LOW BAND GAP DONOR-ACCEPTOR STRATEGIES FOR STABLE n-DOPING POLYMERS

THESIS

Presented to the Graduate Council of
Texas State University-San Marcos
In Partial Fulfillment
of the Requirements

for the Degree

Master of SCIENCE

By

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San Marcos, Texas
August 2011

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ACKNOWLEDGEMENTS

Research is not a solitary undertaking and I could not have accomplished any of this without help. Dr. Jennifer Irvin has been an outstanding advisor from day one, when she showed no hesitation in welcoming me to the group despite my complete lack of laboratory skills. She has given me expert guidance at all hours of the day and diligently proofread hundreds of pages. I would also like to thank the other members of my committee, Dr. Chad Booth and Dr. Luyi Sun, for their input.

The Irvin Group has been a supportive family. Mike Cunningham and Blake Bowden were my mentors day-to-day during my first semester in the lab, teaching me basic skills such as TLC and how to use the Rotovap. Jamie Carberry will conduct electrochemical characterization on my monomers, and has also been a valuable friend. Makda Araya, Leslie Wood, James Warren and Adrian Bergia collaborated with me on reactions or synthesized/purified starting materials that saved me hours of work. Other lab members may have had less influence on my research, but all have contributed to the light-hearted atmosphere in the lab that made work fun (not to mention washing thousands of pieces of glassware that we all knew I dirtied).

Other members of the Texas State University-San Marcos faculty have provided valuable assistance. Dr. David Irvin provided NMR training, as well as expert advice on synthesis and purification. Dr. Todd Hudnall spent hours ensuring that I could obtain NMR spectra during the weeks when the Bruker NMR was being installed. Dr. Chang Ji and Drew Brown assisted when gas chromatography was called for. Dr. William Davis

at Texas Lutheran University and Dr. Ben Shoulders at the University of Texas graciously provided NMR time.

I genuinely appreciate the staff in the Department of Chemistry and Biochemistry whose efforts keep the department and building in order. This staff is cheerful, polite and knowledgeable. Laurie Ellis and the office staff kept me in paper and ink, and provided other assistance as necessary. Dave Fehlis patiently reported dry ice status to me and lent me access to solvent and other supplies and equipment.

I also wish to thank my family and friends who listened when I was stressed out even though they did not understand what I was talking about. Thank you all!

This manuscript was submitted on June 15th, 2011.

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ABSTRACT

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by

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August 2011

SUPERVISING PROFESSOR: JENNIFER A. IRVIN

A promising approach for synthesizing stable n-doping polymers is to alternate electron donating and electron accepting moieties along a conjugated polymer backbone. The donors and acceptors used can be chosen to tailor the properties of the resultant polymer to achieve a low band gap or to increase solubility. This research focuses on the use of thiophene and 3,4-ethylenedioxythiophene donor groups in conjunction with a variety of heterocyclic nitrogen-containing derivatives as acceptors. The high nitrogen heterocycles increase the electron affinity of the polymer while the alternation of the donor and acceptor groups increases conductivity. The monomers are synthesized using transition metal mediated coupling reactions and characterized using nuclear magnetic resonance spectroscopy (NMR) techniques.

CHAPTER 1

INTRODUCTION TO ELECTROACTIVE POLYMERS

History of Electroactive Polymers

When Natta and his colleagues first prepared polyacetylene in 1958, its conductive properties were unexpected because polymers were considered to be insulators.[1] Polyacetylene is a simple polymer, $(CH)_n$, that has alternating double and single bonds along the chain (see Figure 1).[2] The conductive black powder was not easy to work with, so it was not until 1977 when Shirakawa and his research team prepared thin films of polyacetylene that research and development of electroactive polymers (EAPs) began.[2]

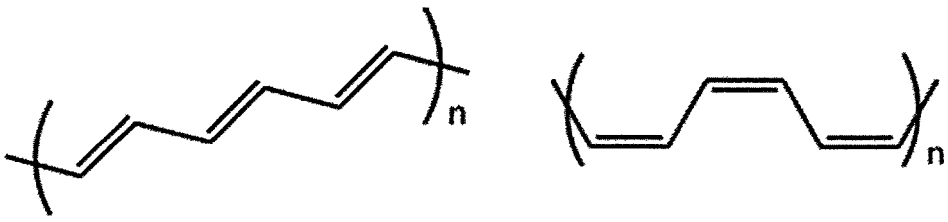


Figure 1: Structures of *trans*-polyacetylene (left) and *cis*-polyacetylene (right)

Shirakawa, MacDiarmid, and Heeger were seeking an organic material which would have the conducting properties of a metal or semi-conductor.[2] Shirakawa and coworkers experimented with both the *cis*-isomer and the more thermodynamically stable *trans*-isomer of polyacetylene in film format.[2] They found that the conductivity increased by several orders of magnitude when the polymer was chemically doped with

arsenic pentafluoride or halogens such as chlorine, bromine or iodine.[2,3] Through experimentation, Shirakawa's team determined that the conductivity of polyacetylene was proportional to dopant concentration at low levels and therefore could be controlled.[3] The team also proposed that replacing the hydrogens of polyacetylene with other substituents could allow for development of many variations of conducting polymers and control of their electronic properties.[3]

Common Electroactive Polymers

In the several decades since Shirakawa, MacDiarmid and Heeger pioneered research in the field of EAPs, a great number of polymers have been synthesized. Some of the most extensively studied classes of conducting polymers are based on polyaniline (PANI), poly(*p*-phenylene) (PPP), and poly(*p*-phenylenevinylene) (PPV) (See Figure 2). Polyheterocycles have also been well investigated, especially variations of polypyrrole (PPy), polythiophene (PT), and poly(3,4-ethylenedioxythiophene) (PEDOT) (See Figure 2).[5,6] These parent polymers are varied by addition of different substituents, such as alkyl or alkoxy groups, to tailor their properties for different applications.

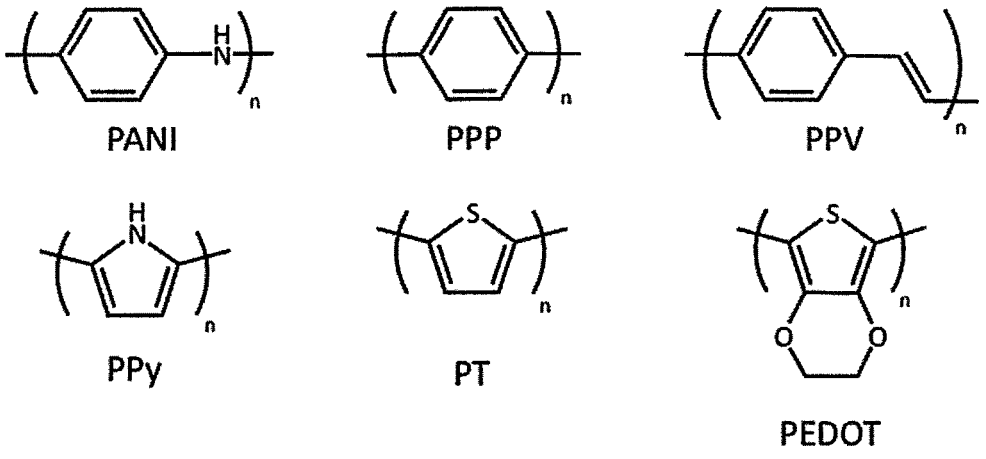


Figure 2: Common electroactive polymers

Band Gap

Whether a material exhibits electronic properties such as conduction or light emission depends on the energy difference between its bonding and antibonding orbitals.[4] The bonding orbitals are also referred to as the valence orbitals, while antibonding orbitals may be called conducting orbitals. In order for the material to be conductive, electrons must be able to acquire enough energy to be promoted from the valence orbitals to the conducting orbitals. Aliphatic or aromatic π orbitals must be present for conductivity to be observed because the energy difference between bonding and antibonding σ orbitals is always too great for electrons to be promoted.[4] The extended conjugation present in the backbone of a polymer leads to many orbitals with similar energies, which blend together to form bands rather than discrete orbitals (see Figure 3).[7,8] The difference in energy between the valence and conducting bands is known as the band gap (E_g). Low band gaps are desirable for ease of excitation of electrons to the electronic state. Conjugation is enhanced in planar molecules because of better alignment of the π orbitals. Thus, planarity of the backbone is desired in electroactive polymers to minimize the band gap.[8,9,10,11,12]

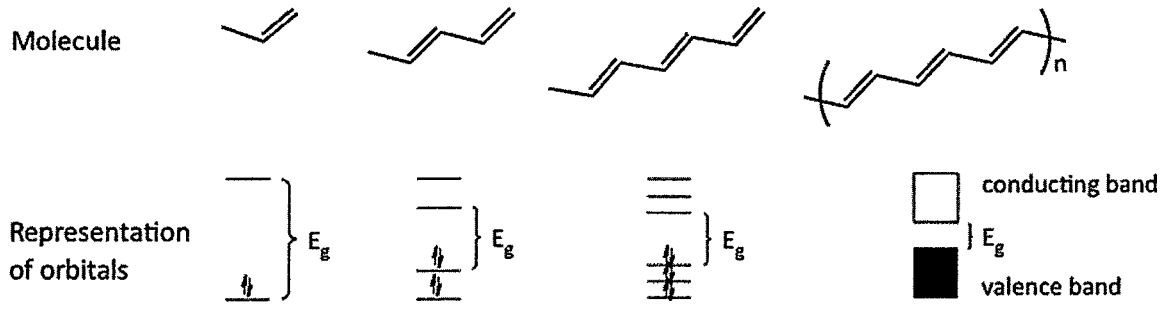


Figure 3: The band gap grows smaller as the length of conjugation increases

Doping is used to reduce the band gap of an EAP by the creation of two new bands between the original valence and conducting bands through hybridization of the orbitals.[13,14] Oxidative doping, known as positive doping or p-doping, removes electrons from the polymer, forming cations along the polymer chain. These positive charges, or holes, are delocalized along the polymer backbone. p-Doping is more common than reductive doping, which is referred to as negative doping or n-doping. An n-doped polymer accepts electrons which are delocalized along the chain. Many useful p-doping polymers have been synthesized,[5,15] but very few usable n-doping polymers have been created. [4,5,9,16,17,18,19,20] The rarity of stable n-doping polymers is generally attributed to the instability of carbanions in the reduced polymer structure.[5,9,17]

Increasing the Stability of n-Doping Polymers

Carbanions are generally unstable. Stability can be increased by delocalizing charge across a conjugated π system.[17] Stability can also be increased when the carbon with the negative charge is bonded to electron withdrawing groups, such as imine nitrogens. There are two general approaches for increasing the stability of the reduced state of a polymer using electron withdrawing groups.

In the first approach, electron withdrawing groups are attached to the polymer as substituents pendant to the main chain (see Figure 4). These pendant groups help to stabilize the carbanions by withdrawing electrons from the polymer backbone. The drawback to this approach is that the charge may become trapped in the pendant groups instead of being transported down the chain. Trapped charge leads to decreased electron mobility and decreased conductivity.[19]

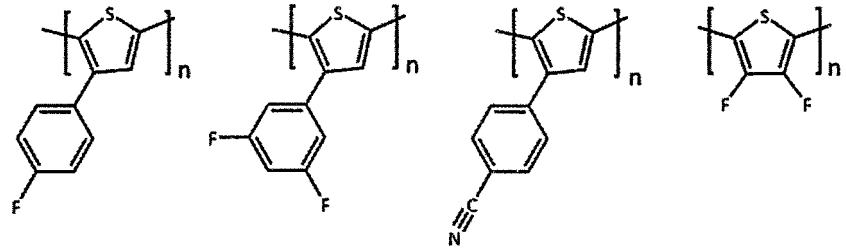


Figure 4: Polymers with pendant electron withdrawing groups[21,22]

The second approach uses electron withdrawing functional groups that are incorporated directly into the polymer backbone, alternating with electron rich (donor) groups (see Figure 5).[7,10,11,12,14,19,23,24] Two donors flank the acceptor group because the donor groups are more readily oxidized, making the monomers more suitable for oxidative polymerization. These polymers are known as D-A-D polymers, which is short for Donor-Acceptor-Donor polymers. Alternating the donor and acceptor groups along the chain creates a push-pull system that prevents charge from becoming trapped. Donor groups should have a low oxidation potential so that they may easily be oxidatively polymerized, while acceptor groups should have a high electron affinity to enhance stability in the negatively charged state. The donor and acceptor moieties can be chosen to engineer properties including band gap, conductivity, absorption color and solubility.[11,14] The ratio of donor to acceptor also seems to influence band gap and the ability to experience n-doping.[12]

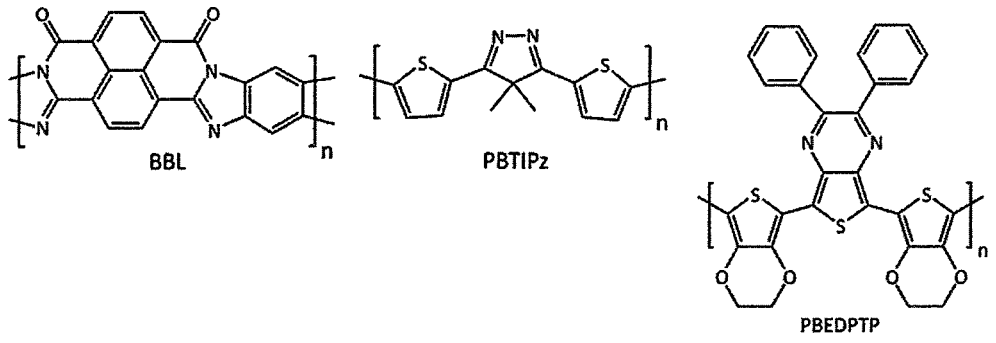


Figure 5: Known donor-acceptor polymers[19,25,26]

Coupling Strategies for Monomer Synthesis

The synthesis of D-A-D monomers requires coupling of several heterocycles, generally two donors and one acceptor. A variety of aryl coupling techniques using transition-metal catalysts have been developed. Stille, Suzuki and Negishi couplings are palladium catalyzed cross-couplings utilizing tin, boron and zinc containing moieties, respectively.[27] Suzuki and Negishi share the 2010 Nobel Prize in Chemistry with Heck for developing the reactions named for them.[28] Sarandeses and coworkers introduced a palladium cross-coupling reaction utilizing a triorganoindium reagent that has also been found to be applicable to a variety of substrates.[29,30,31,32] All of these coupling strategies are believed to undergo the same three basic steps: oxidative addition of the organohalide to Pd(0), transmetallation producing a metal halide, and reductive elimination to generate the new carbon-carbon bond and regenerate the Pd(0) catalyst (see Figure 6).[28,31,33] When indium is used for transmetallation, three ligands can be replaced by halogens; the other metals transfer only a single group.[29,30,31,32]

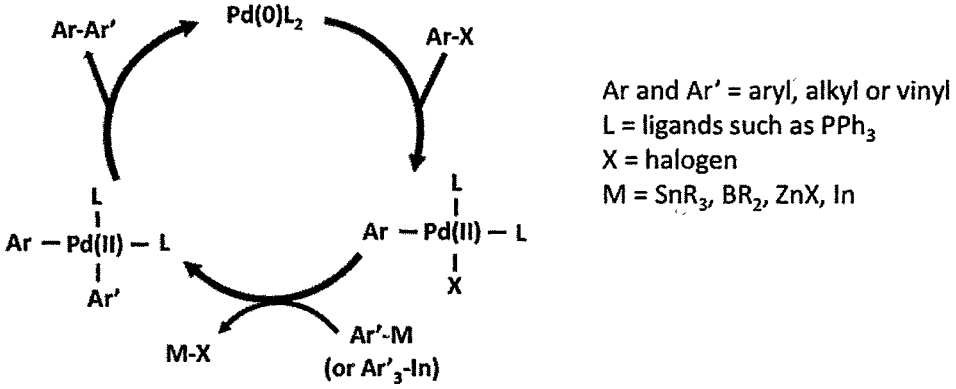


Figure 6: General palladium (0) catalyzed mechanism for carbon-carbon bond formation

Each of these strategies has benefits and drawbacks. While Stille couplings are tolerant of a wide variety of functional groups, the stannyl compounds are extremely

toxic.[28,34] Suzuki couplings are considered non-toxic, but they require synthesis of a boron derivative and addition of a base for transmetallation.[27,33] While Suzuki reactions are compatible with electron withdrawing groups, they are hindered by ortho substituents.[35,36] Negishi reactions require the synthesis of a organozinc reagent, but the resulting compounds are tolerant of a wide range of functional groups on either coupling partner.[34] Sarandeses reactions require preparation of an organoindium reagent and an electrophilic coupling partner, i.e. aryl halides, aryl or vinyl triflates, benzyl bromides and acid chlorides.[29,30,31,32] When nickel catalysts are employed for the coupling of aryl chlorides via Sarandeses reaction, the yields may be improved.[31]

Polymerization

Carbon-carbon bond formation during polymerization of EAPs is rarely accomplished using the coupling methods described above. Catalyzed reactions are expensive but more importantly, many of these polymers are insoluble in common organic solvents, and therefore difficult to process in bulk.[37] An exception to this rule is the Grignard metathesis method (GRIM). GRIM is a nickel (II) catalyzed magnesium-bromine exchange reaction that is employed in polymerization of regioregular polymers from heterocycles.[38] Oxidative polymerization techniques are commonly employed for producing conducting polymers.[5,37] Oxidative polymerization can occur when a potential is applied in the presence of an electrolyte; this process is known as electrochemical polymerization. Chemical oxidative polymerization may be accomplished using oxidizing agents such as ferric chloride, permanganate, or hydrogen peroxide, but the resultant polymers typically exhibit processing limitations due to lack of solubility.[5,37]

Both electrochemical and chemical oxidative polymerization of heterocycles proceed by the same basic mechanism,[5] shown below for thiophene (see Figure 7).

Polymerization is initiated when the oxidant removes an electron from monomer. The radical cation formed may react with another monomer molecule or another radical cation molecule to form dimers. In the case of radical-radical coupling the dimers are dicationic and no longer contain unpaired electrons. When a radical cation reacts with monomer, a radical cationic dimer is formed, which loses a second electron to become a dicationic dimer. The dicationic dimers produced by either type of coupling lose two protons to form the neutral dimer. The process repeats to form polymer.[5]

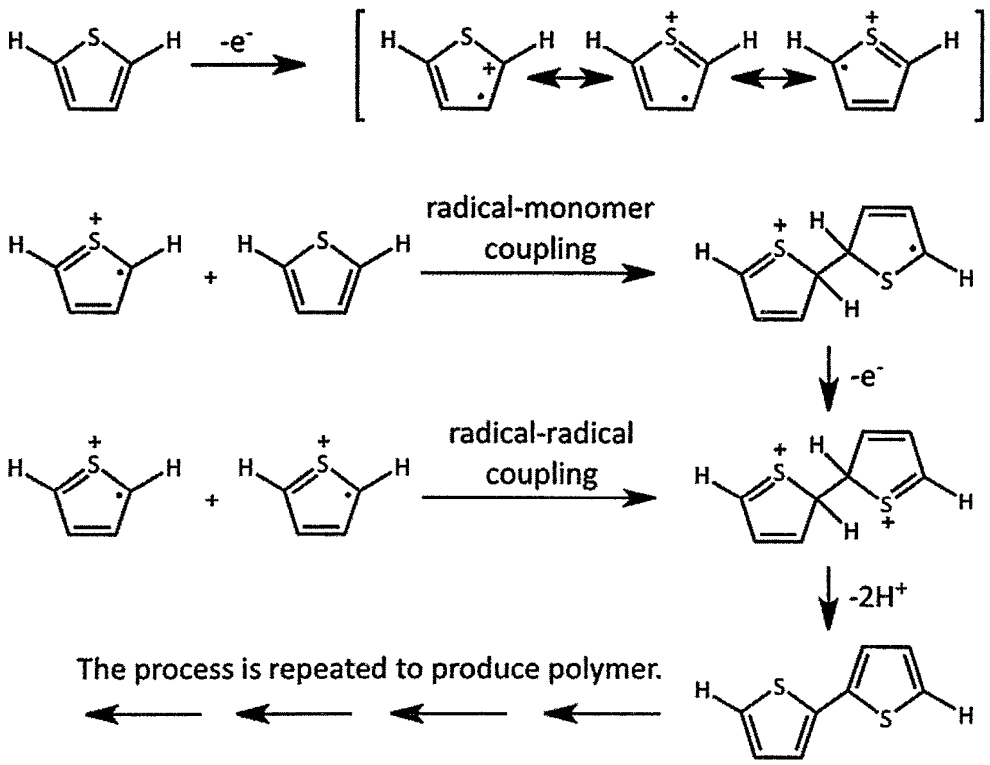


Figure 7: Oxidative polymerization of thiophene[5]

The ease with which a monomer can be oxidatively polymerized depends on its electron density. As electron density increases, the oxidation potential decreases because electron donating groups stabilize the cations formed during oxidation. This is why many

monomers employ the D-A-D approach: the electron deficiencies of the acceptor moieties limit their abilities to undergo oxidative polymerization.[5]

Electropolymerization is often used to create a polymer coating on an electrode for characterization. The conducting form of the polymer is rapidly grown, without use of catalyst. Electropolymerization may also be used for practical applications, since the film thickness can be controlled and patterned electrodes can control polymer placement.[5] The product does not typically require significant purification. Some limitations of this technique are that it is limited by scale, that it requires costly equipment, and that the substrates to be coated must be conductive.[5,37] In addition, some electron deficient monomers will not undergo electrochemical polymerization due to high oxidation potentials.

Chemical oxidative polymerization can be employed when polymerization through electrochemical means is not viable. The reactions are fast, simple and employ relatively mild conditions.[5] The monomer is dissolved in a suitable solvent and a slight excess of oxidant is introduced. The oxidized form of the polymer is produced, usually with noticeable color changes in the solution and precipitation of the product. The insolubility of the EAP limits processability in most cases; the parent polymers polypyrrole, polythiophene, and polyaniline are all insoluble.[37] Solublizing groups attached to the parent monomer can increase solubility of the polymer, but with an associated loss in planarity and therefore conductivity.[5,37]

Polymers may deposit upon the surface of a variety of materials that are immersed in the solution during chemical oxidative polymerization. One benefit to this form of deposition is that it is not limited to conductive materials, and has in fact been applied to

substrates including polymer, glass, fibers, and metal oxides.[37] Reaction conditions can be tailored to minimize the amount of bulk polymer that precipitates while enhancing the amount that is deposited. To eliminate bulk precipitation, the surface to be coated can be pre-treated with oxidant or monomer. When a solution containing the other reactant is introduced, polymerization occurs only on the pre-treated surface.

Applications

Electrochemical Capacitors

An electrochemical capacitor (EC) is a charge storage device in which the oxidation and reduction of electroactive polymers, metal oxides, or carbonaceous materials are used to store electrical energy.[39] An EC device has two electrodes made from EAP, metal oxides or carbon on either side of an electrolyte solution. The electrolyte can be either aqueous or organic.[40] Ionic liquids such as pyrrolidinium and bis(trifluoromethanesulfonyl)imide are a promising alternative to traditional electrolytes, because they show good electrochemical and thermal stability over a wide temperature range and are less volatile than organic solution-based electrolytes.[39] During the charging process, the ions from the electrolyte move toward the electrodes to compensate as the cathode becomes negatively charged and the anode becomes positively charged. When EAPs are utilized as electrodes, charge can be stored throughout the material, as opposed to only at the electrode/electrolyte interface, resulting in greater charge storage capacity.[41]

ECs made from EAPs can be broken down into several types based on the type(s) of polymer(s) used. For maximum voltage output, it is desirable to use a p-doping polymer at one electrode and an n-doping polymer at the other (a so-called type IV EC).[41]

Significant advances in stability of n-doping polymers are required to make this type of EC feasible.[42]

Light Emitting Devices

Light-Emitting Devices (LEDs) have applications in many electronic devices such as cell phones, digital cameras, televisions and other displays.[18] Common organic light emitting diode (OLED) designs use a multi-layer approach, with a cathode and a transparent anode on opposite sides.[18] Sandwiched between the anode and cathode are electron-transport material (ETM), hole-transport material (HTM) and emitter layer (See Figure 8A). When a voltage is applied to the electrodes, holes are injected into the HTM and electrons are injected into the ETM. The holes and electrons that meet create excitons. Some of the excitons emit photons as they decay to the ground state in the emitting layer.[43] The HTM and emitter layers can be combined using a p-type EAP that emits (See Figure 8B), or the ETM and emitter layers could be combined into a n-type emissive EAP (See Figure 8C). If a single material could fulfill the roles of ETM, HTM and emitter, the manufacturing process could be streamlined to the application of a single polymer film (See Figure 8D).[18]

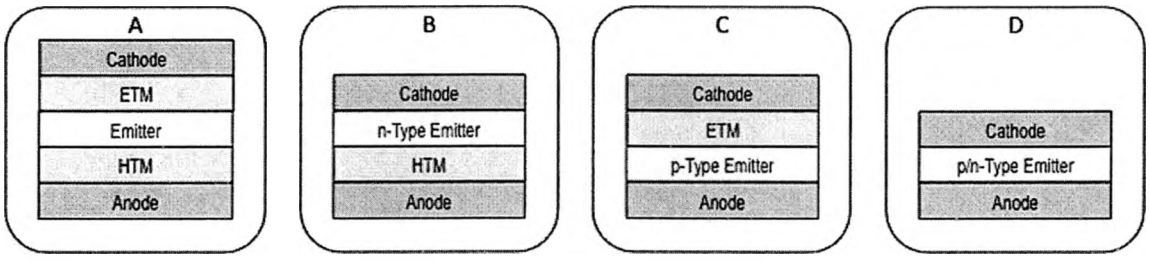


Figure 8: Light emitting device designs[18]

The search for optimal materials for LEDs continues. Using one polymer that is both n-dopable and p-dopable to fulfill the roles of ETM, HTM and emitter could result

in higher efficiency because charge would not have to travel as far to combine. For blue devices, efficiencies in the range of only 4% have been obtained,[43] so there is a large window for improvement. Red, green and blue emitters have all been developed, but the lifetime of all of the known emitters (especially blue) could be improved upon.[43]

Polymer Solar Cells

Polymer solar cells (PSCs) use a mechanism that is similar to that of LEDs, but in reverse, to produce energy from light. Photons of visible light strike an absorptive layer, creating excitons. The excitons, or photoexcited electron-hole pairs, separate into electrons and holes at an acceptor-donor interface. The electrons are transmitted through the acceptor to the anode while the holes are transmitted through the donor material to the cathode to be collected. The transfer time of the exciton must be very short in order to prevent radiative recombination.[4] Bilayer heterojunction devices use very thin films of the donor and acceptor materials to create the interface for separation. Phase separated mixtures of donors and acceptors, known as bulk heterojunctions, more readily allow for the short transfer times required to obtain charge separation.[4,44]

The search for more efficient materials for use in PSCs continues to be the focus for research.[23,45,46] Most bulk-heterojunction PSCs currently use a fullerene derivative as the electron acceptor.[46] Fullerenes have limited absorption, and the small offset between the HOMO of the fullerene and the LUMO of the polymer limits efficiency, so there is impetus to replace them with other materials.[47] Synthesis of stable n-doping EAPs could result in their use as acceptors in PSCs. Presently, EAPs are used as the absorptive and hole transport layer(s) in PSCs. The ideal polymeric material should have a high, broad absorbance to increase photocurrent.[23] A second concern is in increasing charge

separation through optimizing charge transport abilities by tuning the band gap of the polymer.[23,45,46] If charge transport is rapid enough, the absorptive layer could be made thicker, which would also increase the photocurrent.[23]

Motivation for Research

There is a great need for stable n-doping polymers, especially for use in ECs, LEDs, and PSCs.[16,18,41] Therefore, the focus of this research project is the synthesis of monomers containing nitrogen heterocycles for novel donor-acceptor-donor type n-doping polymers, such as BEIPz-TMS, BEIPz, BHexTIPz, B3ETIPz, BTPm, BEPm, B3ETPm, BEBPm and BTBPm (see Figure 9). Seven of the monomers are novel compounds; while BTPm has been reported in literature,[29] its electrochemical characterization was not reported. The higher the electron affinity of the polymer, the greater will be its stability in the reduced state.[19] The electron affinity of these polymers is increased by replacing carbons with imine type nitrogens in the heterocycles.[19]

Monomer synthesis employed several different coupling strategies. An organoindium coupling method was used in the synthesis of BTPm, BEPm, BTBPm, BEBPm, and B3ETPm. Nucleophilic acyl substitution (S_NAc) was used to synthesize BEIPz-TMS, BEIPz, BHexTIPz and B3ETIPz. Once synthesized, the monomers were characterized using Nuclear Magnetic Resonance (NMR) spectroscopy.

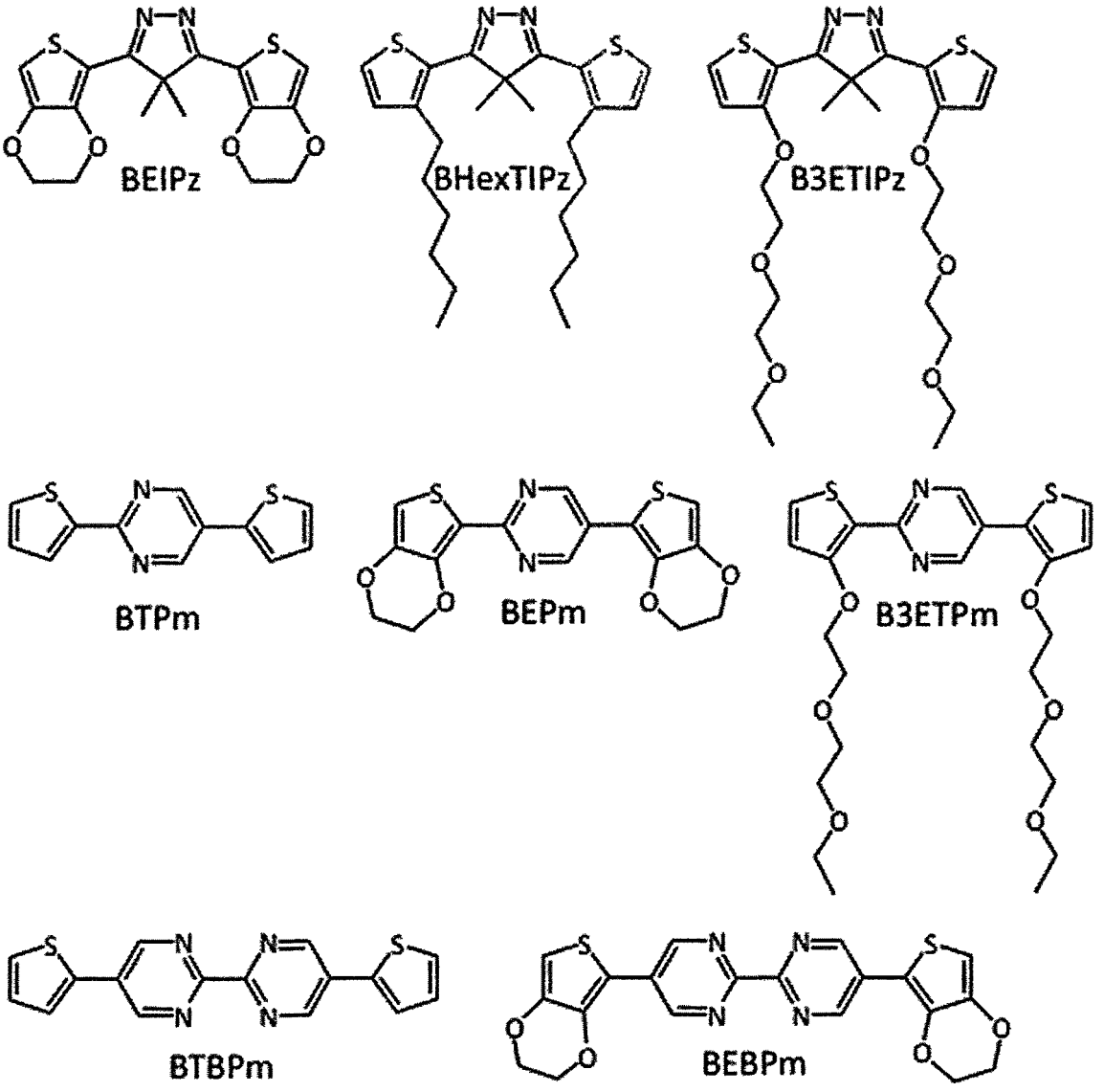


Figure 9: Proposed monomers to be used to synthesize n-doping polymers

CHAPTER II

SYNTHESIS OF BIS-THIENYL ISOPYRAZOLES

Synthetic Method

The isopyrazole series of monomers was derived from bis(thienyl)isopyrazole (BTIPz), a D-A-D monomer produced by Witker and coworkers.[19] The BTIPz monomer was promising because when electropolymerization was accomplished over a broad range, relatively stable n- and p-doping processes were observed, suggesting that transport of both positive and negative ions was occurring throughout the film without significant degradation. The somewhat high oxidation potential of the monomer was attributed to the electron deficiency of the isopyrazole. The isopyrazole moiety was retained, but the donors flanking it were modified to reduce oxidation potential (see Figure 10). The BEIPz monomer was expected to have a lower band gap than that of the original thiophene based structure, because EDOT is known to have a lower oxidation potential than thiophene.[5] The BHTIPz AND B3ETIPz monomers were chosen to increase the solubility of the resultant polymer from that of the original PBTIPz by the addition of solublizing groups at the 3-position of each thiophene, as this would allow for a solution-processable n-doping polymer.

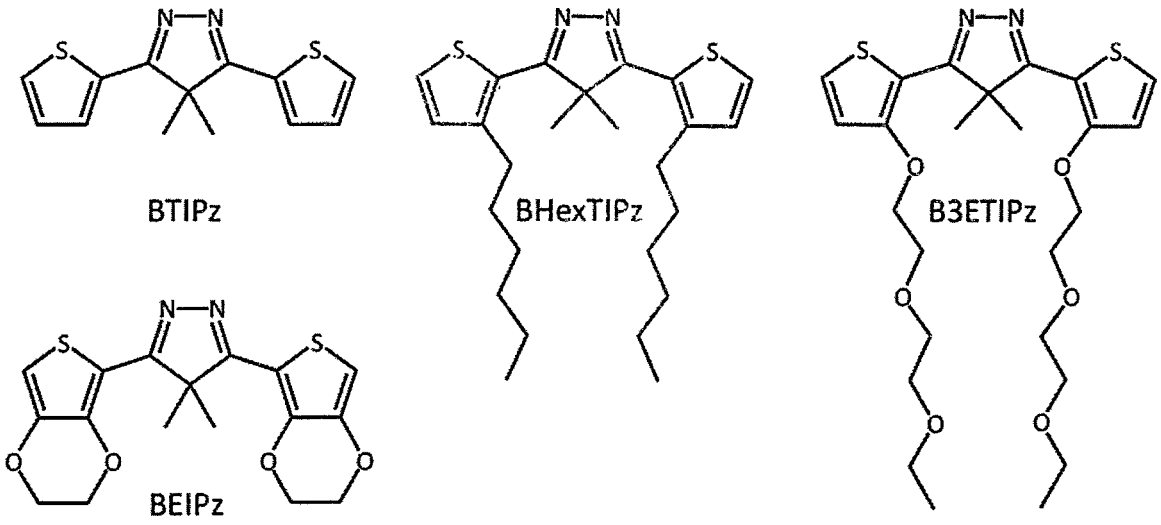
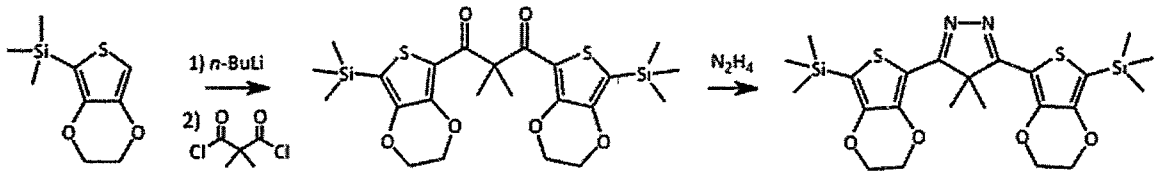


Figure 10: BTIPz and novel thiophene-based isopyrazole monomers

Original attempts at synthesis of the BEIPz monomer in a two step process, such as that set forth by Witker were unsuccessful due to inability to purify the bridged intermediate.[19] Conducting a one-pot synthesis eliminated this problem and allowed for modest yields of trimethylsilyl (TMS) protected BEIPz (see Scheme 1). TMS protecting groups were bonded to the 2-position of the EDOT prior to coupling because the oxidation potential of EDOT caused concern about unintentional side products and decomposition during exposure to oxygen. A later trial reaction without TMS groups resulted in a complex mixture, which appeared to confirm their necessity. A nucleophilic acyl substitution was accomplished without catalyst. Another notable change made to the procedure was increasing the reflux time for the formation of the bridged intermediate, since this is the low-yield step.[19] The ring closure step goes to nearly 100% completion more rapidly. While no mechanism for the ring closure has been postulated in the literature, it seems likely that the process is similar to that of hydrazone formation. The reaction begins with nucleophilic addition of a hydrazine nitrogen to the carbon of one of the carbonyls. A proton transfer occurs between the carbonyl oxygen and the attacking

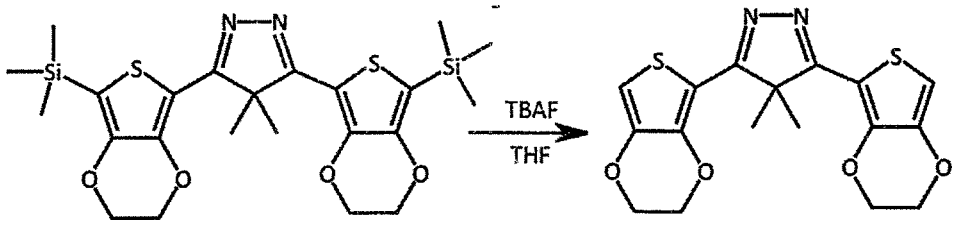
nitrogen, followed by hydrazine base catalyzed dehydration to form an imine. The second nitrogen reacts with the second carbonyl, and the process is repeated to give ring closure.



Scheme 1: One pot reaction scheme for BEIPz-TMS

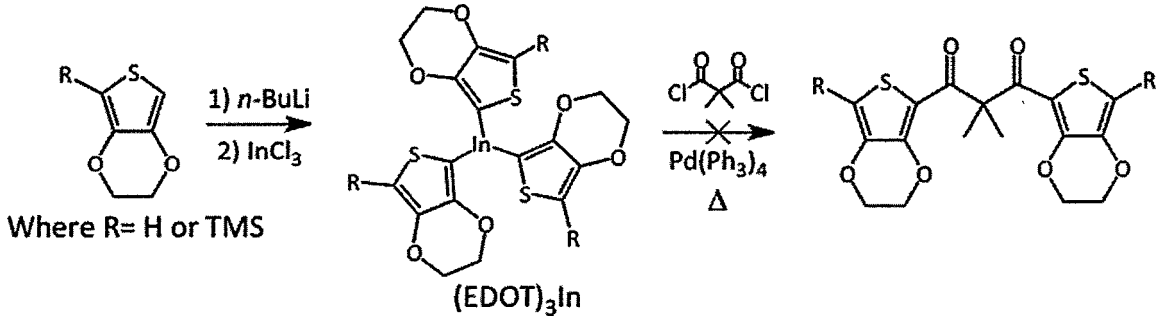
After several attempts with a longer coupling time, we achieved 26% yield of the EDOT version. A Negishi coupling employing $ZnCl_2$ and palladium catalyst was used in the synthetic method reported by Witker for the thiophene version,[19] resulting in a 23% yield. One attempt was made to use the Negishi coupling in synthesis of BEIPz-TMS to increase yields, but the desired product was absent from the proton NMR. Instead, the NMR seemed to show that homocoupling between the EDOT or EDOT-TMS had occurred.

The TMS protecting groups, incorporated to improve monomer stability, are not necessary for electrochemical polymerization of the monomer, and may even be detrimental to film formation. Removal of the TMS groups from the monomer was accomplished using tetrabutylammonium fluoride (TBAF) (see Scheme 2). An attempt to prepare BEIPz in a one pot synthesis directly from 3,4-ethylenedioxythiophene was made in an effort to streamline the procedure for producing the target monomer. Without the TMS groups, the products of the reaction were less soluble in diethyl ether. As mentioned above, more side products were made when TMS was not employed, and purification of the reaction mixture was not successful.



Scheme 2: Deprotection to produce the BEIPz monomer

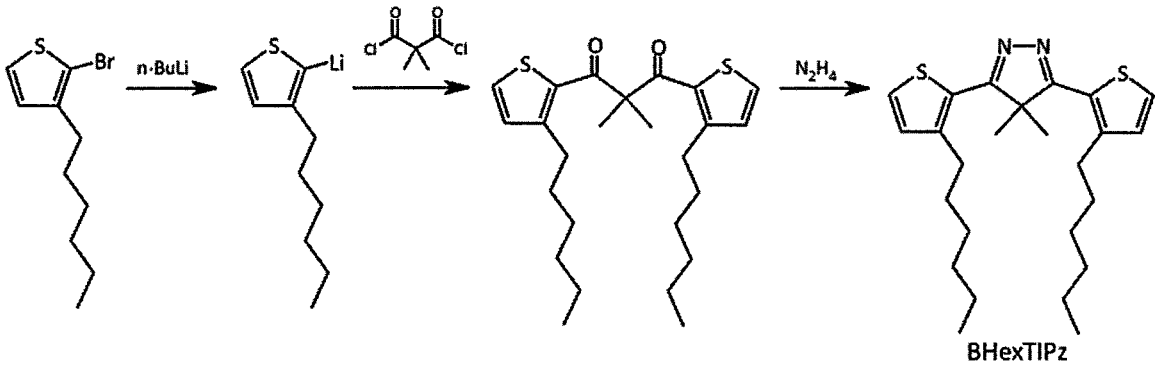
In order to improve yields of BEIPz, Sarandeses coupling was attempted in the synthesis of BEIPz-TMS and BEIPz (see Scheme 3). Proton NMR of the product of the reaction was not consistent with inclusion of the isopyrazole moiety. Dimethyl malonyl chloride does not appear to be a useable substrate for the indium catalyzed reaction, even though Pérez *et al.*[31] reported that ketones could by produced with indium reagents from acid chlorides. However, the examples cited used a Pd (II) catalyst rather than the Pd (0) catalyst employed here. Other factors that could have contributed to the failure of this reaction include insufficient reflux period and the work-up of the carbonyl intermediate prior to ring closure, which is avoided in the one-pot synthesis.



Scheme 3: Sarandeses coupling of EDOT and dimethylmalonyl chloride

Nucleophilic acyl substitution was again employed to synthesize BHexTIPz (see Scheme 4). Proton NMR of the crude product was consistent with the predicted spectrum of the desired product, and the crude yield of this product compared to BEIPz-TMS was greatly improved. However, the addition of the hexyl groups prevented the product from

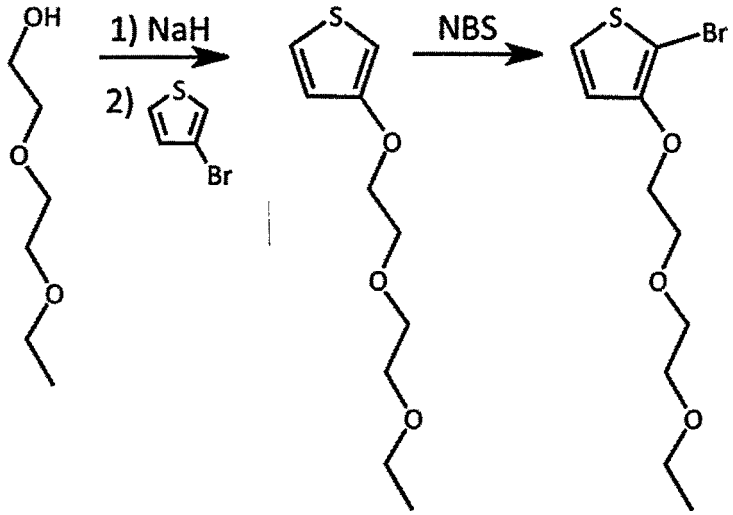
solidifying, enhancing the challenge of purification. Only a few drops of the viscous oil were distilled at 235°C, and the heating seemed to cause degradation, as the NMR spectrum showed that the thienyl proton peaks originally at 6.85 and 7.22 were replaced with peaks at 6.99, 7.34 and 7.37 for both the distillate and the starting material. A sample was submitted for gas chromatography, but a spectrum was not obtained. The operator suggested that the molecular weight was too high for the compound to be suitably volatile. Sublimation produced no solids at temperatures up to 175°C; higher temperatures were not attempted for fear of oligomerization. Chilling to -104°C (dry ice/diethyl ether) also did not produce solids. The product appeared to react on silica gel and alumina, so column chromatography did not achieve separation. Despite all attempts to purify BHexTIPz, separation was not achieved.



Scheme 4: Synthesis of BHexTIPz

Next, an oligoether group derived from 2(2-ethoxyethoxy)ethanol (EEE) was chosen as a solublizing group in place of the hexyl group. The 3-[2-(2-ethoxyethoxy)ethoxy]-thiophene (EEETh) had to be synthesized and brominated prior to coupling (see Scheme 5). Monomer coupling followed the same steps shown for BHexTIPz (see Scheme 4). We anticipated that due to dipole interactions of the oxygens in the chain, this product might solidify more readily than the hexyl version, lending to

easier purification. While proton NMR showed peaks consistent with the desired product, there also appeared to be starting materials present. The product mixture was an oil, similar to that produced for BHexTIPz, and again purification was not achieved.



Scheme 5: Synthesis of 2-bromo-3-[2-(2-ethoxyethoxy)ethoxy]-thiophene

Materials

3,4-Ethylenedioxythiophene (EDOT) was purchased from Aldrich and purified prior to use. Purification included dissolving EDOT in dichloromethane, washing three times with 0.1M HCl, neutralizing with saturated sodium bicarbonate solution, and drying the organic layer over $MgSO_4$. The organic phase was filtered through neutral alumina prior to evaporation under reduced pressure. The EDOT was then vacuum distilled and placed in the freezer under argon until use.

n-Butyl lithium (n-BuLi), anhydrous tetrahydrofuran (THF), dimethylmalonyl chloride, tetrabutylammonium fluoride (TBAF), anhydrous hydrazine, anhydrous sodium carbonate, and 3-hexylthiophene were purchased from Aldrich and used as received. n-Bromosuccinimide was purchased from Acros, recrystallized from water, and dried under vacuum prior to use. Chlorotrimethyl silane, tetrakis(triphenylphosphine) palladium (0)

($Pd(PPh_3)_4$), toluene, 2(2-ethoxyethoxy)ethanol, copper bromide, anhydrous dimethylformamide (DMF), 3-methoxythiophene, *p*-toluenesulfonic acid, phosphorus pentoxide and indium chloride were purchased from Acros and used as received. Diethyl ether, ethyl acetate, hexanes, dichloromethane, cyclohexane, hydrochloric acid, ammonium chloride, sodium bicarbonate and anhydrous magnesium sulfate were used as received from Fischer. 3-Bromothiophene was purchased from both Acros and Alfa Aesar and used as received. Sodium hydride 57-63% oil dispersion was purchased from Alfa Aesar and used as received. Column chromatography and short plug filtration were accomplished using Selecto Scientific 32-63 μm silica gel or Acros 50-200 μm neutral aluminum oxide.

Structural Identification

Structural identification was accomplished via ^{1}H and ^{13}C NMR. EDOT-TMS and BHexTIPz spectra were obtained using a Varian INOVA 400 MHz NMR. Spectra of BEIPz-TMS, BEIPz, EEETh, and Br3ETh were obtained on a Bruker Avance III 400 MHz NMR.

Synthesis

2-Trimethylsilyl-3,4-ethylenedioxythiophene (EDOT-TMS)

Synthesis of this compound was reported by Takasu *et al.*;[48] several deviations from their synthesis were made as noted. EDOT (6.00g, 0.0422 mol) was mixed with 50 mL of anhydrous THF under argon in a three neck flask fitted with an argon inlet. The flask was chilled to -78°C, and 2.5M n-BuLi in hexanes (0.0422 mol, 28.1 mL) was added dropwise. The mixture was stirred for one hour, and then chlorotrimethyl silane (0.0464 mol, 5.9 mL) was added via syringe. The mixture was allowed to warm to room

temperature and stirred for an additional hour, although Takasu reports stirring for 3 hours at room temperature. The published work up required the reaction mixture to be evaporated under reduced pressure and extracted with hexanes.[48] Instead, the reaction mixture was poured into H_2O in a separatory funnel. The aqueous layer was extracted five times with diethyl ether, and the combined organic fractions were dried over $MgSO_4$, filtered and evaporated under reduced pressure. Distillation was unnessary because the product solidified after evaporation. Sublimation yielded a white, crystalline solid (8.05 g, 89%). Mp 49-51°C. ^{1}H NMR ($CDCl_3$) δ 6.55 (s, 1H), 4.18 (s, 4H), 0.28 (s, 9H). Lit: ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.54 (s, 1H), 4.17 (s, 2H), 4.16 (s, 2H), 0.286 (s, 9H).[48]

3,5-Bis-(2-trimethylsilyl-3,4-ethylenedioxythien-5-yl)-4,4-dimethyl isopyrazole (BEIPz-TMS)

A three neck round bottom flask fitted with a condenser, argon inlet, and septum was charged with EDOT-TMS (5.00g, 0.0233 mol) under positive argon flow. Anhydrous THF (50 mL) was added via cannula transfer. The flask was chilled to -78°C. n-BuLi (2.5M in hexanes) (0.0257 mol, 10.3 mL) was added dropwise and stirred for one hour. After one hour, dimethyl malonyl chloride (0.0117 mol, 1.56 mL) was added dropwise via syringe. After 30 minutes, the mixture was stirred for 4 days at reflux. After 4 days, THF was removed by evaporation under reduced pressure. Toluene (50 mL) was added by syringe with vigorous stirring. Anhydrous hydrazine (0.1165 mol, 3.4 mL) was added via syringe and the mixture was stirred at reflux for 3 days. The reaction mixture was washed with H_2O (100 mL), and the aqueous layer was extracted six times with 60 mL portions of diethyl ether. The combined organic layers were dried over sodium carbonate, filtered, and evaporated under reduced pressure. The product was dissolved in a minimum amount of diethyl ether and precipitated into hexanes. After

filtration through paper, the resulting yellow powder (1.65g, 27%) was stored over P_2O_5 in a desiccator. Mp: 240-243°C (dec). ^{1}H NMR ($CDCl_3$) δ 4.30 (m, 4H), 4.23 (m, 4H), 1.69 (s, 6H), 0.29 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 172.81, 146.86, 142.14, 116.79, 113.82, 64.67, 63.96, 59.03, 19.23, 0.92.

3,5-Bis-(3,4-ethylenedioxythiophen-2-yl)-4,4-dimethyl isopyrazole (BEIPz)

BEIPz-TMS (0.700 g, 0.00134 mol) was dissolved in anhydrous THF (10 mL) in a three neck flask fitted with an argon inlet under positive argon flow. TBAF (1M in THF, 0.00281 mol, 2.81 mL) was added dropwise via syringe and the mixture was stirred for 15 minutes at room temperature. The reaction mixture was poured into H_2O and extracted with dichloromethane. The organic layers were dried over sodium carbonate, filtered and evaporated under reduced pressure. The resultant solid was dissolved in a minimum amount of dichloromethane and precipitated into hexane. After filtration, the orange-yellow powder (0.3456g, 69%) was dried under vacuum at 65°C overnight to remove residual solvent. Mp: 236-238°C (dec.). ^{1}H NMR ($CDCl_3$) δ 6.49 (s, 2H), 4.33-4.35 (m, 4H), 4.22-4.24 (m, 4H), 1.70 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 173.01, 141.67, 141.66, 109.79, 104.28, 64.97, 64.06, 59.06, 18.80.

3,5-Bis-(3-hexylthiophen-2-yl)-4,4-dimethyl isopyrazole (BHexTIPz)

The procedure used to synthesize BEIPz-TMS was followed using 3-hexylthiophene (0.020 mol, 5.00 g), THF (125 mL), 2.5M n-BuLi (0.022 mol, 8.89 mL), and dimethyl malonyl chloride (0.010 mol, 1.35 mL). The product was a viscous red oil at room temperature. Purification was attempted via recrystallization in a diethyl ether/dry ice bath, sublimation, and distillation without success. Column chromatography was also implemented using neutral alumina solid phase with

cyclohexane:diethyl ether mobile phase. The product reacted with the column, producing many additional spots which were observed via TLC. Even using approximately 6 mL aliquots, separation was not achieved. The compound was not successfully purified for electrochemistry or elemental analysis. ^{1}H NMR ($CDCl_3$) δ 7.22 (dd 1H), 6.92 (m 2H), 2.62 (t, 4H), 1.57-1.72 (overlapping multiplets, 8H), 1.30 (s, 6H), 1.08-1.26 (overlapping multiplets, 8H), 0.88 (t, 6H).

3-[2-(2-Ethoxyethoxy)ethoxy]-thiophene (EEETh)

Several methods were employed for synthesis of this compound. First, a transetherification similar to that reported by Guo[49] was attempted using 3-methoxythiophene. 3-Methoxythiophene (0.0219 mol, 2.16 mL) was dissolved in toluene (50 mL) in a flame dried 3-neck flask under argon. Toluenesulfonic acid (0.00219 mol, 0.417 g) was added along with 2-(ethoxyethoxy)ethanol (0.0438 mol, 5.93 mL). The mixture was heated to reflux and stirred overnight. The pale brown mixture was poured into H_2O in a separatory funnel. The organic layer was separated and washed with a second aliquot of H_2O. The aqueous washes were combined and extracted twice with dichloromethane (60mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield a brown oil. The oil was decolorized with activated carbon and purified on a silica column with 75:25 hexanes:ethyl acetate eluent. A slightly yellow oil (0.701 g, 15%) was obtained.

In an effort to improve yield, the synthesis as reported by Lai[50] (with a reported crude yield of 82%) was attempted. Sodium hydride, 57-63% in mineral oil, (0.118 mol, 4.7 g) was added to a flame dried 3 neck flask under positive argon flow. Anhydrous dimethylformamide (20 mL) was added via syringe. The mixture was chilled to 0°C in a

ice/water bath prior to the dropwise addition of 2-(2-ethoxyethoxy)ethanol (EEE) (0.393 mol, 53.3 mL) using a constant pressure addition funnel over a 30 minute period. When addition of EEE was complete, the reaction mixture was allowed to warm to room temperature and stirred for one hour. 3-Bromothiophene (0.0786 mol, 12.8 g) was added via syringe along with copper bromide (0.00786 mol, 1.13 g) under positive argon flow. This mixture was heated to 110°C for 30 minutes, at which time the reaction was allowed to cool prior to addition of 1M NH_4Cl solution (75 mL). After stirring 10 minutes, this mixture was extracted three times with diethyl ether (70 mL portions). The organic extracts were combined and dried over $MgSO_4$, filtered and evaporated under reduced pressure. Purification was accomplished using column chromatography as described above to yield a slightly yellow oil (2.13 g, 12.5%). The reaction was repeated using the same amounts of reactants but substituting tetrahydrofuran for DMF and heating the reaction to reflux for 2 days. The quenched reaction was washed with ~1M sodium hydroxide rather than H_2O. After purification 1.74 g of oil (10.2%) was obtained.

Due to the low yields of the previous methods, another attempt was made to synthesize EEETh by a new procedure. EEE (50 mL) was added under positive argon pressure to a flame dried 3 neck flask. A water bath was used to dissipate heat as, under positive argon flow, NaH (57-63% in mineral oil, 0.0801 mol, 3.20 g) was added in small portions. Hydrogen gas was evolved during addition. This mixture was stirred for 2 hours at room temperature and gradually became dark red in color. CuBr (0.0534 mol, 7.50 g) was added under positive argon flow, followed by slow addition of 3-bromothiophene (0.0534 mol, 5.00 mL). This was heated to reflux and stirred overnight. The product was quenched with ammonium chloride solution, extracted with diethyl

ether, dried over $MgSO_4$, filtered and reduced prior to purification on a silica column with 75:25 hexane:ethyl acetate eluent to yield 6.11 g (53%) of yellow oil. ^1H NMR ($CDCl_3$) δ 7.13 (m, 1H), 6.75 (m, 1H), 6.24 (m, 1H), 4.10 (t, 2H), 3.82 (t, 2H), 3.69 (t, 2H), 3.60 (t, 2H), 3.52 (m, 2H),1.20 (t, 3H). Lit: ^1H NMR 300 MHz ($CDCl_3$) δ 7.16 (m, 1H), 6.78 (m, 1H), 6.25 (m, 1H), 4.12 (t, 2H), 3.84 (t, 2H), 3.71 (t, 2H), 3.61 (t, 2H), 3.52 (m, 2H), 1.21 (t, 3H).[50]

2-Bromo-3-[2-(2-ethoxyethoxy)ethoxy]-thiophene (Br3ETh)

A 250 mL 3 neck flask fitted with air inlet valve and stir bar was flame dried and charged with THF (30 mL) and glacial acetic acid (30 mL). EEETh (0.0271 mol, 5.86 g) was added via syringe and the mixture was chilled to 0°C in an ice/water bath. N-Bromosuccinimide (0.0266 mol, 4.27g) was added over 30 minutes using a constant pressure powder addition funnel. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was evaporated at reduced pressure to remove THF. The remaining volume was extracted with diethyl ether (70 mL portions) three times. The organic extracts were combined and washed with saturated sodium bicarbonate solution (100 mL portions) four times, and H_2O (70 mL) once. The organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to yield a greenish oil (7.46 g, 95%). The oil was dissolved in ether and decolorized over activated carbon, filtered through silica gel and evaporated under reduced pressure to yield a yellow oil. ^1H NMR (CD_2Cl_2) δ 7.15 (d, 1H), 6.72 (d, 1H), 4.10 (t, 2H), 3.69 (t, 2H), 3.58 (t, 2H), 3.48 (t, 2H), 3.42 (m, 2H),1.09 (t, 3H). ^{13}C NMR (CD_2Cl_2) δ 154.90, 124.76, 118.24, 92.01, 72.07, 71.31, 70.22, 70.14, 66.85, 15.38.

Bis-(3-[2-(2-ethoxyethoxy)ethoxy]-thiophen-2-yl)-4,4-dimethyl isopyrazole (B3ETIPz)

Synthesis followed the same steps as described for BEIPz-TMS using the following quantities. Br3ETh (0.0101 mol, 3.00g) in THF (20 mL), n-BuLi (0.0111 mol, 4.46 mL of 2.5M in hexanes), and dimethyl malonyl chloride (0.00507 mol, 0.676 mL). The THF was evaporated under reduced pressure prior to addition of toluene (20 mL) and hydrazine (0.0507 mol, 1.49 mL). After 36 hours, the reaction was cooled to room temperature and washed with H_20 (100 mL). The water layer was extracted with ether (4X, 100 mL) and NaCl was added to remove the emulsion. The aqueous layer was subsequently extracted with chloroform (2X, 75 mL). The organic extracts were separately dried over $MgSO_4$, filtered and evaporated under reduced pressure. Precipitation into hexanes did not produce solids that could be collected by filtration. Dissolving the product in diethyl ether and chilling the solution in a dry ice/diethyl ether bath to -104°C did not produce crystals. Thin layer chromatography did not suggest separation by column chromatography would be successful. Distillation was not attempted due to the anticipated high boiling point (based on the high boiling point observed for the EEETh starting material) and for fear of degradation and oligomerization. The proton NMR spectrum of the crude mixture is consistent with that of the desired product as well as impurities from starting material or biproducts.

CHAPTER III

SYNTHESIS OF BIS-THIENYL PYRIMIDINES

Synthetic Method

Several D-A-D molecules were targeted using the pyrimidine moiety as the acceptor species between thiophene-based donor groups. While 2,5-bis(thiophen-2-yl)-pyrimidine (BTPm) has been previously reported,[25] its electronic properties had not been reported. Because of the nitrogen rich heterocycle sandwiched between the electron rich thiophenes, the structure appeared promising as an n-doping monomer. Again, variations in structure were proposed to decrease band gap and increase conductivity and solubility (see Figure 11).

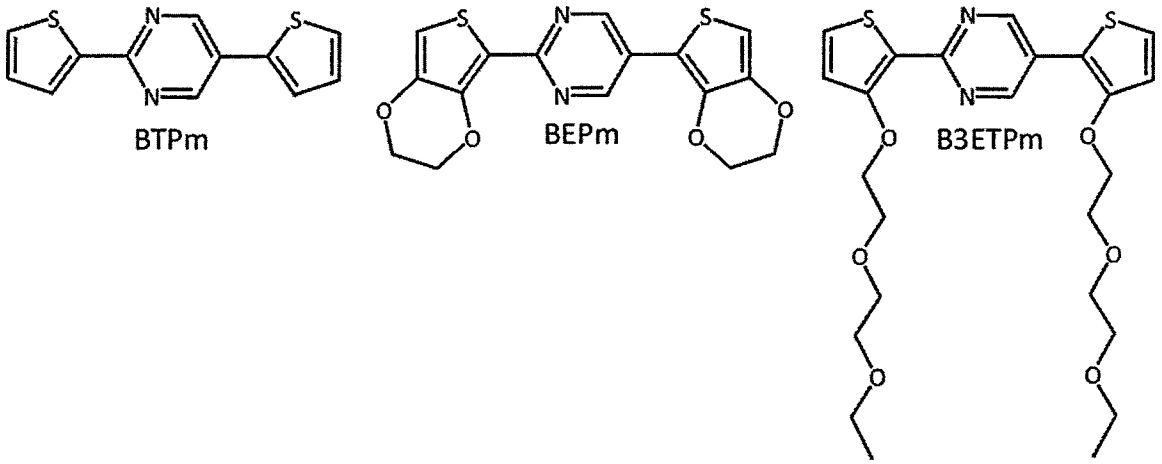
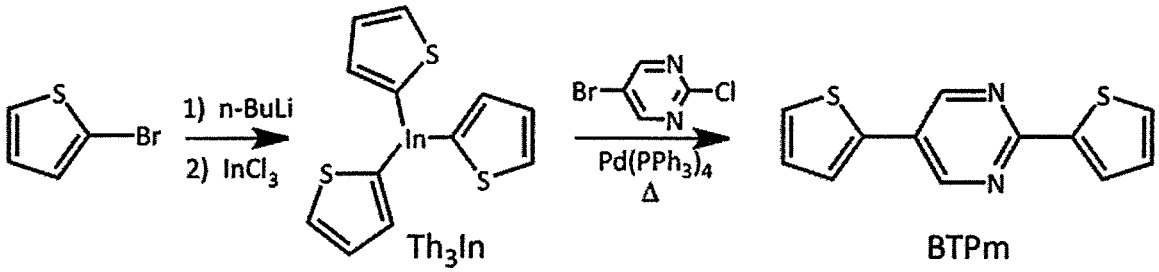


Figure 11: BTPm and the novel pyrimidine monomers

BTPm was synthesized according to a procedure reported by Mosquera *et al.*[29] In this procedure, a thienyl indium moiety is prepared and then coupled to 5-bromo-2-

chloro-pyrimidine using a palladium catalyst (see Scheme 6). Proton NMR and melting point of the product were consistent with those reported by Mosquera.[29]



Scheme 6: Synthetic scheme for BTPm

The EDOT analog, BEPm, was prepared following the same general procedure. Purification of this compound was accomplished by filtering through a short plug of silica and recrystallization from acetonitrile to produce fine yellow needles.

Attempts were made to prepare a soluble version of BTPm utilizing an oligo ether side chain, B3ETPm, via Sarandeses' indium-based coupling. While peaks consistent with B3ETPm were observed in the ^{1}H NMR spectrum of the product, isolation and purification of the desired product proved elusive.

Materials

2-Bromothiophene was purchased from Acros and used as received. 5-Bromo-2-chloropyrimidine was purchased from TCI and used as received. Sources and purification techniques for all other reagents mentioned herein are provided in Chapter II.

Structural Identification

Structural identification was accomplished via ^{1}H and ^{13}C NMR. A Varian UNITY 300+ was used for BEPm spectra. All other spectra were obtained using a Bruker Avance III 400 MHz instrument.

Synthesis

2,5-Bis-(thiophen-2-yl)-pyrimidine (BTPm)

As reported by Mosquera,[29] 2-bromothiophene (0.0155 mol, 2.53 g) was mixed with dry THF (25 mL) in a three neck flask under argon. The flask was chilled to -78°C, and n-BuLi (2.5M in hexanes) (0.0675 mol, 6.8 mL) was added dropwise by syringe. After stirring for one hour, a 0.05M $InCl_3$ solution in THF (0.00569 mol, 1.3 g) was added via cannula transfer. This mixture was stirred an additional hour at -78°C, then allowed to warm to room temperature with stirring for one more hour. A second three neck flask with argon inlet and stir bar was charged with 5-bromo-2-chloropyrimidine (0.00517 mol, 1.00 g) under positive argon flow. THF (10 mL) and $Pd(PPh_3)_4$ (0.130 mmol, 0.15g) were added. The thienyl indium mixture from the first flask was slowly added to the 5-bromo-2-chloropyrimidine mixture in the second flask via cannula transfer. The combined mixture was heated to reflux overnight, and the progress was monitored by TLC to ensure that the starting materials had been consumed. After 18 hours, methanol (1 mL) was injected to the reaction flask to quench the reaction. The mixture was evaporated under reduced pressure to yield a yellow solid (0.78 g, 62%). The crude product was dissolved in dichloromethane and washed with 5% HCl. The aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with saturated ammonium chloride solution, followed by brine. The organic phase was then dried over $MgSO_4$, filtered and evaporated under reduced pressure. After TLC plates showed an improved separation using methylene chloride, a deviation was made from the reported purification method which used 15:85 ethyl acetate:hexanes eluent. The BTPm fraction was further purified by recrystallization from methylene

chloride. Mp 195-197°C (Lit.[25]: 200-203). ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 2H), 8.02 (dd, 1H), 7.48 (dd, 1H), 7.40 (td, 2H), 7.16 (td, 2H). (Lit: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.91 (s, 2H), 8.03 (dd, 1H), 7.50 (dd, 1H), 7.42 (br t, 2H), 7.17 (br t, 2H)).[29]

2,5-Bis-(3,4-ethylenedioxythiophen-2-yl)-pyrimidine (BEPm)

Synthesis was adapted from Mosquera *et al.*[29] EDOT (0.0210 mol, 2.98 g) was mixed with anhydrous THF (30mL) in a flame dried 3-neck flask fitted with an air inlet adapter and stir bar. The mixture was chilled to -78°C in a dry ice/acetone bath prior to dropwise addition of n-BuLi solution in hexanes (2.5M in hexanes, 0.0230 mol, 9.22 mL). After stirring for two hours, 0.05M $InCl_3$ solution in THF (0.00768 mol, 154 mL) was added via cannula transfer. This mixture was stirred an additional hour at -78°C, then allowed to warm to room temperature for one more hour of stirring. Another 3-neck flask with stir bar, air inlet adapter, and condenser was flame dried and charged with 5-bromo-2-chloropyrimidine (0.00698 mol, 1.35 g) and dry THF (15 mL). $Pd(PPh_3)_4$ catalyst was added to this flask (0.15 g) before the $In(EDOT)_3$ mixture was transferred in by cannula. The complete mixture was heated to reflux overnight. The reaction was quenched with a few milliliters of methanol and evaporated under reduced pressure to yield a chalky yellow solid. The solid was dissolved in 50 mL dichloromethane and washed with 5% HCl (50 mL), saturated NH_4Cl solution (50 mL) and brine (50 mL). The organic layer was then dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a brown solid. This solid was passed through a short plug of silica. The first pale green eluate was set aside, and the second amber eluate collected. Evaporation left a yellow solid which was recrystallized from acetonitrile to yield 1.21g (48% yield) of pale yellow needles. Mp 221-223°C. ^{1}H NMR ($CDCl_3$) δ 9.022 (s, 2H), 6.517 (s, 1H),

6.381 (s, 1H), 4.240-4.449 (doublet of multiplets, 8H). ^{13}C NMR ($CDCl_3$) δ 158.247, 153.208, 142.378, 142.254, 142.174, 139.887, 123.843, 117.194, 110.465, 103.772, 99.373, 65.442, 64.830, 64.335, 64.182. Elemental Analysis: Anal. Calculated: C, 53.32%, H, 3.36%, N, 7.77%, S, 17.79%. Found: C, 53.13%, H, 3.46%, N, 7.70%, S, 18.50%.

Bis-2,5-(3-[2-(2-ethoxyethoxy)ethoxy]-thiophen-2-yl)-pyrimidine (B3ETPm)

The procedure used to synthesize BTPm and BEPm was followed using Br3ETh (0.00675 mol, 2.0 g) in THF (12 mL), n-BuLi (2.5M in hexanes) (0.00743 mol, 3.0 mL), $InCl_3$ (0.00230 mol, 0.508 g) dissolved in THF (46 mL), BCPm (0.00338 mol, 0.653 g), and $Pd(PPh_3)_4$ (1.35×10^4 mol, 0.156 g). Upon extraction, drying, filtration and evaporation a red oil was obtained. A proton NMR of the crude mixture indicated that single couplings of the thiophene moiety to the pyrimidine at both the 2- and 5-positions had taken place, but that the desired triaryl compound was not obtained (see Appendix).

CHAPTER IV

SYNTHESIS OF BIS-THIENYL BIPYRIMIDINES

Synthetic Method

The bipyrimidine series of monomers was designed to incorporate two acceptor moieties rather than a single one. This adaptation was chosen to test the difference in properties when the ratio of donor to acceptor was decreased. It was expected that the bipyrimidine versions would have a higher electron affinity, which might lead to enhanced reduction processes. Fu[12] proposed that the 1:1 ratio of donor to acceptor would result in a better n-doping polymer, but at the cost of a higher band gap. Both thiophene and EDOT versions were attempted (see Figure 12).

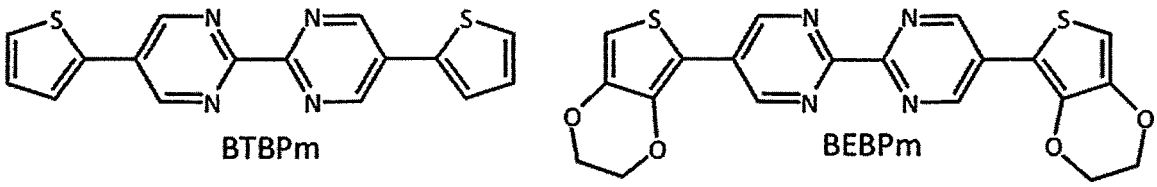
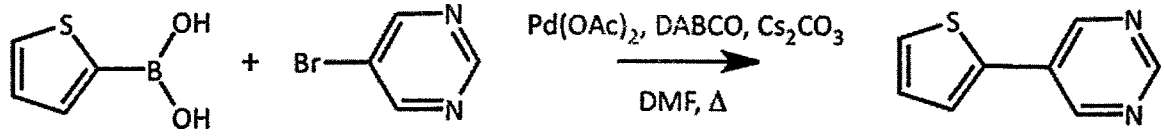


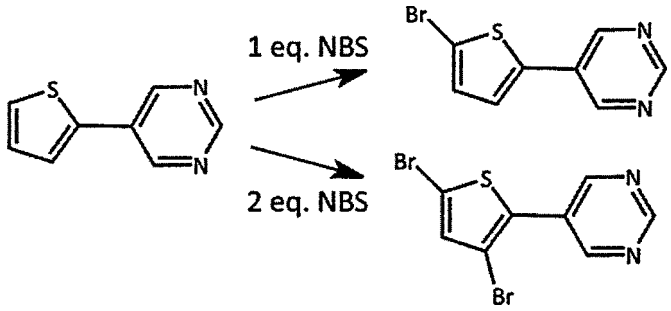
Figure 12: Proposed bipyrimidine monomers

Several synthetic routes for BTBPm have been proposed and attempted. This monomer proved challenging to synthesize. The difficulty stems, at least in part, from the electron density of the lone pairs on the nitrogens in the pyrimidine rings. In the first attempt at synthesis, a Suzuki reaction was successfully used to couple 5-bromopyrimidine with 2-boronic acid thiophene (see Scheme 7).



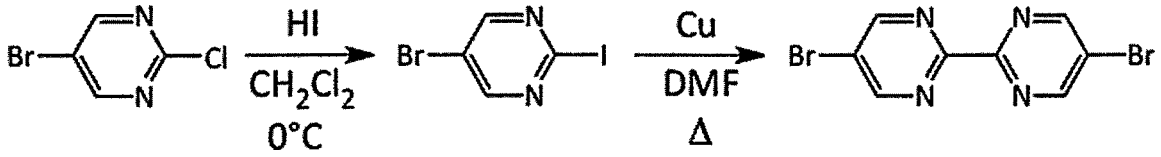
Scheme 7: Suzuki coupling of 2-boronic acid thiophene with 5-bromopyrimidine

The product, 5-thien-2-yl pyrimidine, was purified, and bromination at the 2-position of the pyrimidine was undertaken (see Scheme 8). Bromination occurred at the 5-position of the thiophene, followed by the 3-position of the thiophene instead. Thus, it was determined that 2-halogenated pyrimidines were necessary as starting materials.



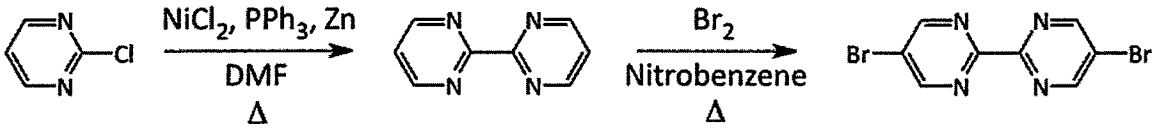
Scheme 8: Bromination of 5-thiophen-2-yl pyrimidine with 1 and 2 equivalents of NBS

Another attempt approached the synthesis from the inside out. An Ullmann coupling of 5-bromo-2-chloropyrimidine was attempted to produce 5,5'-dibromo-2,2'-bipyrimidine as reported by Vlád (see Scheme 9).[51] The product mixture had such great complexity and such little mass that separation was not successful in producing the desired material for further reaction.



Scheme 9: Ullman coupling to produce 5,5'-bromo-2,2'-bipyrimidine

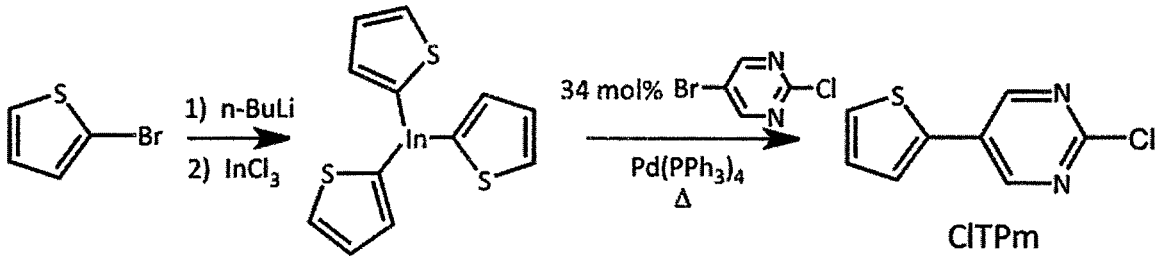
Continuing with an inside-out approach, 2-chloropyrimidine was reductively coupled to produce bipyrimidine (see Scheme 10).[52] Bromination of the bipyrimidine would be followed by a Suzuki or Stille coupling to produce the BTBPm. There are two main routes for bromination of bipyrimidine in literature. The first approach[53] is a pressurized reaction in neat bromine with an 85% reported yield of the doubly brominated product, but due to the very small scale of reaction possible, this route was not undertaken. The second option has only a 15% yield of the 5,5'-dibromo-2,2'-bipyrimidine, but is accomplished at atmospheric pressure.[52] This was the procedure chosen, and results were not optimal. Yields of the desired compound were low, as expected, and the separation of the singly and doubly brominated bipyrimidine was difficult. In the end, this route was not deemed useful in producing enough brominated bipyrimidine to continue with this scheme.



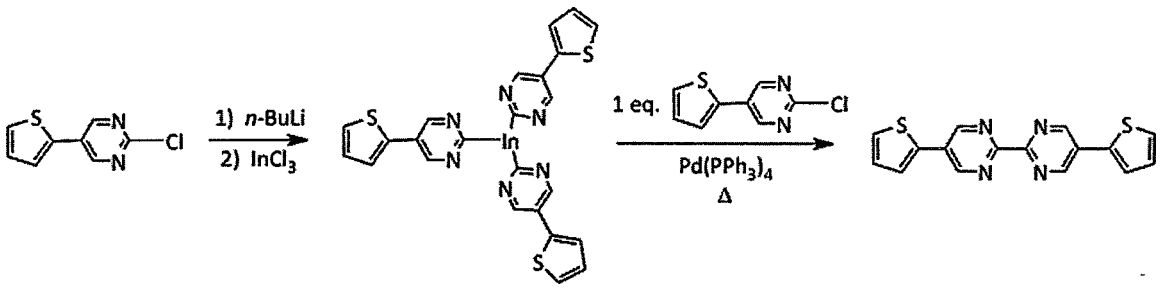
Scheme 10: Inside-out approach to synthesis of BTBPm

The procedure for making 2-chloro-5-(thiophen-2-yl)pyrimidine by Sarandeses coupling was attempted (see Scheme 11).[29] This reaction is conducted in the same manner as that used to produce BTPm in Chapter II, except the ratio of Th_3In to 5-bromo-2-chloropyrimidine is decreased to 40%. Thin layer chromatography (TLC) showed the resulting product mixture was too complex for separation via column chromatography as reported in the paper. When the amount of thienyl lithium used was decreased to 34%, the desired chlorinated bi-aryl was produced (see Scheme 11). This intermediate was submitted to a second Sarandeses reaction to produce BTBPm which was not successful

(see Scheme 12). A proton NMR of the resultant mixture contained mostly starting materials.



Scheme 11: Synthesis of ClTPm via Sarandeses route



Scheme 12: A second Sarandeses coupling to produce BTBPm

The EDOT analog, BEBPm was synthesized from EDOT in the same manner as BTBPm (see Scheme 12). A Sarandeses coupling was used to produce the 2-chloro-5-(3,4-ethylenedioxythiophen-2-yl)-pyrimidine (ClEPm) which was purified prior to symmetric coupling in an attempt to produce the D-A-A-D monomer by Sarandeses coupling. The desired product was not synthesized.

Materials

Copper powder was purchased from Fisher and activated as described by Vlád:[51] copper (20 g) was placed in a fritted funnel and activated by washing with 100 mL each of a 1:1 mixture of acetone and 12M HCl, acetone, distilled water, 5% ammonia solution, ethanol (until the filtrate was no longer blue), acetone, and ether before being dried under vacuum.

Ethylene glycol dimethyl ether (glyme) was purchased from Acros and distilled over calcium hydride prior to use. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purchased from Aldrich and used as received. 2-Thiopheneboronic acid, palladium (II) acetate ($Pd(OAc)_2$), calcium hydride and cesium carbonate were purchased from Acros and used as received. 5-Bromopyrimidine was purchased from Acros and purified via sublimation prior to use. Sodium thiosulfate was purchased from Fisher and used as received. See Chapter II for information on all other reagents used.

Structural Identification

Structural identification was accomplished via ^{1}H and ^{13}C NMR. Spectra for 5-bromo-2-pyrimidin-5-yl-thiophene, 3,5-dibromo-2-pyrimidin-5-yl-thiophene, 5-bromo-2-iodopyrimidine, the Ullmann coupling of 5-bromo-2-iodopyrimidine, and 2,2'-bipyrimidine were obtained on a Varian INOVA 400 MHz instrument. Remaining spectra were obtained using a Bruker Avance III 400 MHz instrument.

Synthesis

5-(Thiophen-2-yl)-pyrimidine

Synthesis followed procedures published by Li et. al.[54] A three neck flask fitted with a condensor and argon inlet was charged with dry DMF (120 mL) via cannula transfer. 5-Bromopyrimidine (0.0126 mol, 2.00 g), 2-thiopheneboronic acid (0.0176 mol, 2.25 g), $Pd(OAc)_2$ (0.377 mmol, 0.0847 g), DABCO (0.755 mmol, 0.0847 g), Cs_2CO_3 (0.0377 mol, 12.3 g) were added under positive argon flow. The mixture was heated to reflux and stirred overnight. Completion was monitored by TLC to verify starting materials had been consumed. The reaction mixture was poured into diethyl ether and washed with distilled H_2O. The water layer was extracted with diethyl ether three times.

The combined ether layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield 5-(thiophen-2-yl)-pyrimidine (1.81 g, 89%). Sublimation produced white crystals. Mp: 75.5-78.0°C. (Lit:[54] 77.2-78.0°C) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.05 (s, 1H), 8.88 (s, 2H), 7.39 (dd, 1H), 7.36 (dd, 1H), 7.11 (m, 1H). (Lit:[54] ($CDCl_3$, 400 MHz) δ 9.13 (s, 1H), 8.96 (s, 1H), 7.46 (dd, 2H), 7.43 (d, 1H), 7.18 (t, 1H)). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 157.2, 153.4, 136.2, 128.6, 127.3, 125.2.

5-Bromo-2-(pyrimidin-5-yl)-thiophene

5-(Thiophen-2-yl)-pyrimidine (3.08 mmol, 0.500 g) was added to a three neck flask under positive argon flow. Anhydrous THF was added via syringe (5 mL). Two equivalents of NBS (6.17 mmol, 1.10 g) in THF (18 mL) were added to the flask via syringe. The mixture was stirred for 36 hours at room temperature, and then quenched by pouring into sodium thiosulfate solution in a separatory funnel. The aqueous layer was extracted with chloroform (4X, 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The brown solids were recrystallized from methanol. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.12 (s, 1H), 8.86 (s, 2H), 7.13 (dd, 2H), 6.88 (dd, less than 1H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 157.6, 153.4, 137.8, 131.7, 128.2, 125.9, 114.7.

5-Bromo-2-iodopyrimidine

Synthesis was adapted from the procedure described by Vlád and Goodby *et al.*,[51,55] but modified by addition of excess acid and stirred for a longer interval. Hydroiodic acid (47%, 120 mL) was chilled to -10°C. Methylene chloride (42 mL) was poured into an Erlenmeyer flask and chilled to 0°C in an ice water bath. 5-Bromo-2-chloropyrimidine (13.5 g) was dissolved in the dichloromethane, and the chilled HI was

added in a dropwise fashion. While Vlád and Goodby[51,55] reported that the reaction was complete in 5 hours, the reaction required 4 days to complete when reproduced. The reaction progress was monitored by NMR until no BCPm remained. The reaction mixture was quenched by the careful addition of potassium carbonate until no more gas was evolved. Saturated sodium thiosulfate solution was poured into the flask until the mixture was off-white. The aqueous layer was separated and washed with dichloromethane (5X, 100 mL). The combined organic phases were dried over potassium carbonate, filtered, and evaporated under reduced pressure to yield a white solid. The crude solid was recrystallized from petroleum ether to yield fine white needles (14.1 g, 71%). Mp: 100-101°C (Lit:[54] 101-102°C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.55 (s, 2H).

5,5'-Bromo-2,2'-bipyrimidine

Synthesis was first attempted following the Ullman coupling procedure described by Vlád.[51] Activated copper (10.0 g) was added to a three neck flask under positive argon flow along with 5-bromo-2-iodopyrimidine (12.0 g). Dry dimethylformamide was added via syringe (35 mL). The reaction mixture was heated at 90°C for 3.5 hours. The argon inlet was then exchanged for a column packed with calcium chloride. An additional portion of copper was added (1.75 g) and stirring continued for another 3.5 hours. The temperature was then increased to 120°C for two more hours. The reaction was allowed to cool to room temperature, and then placed in an ice bath. The chilled mixture was poured into a KCN solution in ammonia (13.5 g, 70 mL 25% ammonia), and the mixture was filtered. The solids were poured into a second KCN solution of the same concentration, and filtered again. KCN (0.5 g) was added to the filtrate, which was then extracted with chloroform (5X, 200 mL). The combined organic extracts were dried over

potassium carbonate, filtered and evaporated under reduced pressure. The resulting solid dissolved partially in 90:10 ethyl acetate:chloroform. The insoluble black solids were set aside, and the soluble portion recrystallized. The solid mixture was of such small mass and great complexity that separation was not achieved (see Spectrum 16, Appendix I).

2,2'-Bipyrimidine

Synthesis reported by Schwab and coworkers was followed.[52] Dimethyl formamide (DMF) was degassed overnight by sparging with argon. Triphenylphosphine (0.1128 mol, 29.59 g), nickel chloride hexahydrate (0.02821 mol, 6.666 g) and zinc (0.05641 mol, 3.688 g) were placed under vacuum for 20 minutes before being added to the DMF under positive argon flow. This mixture was stirred for one hour prior to addition of freshly sublimed 2-chloropyrimidine (0.1128 mol, 12.92 g) under positive argon flow. After stirring for 1 hour at room temperature, the reaction mixture was heated at 50°C for over 50 hours. Work up began by filtering the mixture through celite and rinsing with chloroform. The filtrate was vacuum distilled to remove the DMF. The resultant dark, reddish solid was then suspended in a solution of EDTA (75g) in 7% ammonia (200 mL). This aqueous layer was extracted with 70 ml aliquots of diethyl ether to remove the triphenylphosphine until no residue remained when a drop was placed on a watch glass (approximately 12 washes). The aqueous layer was further extracted with chloroform washes to remove the products. The chloroform extracts were dried over $MgSO_4$, decolorized with activated charcoal, filtered and evaporated under reduced pressure. Sublimation was used to purify the 2,2'-bipyrimidine to a white crystalline solid (2.45 g, 19%). Mp: 109-110 (Lit.:[52] 113-115°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.0 (s, 2H), 7.4 (t, 4H). (Lit:[52] ($CDCl_3$, 300 MHz) δ 9.02 (d, 2H), 7.44 (t, 4H)).

2-Chloro-5-(thiophen-2-yl)-pyrimidine (ClTPm)

Synthesis followed the procedure described for 2,5-bis(thiophen-2-yl)-pyrimidine, with the exception that only 34% mol percent of thienyl indium to pyrimidine was used, because all three ligands on the organolithium compound are transferred.[29,30,31,32] 2-Bromothiophene (0.0310 mol, 3.00 mL), n-BuLi (2.5 M in hexanes, 0.0342 mol, 13.6 mL), $LiCl_3$ (0.0310 mol, 2.5 g), and 5-bromo-2-chloropyrimidine (0.0304 mol, 5.88 g) were used in the reaction to produce 1.2 g (20%) of yellow powder. Mp: 119-121°C. (Lit:[29] 122-125°). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.90 (s, 2H), 7.45 (d, 1H), 7.38 (d, 2H), 7.15 (dd, 2H). (Lit:[29] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.82 (s, 2H), 7.47 (br d, 1H), 7.41 (br d, 1H), 7.18 (dd, 1H)).

5,5'-Bis-(thiophen-2-yl)-2,2'-bipyrimidine (BTBPm)

A 100 mL Schlenk flask was flame dried and backfilled with argon. ClTPm (0.00305 mol, 0.600 g) was added under positive argon flow. Freshly distilled ethylene glycol dimethyl ether (glyme) was transferred into the schlenk flask via cannula transfer. Since the freezing point of glyme is 6°C, a dry ice/acetone bath could not be used during lithiation. Instead, the reaction flask was cooled in an ice bath, maintained at 5-8°C. n-BuLi (2.5 M in hexanes, 0.00336 mol, 1.34 mL) was added via syringe. After the mixture was stirred for one hour in an ice bath, indium chloride (0.05 M in glyme, 0.00305 mol, 0.675 g) was transferred into the reaction flask via cannula transfer. The reaction was stirred for one hour in an ice bath and one hour at room temperature. A 250 mL three neck flask fitted with a condenser was flame dried and charged with the remaining ClTPm (0.00305 mol, 0.600 g) and $Pd(PPh_3)_4$ (0.00915 mM, 0.11 g) under positive argon flow. The ClTPm and catalyst were dissolved with 10 mL of glyme via

syringe. The organolithium reagent was transferred into the 250 mL flask after its second hour of stirring via cannula transfer. The reaction was heated to reflux and stirred for 3 days. At this time, the reaction was quenched with MeOH (3 mL), evaporated to remove glyme, and dissolved in dichloromethane. The dichloromethane solution was washed consecutively with 200 mL each of 5% HCl, saturated NH_4Cl, and brine, dried over $MgSO_4$, filtered and evaporated to dryness. A proton NMR of the crude product showed that the starting materials were present as well as other impurities, but that no coupling had occurred.

2-Chloro-5-(3,4-ethylenedioxythiophen-2-yl)-pyrimidine (ClEPm)

A 250 mL 3 neck flask was flame dried under vacuum and charged with EDOT (0.0275 mol, 3.91 g) and anhydrous THF (36 mL) via syringes. The flask was placed in a dry ice/acetone bath to chill to -78°C, then n-BuLi (2.5M in hexanes, 0.03025 mol, 12.1 mL) was added dropwise via syringe. This mixture was stirred for one hour at -78°C. A solution of $InCl_3$ (0.0101 mol, 2.2 g) in THF (201.6 mL) was made in the glove box. The $InCl_3$ solution was transferred into the reaction flask via cannula transfer. This mixture was stirred for one hour at -78°C, then warmed to room temperature and stirred an additional hour. A second three neck flask was flame dried under vacuum and charged with BCPm (0.0275 mol, 5.32 g) and $Pd(PPh_3)_4$ (0.000275 mol, 0.32 g) under positive argon flow. THF (20 mL) was added via cannula to dissolve the BCPm. The $In(EDOT)_3$ solution from the first flask was transferred via cannula into the flask containing BCPm and catalyst. The final mixture was stirred at reflux for 2 days. After this time, the reaction mixture was allowed to cool to room temperature and quenched with methanol (3 mL). The flask was evaporated to dryness under reduced pressure. The tan solids

were dissolved in dichloromethane and washed with 5% HCl (200 mL), saturated NH_4Cl solution (200 mL), and brine (200 mL) in succession. The brown organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield the crude product (6.2g, 89% yield). Purification was accomplished by dissolving the crude solid in a minimum amount of dichloromethane and precipitating into hexanes. The filtrate from the first precipitation was concentrated and reprecipitated. Sublimation of the light tan solids yielded 4.24g (61%) of white crystalline solid. Mp: 160-162°C (dec). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.88 (s, 2H), 6.44 (s, 1H), 4.33 (m, 2H), 4.26 (m, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 158.03, 155.46, 142.36, 140.66, 126.68, 108.56, 100.65, 65.07, 64.34.

5,5'-Bis-(3,4-ethylenedioxythiophen-2-yl)-2,2'-bipyrimidine (BEBPm)

Negishi and Sarandeses methods were each used for the coupling of ClEPm. In the Negishi approach, a 50 mL three neck flask with air inlet, stir bar and condenser was flame dried and charged with ClEPm (0.00295 mol, 0.750 g) under positive argon flow. THF (20 mL) was added via syringe. The reaction mixture was chilled to -78°C prior to the dropwise addition of n-BuLi (2.5M in hexanes, 0.00324 mol, 1.30 mL) via syringe. After stirring one hour, $ZnCl_2$ (0.5M in THF, 0.00353 mol, 7.1 mL) was added dropwise via syringe. After addition, the mixture was stirred one hour at -78°C, and an additional hour at room temperature. The second portion of ClEPm (0.00295 mol, 0.750 g) was added with $Pd(PPh_3)_4$ (0.000059 mol, 0.068g) under positive argon flow. The reaction mixture was stirred at reflux for three days. Once cooled to room temperature, the reaction mixture was poured into saturated sodium bicarbonate solution (150 mL). Dichloromethane (100 mL) was added, and the phases were separated. The organic layer

was washed with another aliquot of bicarbonate (50 mL) and then with brine (150 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The reddish solids from this reaction were combined with those obtained below and subjected to soxhlet extraction with benzene. Soxhlet extraction was ineffective at purification; the solids remaining in the thimble appeared to have oxidized, as they were discolored and less soluble in dichloromethane and chloroform. Finally, the remaining product mixture was dissolved in a minimum amount of dichloromethane and precipitated into warm toluene, but the desired product was not evident in the ^1H NMR spectrum.

Synthesis of B3ETPm was also attempted using the Sarandeses approach. A 250 mL three neck flask was fitted with a stir bar and air inlet adapter and flame dried. The flask was charged with ClEPm (0.00393 mol, 1.00 g) under positive argon flow. THF was added via cannula transfer (100 mL). The mixture was chilled to -78°C prior to the dropwise addition of n-BuLi (2.5M in hexanes, 0.00432 mol, 1.73 mL). The mixture was stirred one hour at -78°C while $InCl_3$ (0.00144 mol, 0.318 g) was dissolved in THF (29 mL). The $InCl_3$ solution was transferred via cannula into the reaction flask. The mixture was stirred for one hour at -78°C, then an additional hour at room temperature. A second portion of ClEPm (0.00393 mol, 1.00 g) and $Pd(PPh_3)_4$ (0.0004 mol, 0.2 g) were added under positive argon flow to the red organoindium solution. A condenser was placed on the flask, which was stirred at reflux for two days. The reaction was cooled to room temperature and quenched with methanol (2 mL). The reaction flask was evaporated under reduced pressure to dryness. The reddish solids were then dissolved in chloroform and washed with 5% HCl (50 mL), saturated NH_4Cl (50 mL) and brine (50 mL) in

sequence. The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield a reddish brown solid. ^1H NMR showed that this crude solid was similar to that obtained from the Negishi coupling, so the two were combined for purification, which is described above. The product was not isolated.

CHAPTER V

CONCLUDING REMARKS

Synthesis

Several target monomers, BEIPz-TMS, BEIPz, BTPm and BEPm, were synthesized and isolated. BTPm and BEPm were made in reasonable yields (62% and 48% respectively); the yield of BEIPz-TMS is lower (26%), but still higher than the yield reported in the literature for a similar compound. BEIPz is derived from the deprotection of BEIPz-TMS, so its yield is still lower compared to the starting materials used. BHexTIPz, B3ETIPz and B3ETPm may have been successfully synthesized, but isolation was not achieved. The bipyrimidines also proved challenging to synthesize.

While a Negishi coupling was used in the published procedure for BTIPz synthesis, we found there was no real difference in yield when the reaction was uncatalyzed and allowed to continue for several days. We found that a shorter reflux than reported was sufficient to effect ring closure. Alternate coupling strategies should be pursued if enhanced yields are desired.

The Sarandeses coupling technique proved to be a very valuable tool for carbon-carbon bond formation. All of the pyrimidine monomers and the bi-aryl starting materials for the bipyrimidine monomers were synthesized using this triorganoindium

technique. This coupling strategy is proposed to follow the basic mechanism for palladium catalyzed cross-coupling reactions, yet it is not as widely used as the Stille, Suzuki or Negishi reactions. Attempts to apply the Sarandeses coupling to the isopyrazole series of monomers were unsuccessful, suggesting that dimethyl malonyl chloride is not a suitable coupling partner.

Our experimentation with the Sarandeses coupling was limited to the use of $Pd(PPh_3)_4$ as a catalyst. Other palladium and nickel catalysts have been shown to work in Sarandeses coupling.[29,30,31,32] Perez found that chlorohalides could be coupled more efficiently using nickel (0) catalysts at 5 mol% loading.[31] It is possible that switching catalysts could increase yields and lend to easier purification of the bipyrimidines.

Another variable is the solvent in which the reaction is accomplished. All of the couplings except for that of the BTBPm were accomplished in THF, so the temperature at which the reaction refluxed was limited. BTBPm was accomplished using glyme rather than THF, to see if the higher boiling point of the solvent would improve yields. However, glyme also has a high melting point, so lithiation cannot be accomplished at the usual temperature of -78°C. DMF is another alternative for a higher boiling solvent, which was not employed due to its difficulty in removal and incompatibility with lithiation. The use of alternate solvents, or a combination of solvents during different reaction steps, may help to optimize yields.

The hexyl and EEE solublizing groups may serve the intended purpose to yield soluble polymers, but this was not able to be determined due to difficulties in isolating the products. The alkyl tails restrict purification via column chromatography. Since the products are oils, sublimation and recrystallization were not useful. The molecular

weights of the monomers suggest that each has a high boiling point, and the heat required for distillation may cause degradation or oligomerization of the product. This was shown for BHexTIPz.

Future Work

Several improvements to the synthetic method were suggested above. Optimizing the use of solvent and catalyst for the Sarandeses reaction may result in synthesis and isolation of the bipyrimidine and B3ETPm monomers. If Sarandeses coupling is still unsuccessful, Grignard or Ullmann couplings of the bipyrimidines should be attempted from the 2-chloro-5-(thiophen-2-yl)-pyrimidine and 2-chloro-5-(3,4-ethylenedioxythiophen-2-yl)-pyrimidine biaryls.

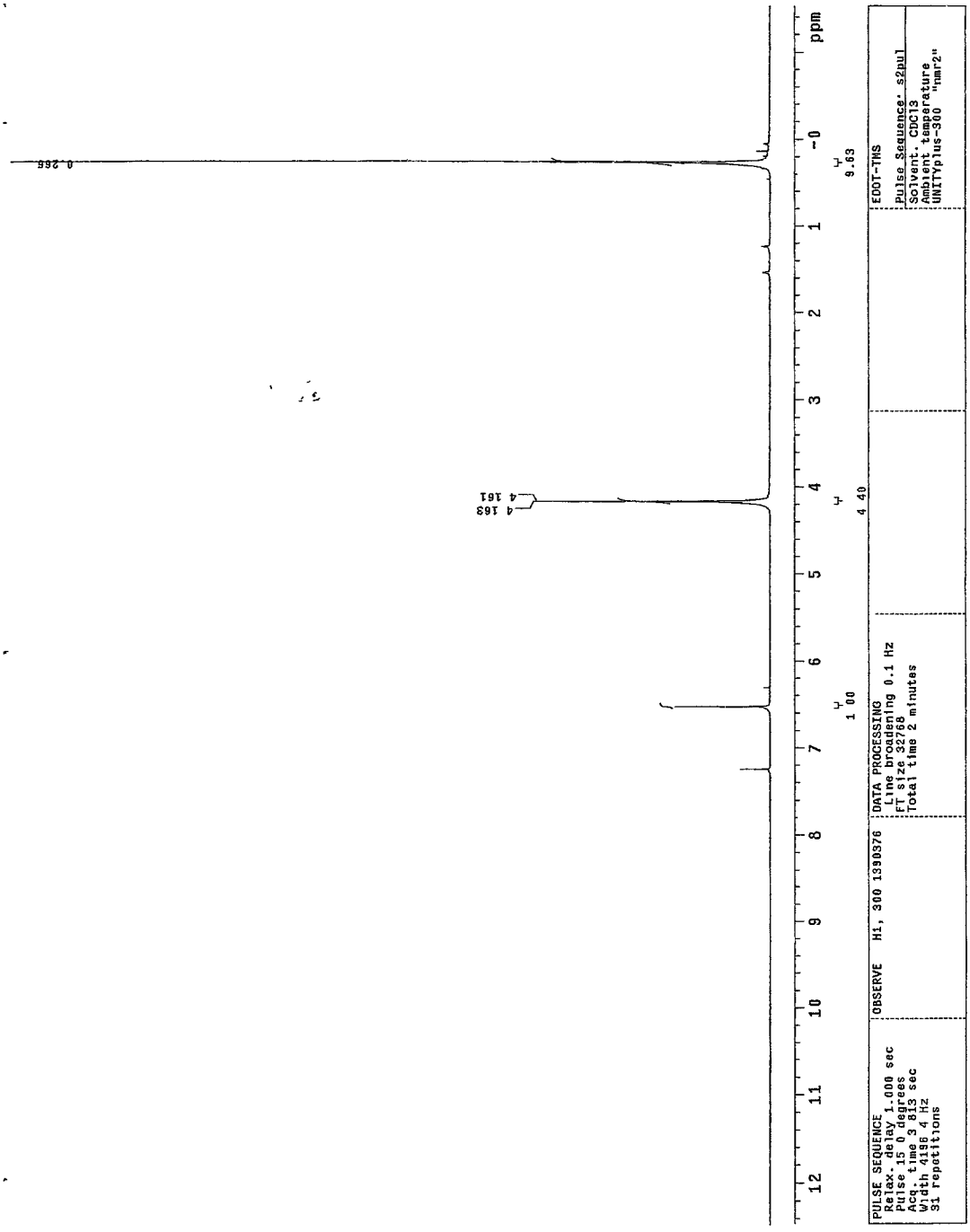
The scope of this research was limited to synthesis of the monomers. Next, the monomers must be electrochemically characterized to determine their conductive properties, such as oxidation potential, band gap and current response to applied voltage. Repeated cyling of the polymer can determine whether the n-doping and p-doping processes are stable and reversible.

If a purification method for the BHexTIPz and B3ETIPz monomers could be discerned, the monomers could be submitted to chemical oxidative polymerization in addition to electrochemical polymerization. The molecular weight of the product of the chemical oxidation could be determined by end group analysis through proton NMR, gel permeation chromatography, or viscosity measurements. Solubility tests would be accomplished in a variety of common organic solvents.

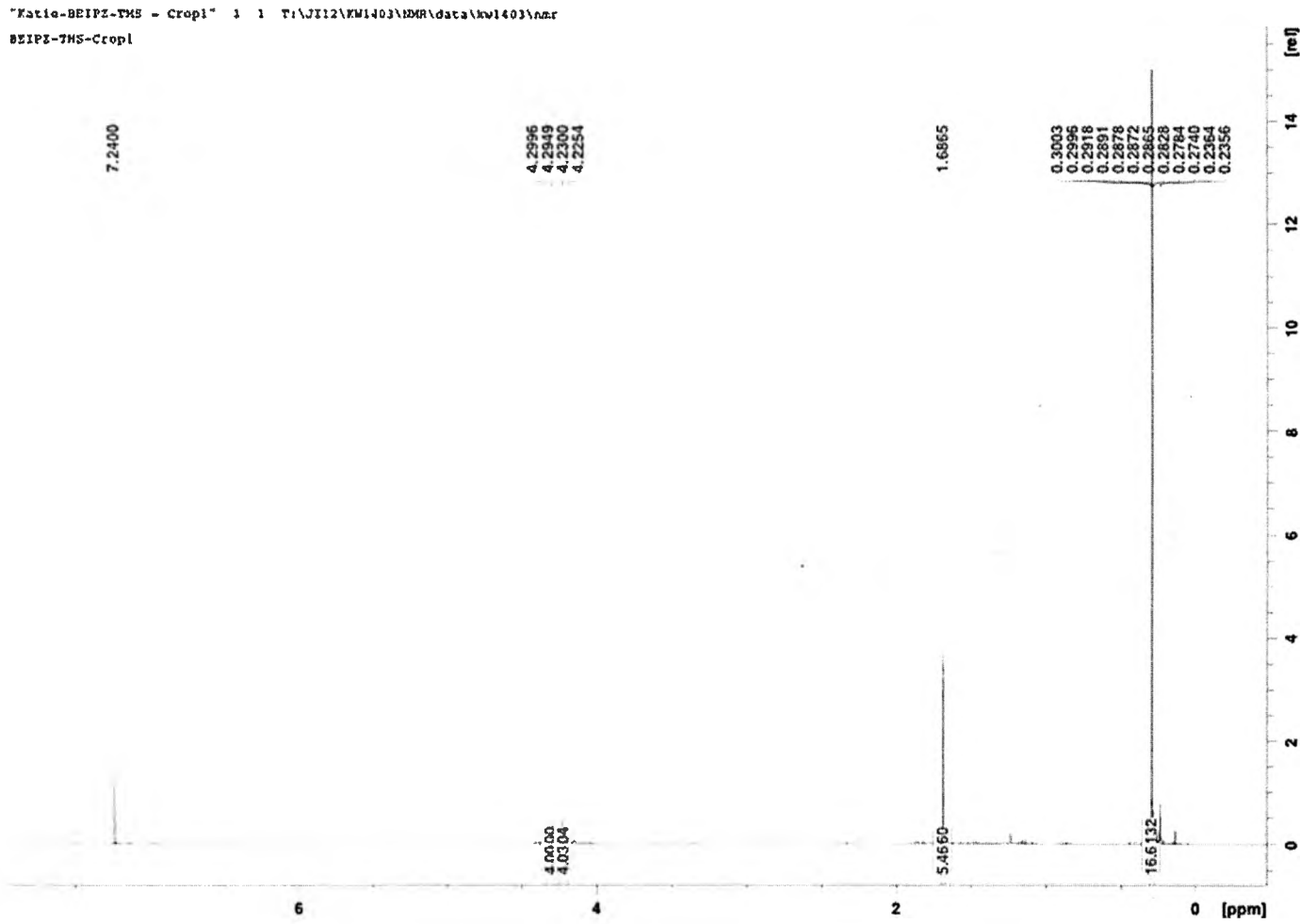
APPENDIX A

NUCLEAR MAGNETIC RESONANCE SPECTRA

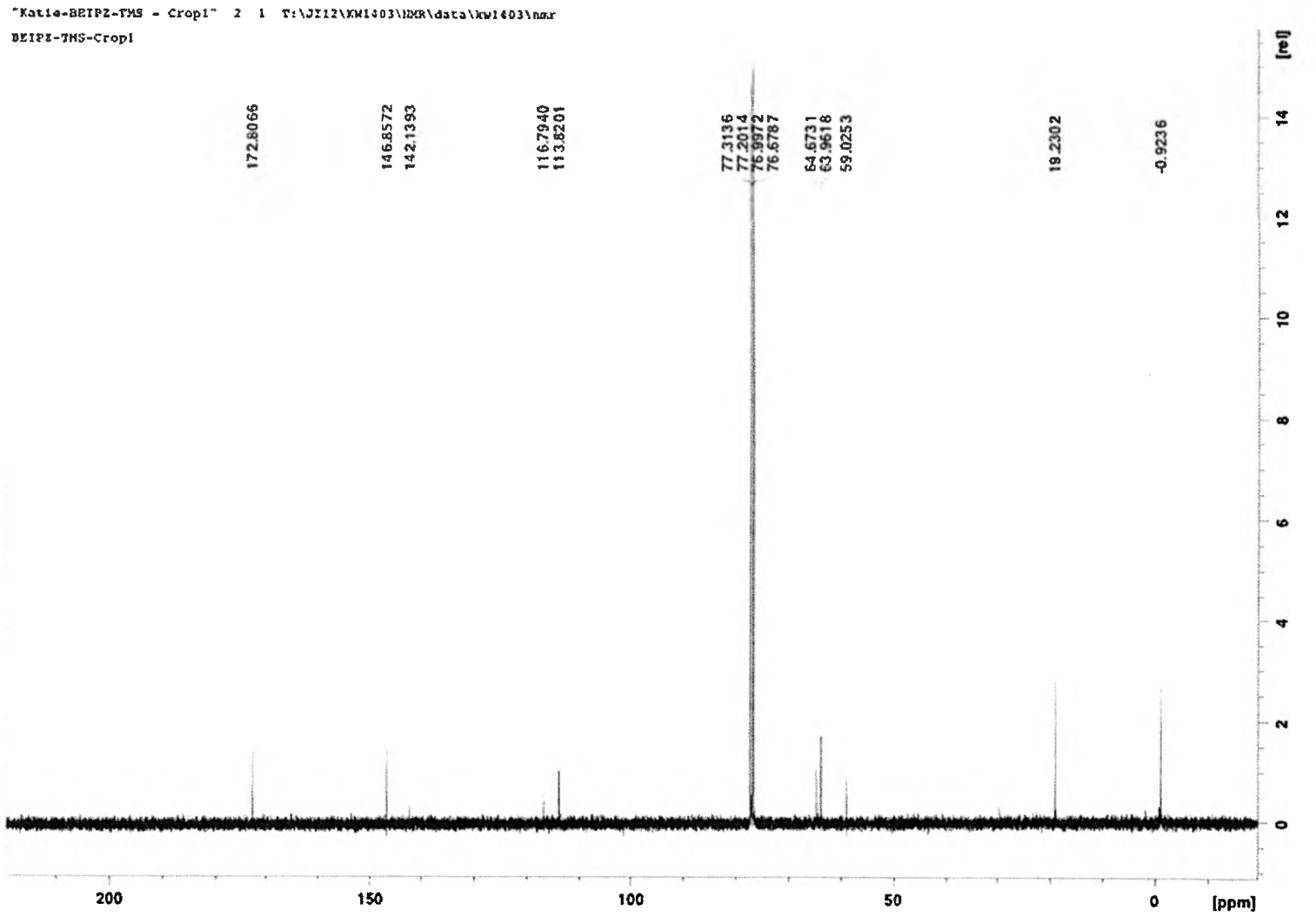
Spectrum **Page**



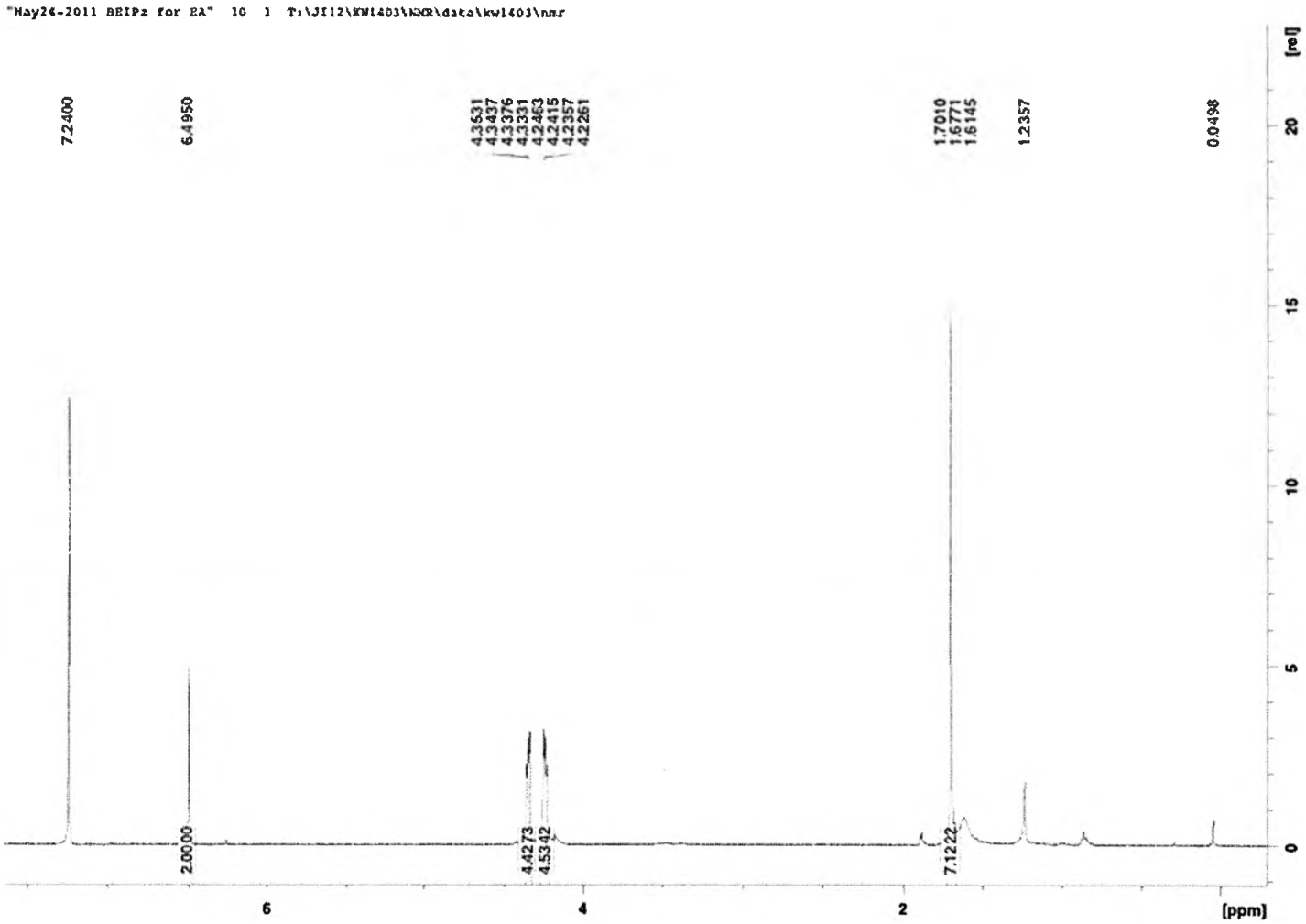
Spectrum 1: EDOT-TMS ^{1}H NMR in $CDCl_3$



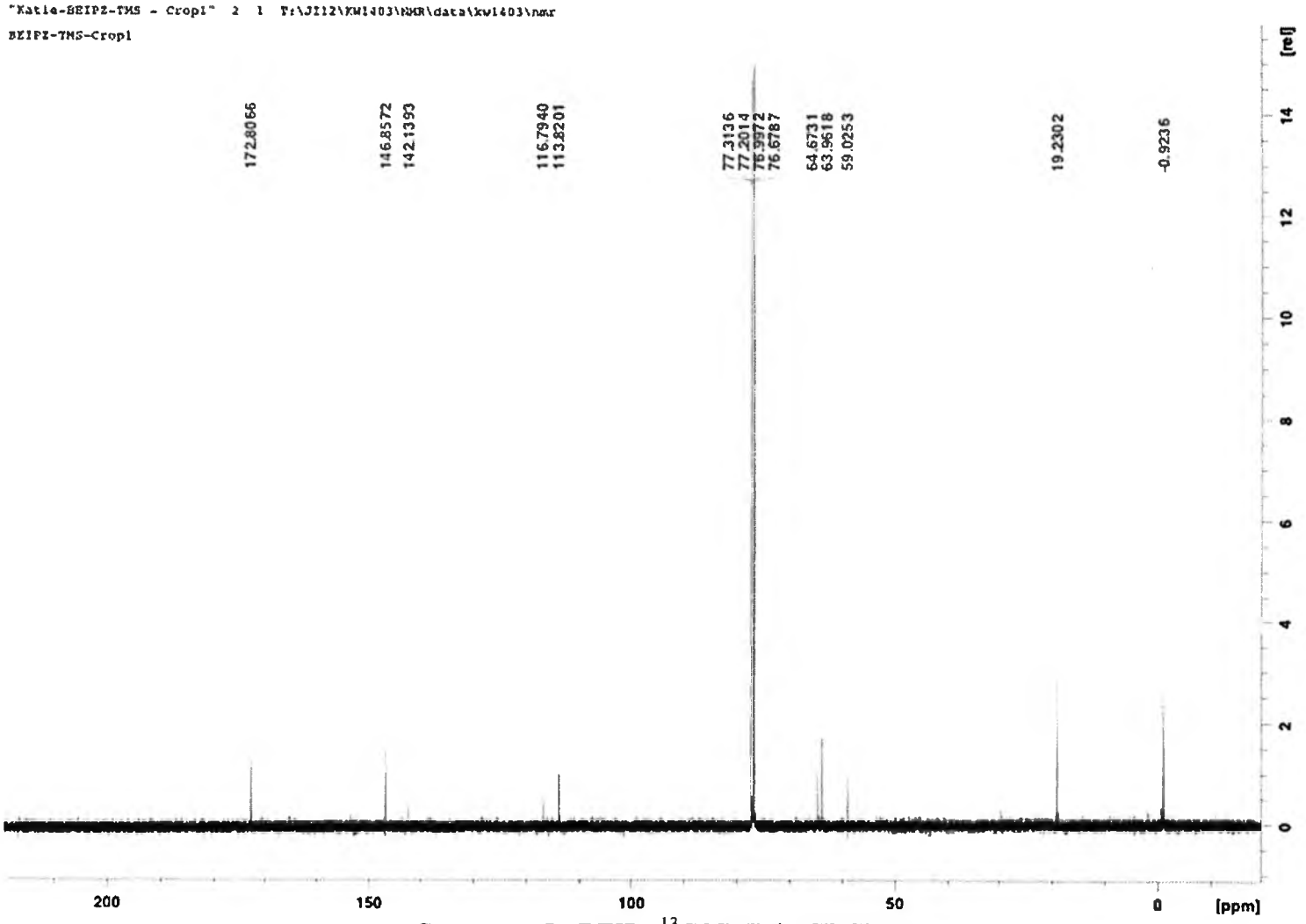
Spectrum 2: BEIPz-TMS ^{1}H NMR in $CDCl_3$



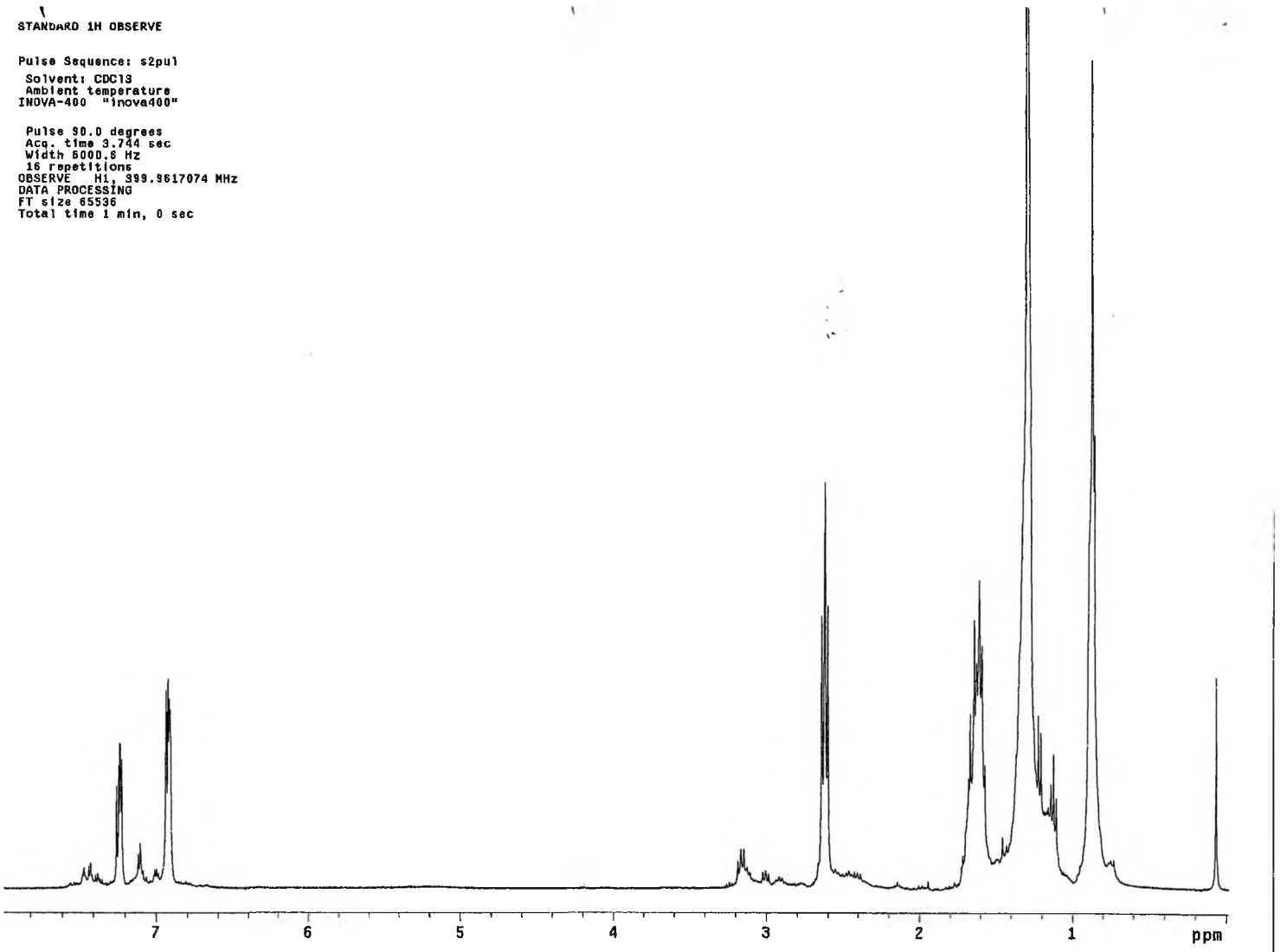
Spectrum 3: BEIPz-TMS ^{13}C NMR in $CDCl_3$



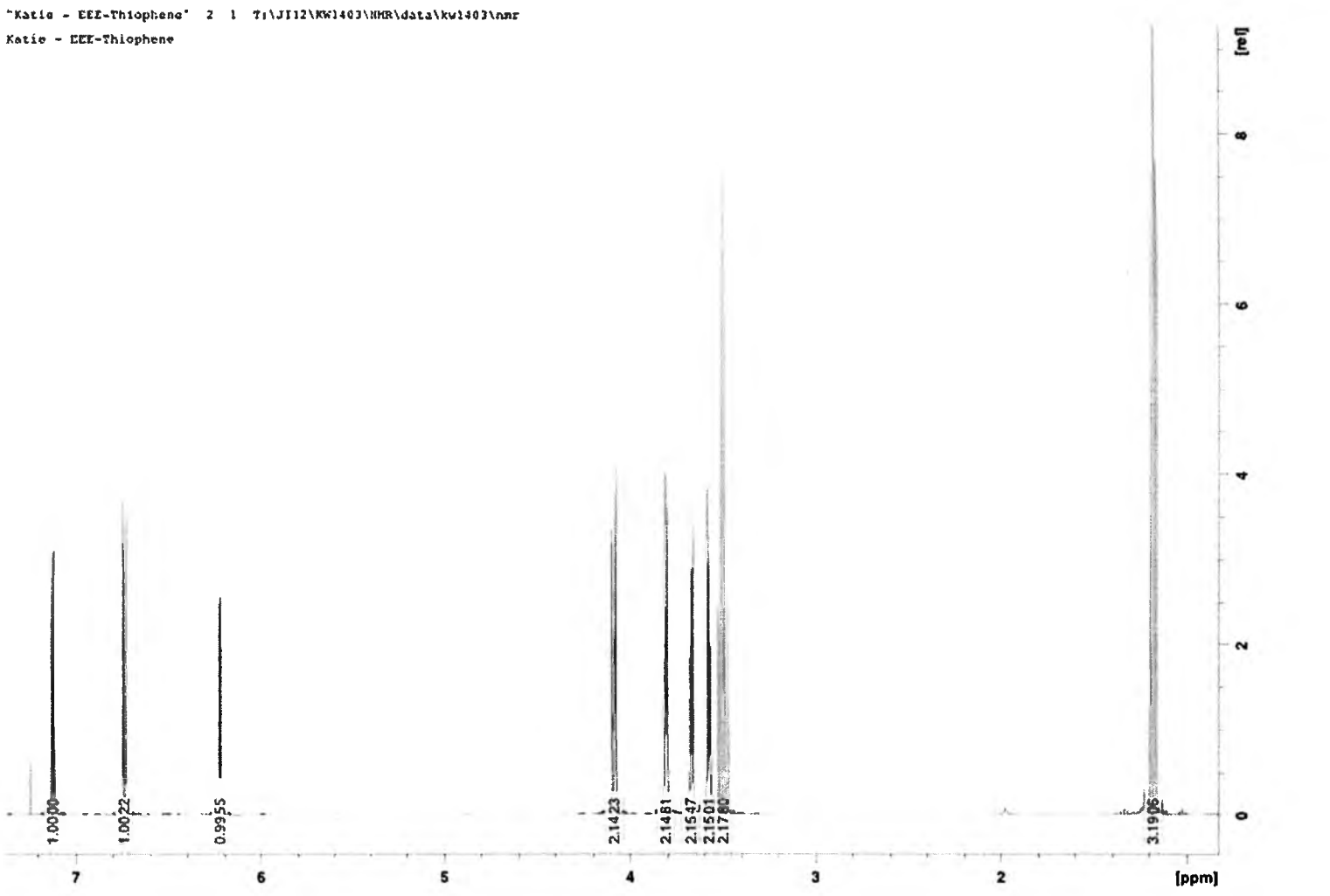
Spectrum 4: BEIPz ^{1}H NMR in $CDCl_3$



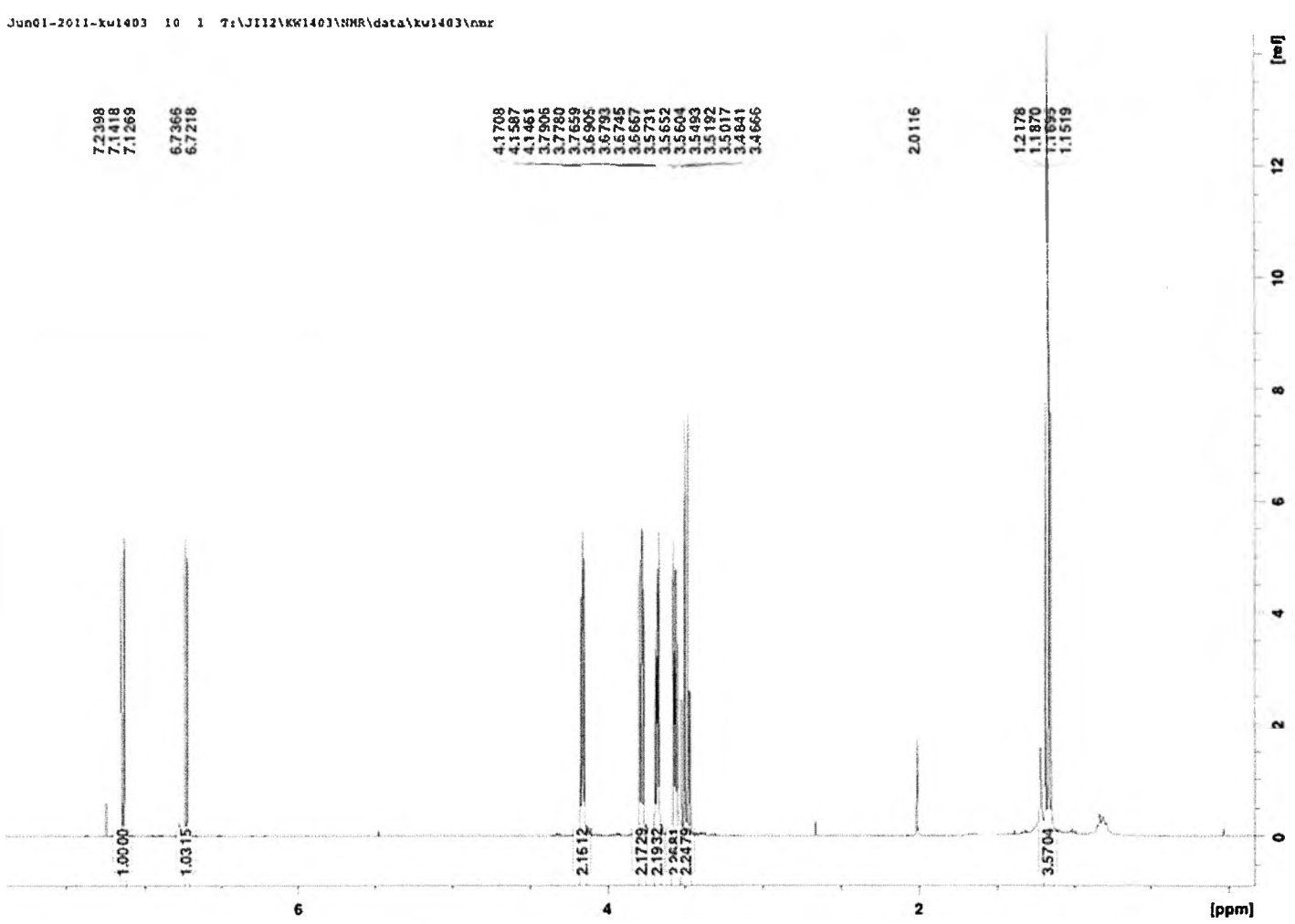
Spectrum 5: BEIPz ^{13}C NMR in $CDCl_3$



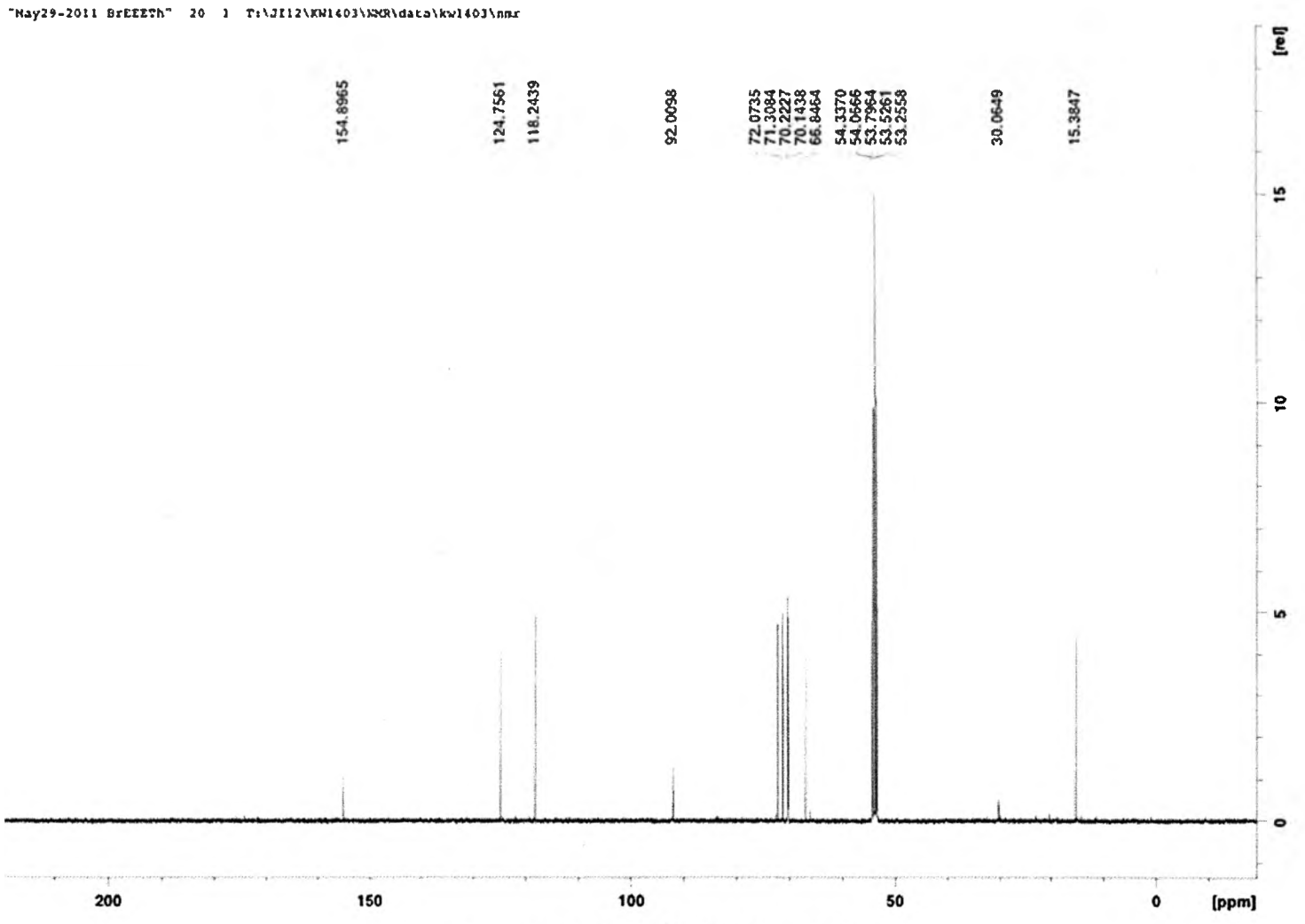
Spectrum 6: BHexTlPz ^{1}H NMR in $CDCl_3$



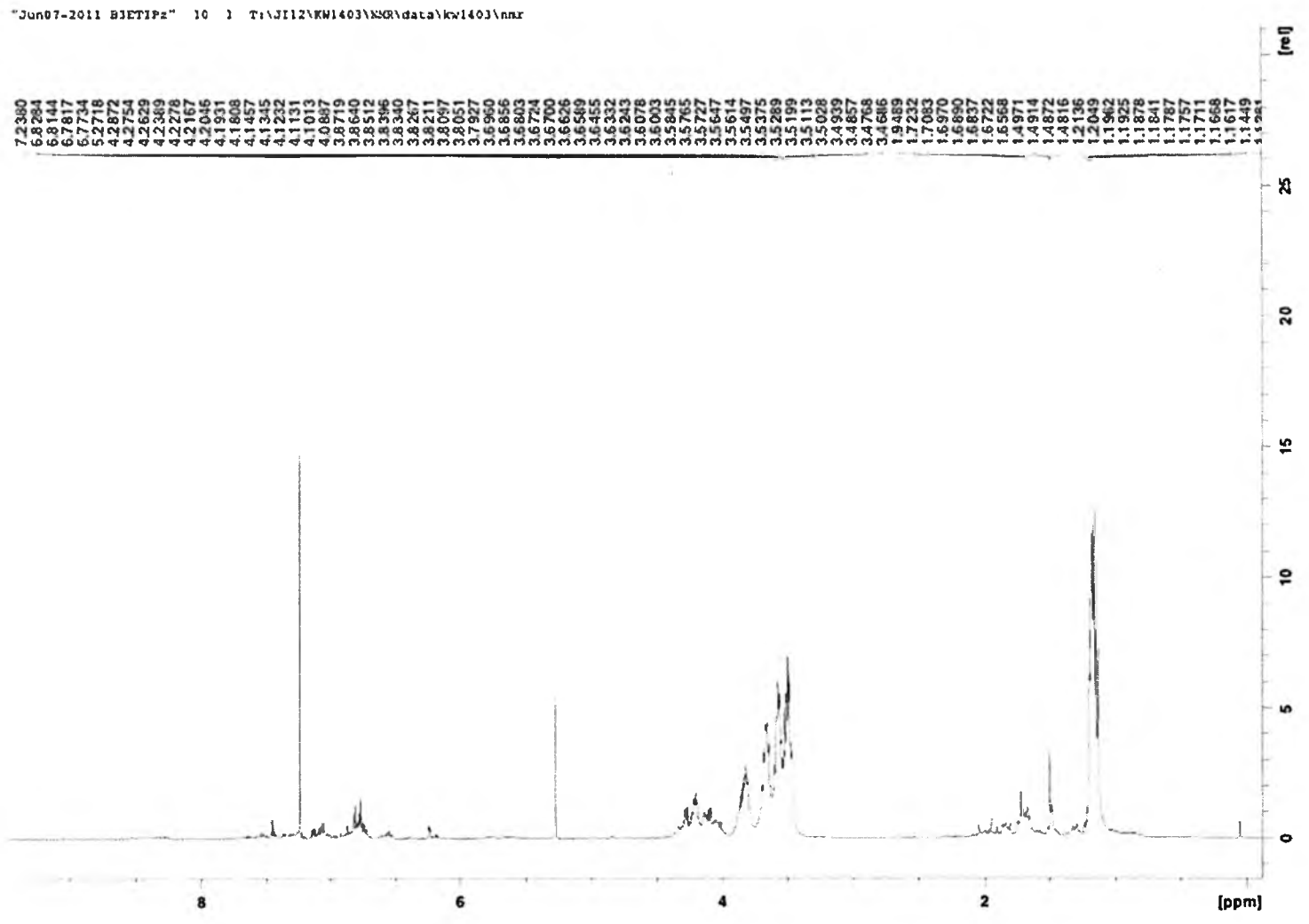
Spectrum 7: EEEThiophene ^{1}H NMR in $CDCl_3$



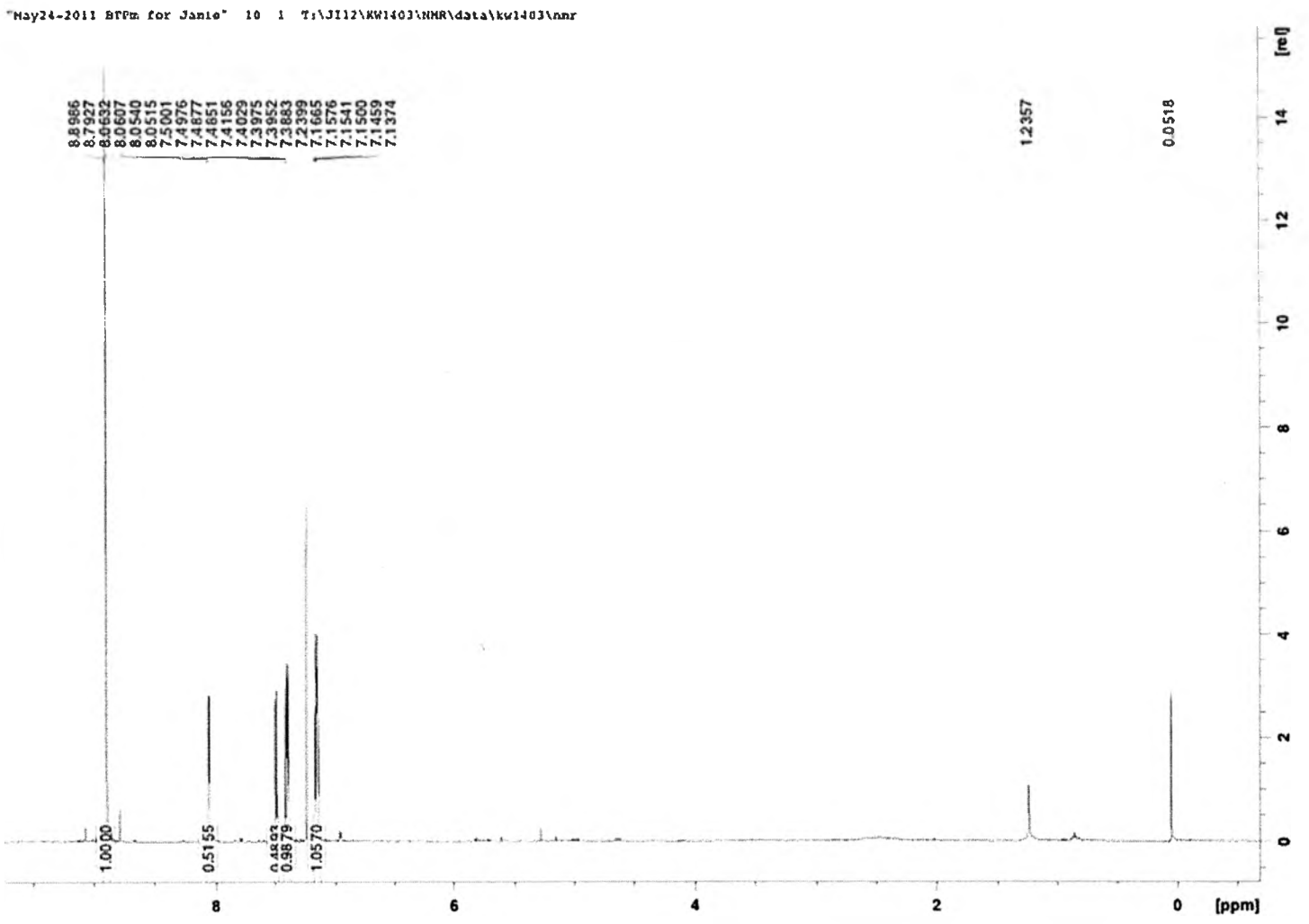
Spectrum 8: Br3ETh ^{1}H NMR in CD_2Cl_2



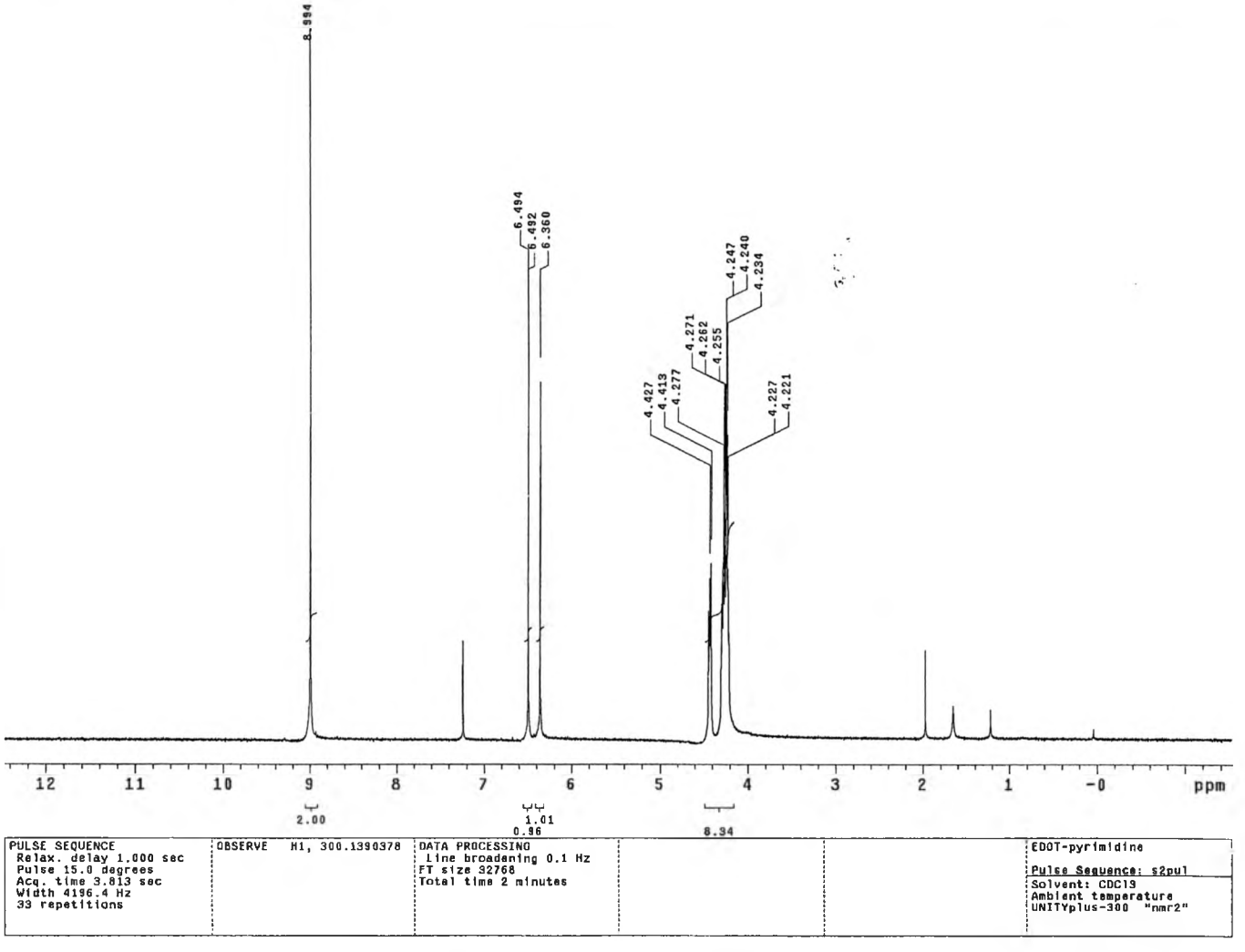
Spectrum 9: Br3ETh ^{13}C NMR in CD_2Cl_2



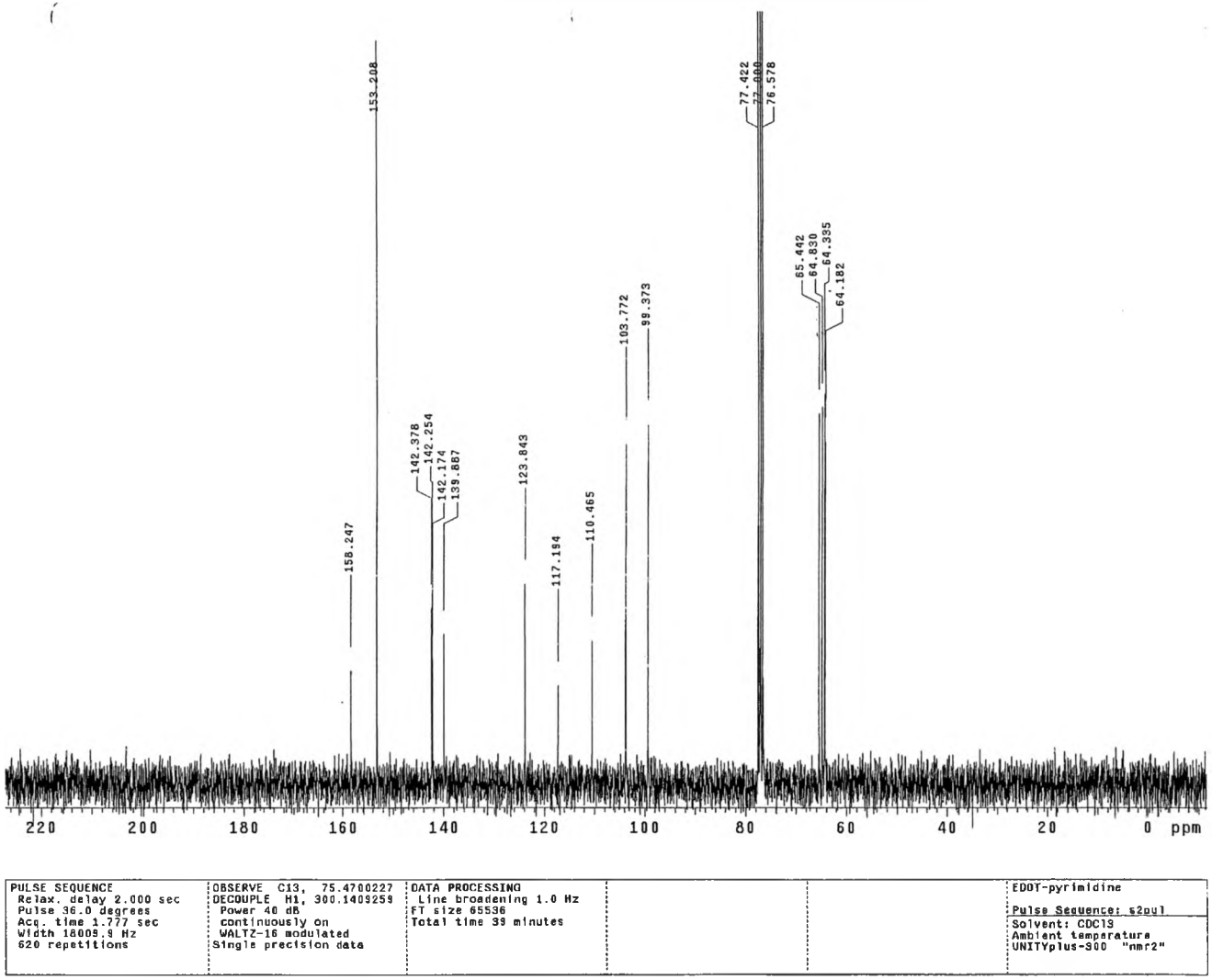
Spectrum 10: B3ETIPz ^{1}H NMR in $CDCl_3$



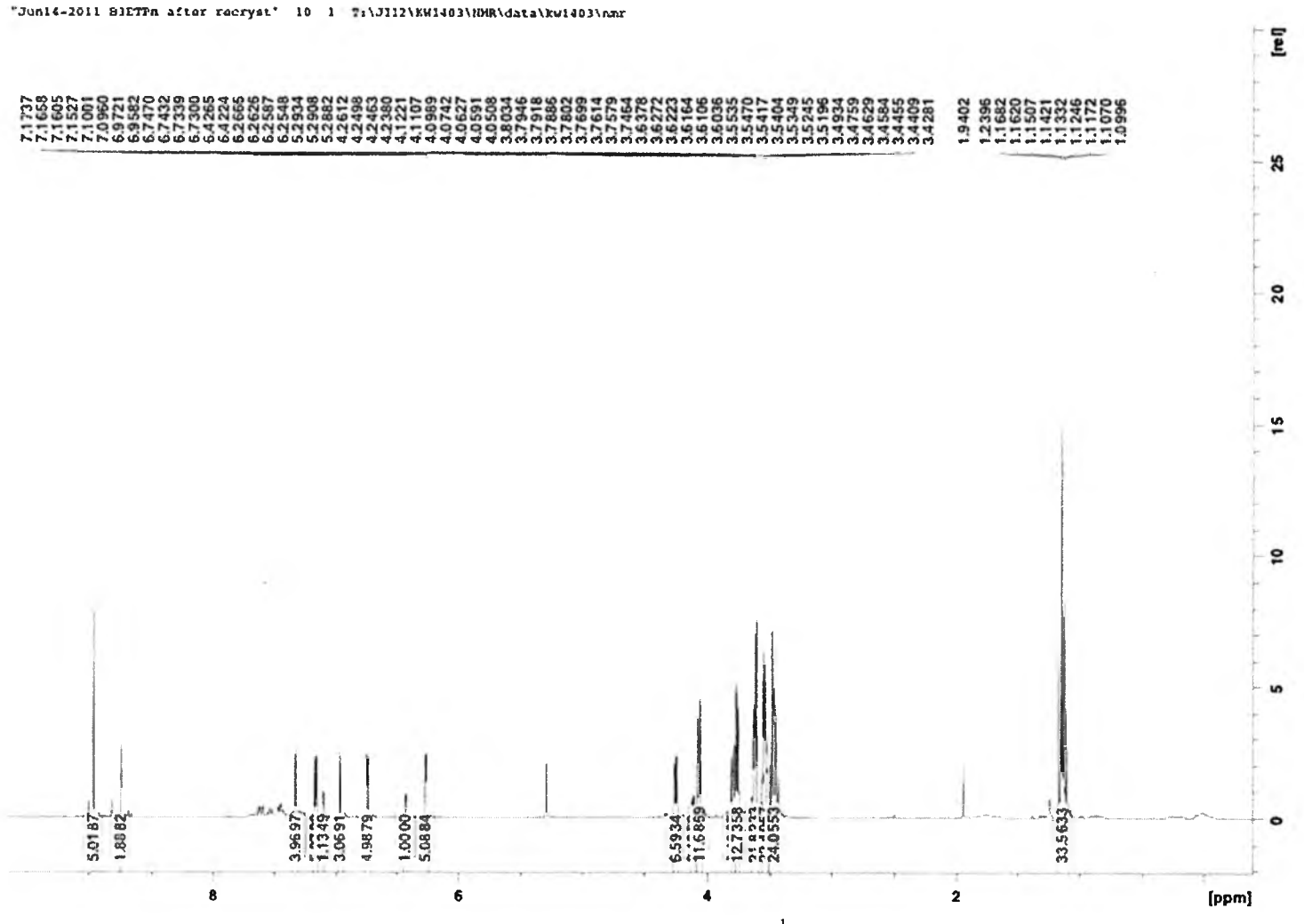
Spectrum 11: BTPm ^{1}H NMR in $CDCl_3$



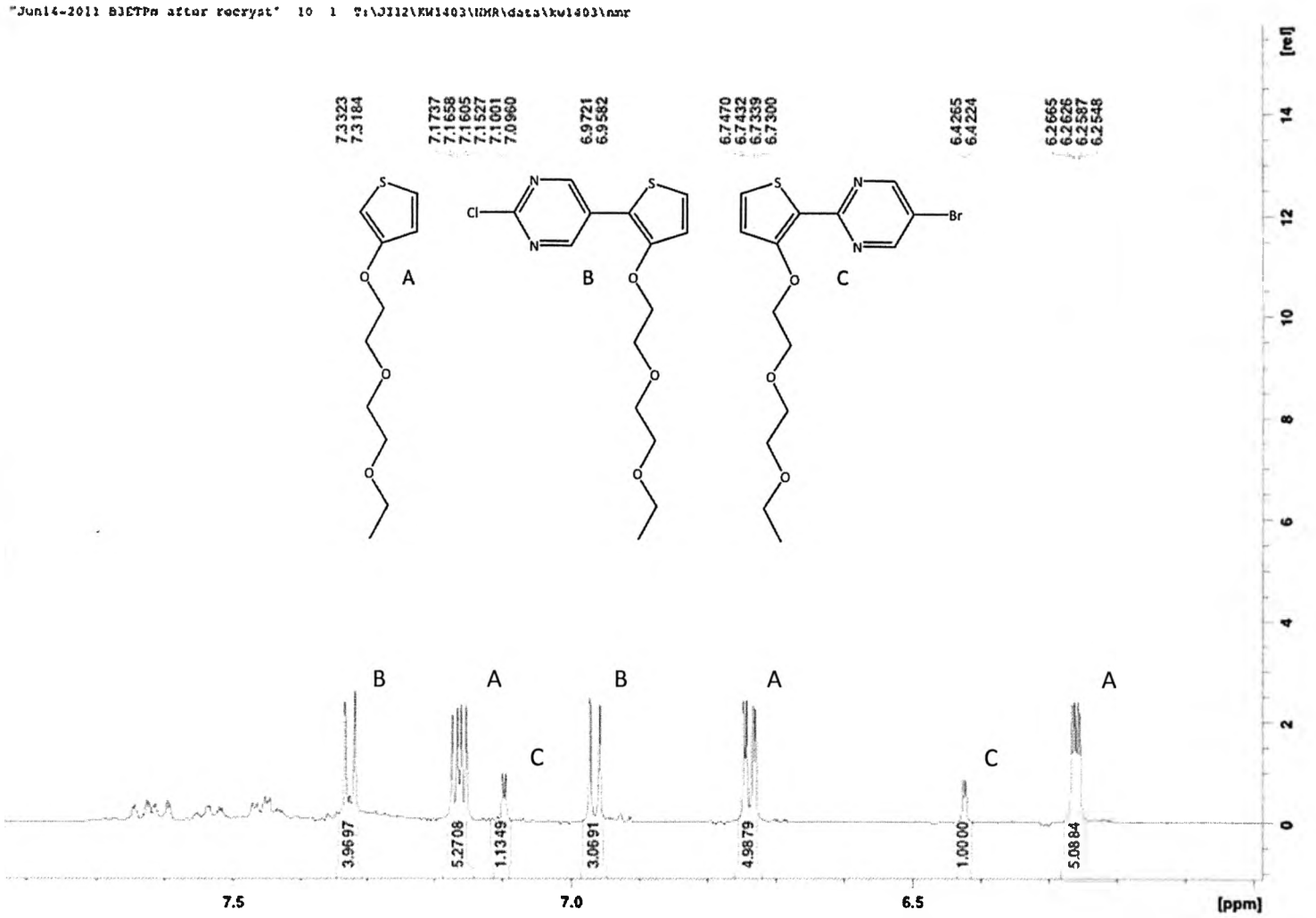
Spectrum 12: BEPm ^{1}H NMR in $CDCl_3$



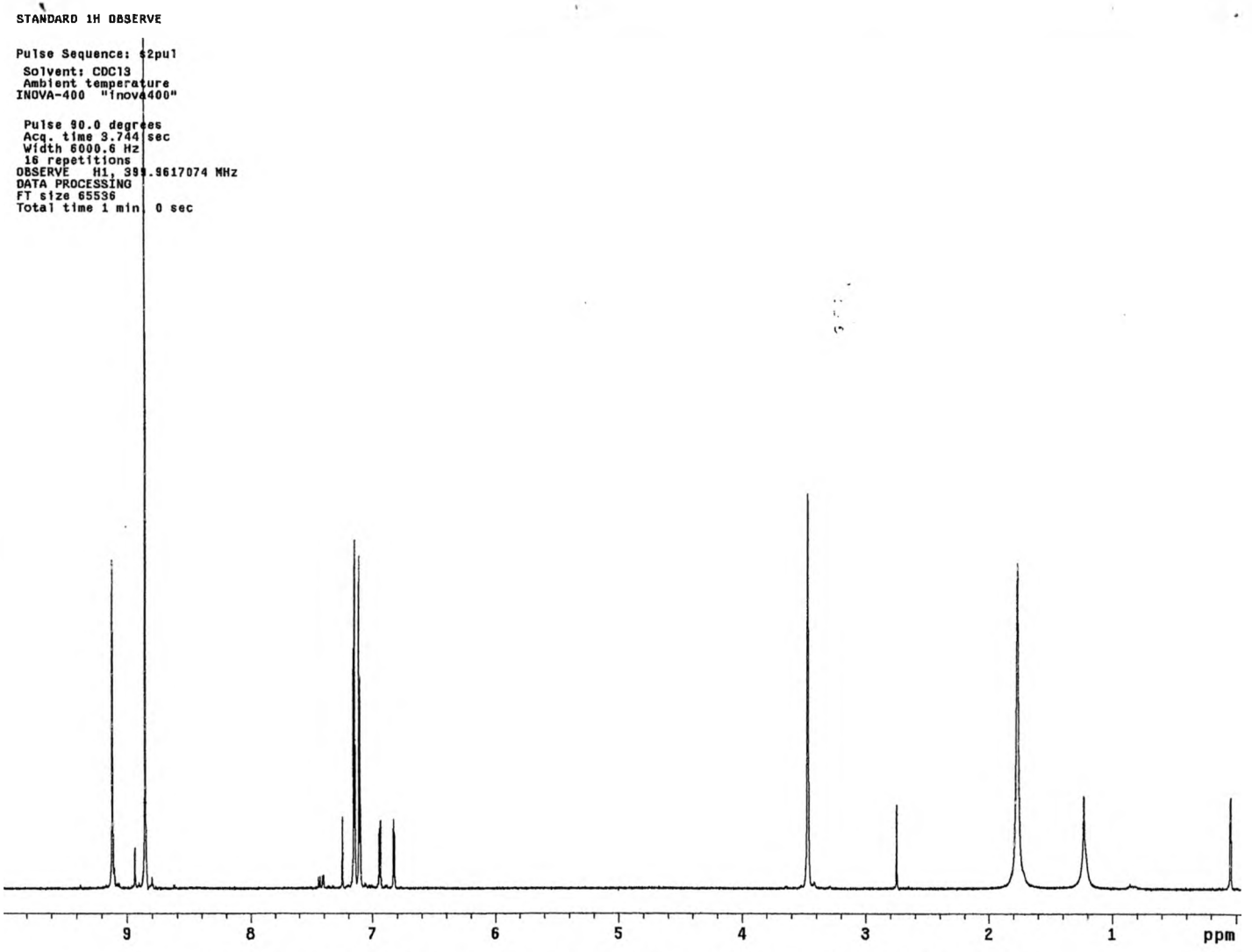
Spectrum 13: BEPm ^{13}C NMR in $CDCl_3$



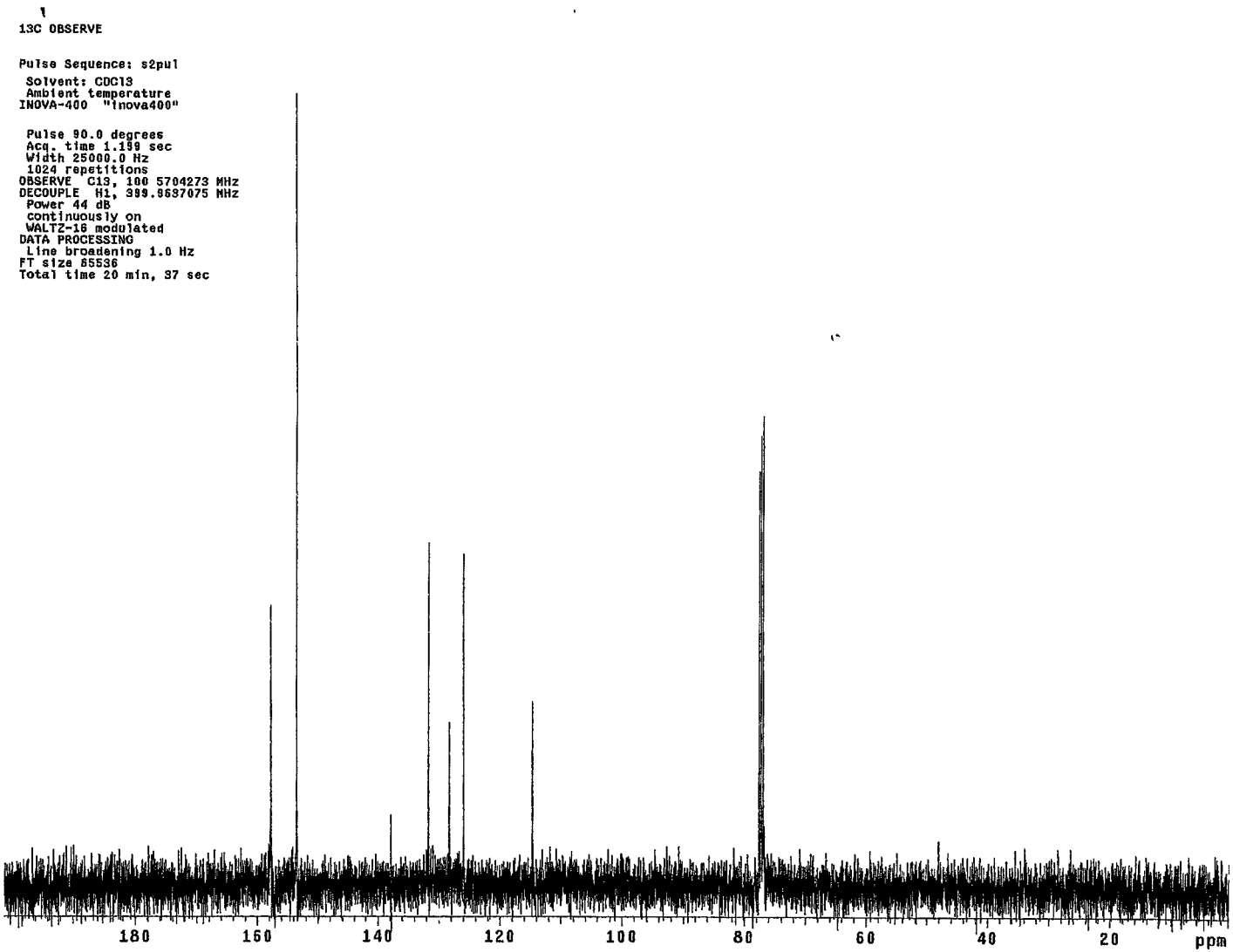
Spectrum 14: B3ETPm reaction mixture ^{1}H NMR in CD_2Cl_2



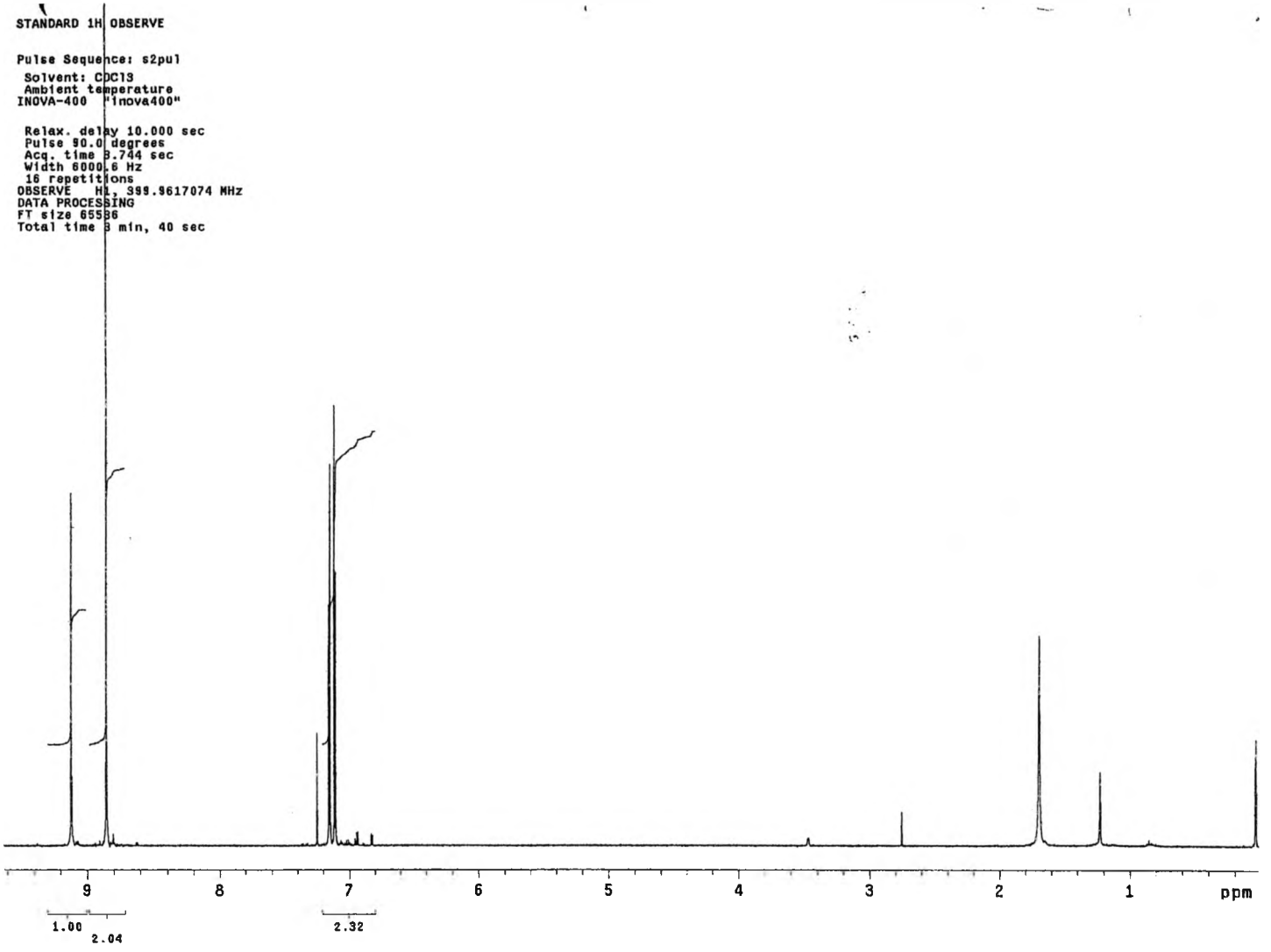
Spectrum 15: B3ETPm reaction mixture thiophene region ^{1}H NMR in CD_2Cl_2



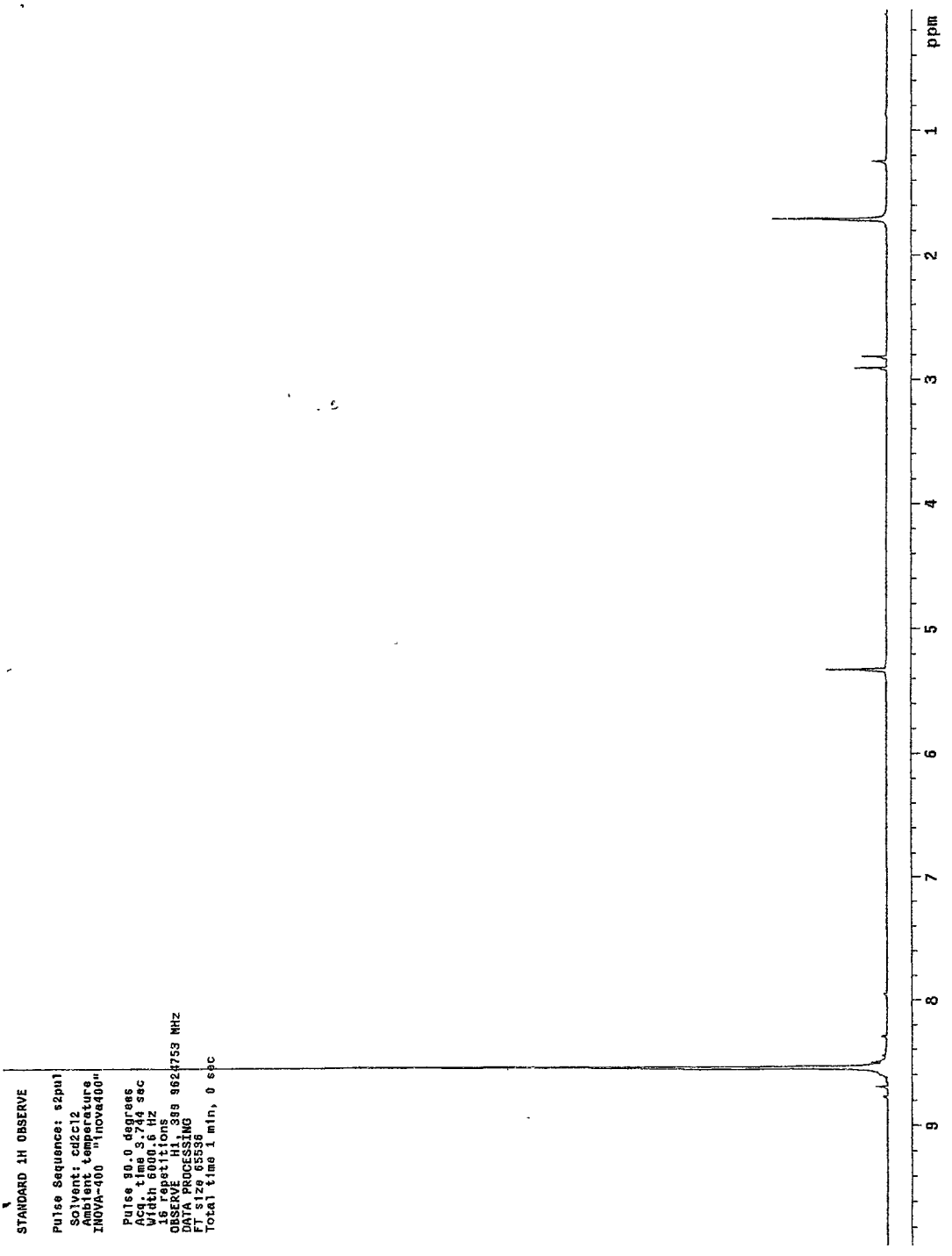
Spectrum 16: 5-Bromo-(2-pyrimidin-5-yl)-thiophene ^{1}H NMR in $CDCl_3$



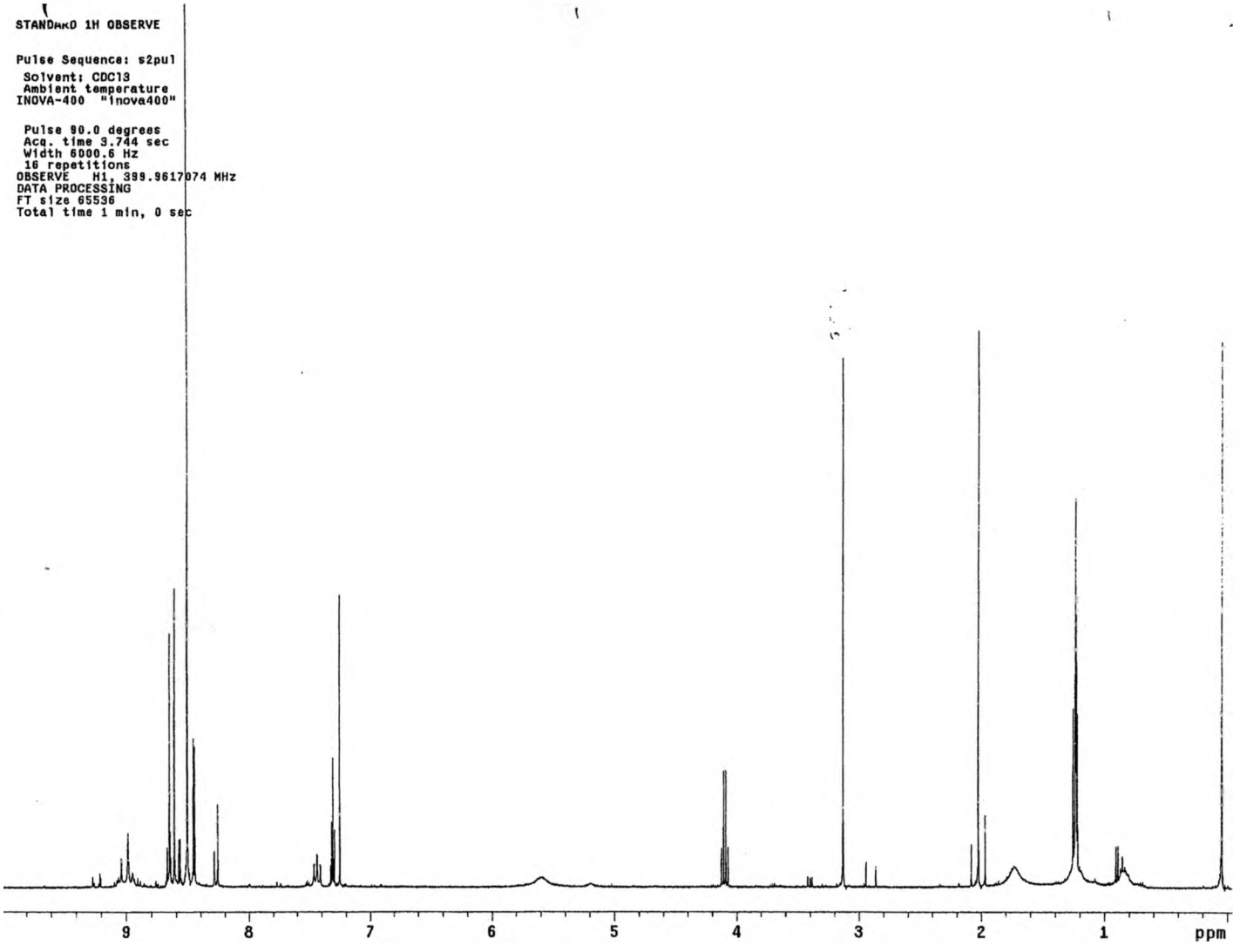
Spectrum 17: 5-Bromo-2-(pyrimidin-5-yl)-thiophene ^{13}C NMR in $CDCl_3$



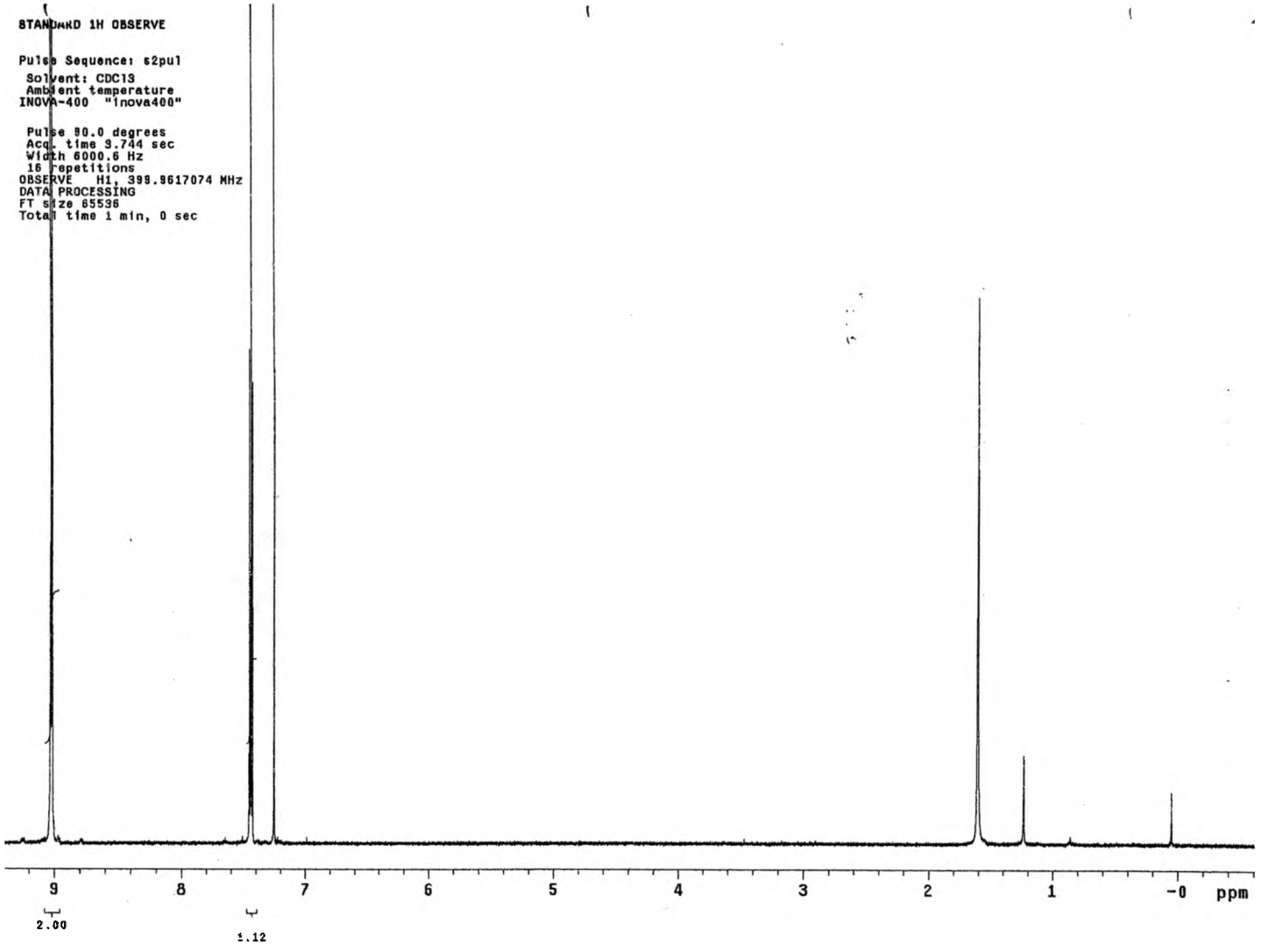
Spectrum 18: 3,5-Dibromo-2-(pyrimidin-5-yl)-thiophene ^{1}H NMR in $CDCl_3$



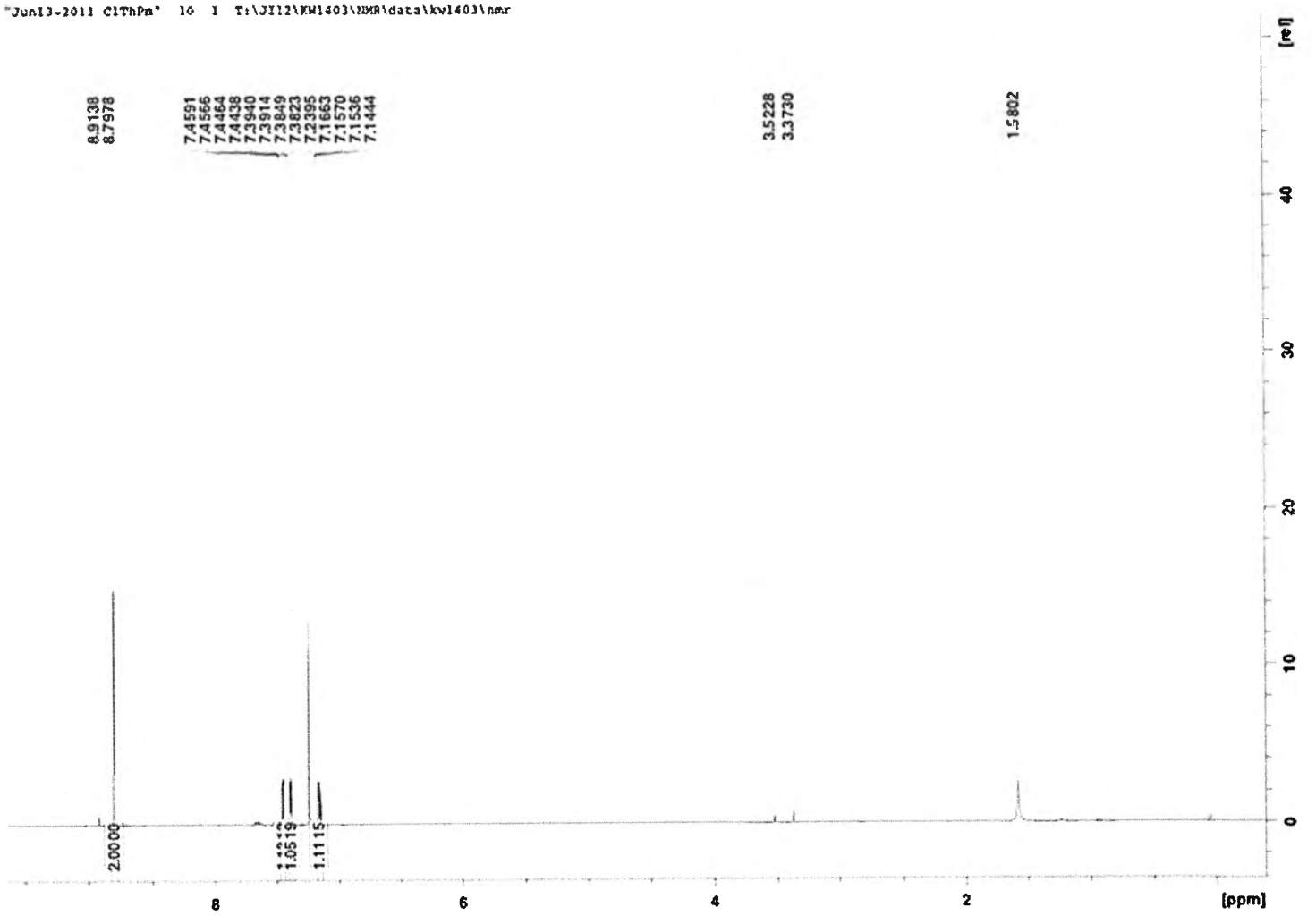
Spectrum 19: 5-Bromo-2-iodopyrimidine ^{1}H NMR in CD_2Cl_2



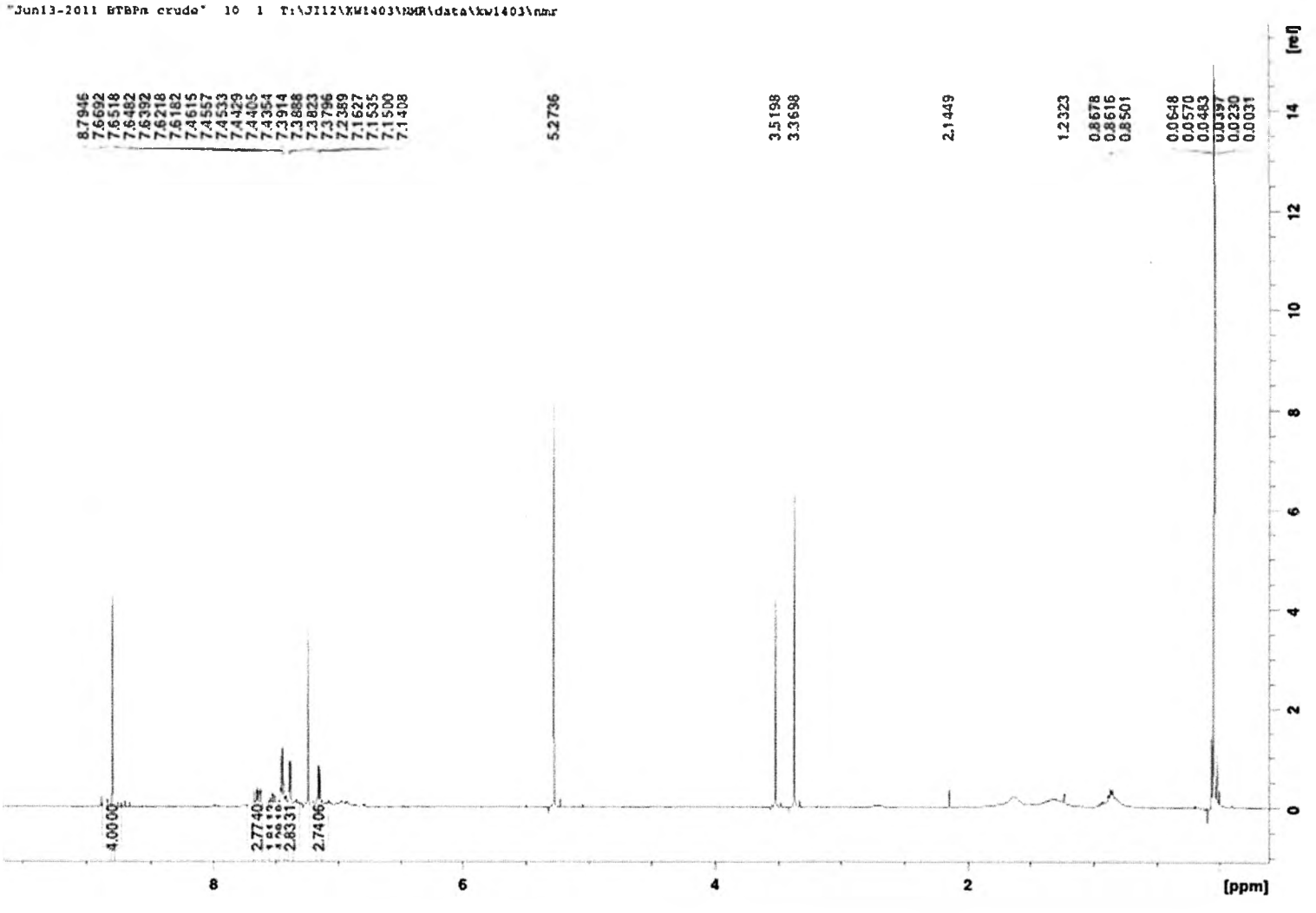
Spectrum 20: Ullmann coupling of 5-bromo-2-iodopyrimidine ^{1}H NMR in $CDCl_3$



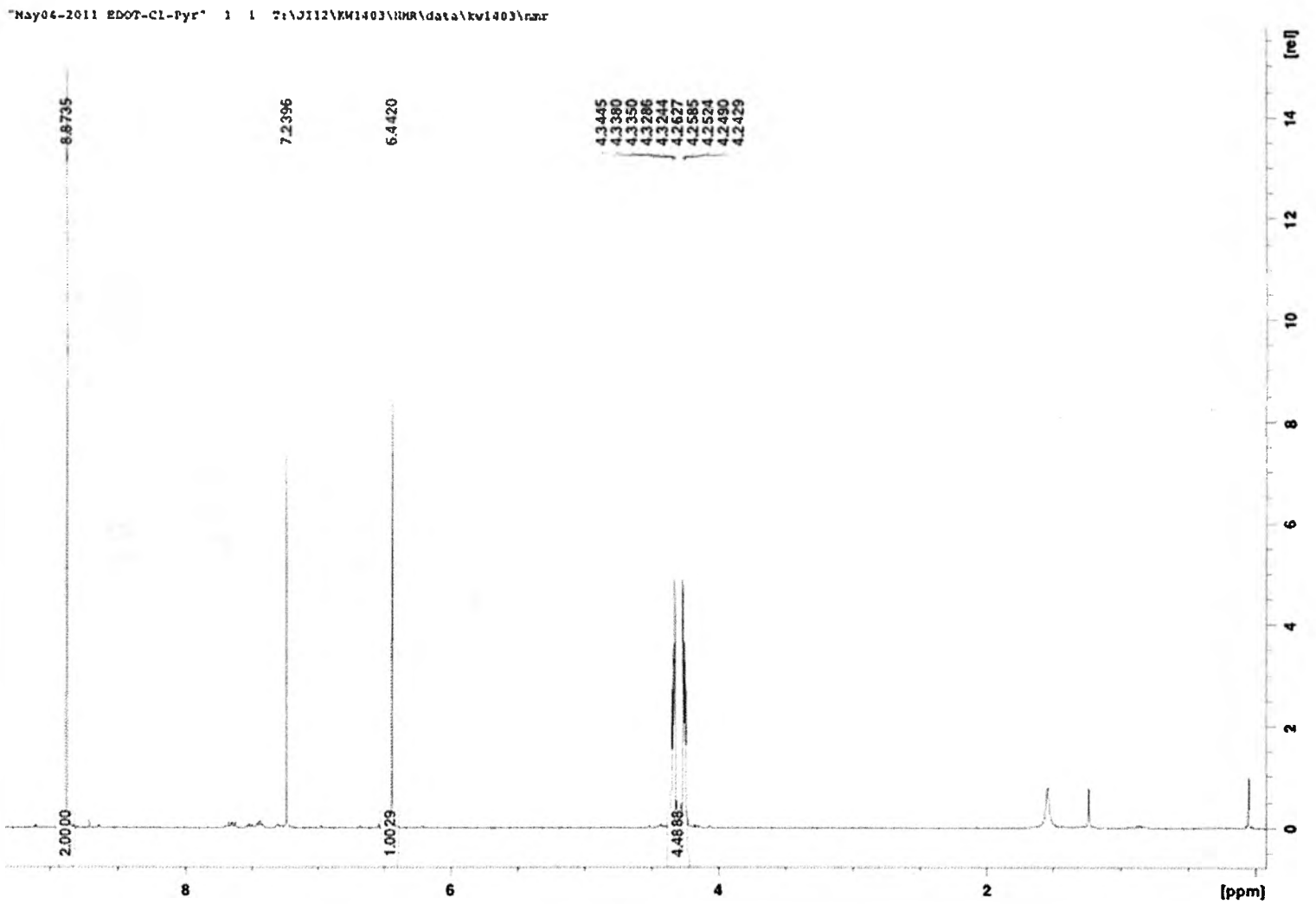
Spectrum 21: 2,2'-Bipyrimidine ^{1}H NMR in $CDCl_3$



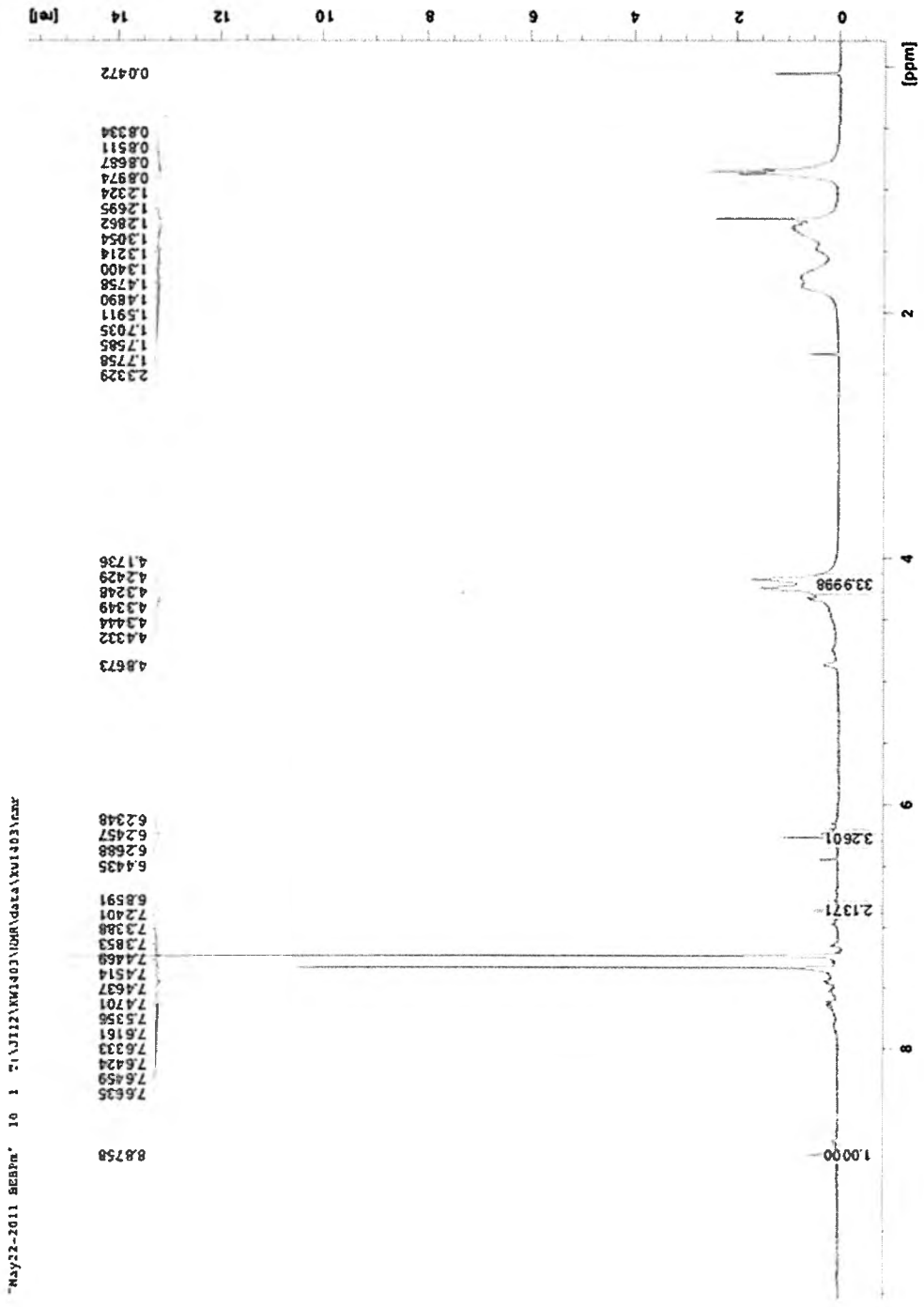
Spectrum 22: 2-Chloro-5-(thiophen-2-yl)-pyrimidine ^{1}H NMR in $CDCl_3$



Spectrum 23: BTBPm reaction product in ^{1}H NMR in $CDCl_3$



Spectrum 24: 2-Chloro-5-(3,4-ethylenedioxythiophen-2-yl)-pyrimidine ^{1}H NMR in $CDCl_3$



Spectrum 25: The product from the BEBPm reaction ^{1}H NMR in $CDCl_3$

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VITA

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