalent. Likewise the signals due to C-3' and C-5' overlap as these carbon atoms are also equivalent. The remaining carbon signals agree with the structures assigned to the compounds.

Table 4 . 1H-NMR (400.13 MHz, $CDCL_3$) data (δ_{ppm}) of compound **28** and **29**

28	**29**
7.54 (*d*, J = 8.4 Hz, 2H, H-2', H-6')	7.56 (*d*, J = 8 Hz, 2H, H-2', H-6')
7.38 (*m*, 3H, H-2, H-4, H-5)	7.42 (*m*, 3H, H-2, H-4, H-5)
6.95 (*d*, J = 8.4 Hz, 2H, H-3', H-5')	7.25 (*d*, J = 8 Hz, 2H, H-3', H-5')
4.01 (*t*, J = 6.4 Hz, 2H, H-2'')	2.67 (*t*, J = 4 Hz, 2H, H-1'')
1.83 (q, 2H, H-3'')	1.69 (*q*, 2H, H-2'')
1.50-1.33 (*m*, 10H, H-4'', H-5'', H-6'', H-7'', H-8'')	1.45-1.30 (*m*, 10H, H-3'', H-4'', H-5'', H-6'', H-7'')
0.93 (*t*, 3H, H-9'')	0.94 (*t*, 3H, H-8'')

Compound **26** was transformed to the bithiophene **31** by employing the sequence of reactions depicted in Scheme 17. Thus, iodination of **26** with I_2 and HgO followed by a Stille coupling of the iodide **31** with 2-(tributylstannyl)thiophene in the presence of $PdCl_2(PPh_3)_2$ as a catalyst afforded compound **31**, which was purified by silica gel column chromatography using CH_2Cl_2:MeOH (100:1) as eluent.



Scheme 17. Synthesis of monomer **31**.

The ^{1}H-NMR spectrum (Table 5) of compound **31** revealed proton resonances at δ 7.24 (*d*) and 6.87 (*d*), each integrating for two protons, due to the protons on the phenyl ring. The doublets at δ 7.21 (1H) and 7.01 (1H) are attributed to H-5 and H-4, respectively. The remaining thiophene proton resonances appeared as doublet of doublets at δ 7.14, 6.95 and 6.90 (*dd*) and are assigned to H-5', H-4' and H-3', respectively. The ^{13}C-NMR spectrum (Table 6) of compound **31** showed 17 carbon resonances of which 12 appeared in the aromatic region. The DEPT-135 spectrum revealed that of the twelve carbon resonances in the aromatic region, five are due to quaternary carbon atoms and seven are due to methine carbons. It was thus apparent that the signals due to C-3'' and C-5'' overlapped δ 114.5 and those of C-2'' and C-6'' overlapped at δ 130.6. The down-field carbon signal at δ 158.2 is attributed to the oxygenated quaternary carbon atom (C-4''). The aliphatic carbon resonances appeared at δ 59.1 (OCH_3), 67.7, 69.8, 70.8 and 71.9 confirming the presence of the 1,4,7-trioxaoctyl side chain.

Table 5. ^{1}H-NMR (400.13, $CDCl_3$) data (δ_{ppm}) of compounds **26**, **30**, and **31.**

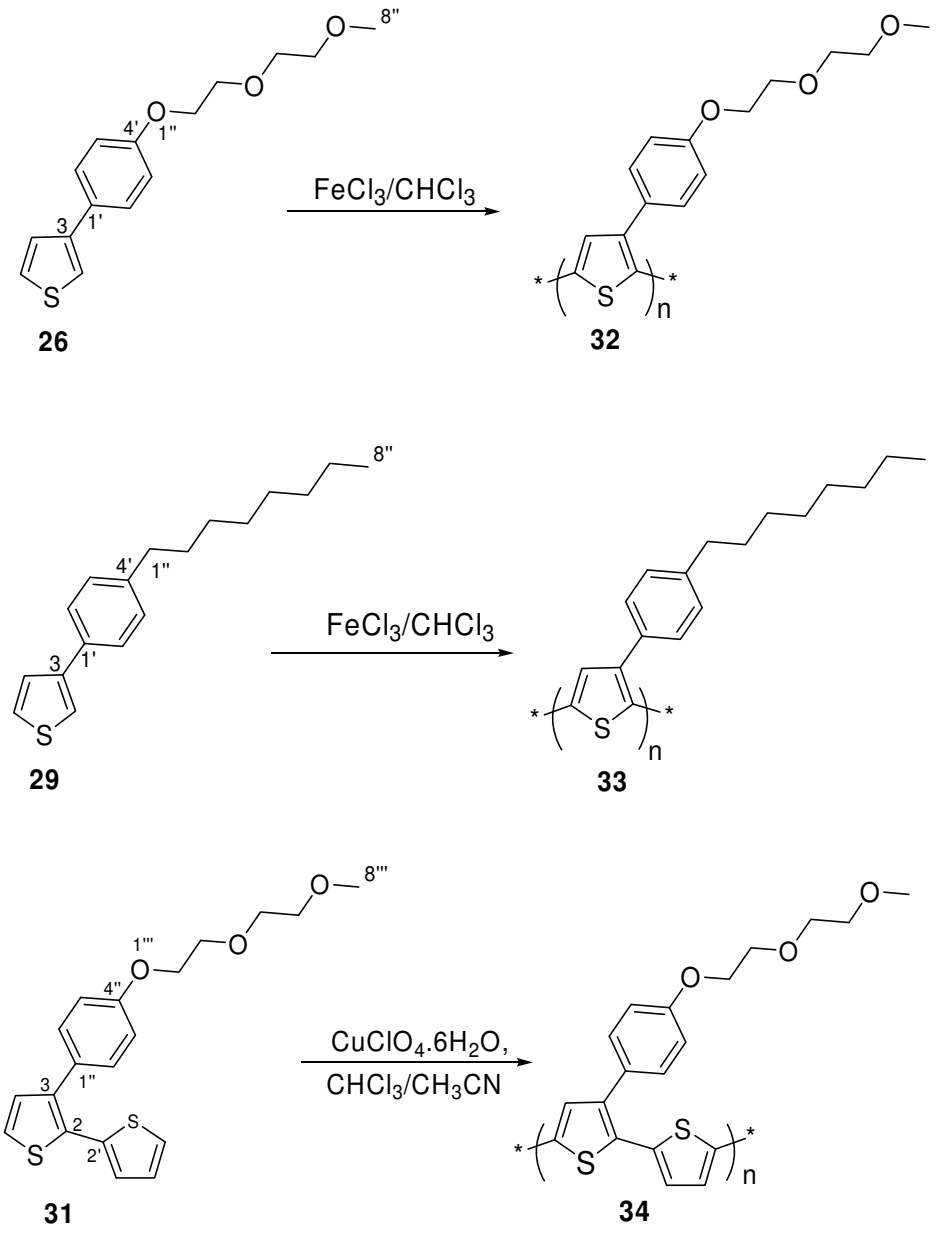
26	**30**	**31**	
7.54	7.48	7.24	3.70
(*d*, *J* = 8.8 Hz, 2H, H-2', H-6')	(*d*, *J* = 5.6 Hz, 1H, H-5)	(*d*, *J* = 8.8 Hz, 2H, H-2'', H-6'')	(*t*, *J* = 4 Hz, 2H, H-5''')
7.35-7.40	7.44	7.21	3.56
(*m*, 3H, H-2, H-4, H-5)	(*d*, *J* = 8.8 Hz, 2H, H-2', H-6')	(d, *J* = 5.2 Hz, 1H, H-5)	(*t*, *J* = 4. Hz, 2H, H-6''')
6.97	6.99	7.14	3.37
(*d*, *J* =8.8 Hz, 2H, H-3', 5')	(*d*, *J* = 8.8 Hz, 2H, H-3', H-5')	(*dd*, *J* = 5.2, 1.2 Hz, 1H, H-5')	(*s*, 3H, H-8''')
4.19	6.94	7.01	
(*t, J* = 4.8 Hz, 2H, H-2'')	(*d*, *J* = 5.6 Hz, 1H, H-4)	(*d*, *J* = 5.2 Hz, 1H, H-4)	
3.90	4.21	6.95	
(*t*, *J* = 4.8 Hz, 2H, H-3'')	(*t*, *J* = 4.8 Hz, 2H, H-2'')	(*dd*, *J* = 3.6, 1.2 Hz, 1H, H-3')	
3.76	3.91	6.90	
(*t*, *J* = 4.4 Hz, 2H, H-5'')	(*t*, *J* = 4.8 Hz, 2H, H-3'')	(*dd*, *J* = 3.6, 5.2 Hz, 1H, H-4')	
3.61	3.75	6.87	
(*t*, *J* = 4.4 Hz, 2H, H-6'')	(*t*, *J* = 4.4 Hz, 2H, H-5'')	(*d*, *J* = 8.8 Hz, 2H, H-3'', H-5'')	
3.43	3.61	4.13	
(s, 3H, H-8'')	(*t*, *J* = 4.8 Hz, 2H, H-6'')	(*t*, *J* = 4.8 Hz, 2H, H-2''')	
	3.42	3.84	
	(*s*, 3H, H-8'')	(*t*, *J* = 4.8 Hz, 2H, H-3''')	

Table 6. C^{13}-NMR (100.6 MHz, $CDCl_3$) data (δ_{ppm}) of compounds **26**, and **28**- **31**.

C	26	28	29	30	31
2	118.9	118.5	119.5	72.6	138.7
3	141.9	142.1	142.4	146.4	131.0
4	126.2	126.2	126.0	131.0	125.6
5	126.0	126.0	126.0	137.8	127.1
1’	128.9	128.5	133.3	129.1	------
2’	127.5	127.5	126.3	129.9	136.1
3’	114.9	114.8	128.8	114.4	126.4
4’	158.0	158.3	142.0	158.3	130.4
5’	------	------	------	------	123.9
6’	------	-------	------	------	------
1’’	------	6.81	35.6	-------	128.7
2’’	67.5	31.8	31.9	67.4	130.6
3’’	69.8	29.4	31.5	69.7	114.5
4’’	------	29.3	29.5	-----	158.2
5’’	70.8	29.2	29.39	70.8	-------
6’’	71.9	26.0	29.32	72.0	-------
7’’	-----	22.68	22.7	------	-------
8’’	59.1	14.1	14.1	59.1	-------
1’’’	-----	------	-----	------	-------
2’’’	-----	------	-----	------	67.3
3’’’	-----	------	-----	------	69.8
4’’’	-----	------	------	------	------
5’’’	-----	------	------	------	70.8
6’’’	------	-------	------	------	71.9
7’’’	------	-------	------	------	------
8’’’	------	-------	-------	------	59.1

The infrared spectrum (IR) of the monomers **26**, **29** and **31** revealed the presence of aromatic ring and an ether linkage. Absorption arising from C-H stretching in the alkane occurs in the general region of 3000-2840 cm^{-1}. Therefore, the strong absorption bands occurring at 2950 and 2875 cm^{-1} were because of C-H stretching vibrations of the aliphatic chains of the compounds. In the aliphatic ether region strong absorption band at 1150-1085 cm^{-1}were characteristics of the C-O-C ether linkage and strong absorption bands at 1000-1050 cm^{-1} were also the Aryl-O-CH_2 stretching vibrations. Moreover, all the mono substituted of thiophene compounds have two absorption bands of variable intensity, often medium-to-strong intensity, one at regions 745-695 cm^{-1} and the other at 700-600 cm^{-1} possibly due to the out of plane bending of the =C-H group.

Three polymers, namely, poly[3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene] (**32**), poly[3-(4'-octylphenyl)thiophene] (**33**), and ploy[3-(4''-(1''',4''',7'''-trioxaoctyl)phenyl)-2,2'-bithiophene] (**34**) were synthesized starting from monomers **26**, **29**, and **31,** respectively, using the oxidative polymerization technique as shown in Scheme 18. Ferric chloride was used for the syntheses of polymers **32** and **33** while copper(II) perchlorate hexahydrate was employed for the synthesis of polymer **34**. After the reactions were complete, the doped polymers were obtained by precipitation from MeOH. These materials were suspended in chloroform and were dedoped by washing with conc. ammonia solution and a 0.05 M solution of EDTA. The polymers were reprecipitated from MeOH and were subjected to Soxhlet extraction with diethyl ether (to remove lower molecular weight oligomers and irregular materials) and $CHCl_3$. Reprecipitation of the $CHCl_3$ extract from MeOH afforded the polymers.



Scheme 18. Oxidative polymerization of compounds **26**, **29** and **31**.

Polymer **32** was obtained as a dark colored solid. The chloroform solution of the polymer had a deep-red color while the color became darker upon evaporating the chloroform. When a chloroform solution of the polymer was exposed to 365 nm UV light it gave an orange fluorescence. The UV-Vis spectrum of the polymer in chloroform showed an absorption maximum at 447 nm and when compared with the monomer, which had an absorption maximum

at 309 nm, the absorption maximum of the polymer had red-shifted due to the increase in conjugation (Table 7).

Table 7. UV-VIS and other characteristics of polymers **32**-**34**.

Compound	**Physical state**	**Mp(^{o}C)**		**UV-VIS spectrum (nm)**	
		monomer	polymer	monomer	polymer
32	Dark solid	70-72.2	191-193	309	447
33	Dark-blueblack solid	54.6-57.6	> 300	297	462
34	Dark-red powder	------	177-180	306	417

The polymerization of **29** was achieved by slow addition of a slurry of $FeCl_3$ in chloroform in to the solution of the monomer in chloroform at room temperature. The doped polymer was precipitated from MeOH and was then dedoped by suspending the polymer in $CHCl_3$ and washing it exhaustively with conc. ammonia solution and 0.05 M EDTA. Polymer **33** was obtained as a dark blue black solid. A solution of the polymer in chloroform had a red-brown color but when the polymer was allowed to dry it had a deep blue black color. Exposing a dilute chloroform solution of the polymer to the 365 nm UV light gave a deep orange fluorescence. The UV-VIS spectrum of the polymer in chloroform solution had an absorption maximum at 462 nm.

The oxidative polymerization of compound **31** was effected with $CuClO_4.6H_2O$ using a mixture of acetonitrile and $CHCl_3$ as a solvent. As described above, the doped polymer was precipitated from MeOH and was washed with conc. ammonia and a solution of EDTA to dedope it. Polymer **34** was obtained as a dark-red powder. A chloroform solution of this polymer had an orange fluorescence when exposed to a long wavelength UV radiation. The UV-Vis spectrum of polymer **34** in $CHCl_3$ exhibited an absorption maximum at 417 nm.

5. Conclusion

Polythiophenes attract considerable attention because of their high electrical conductivity, environmental stability, the ease of derivatization and ability to be polymerized by a variety of chemical and electrochemical methods. But because unsubstituted polythiophenes were found to be intractable, there was a need for structural modification in order to make processable polymers. In the present work, three phenyl-substituted polythiophenes were synthesized starting from 3-phenyl-substituted thiophenes. The phenyl groups contained alkyl, alkoxy and trioxaoctyl side chains. Both Suzuki and Grignard coupling reactions were employed in the syntheses of the monomers. The polymerization reactions were carried out by oxidative polymerization using ferric chloride and copper(II) perchlorate hexahydrate as oxidants. All three polymers were soluble in chloroform and were also meltable thus they are processable. The strong fluorescence of solutions of the polymer when irradiated with long-wavelength UV light suggests that they might find applications as light emitting materials. The physical properties of these polymers will be studied in collaboration with physicists.

6. Experimental

6.1. Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ and were reported in δ units. The UV-Vis spectra of the monomers and the polymers were recorded in chloroform using SPECTRONIC GENESYS 2PC spectrophotometer. Infrared spectra were obtained using a PERKIN-ELMER infrared spectrometer. IR spectra of the crystalline compounds were obtained as KBr pellets and the oily compounds as thin films. Melting points were measured using Mettler Toledo FP82HT hot stage with FP90 central processor Leica Galen^{TM} III microscope. The melting points were uncorrected.

6.2. Reagents

1, 4-Dibromobenzene, 4-bromophenol, 3-bromophenol, 2-bromophenol, *n*-octyl bromide, NBS, Mg turnings, anhyd. Na_2SO_4, ethyl acetate, 2(tributylstannyl)thiophene, *n*-butyl lithium (2.5M in hexane), tributylborate, 3-bromothiophene, $CDCl_3$, NiC_2(dppp) and 2-(2-methoxyethoxy)ethanol were bought from Aldrich and were used as received. *n*-Pentane, acetone, DME, petroleum sprit (40-60 ^{o}C), $PdCl_2$ and CH_2Cl_2 were purchased from BDH and were used as received. $SOCl_2$ was obtained from Riedel-de Haën. Tetrahydrofuran used for the synthesis of 3-bromothiophene and for the Grignard coupling was dried over Na-benzophenone under nitrogen atmosphere. Analytical grade chloroform and methanol purchased from BDH were used for the polymerization reactions. Silica gel 60 (43-63 μm) was used as a stationary phase for column chromatography. 0.25 mm silica gel pre-coated plates (Fluka) were used for thin layer chromatography. All solvents used for column and flash chromatography were used as received without prior distillation.

6.3. Procedures

Preparation of tetrakis(triphenylphosphin)Palladium(0)

Palladium chloride (1.0 g) was dissolved in DMSO (68 mL.) and triphenylphosphine (7.4 g) was added and the mixture was heated over an oil bath. The system was kept under nitrogen atmosphere and was heated at 140 ^{o}C until complete solublization occurred. The heated oil bath was taken away and the solution was stirred rapidly for 15 minutes. Then, hydrazine hydrate ($H_2NNH_2.xH_2O$) (1.2 mL.) was slowly added over a period of 1 minute, during which a vigorous evolution of N_2 took place indicating reaction. The dark solution was cooled by a water bath and was left to cool by it self after crystallization was observed. After the mixture was reached room temperature, it was filtered under nitrogen atmosphere on affine sintered glass funnel and washed with two 15 mL. portion of ethanol and two 15 mL. portion of diethyl ether successively. Finally the compound was dried and weighed to give (5.765 g) pure greenish yellow crystalline solid which was stored under nitrogen atmosphere.

Synthesis of 1-chloro-2-(2-methoxyethoxy)ethane (**14**)

2-(2-Methoxyethoxy)ethanol (40 ML, 40.1 g, 0.336 mol) was placed in three-necked round-bottomed flask and to it was added pyridine (30 mL). While stirring the mixture $SOCl_2$ (48 mL) was added drop wise from a pressure equalizing dropping funnel. After the addition of the $SOCl_2$ was complete the mixture was stirred for several hours. Diethyl ether was added to the reaction mixture to precipitate the pyridinium chloride and the ether soluble portion was decanted and the residue was washed several times with diethyl ether. Careful addition of water into the ether solution removed the unreacted $SOCl_2$. The ether solution was separated, dried over anh. Na_2SO_4 and the solvent was removed using a rotary evaporator. The residue was distilled under reduced pressure and the compound boiling at 58 - 64 ^{o}C was collected and a total of 27.9 g (60.1%) of the chloride was obtained as a colorless liquid. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.55 (*t*, *J* = 5.6 Hz, 2H, H-2), 3-48-3.44 (*m*, 4H, H-4, H-5), 3.36 (*t*, *J* = 4 Hz, 2H, H-1), 3.18 (*s*, 3H, H-7). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 71.9 (C-5), 71.4 (C-4), 70.5 (C-2), 58.6 (C-7), 42.5 (C-1).

Synthesis of 2-(1',4',7'-trioxaoctyl)bromobenzene (**15**)

To a mixture of 2-bromophenol (10 g, 57.8 mmol) in 60 mL of DMF, anhydrous K_2CO_3 (34 g) was added and the mixture was heated to 100 ^oC. To this was added compound **14** (10.1 mL) dropwise from a pressure equalizing dropping funnel. The mixture was heated under nitrogen atmosphere for 8 hr., cooled to room temperature and the K_2CO_3 was separated by suction filtration. The filtrate was acidified with 2 M HCl and extracted with diethyl ether three times. The combined ether extract was washed with 1 M NaOH (to remove unreacted phenolic material) and brine (conc. NaCl) solution, dried over anhydrous Na_2SO_4. and the ether was removed by rotary evaporation to afford 8.71 g (48.5%) of a colorless liquid product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.25 (*dd*, *J* = 8, 1.6 Hz, 1H, H-6), 7.14 (*dt*, *J* = 7.8, 1.6 Hz, 1H, H-4), 6.82 (*dd*, *J* = 8, 1.2 Hz, 1H, H-5), 6.72 (*dt*, *J* = 7.8, 1.2 Hz, 1H, H-3), 4.07 (*t*, *J* = 4.8 Hz, 2H, H-2'), 3.80 (*t*, *J* = 4.8 Hz 2H, H-3'), 3.67 (*t*, *J* = 4.2 Hz, 2H, H-5'), 3.47 (*t*, *J* = 4.2 Hz, 2H, H-6'), (*s*, 3H, H-8'). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 155.2 (C-2), 133.2 (C-6), 128.4 (C-4), 122.0 (C-5), 113.5 (C-3), 112.0 (C-1), 71.9 (C-6'), 70.9 (C-5'), 69.4 (C-3'), 69.0 (C-2'), 58.8 (C-8').

Synthesis of 3-(1',4',7'-trioxaoctyl)bromobenzene (**16**)

The same procedure like that employed for the synthesis of compound **15** was used except that 3-bromophenol (10 g, 57.8 mmol) was used to afford compound **16** (9.67 g, 61%) as an oily liquid. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.03-7.11 (*m*, 3H, H-2, H-5, H-6), 6.84 (*m*, 1H, H-4), 4.07 (*t*, *J* = 4.8 Hz, 2H, H-2), 3.81 (*t*, *J* = 4.8 Hz, 2H, H-3), 3.67 (*t*, *J* = 4 Hz, 2H, H-5'), 3.53 (*t*, *J* = 4 Hz, 2H, H-6'), 3.36 (*s*, 3H, H-8'). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 159.5 (C-3), 130.5 (C-5), 123.9 (C-1), 122.7 (C-6), 117.9 (C-2), 113.5 (C-4), 71.9 (C-6'), 70.7 (C-5'), 69.5 (C-3'), 67.6 (C-2'), 59.0 (C-8').

Synthesis of 4-(1',4',7'-trioxaoctyl)bromobenzene (**17**)

Similar procedure like that of compound **15** was employed except that 4-bromophenol (10 g, 57.8 mmol) was used to obtain compound **17** as an oily liquid, which gave a white crystalline solid (10.0 g, 63.1%) upon cooling. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.20 (*d*, *J* = 8.8 Hz, 2H, H-2, H-6), 6.65 (*d*, *J* = 8.8 Hz, 2H, H-3, H-5), 3.92 (*t*, *J* = 4.8 Hz, 2H, H-2'), 3.67 (*t*, *J* = 4.8 Hz, 2H, H-3'), 3.54 (*t*, 2 *J* = 4.4 Hz, H, H-5'), 3.41 (*t*, *J* = 4.4 Hz, 2H, H-6'), 3.23 (*s*, 3H, H-8'). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 157.8 (C-4), 132.0 (C-2, C-6), 116.3 (C-3, C-5), 112.7 (C-1), 71.8 (C-6'), 70.5 (C-5'), 69.4 (C-3'), 67.5 (C-2'), 58.8 (C-8').

Synthesis of 1,3-bis(1',4',7'-trioxaoctyl)benzene (**18**)

Resorcinol (10 g, 90.81 mmol), K_2CO_3 (53.4 g), DMF (120 mL) were mixed and heated at 100 ^{o}C. Compound **14** (25.17 g, 0.182 mol) was added dropwise into the reaction mixture from a pressure-equalizing dropping funnel. After *ca.* 8 h, the mixture was cooled and was then worked up as described for the synthesis of compound **15**. Compound **18 (**17.75 g, 62.19%) was obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.10 (*dd*, *J* = 6.8, 2.8 Hz, 1H, H-5), 6.48 (*d*, 2H, H-6), 6.45 (*d*, J = 2.8 Hz, 1H, H-2), 4.03 (*t*, *J* = 4.8 Hz, 4H, H-2'), 3.76 (*t*, *J* = 4.8 Hz, 4H, H-3'),3.63 (*t*, *J* = 4 Hz, 4H, H-5'), 3,50 (*t*, *J* = 4 Hz, 4H, H-6'), 3.32 (*s*, 3H, H-8'). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.8 (C-1, C-3), 129.6 (C-5), 106.8 (C-4, C-6), 101.5 (C-2), 71.8 (C-6'), 70.4 (C-5'), 69.4 (C-3'), 67.2 (C-2'), 58.6 (C-8').

Synthesis of 2,4-bis(1',4',7'-trioxaoctyl) bromobenzene (**19**)

In a 250 mL round-bottomed flask, compound **18** (17g, 54.08 mmol) was dissolved in DMF (100 mL). To the resulting solution, NBS (9.6 g, 55.16 mmol) dissolved in DMF (30 mL) was added drop wise. The mixture was allowed to stir at room temperature in the dark under nitrogen atmosphere for 24 h. The resulting mixture was acidified with 2 M HCl and the mixture was extracted with diethyl ether several times. The combined ether extract was dried over anhydrous Na_2SO_4 and the ether was removed to give compound **19** (14.0 g, 65%) as yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.24 (*d*, *J* = 8.8 Hz, 1H, H-6), 6.27 (*dd*, *J* = 8.8, 2.4 Hz, 1H, H-5), 6.43 (*d*, *J* = 2.4 Hz, 1H, H-3), 3.88-3.82(*m*, 4H, H-2'), 3.62-3.56 (*m*, 4H, H-3'), 3.51-3.43 (*m*, 4H, H-5'), 3.31-3.30 (*m*, 4H, H-6'), 3.12 (s, 3H, H-8'). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.9 (C-4), 155.4 (C-2), 132.5 (C-6), 106.9 (C-5), 102.1 (C-1), 101.2 (C-3), 71.5/71.4(C-6'), 70.3/70.0 (C-5'), 69.0/68.9 (C-3'), 67.3/68.5 (C-2').

Synthesis of 1-bromo-4-octyloxybenzene **(20)**

To a solution of *p*-bromophenol (**12**) (10 g, 0.578 mol) in DMF (60 mL), anh. K_2CO_3 (34 g) was added. The mixture was heated at 100 ^{o}C and *n*-octyl bromide (10.10 mL, 1% excess) was added drop wise from a pressure equalizing dropping funnel. The mixture was heated for 5 h under nitrogen atmosphere, cooled to room temperature and filtered by suction. The filtrate was acidified with 2 M HCl and extracted with diethyl ether three times. The combined ether extract was washed with 1 M NaOH and brine solution, dried over anh. Na_2SO_4 and the ether was removed to afford compound **20** (12.76 g, 77. 4%) as a yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38 (*d*, *J* = 9.2 Hz, 2H, H-2), 6.80 (*d*, *J* = 9.2 Hz, 2H, H-3), 3.93 (*t*, *J* = 6.8 Hz, 2H, H-2'), 1.71 (*q*, 2H, H-3'), 1.30-1.10 (*m*, 10H, H-4', H-5', H-6', H-7', H-8'), 0.9 (*t*, 3H, H-9'). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.3 (C-4), 132.1 (C-6, C-2), 116.3 (C-3, C-5), 112.5 (C-1), 68.2 (C-2'), 31.8 (C-3'), 29.4 (C-4'), 29.2 (C-5'), 26.0 (C-6'), 22.7 (C-7'), 14.1 (C-8').

Synthesis of 1-bromo-4-octylbenzene (**22**)

To a mixture of Mg (1.89 g, 0.078 mol) and THF (30 mL) in a three-necked round-bottomed flask kept under nitrogen atmosphere, *n*-octyl bromide (15.15 g, 0.078 mol) in THF (20 mL) was added at such rate that the reaction mixture maintained self-refluxing. After the addition was complete, the mixture was further refluxed in an oil bath for 30 min. The solution was then transferred (through a transfer needle) to the mixture containing 1,4-dibromobenzene (**21**) (20.13 g, 0.078 mol), $PdCl_2$(dppf) (0.60 g, 0.7 mol) and THF (40 mL), which was also kept under nitrogen atmosphere. The resulting mixture was refluxed overnight, cooled to room temperature and was poured into water. After removing of the catalyst residue by filtration, the filtrate was extracted with diethyl ether. The ether layer was washed with water and dried over anh. Na_2SO_4. The ether was evaporated and the resulted liquid was distilled under reduced pressure ($1.3x10^{-1}$-1.1x10-^{1}) and the material that boiled at 98 -102 ^{o}C was collected to give compound **22** (11.61 g, 55.6%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (*d*, *J* = 8.4 Hz, 2H, H-2, H-6), 6.96 (*d*, *J* = 8.4 Hz, 2H, H-3, H-5), 2.49 (*t*, *J* = 4 Hz, 2H, H-1'), 1.57 (*q*, 2H, H-2'), 1.27 (*m*, 10H, H-3', H-4', H-5', H-6',H-7'), 0.9 (*t*, 3H, H-8'). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141 (C-4), 131.3 (C-2, C-6), 130.2 (C-3, C-5), 119.4 (C-1), 35.5 (C-1'), 32.1 (C-2'), 31.5 (C-3'), 29.6 (C-4'), 29.5 (C-5'), 29.4 (C-6'), 22.9 (C-7'), 14.3 (C-8').

Synthesis of 3-thiopheneboronic acid (**23**)

3-Bromothiophene (12 g, 0.074 mol) was placed in a 500 mL round-bottomed flask and was dissolved in dry THF (137 mL). The mixture was cooled to -78 ^{o}C and a 2.5 M solution of *n*-butyl lithium (45.9 mL) was added at once. After stirring for 3 minutes, tributyl borate (19.8 mL) was added at once. The stirring continued overnight and the temperature was allowed to rise to room temperature. The mixture was then acidified with 1M HCl the THF layer was separated and the aqueous layer was extracted three times with diethyl ether. The combined ether extract was placed in a separatory funnel and was extracted three times with 1M NaOH. The combined NaOH extract was acidified with 1M HCl and was extracted three times with diethyl ether. The

combined ether extract was washed with distilled water, dried over anh. Na_2SO_4, and the ether was removed under reduced pressure to afford compound **23** as a white solid (4.66 g, 51.46%).

Synthesis of 3-(2'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**24**)

In a 500 mL three-necked round-bottomed flask compound **15** (4.36 g, 0.0158 mol) was dissolved in DME (54.09 mL) and to it was added tetrakis (triphenylphosphine)Pd(0) (0.253 g, 0.226 mmol). The mixture was kept under nitrogen atmosphere and was stirred for 10 min. 3-Thiopheneboronic acid (2.5 g, 0.0195 mmol) (5 mol% excess) was added followed by 1 M $NaHCO_3$ (43.28 mL). The resulting mixture was heated under reflux and the progress of the reaction was followed by TLC. After 5 h the reaction mixture was cooled to room temperature and DME was removed with a rotary evaporator. Water was added to the residue and the mixture was extracted with diethyl ether five times. The ether extract was washed with distilled water, dried over anh. Na_2SO_4 and the ether was removed to afford a dark-brown oil (4.48 g). The crude product was flash-chromatographed over silica gel using CH_2Cl_2:ethyl acetate (4.3:0.7) as eluent. Compound **24** was not obtained in a pure form and all attempts to purify the compound by column chromatography did not result in a pure compound as the impurity had a similar TLC Rf value like the desired product.

Synthesis of 3-(3'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**25**)

A similar procedure as described above for the synthesis of **24** was followed for the synthesis of compound **25**. Thus, to a mixture of compound **16** (9.65 g, 0.0350mmol) and tetrakis(triphenylphosphine)Pd(0) (1.2167 g) in DME (150 mL), 3-thiopheneboronic acid (4.7 g) (5 mol% excess), and 1 M $NaHCO_3$ (125 mL.) were added and the mixture was heated under reflux. The crude product was obtained as yellow oil (4.5 g), which turned out to be a mixture of compounds that proved to be very difficult to separate by silica gel column chromatography.

Synthesis of 3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**26**)

A similar procedure as described for the synthesis of **24** above was followed for the synthesis of compound **26**. Thus, compound **17** (9 g, 0.0327 mol), tetrakis(triphenylphosphine)Pd(0) (0.377 g), 3-thiopheneboronic acid (4.25 g, 0.0332 mmol) 1M $NaHCO_3$ (100 mL.) were employed. The crude product was brown oil, which was purified by column filtration over silica gel using CH_2Cl_2 as eluent. The resulting compound was recrystallized from methanol to afford compound **26** (3.24 g, 35%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (*d*, *J* = 8.8 Hz, 2H, H-2', H-6'), 7.35-7.40 (*m*, 3H, H-2, H-4, H-5), 6.97 (*t*, *J* = 8.8 Hz, 2H, H-3', H-5'), 4.19 (*t*, *J* = 4.8 Hz, 2H, H-2''), 3.90 (*t*, *J* = 4.8 Hz, 2H, H-3''),3.76 (*t*, *J* = 4.4 Hz, 2H, H-5''), 3.61 (*t*, *J* = S4.4 Hz, 2H, H-6''), 3.43 (*s*, 3H, H-8''). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.0 (C-4'), 141.9 (C-3), 128.9 (C-1'), 127.5 (C-2'), 126.2 (C-4), 126.0 (C-5), 118.9 (C-2), 114.9 (C-3'), 71.9 (C-6''), 70.8 (C-5''), 69.8 (C-3''), 67.5 (C-2''), 59.1 (C-8'').

Synthesis of 3-(2',4'-bis(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**27**)

A similar procedure as described for the synthesis of **24** was followed to synthesize compound **27**. Thus, compound **19** (14 g, 0.036 mol), tetrakis(triphenylphosphine)Pd(0) (0.404 g), 3-thiopheneboronic acid (5.0 g, 0.039 mol), 1M $NaHCO_3$ (120 mL.) were employed. The crude product was a brown oil (13.78 g) and efforts to obtain compound **27** in a pure form by column chromatography over silica gel using CH_2Cl_2 : diethyl ether (4.5:0.5) failed to give a reasonably pure product.

Synthesis of 3-(4'-octoxyphenyl)thiophene (**28**)

To Mg (0.511 g, 0.021 mol) in dry THF (15 mL.), compound **20** (6 g, 0.021 mol) in THF (10 mL.) was added drop wise from a pressure equalizing dropping funnel. The mixture was kept under nitrogen atmosphere and after the addition of compound **20** was complete, the mixture

was heated under reflux for *ca* 30 min. The resulting Grignard reagent was transferred using a transfer needle to a mixture of 3-bromothiophene (3.242 g, 0.0210 mol) and $NiCl_2$(dppp) (0.51 g) (5 mol%) in THF. The resulting mixture was refluxed for 2 h The mixture was then cooled and saturated NH_4Cl was added. It was then extracted with diethyl ether several times. The combined ether extract was washed with brine solution, dried over anh. Na_2SO_4 and the ether was removed. The resulting solid product was recrystallized from isopropanol to afford compound **28** (3.54 g) as a white solid. Further purification of compound **28** by silica gel column chromatography using CH_2Cl_2:petroleum sprit (4:1) resulted in pure white crystalline compound **28** (1.405 g, 23. 23%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (*d*, *J* = 8.4 Hz, 2H, H-2'), 7.38 (*m*, 3H, H-2, H-4, H-5), 6.95 (*d*, *J* = 8.4 Hz, 2H, H-3'), 4.01 (*t*, *J* = 6.4 Hz, 2H, H-2''), 1.83 (*q*, 2H, H-3''), 1.50-1.33 (*m*, 10H, H-4'', H-5'', H-6'', H-7'', H-8''), 0.93 (*t*, 3H, H-9''). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.3 (C-4'), 142.1 (C-3), 128.5 (C-1'), 127.5 (C-2'), 126.2 (C-4), 126.0 (C-5), 118.9 (C-2), 114.8 (C-3'), 68.1 (C-1''), 31.8 (C-2''), 29.4 (C-3''), 29.3 (C-4''), 29.2 (C-5''), 26.0 (C-6''), 22.68 (C-7''), 14.1 (C-8'').

Synthesis of 3-(4'-octylphenyl)thiophene (**29**)

A similar procedure as described above for the synthesis of compound **28** was followed to synthesize compound **29**. Thus, compound **22** (9 g, 0.0334 mol), Mg (0.811 g, 0.0334 mol) in THF (20 mL.), 3-bromothiophene (5.445 g, 0.0334 mol) and $NiCl_2$(dppp) (0.9052 g) were used. The crude product was applied on to a column packed with silica gel and was eluted using a mixture of toluene:*n*-pentane (0.05:5). After the solvent was removed a white crystalline solid compound **29** (2 g, 22%) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56 (*d*, *J* = 8 Hz, 2H, H-2'), 7.42 (*m*, 3H, H-2, H-4, H-5), 7.25 (*d*, *J* = 8 Hz, 2H, H-3'), 2.67 (*t*, *J* = 4.0 Hz, 2H, H-1''), 1.69 (*q*, 2H, H-2''), 1.45-1.30 (*m*, 10H, H-3'', H-4'', H-5'',H-6'',H-7''), 0.94 (*t*, 3H, H-8''). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.4 (C-3), 1142.0 (C-4'), 133.3 (C-1'), 128.8 (C-3'), 126.3 (C-2'), 126.0 (C-4, C-5), 119.5 (C-2), 35.6 (C-1''), 31.9 (C-2''), 31.5 (C-3''), 29.5 (C-4''), 29.39 (C-5''), 29.32 (C-6''), 22.7 (C-7''), 14.1 (C-8'').

Synthesis of 2-iodo-3-[4'-(1'',4'',7''-trioxaoctyl)phenyl]thiophene (**30**)

To an ice cold solution of compound **26** (1.5 g, 5.388 mol), in toluene (50 mL.) was added a mixture of I_2 (1.71 g, 6.74 mmol) and HgO (1.46 g, 6.74 mmol). The mixture was stirred for 13 h, monitoring the progress of the reaction by TLC. Small amount of a mixture of I_2 and HgO was added until the starting material disappeared completely. The reaction mixture was then filtered and the filtrate was washed with 5% $Na_2S_2O_3$ and water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford compound **30** (2.21 g, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (*d*, *J* = 5.6 Hz, 1H, H-5), 7.44 (*d*, *J* = 8.8 Hz, 2H, H-2', H-5'), 6.99 (*d*, *J* = 8.8 Hz, 2H, H-3', H-5'), 6.94 (*d*, *J* = 5.6 Hz, 1H, H-4), 4.21 (*t*, *J* = 4.8 Hz, 2H, H-2''), 3.91 (*t*, *J* = 4.8 Hz, 2H, H-3'') 3.75 (*t*, *J* = 4.4 Hz, 2H, H-5''), 3.61 (*t*, *J* = 4.8 Hz, 2H, H6''), 3.42 (*s*, 3H, H-8''). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.3 (C-4'), 146.4 (C-3), 137.8 (C-5), 131.0, (C-4), 129.9 (C-2'), 129.1 (C-1'), 114.4 (C-3'), 72.6 (C-2), 72.0 (C-6''), 70.8 (C-5''), 69.7 (C-3''), 67.4 (C-2''), 59.1 (C-8'').

Synthesis of 3-[4''-(1''', 4''',7'''-trioxaoctyl)phenyl]-2,2'-bithiophene (**31**)

To a solution of compound **30** (2.1 g, 5.19 mmol) and 2(tributylstannyl)thiophene (1.8 mL., 2.034 g) in toluene (22 mL.), $PdCl_2(PPh_3)$ (0.100 g) was added. The mixture was refluxed under nitrogen atmosphere and the progress of the reaction was monitored by TLC. After 12 h., the solvent was removed and the residue was mixed with hexane. The solid precipitate was filtered by suction to afford 3 g of a crude product. The crude product was applied on a column of silica gel and was eluted using CH_2Cl_2:MeOH (100:1). Compound **31** (0.71 g ,36%) was obtained as pure oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.24 (*d*, *J* = 8.8 Hz, 2H, H-2'', H-6''), 7.21 (*d*, *J* = 5.2 Hz, 1H, H-5), 7.14 (*dd*, *J* = 5.2, 1.2 Hz, 1H, H-5'), 7.01 (*d*, *I* = 5.2 Hz, 1H, H-4), 6.95 (*dd*, *J* = 1.2, 3.6 Hz,1H, H-4'), 6.90 (*dd*, *J* = 1.2, 3.6 Hz, 1H, H-3'), 6.87 (*d*, *J* = 8.8 Hz, 2H, H-3'', H-5''), 4.13 (*t*, *J* = 4.8 Hz, 2H, H-2'''), 3.84 (*t*, *J* = 4.8 Hz, 2H, H-3'''), 3.70. (*t*, *J* = 4 Hz, 2H, H-5'''), 3.56 (*t*, *J* = 4 Hz, 2H, H-6'''), 3.37 (*s*, 3H, H-8'''). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.2 (C-4''), 138.7 (C-2), 136.1 (C-2'), 131.0 (C-3), 130.6 (C-2''), 130.4 (C-4'), 128.7 (C-1''), 127.1

(C-5), 126.4 (C-3'), 123.9 (C-5'), 114.5 (C-3''), 71.9 (C-6'''), 70.8 (C-5'''), 69.8 (C-3'''), 67.3 (C-2'''), 59.1 (C-8''').

Synthesis of poly[3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene] (**32**)

To compound **26** (450 mg, 1.62 mmo) in $CHCl_3$ (12 mL) kept under nitrogen atmosphere, a slurry of $FeCl_3$ (1.08 g, 6.48 mmol) in $CHCl_3$ (12 mL) was added over a period of 2h. The mixture was stirred for an additional 2:30 h. and was poured in to methanol. The precipitate was collected by filtration and was dissolved in$CHCl_3$ and washed with conc. NH_3 (6 times), 0.05 M EDTA (twice) and distilled water (twice). The $CHCl_3$ solution was concentrated to a small volume and the polymer was precipitated from methanol. The resulting solid was Soxhlet extracted with diethyl ether and chloroform. The chloroform solution was concentrated to a small volume and the polymer was reprecipitated from MeOH to afford polymer **32** as a dark-colored solid (95 mg).

Synthesis of poly[3-(4'-octylphenyl)thiophene] (**33**)

To compound **29** (450 mg, 1.65 mmol) in $CHCl_3$ (12 mL.) kept under nitrogen, a slurry of $FeCl_3$ (1.1027 g, 6.6 mmol) in$CHCl_3$ was added over a period of 2 h. The mixture was allowed to stir for an additional 2:30 h. and was poured in to methanol. The precipitate was collected by filtration and was dissolved in $CHCl_3$ and washed with conc.NH_3 (6 times), 0.05M EDTA (twice) and distilled water (twice). The $CHCl_3$ solution was concentrated to a small volume and the polymer was precipitated from methanol. The dark-colored solid was Soxhlet extracted with diethyl ether and chloroform. The chloroform extract was concentrated to a small volume and the polymer was reprecipitated from MeOH to afford polymer **33** (146 mg) as dark blue-black solid.

Synthesis of poly[3-(4’’-(1’’’,4’’’,7’’’-trioxaoctyl)phenyl)-2,2’-bithiophene] (**34**)

To compound **31** (280 mg, 0.777 mmol) in $CHCl_3$ kept under nitrogen atmosphere, a slurry of $CuClO_4.6H_2O$ (1.152 g, 3.108 mmol) in $CHCl_3$ and a small amount of acetonitrile was added with a syringe over a period of 2 h at constant interval of time. After the addition was complete, the mixture was stirred for an additional 2:30 h. and was poured in to methanol. The precipitate was then collected by membrane filtration and dissolved in $CHCl_3$ and was washed with conc. NH_3 (four times) and distilled water (twice). The chloroform solution was concentrated to a small volume and the polymer was precipitated by slow addition into MeOH to afford polymer polymer **34** (100 mg) as a dark-red solid.

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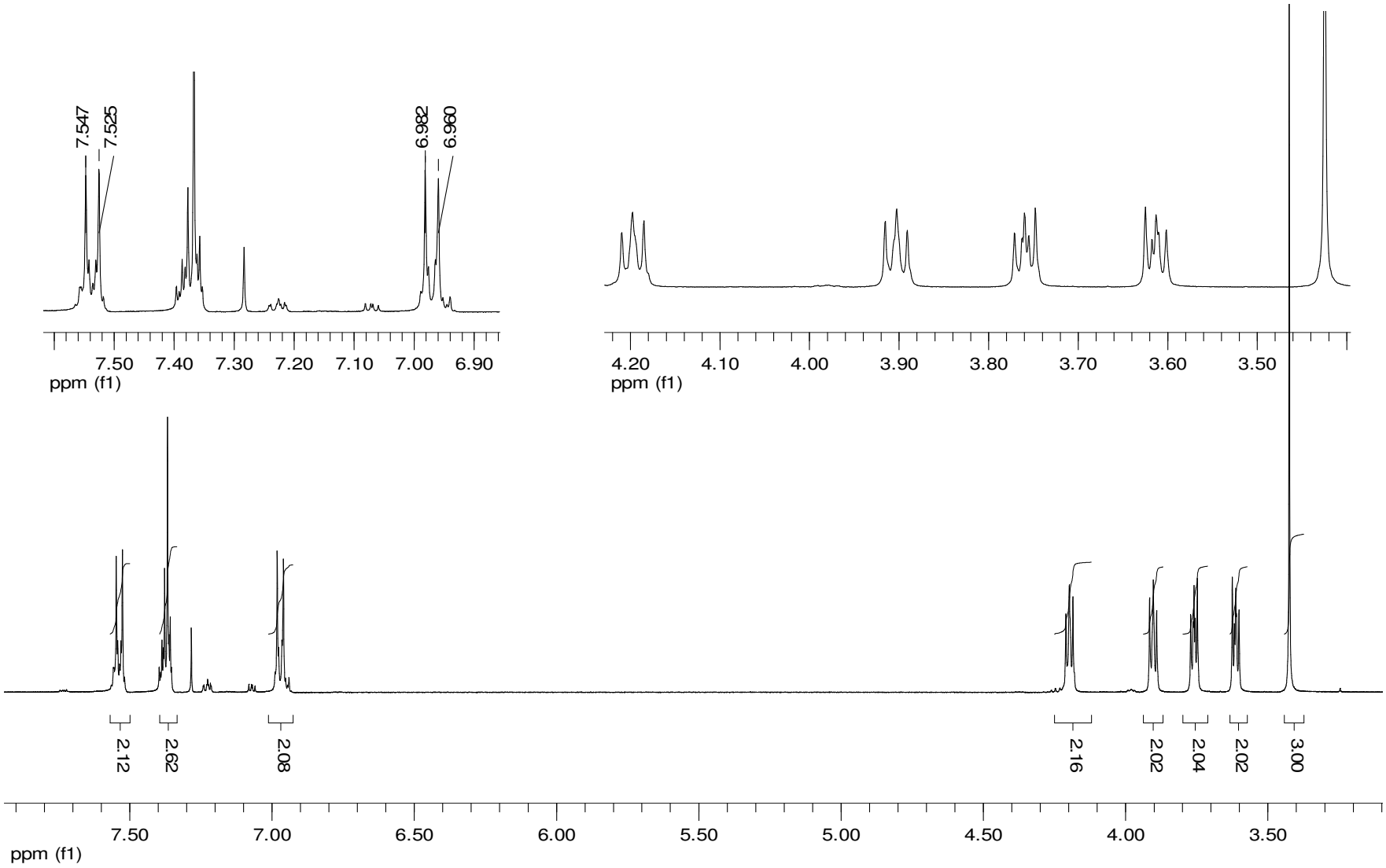
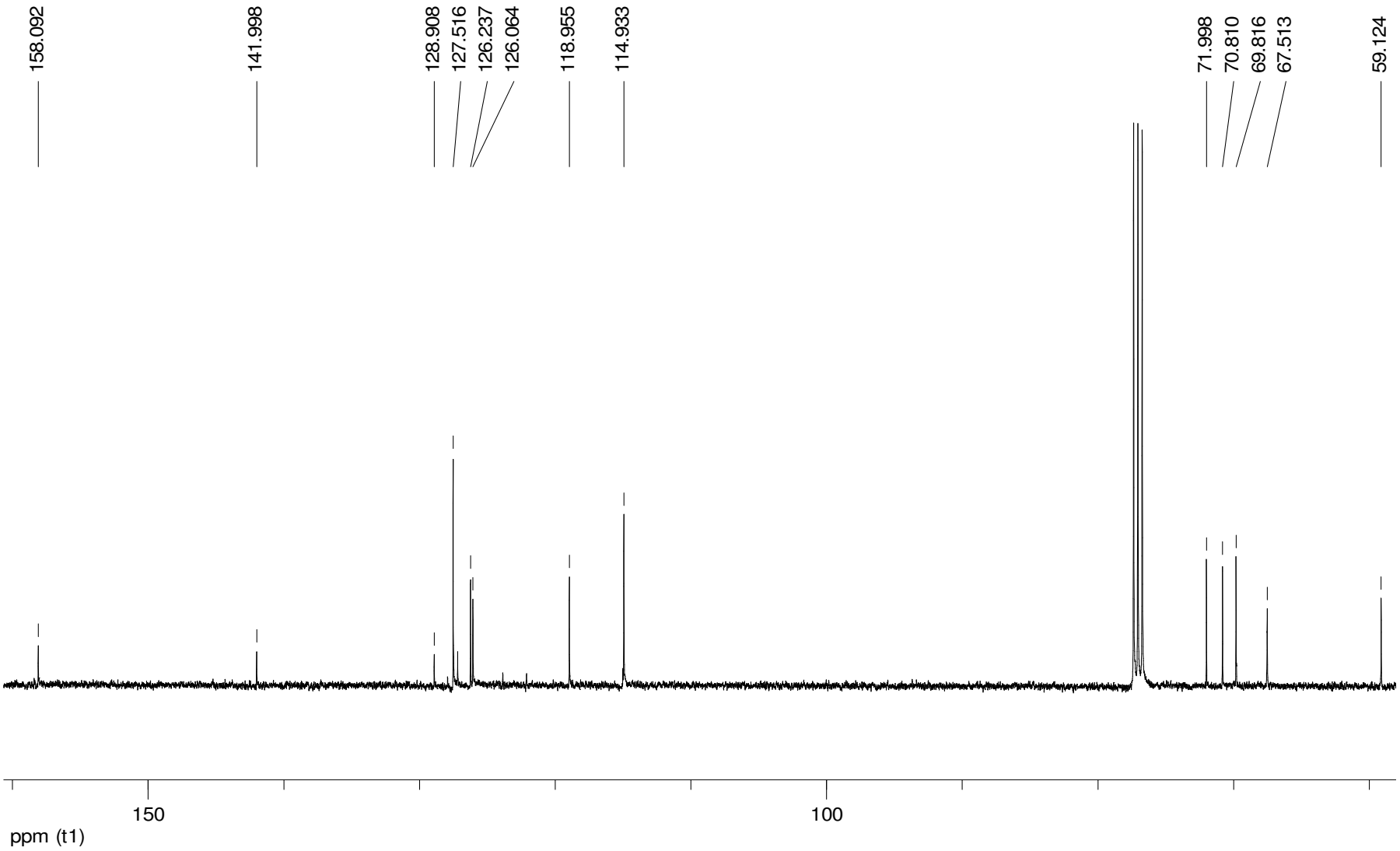
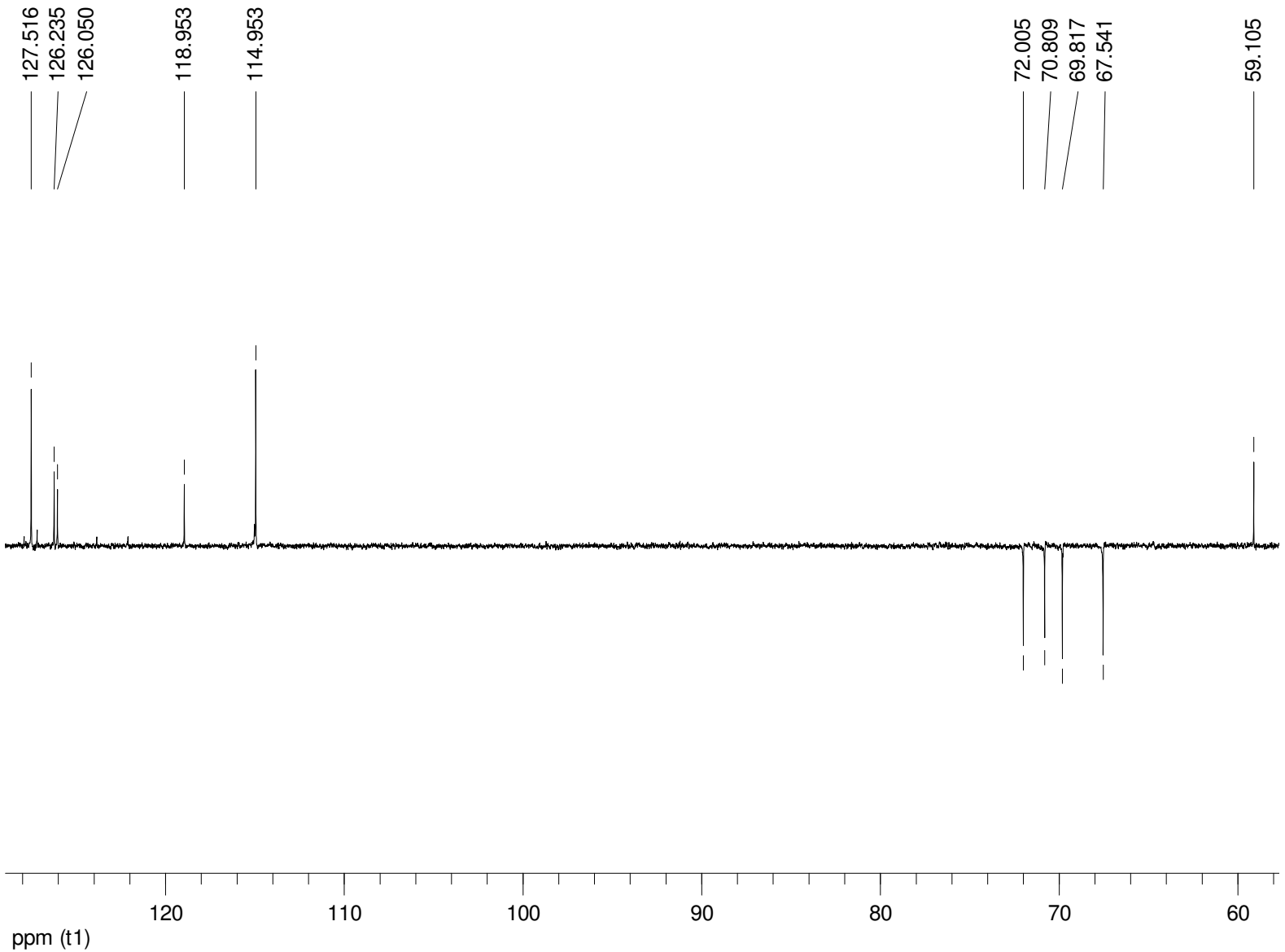
8. Appendices



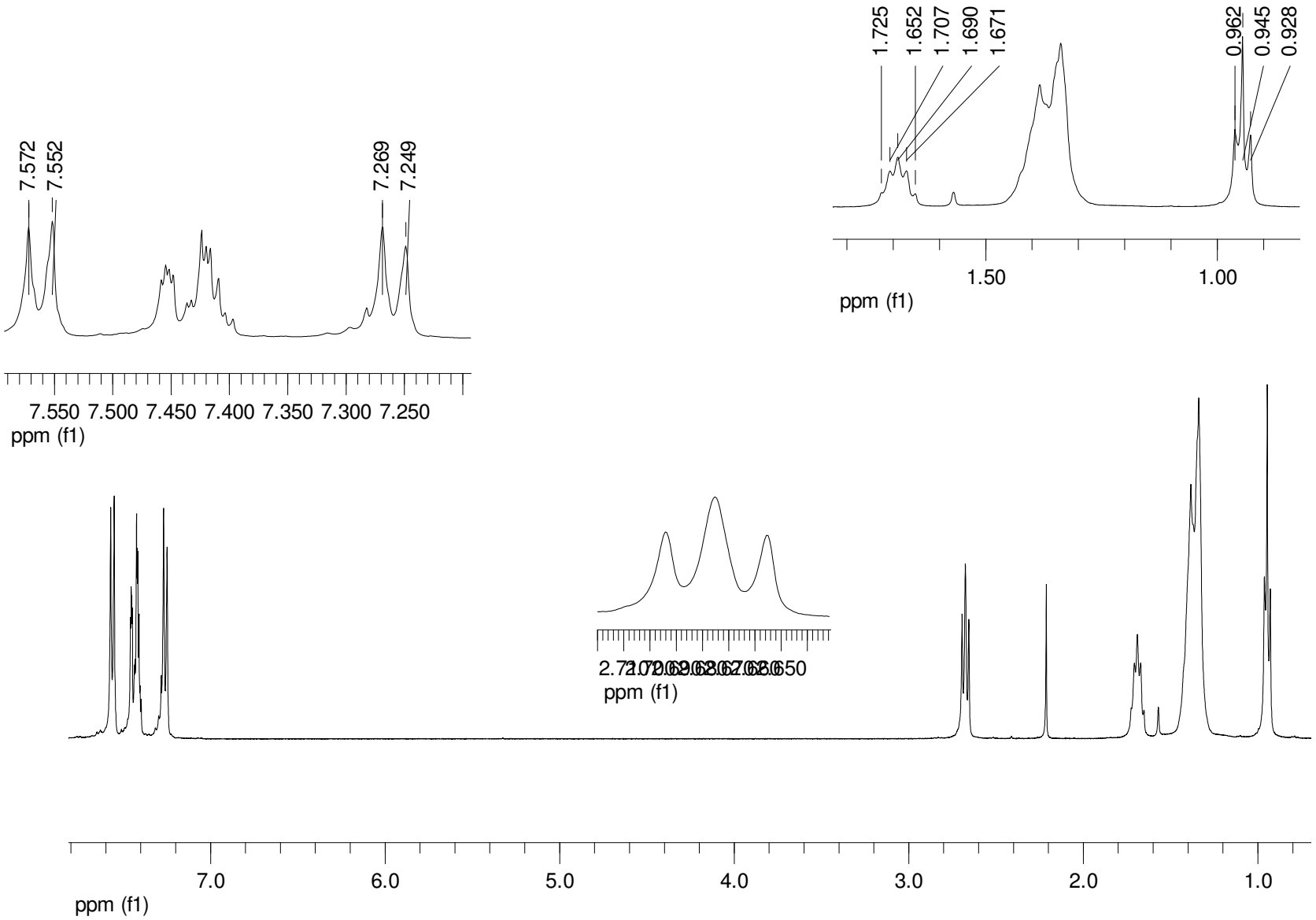
Appendix 1. The ^{1}H-NMR spectrum of 3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**26**).



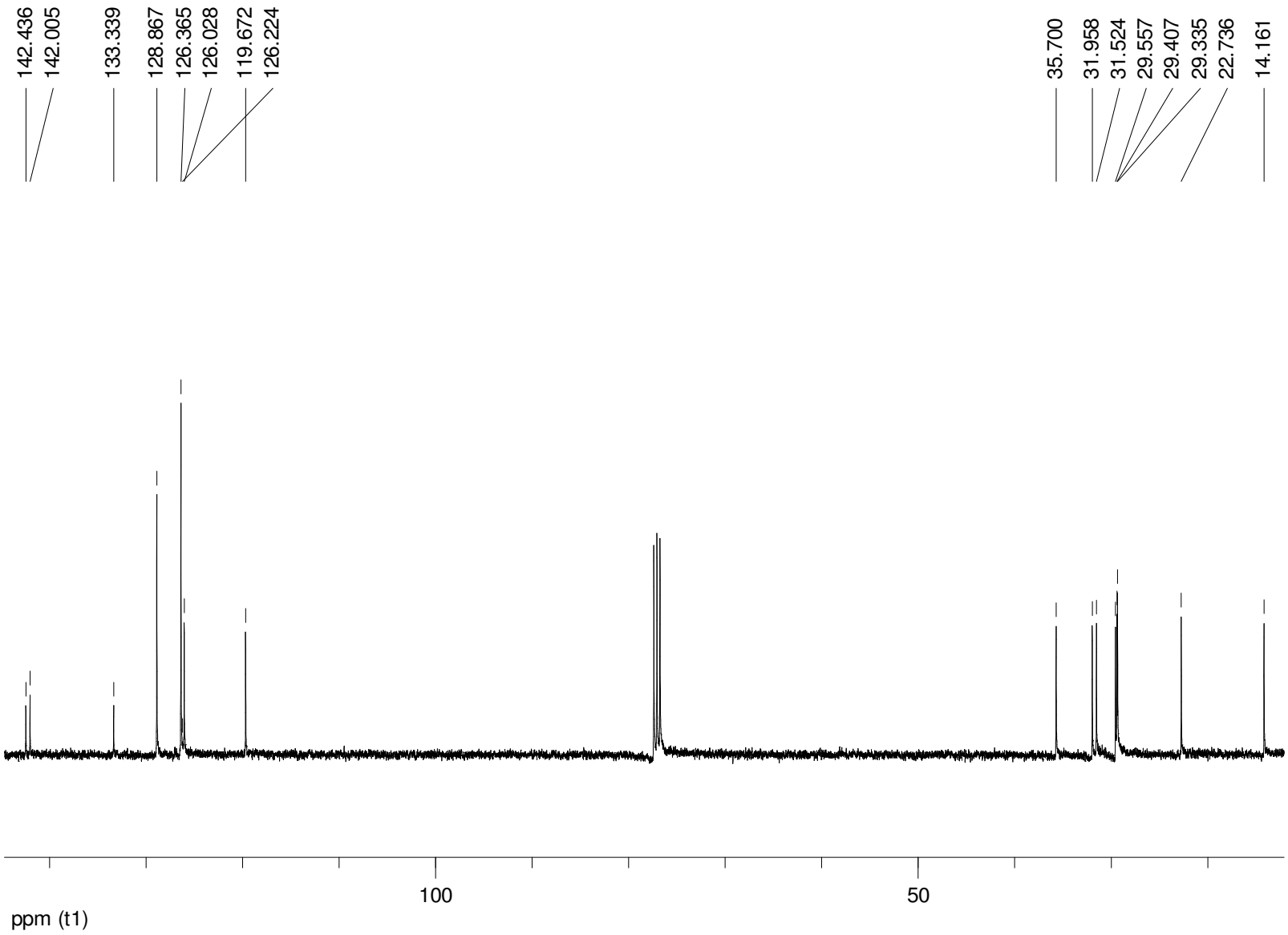
Appendix 2. C^{13}-NMR spectrum of 3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**26**).



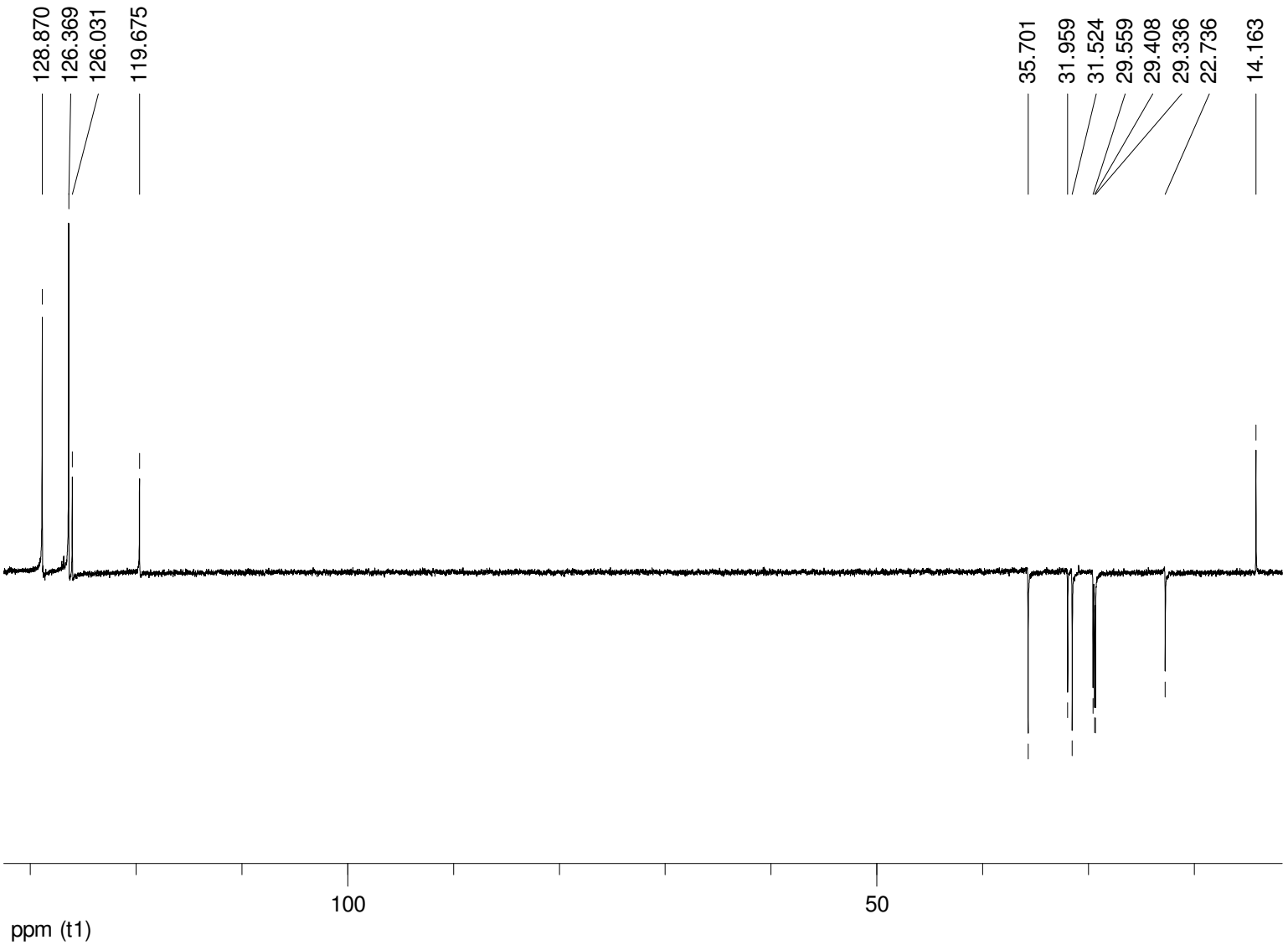
Appendix 3. DEPT-135 spectrum of 3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene (**26**).



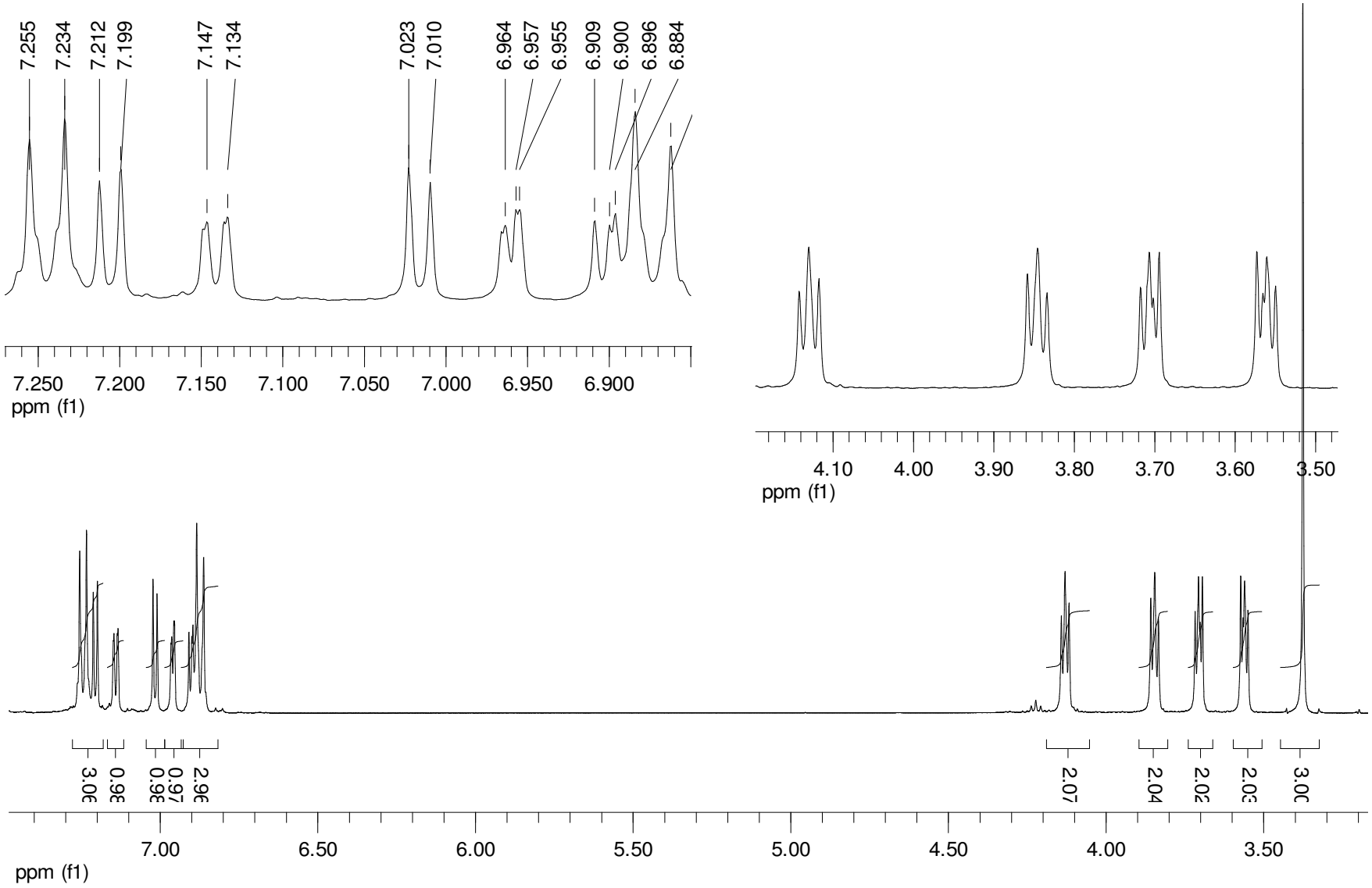
Appendix 4. ^{1}H-NMR spectrum of 3-(4'-octylphenyl)thiophene (**29**).



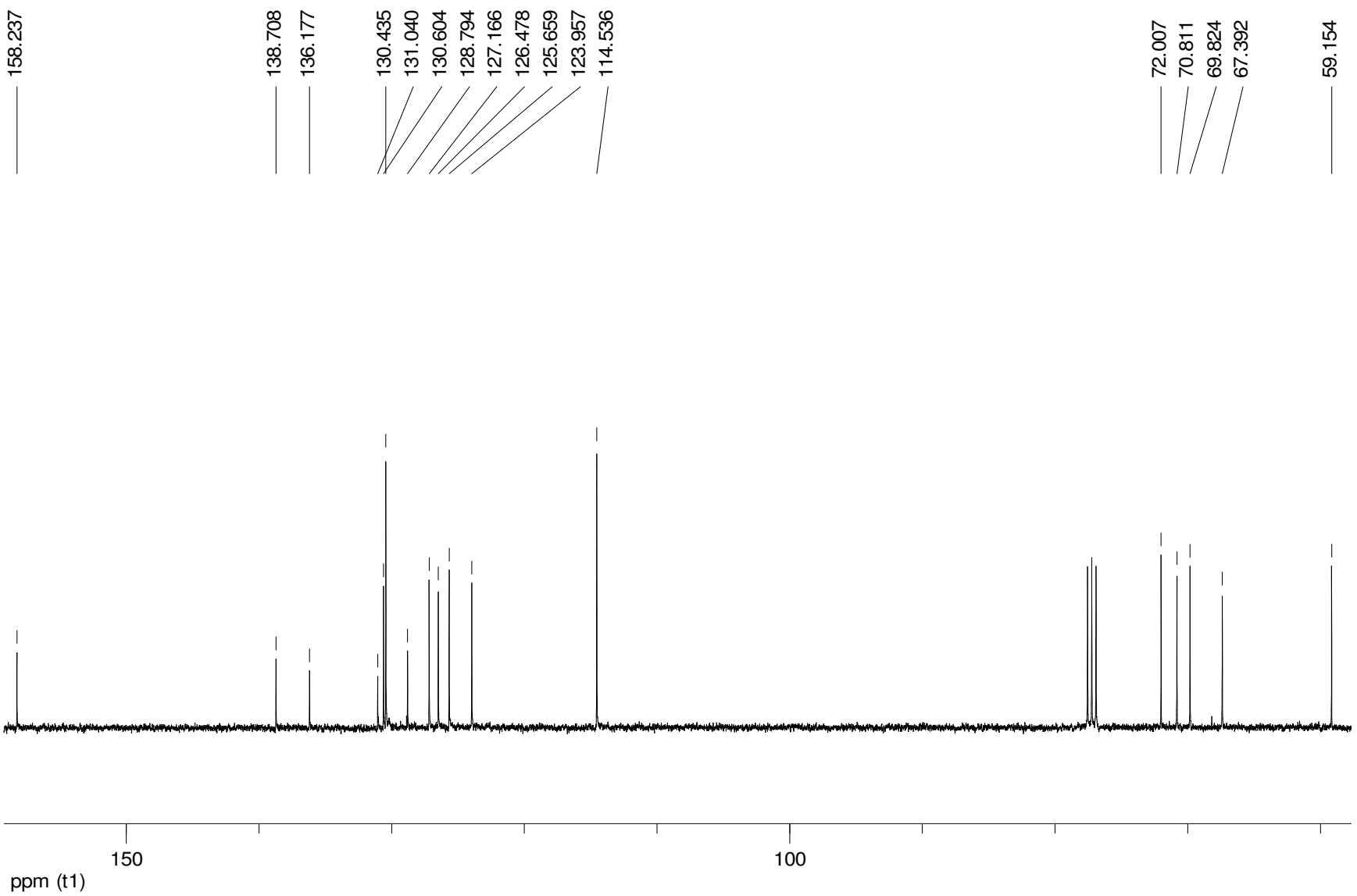
Appendix 5. C^{13}-NMR spectrum of 3-(4'-octylphenyl)thiophene (**29**).



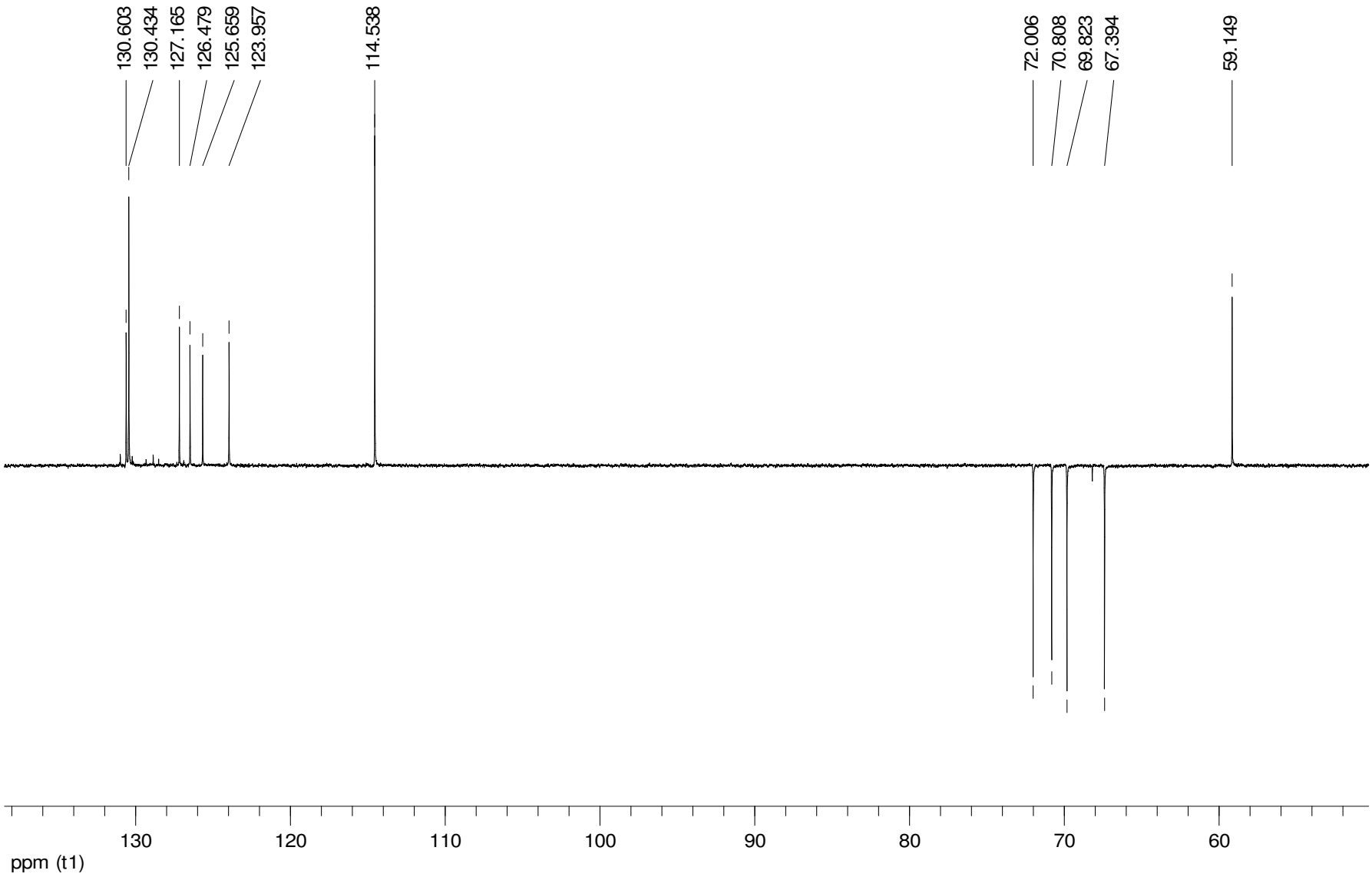
Appendix 6. DEPT-135 spectrum of 3-(4'-octylphenyl)thiophene (**29**).



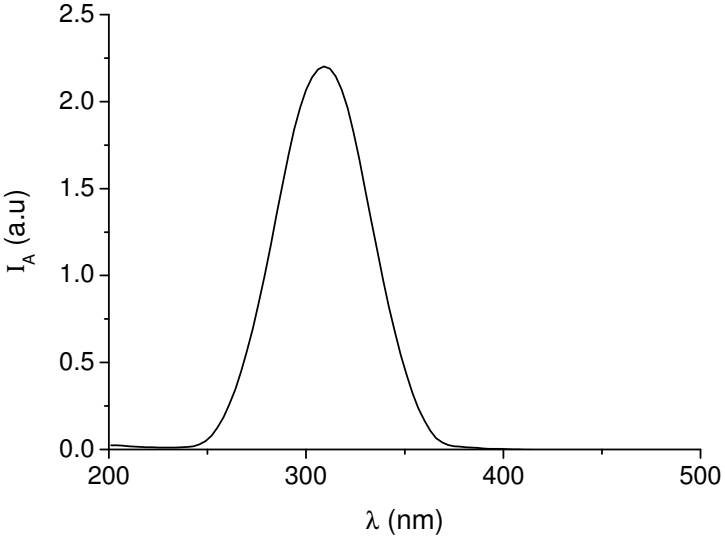
Appendix 7. 1H-NMR spectrum of 3-[4''-(1''', 4''',7'''-trioxaoctyl)phenyl]-2,2'-bithiophene (**31**).



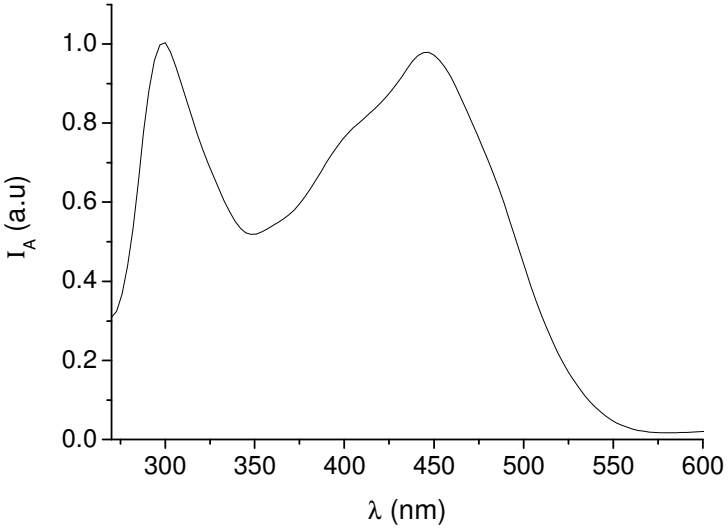
Appendix 8. C^{13}-NMR spectrum of 3-[4''-(1''', 4''',7'''-trioxaoctyl)phenyl]-2,2'-bithiophene (**31**).



Appendix 9. DEPT-135 spectrum of 3-[4’’-(1’’’, 4’’’,7’’’-trioxaoctyl)phenyl]-2,2’-bithiophene (**31**).

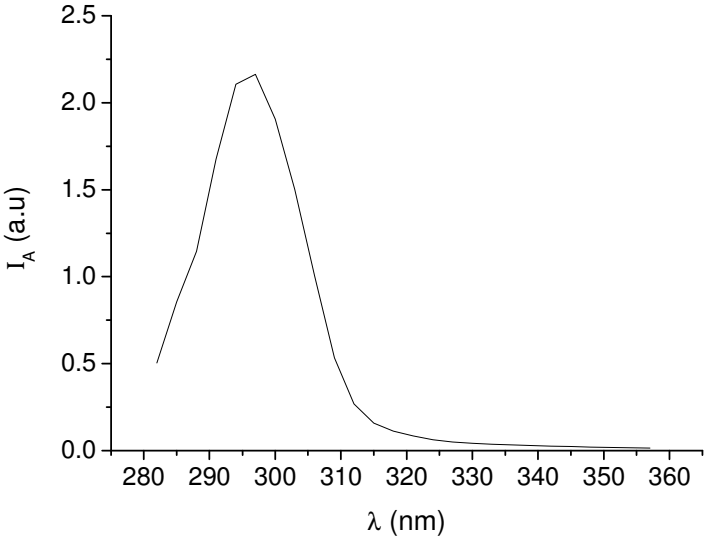


Compound **26**

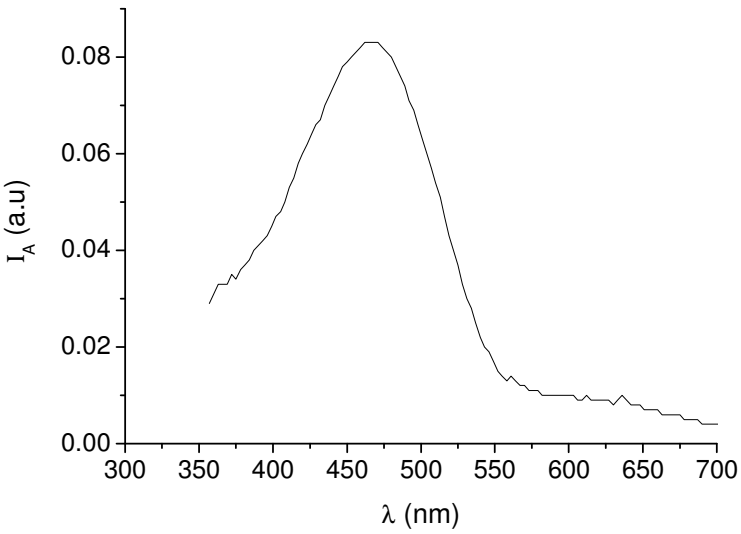


Compound **32**

Appendix 10. UV-Vis spectrum of compound **26** and **32.**

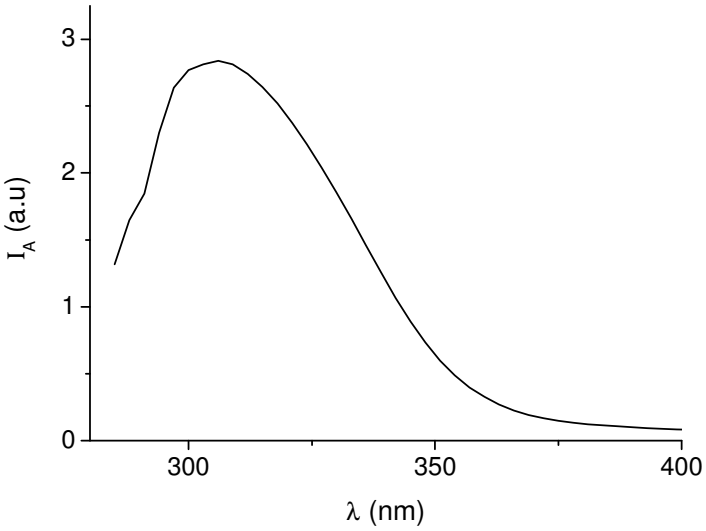


Compound **29**

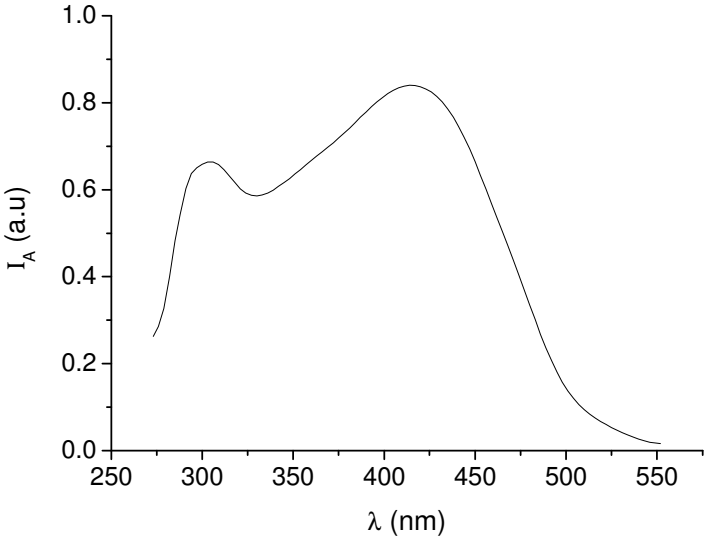


Compound **33**

Appendix 11. UV-Vis spectrum of compound **29** and **33.**



Compound **31**



Compound **34**

Appendix 12. UV-Vis spectrum of compound **31** and **34.**