Efficient Synthesis of Symmetric Oligothiophenes via Decarboxylative and Suzuki Cross-Coupling Reactions

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ABSTRACT

Efficient Synthesis of Symmetric Oligothiophenes via Decarboxylative and Suzuki Cross-Coupling Reactions

Venelin Petkov

Organic semiconductors (OSC) have become an integral part of modern society and have found applications in various electronics such as organic photovoltaic cells (OPVC), organic light-emitting diodes (OLED) and flexible organic field-effect transistors (FOFET). Although poly-3-hexylthiophene (P3HT) is one of the most widely used OSCs, interest in oligothiophenes has surged recently as they can be used as effective models to study P3HT. The most widely used methods for the synthesis of oligothiophenes are Kumada, Stille and Suzuki cross-coupling (CC) reactions. These methods are well-explored and robust however, the Stille and Kumada processes come with a variety of disadvantages as well as environmental and health risks such as requiring harsh conditions and producing toxic metallic waste. In this work, we aimed to investigate and compare two different cross-coupling methodologies for the synthesis of oligothiophenes that do not produce harmful byproducts while also having simple and convenient reaction procedures. Using both decarboxylative cross-coupling (DCC) and Suzuki cross-coupling, symmetric oligothiophenes of lengths between 3 and 12 thiophene units have been sequentially synthesized at scales between 0.1 mmol and 1.4 mmol. Individual functionalized monomers were coupled to di-halogenated thiophene cores utilizing a double Pd-catalyzed cross-coupling reaction. The resulting oligomers were then di-brominated using multi-solvent systems with average reaction times of 30 minutes leading to complete conversions without the need for purification. Combining the DCC/Suzuki cross-coupling with the dibromination reaction, an odd sequence of 3, 5, 7, 9 and 11-unit oligothiophenes as well as an even sequence of 4, 6, 8, 10 and 12-unit oligothiophenes were sequentially synthesized in very good yields (70% to 92%). To our knowledge, 4 of the synthesized compounds have not been previously reported, namely **9T**, **11T**, **DiBr-7T** and **DiBr-9T**.

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List of Abbreviations

*μ*w: Microwave Irradiation....30
2-KEH: Potassium 2-Ethylhexanoate....41
2-MeTHF: 2-Methyltetrahydrofuran....50
3AT: 3-Alkylthiophene....14
3HT: 3-Hexylthiophene....3
AcOH: Acetic Acid....49
Ar: Aryl Functional Group....10
$B(OMe)_3$: Trimethyl Borate....52
B2Pin2: Bis(pinacolato)diboron....20
Bpin: 4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane....20
CC: Cross-Coupling....9
$CHCl_3$: Chloroform....49
CMD: Concerted-Metalation-Deprotonation....24
COOH: Carboxylic Acid Functional Group....30
COOK: Potassium Carboxylate Functional Group....31
CPX: Charge-transfer complex....7
DArP: Direct-Arylation-Polymerization....26
DMA: *N*,*N*-Dimethylacetamide....37
DMF: *N*,*N*-Dimethylformamide....34
dppb: 1,2-Bis(diphenylphosphino)butane....27
dppf: 1,1'-Ferrocenediyl-Bis(diphenylphosphine)....50
dppp: 1,3-Bis(diphenylphosphino)propane....11
E_{dist}: Free Energy of Distortion....25
E_{int}: Free Energy of Interaction....25
equivs. : Equivalents of Reactant....36
EtOAc: Ethyl Acetate....23
EtOH: Ethanol....54
F_4TCNQ: 2,3,5,6-Tetrafluoro-7,7,8,8-Tetracyanoquinodimethane....7
FCT: Fractional Charge Transfer....8
FTIR: Fourier Transform Infrared Spectroscopy....7

GCMS: Gas Chromatography-Mass Spectrometry 39
HH: Head-to-Head 3
HOMO: Highest Occupied Molecular Orbital 7
HRMS: High-Resolution Mass Spectrometry 60
HT: Head-to-Tail 3
ICT: Integer Charge Transfer 7
i-Pr: *iso*-Propyl Functional Group 20
KOAc: Potassium Acetate 50
KOPiv: Potassium Pivalate 50
L: L-Type Ligand 25
LUMO: Lowest Unoccupied Molecular Orbital 7
MX: Metal-Halogen Salt 11
NBS: N-Bromosuccinimide 16
n-Bu: *normal*-Butyl Functional Group 17
NMR: Nuclear Magnetic Resonance 36
OAc: Acetate Functional Group 26
$OBpin_2$: 2,2'-Oxybis(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane) 51
OFET: Organic Field Effect Transistors 2
OLED: Organic Light Emitting Diode 2
OLET: Organic Light Emitting Transistors 7
OPVC: Organic Photovoltaic Cells 2
OR: Alcohol Functional Group 19
OSCP: Organic Semiconducting Polymer 2
OT: Oligothiophene 2
o-tolyl: *ortho*-Tolyl/2-Methylphenyl 46
P3AT: Poly-3-Alkylthiophene 3
P3BT: Poly-3-Butylthiophene 3
P3DDT: Poly-3-Dodecylthiophene 4
P3HT: Poly-3-Hexylthiophene 5
P3OT: Poly-3-Octylthiophene 5
PA: Polyacetylene 2
PivOH: Pivalic Acid 24

PPh_2: Diphenylphosphine 21
PT: Polythiophene 2
PTC: Phase-Transfer Catalyst 21
QT: Quaterthiophene 7
RCOO: Carboxylate Functional Group 25
RRa: Regio-Random 3
RRe: Regio-Regular 3
S_EAr: Electrophilic Aromatic Substitution 24
t-Bu: *tert*-Butyl Functional Group 30
TCV: Tricyanovinyl 21
THF: Tetrahydrofuran 36
TMPMgCl·LiCl: 2,2,6,6-Tetramethylpiperidinylmagnesium Chloride Lithium Chloride 36
TS: Transition State 24
TT: Tail-to-Tail 3
X: Halogen Atom 10
Δ: Conventional Heating 50

Chapter 1 – Introduction

1.1 Organic Semiconductors and Polythiophenes

Human fascination with electromagnetic phenomena dates back to some of the earliest hominids. From one of our earliest major discoveries—fire, which emerged just under a million years ago[1]—to the advent of electricity, the backbone of modern civilization, the photon-emitting dance of electrons has long captivated our imagination. It is, in fact, the motion of electrons that is responsible not only for the colors we perceive in the world[2] but also for the extraordinary pace of scientific and technological progress in recent history, enabled by electricity. However, electricity alone is not sufficient as it requires suitable materials to channel and control it. From an electrical standpoint, materials fall into three primary categories: conductors, semiconductors, and insulators. Semiconductors bridge the gap between conductors and insulators in terms of electrical behavior, with band gaps typically ranging from 0.1 to 3.0 eV and conductivities between 10^{-8} and 10^{3} S/cm (**Figure 1**).[3,4] Conductors, by contrast, possess no band gap and high conductivity, while insulators have large band gaps and negligible conductivity. Semiconductors are fundamental to virtually all modern electronics. Among them, silicon stands as the most common and widely utilized material[5–8], with a band gap of 1.12 eV and a strong response to both n-type and p-type doping.[5,9] As such, it is integral to the fabrication of transistors which are the core components of modern computer processors.[7,9] Despite its utility, silicon has several limitations. For instance, silicon chips are produced from delicate thin wafers that cannot be directly exposed to the environment: excess pressure can cause them to crack, dust particles can compromise entire production batches, and even direct skin contact can render a wafer unusable.[5,10–12] Additionally, silicon's rigid nature and the often complex and costly fabrication methods[6,11,13] have fueled interest in alternative materials with more versatile physical properties and simpler manufacturing processes. This is where organic semiconductors (OSCs) come into play. OSCs are organic materials that exhibit semiconductor-like electrical behavior, combined with advantages such as mechanical flexibility, structural tunability via organic synthesis, lower production costs, and simpler processing requirements.[4,14,15] The most commonly used building blocks for OSCs are π-conjugated polymers. However, not all polymers qualify as semiconductors. In fact, most organic molecules are electrical insulators unless doped with one notable exception being derivatives of 7,7,8,8-tetracyanoquinodimethane (TCNQ).[16]

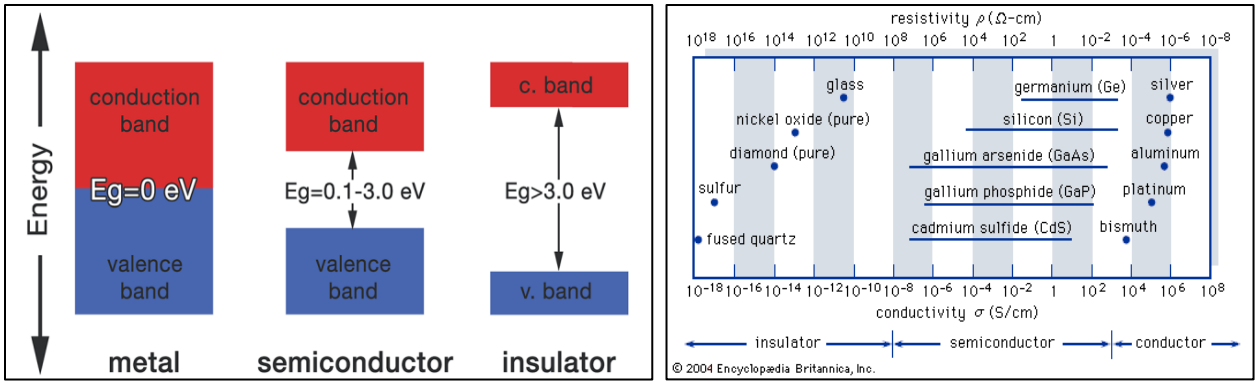
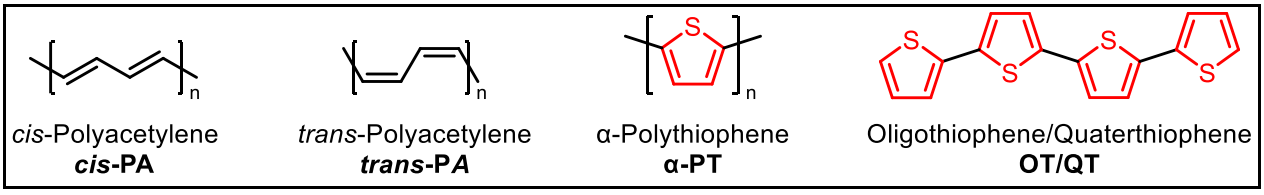


Figure 1: Bandgap Energies and Conductivities of Insulators, Semiconductors and Conductors[3,8](Image credits to *RSC Adv.* **2015**, *5*, 11611 and Encyclopedia Britannica)

The first demonstration of a polymer with metal-like conductivity was made in 1977 by the group of Alan MacDiarmid, Alan J. Heeger and Hideki Shirakawa (**Figure 2**) when they reported their work on doped polyacetylene (PA).[17,18] This discovery is mainly responsible for the large variety of organic semiconducting polymers (OSCPs) available today. Using controlled polymerization reaction conditions, they synthesized two isomers of the simplest π-conjugated polymer, namely *cis*- and *trans*-PA.[19] Their synthesis produced a crystalline product which, when doped using halogen/AsF_5 vapor, presented an increased conductivity by up to eleven orders of magnitude (from $1.7*10^{-9}$ S/cm to $1.2*10^{3}$ S/cm for cis-PA doped with AsF_5 vapor).[18,20] This was particularly important because this transition takes undoped PA from an insulator in terms of conductivity into the range of metallic conductors (**Figure 1**) and the previously mentioned TCNQ derivatives.[18] For their work on developing the first OSCPs, Alan MacDiarmid, Alan J. Heeger and Hideki Shirakawa were awarded the 2000 Nobel Prize in chemistry.[21]



cis-Polyacetylene **cis-PA** | *trans*-Polyacetylene ***trans*-PA** | α-Polythiophene **α-PT** | Oligothiophene/Quaterthiophene **OT/QT**

Figure 2: Structures of Polyacetylene Isomers and Thiophene-Based Polymers

From there, research into semiconducting polymers led to the development of thiophene-based polymers and oligomers (**Figure 2**), also known as polythiophenes (PTs) and oligothiophenes (OTs), which have become the most widespread OSCPs. Polythiophenes have been applied to a variety of devices, the most prevalent being organic solar cells (OPVCs)[22], organic field-effect transistors (OFETs)[23], and organic light-emitting diodes (OLEDs)[24] along with varied applications

in biotechnology[25]. As previously mentioned, OSCPs provide certain benefits due to their malleability and flexibility, which have allowed for the development of modern applications of PT in printable OPVCs[26,27] and flexible electronics.[28,29] Thiophene is particularly well suited for these applications for multiple reasons, some of them being its ease of chemical modification as well as ease of polymerization through transition-metal catalyzed cross-couplings, structural stability of resulting PTs which exhibit favorable π-conjugation, high polarizability of the sulfur atom and efficient stacking of polymer structures.[30] Being organic molecules, PTs have the advantage of tuneability through chemical modification (functionalization through chemical reactions). This has generated a wide variety of PTs that can be used for many different and specific scenarios. The primary focus of this work will be a subset of PTs, specifically those based on 3-hexylthiophene (3HT).

1.1.1 *Poly-3-Alkyl Thiophenes*

Poly-3-alkylthiophenes (P3ATs) are a class of PTs that have been extensively studied and have found numerous applications. However, for these applications to be realized, the PT must be in the form of thin-films, which requires the PT to be either fusible or soluble in organic solvents.[31] The early syntheses of PT in 1980 yielded unsubstituted α-PTs (**Figure 2**) which would precipitate out of the reaction solution and were not soluble in any organic solvents.[32,33] Doping with I_2 vapor produced conductivities of 0.1 S/cm at best without thermal treatment.[33] Shortly after, the Elsenbaumer group reported the synthesis and I_2 doping of poly-3-butylthiophene (P3BT) along with other P3ATs.[34] This was a particularly important since I_2-doped P3BT had a conductivity of 4 S/cm along with the added benefit of being soluble in organic solvents and therefore processable into thin-films, while polymers with shorter alkyl chains did not possess the same benefit.[34,35] Unfortunately, the newly synthesized P3AT samples were not imparted any particular orientation during synthesis, resulting in random orientations of the 3-alkyl chains within the polymer. This led to the classification of P3ATs into different groups (**Figure 3**), particularly three groups for thiophene dimers which could be further coupled to create four distinct trimers.[36] The three dimer groups are **Head-to-Head** (HH), **Head-to-Tail** (HT) and **Tail-to-Tail** (TT). These three groups can be further combined to create HT-HT, TT-HT, HT-HH, and TT-HH triads.[37] In this naming scheme, the “head” is C2 adjacent to the alkyl chain and the “tail” is C5. Out of the four trimer motifs, the HT-HT is the most sought-after and of highest importance, its other name being Regio-Regular P3AT (RRe-P3AT). The three other motifs are also known as Regio-Random P3AT (RRa-P3AT).

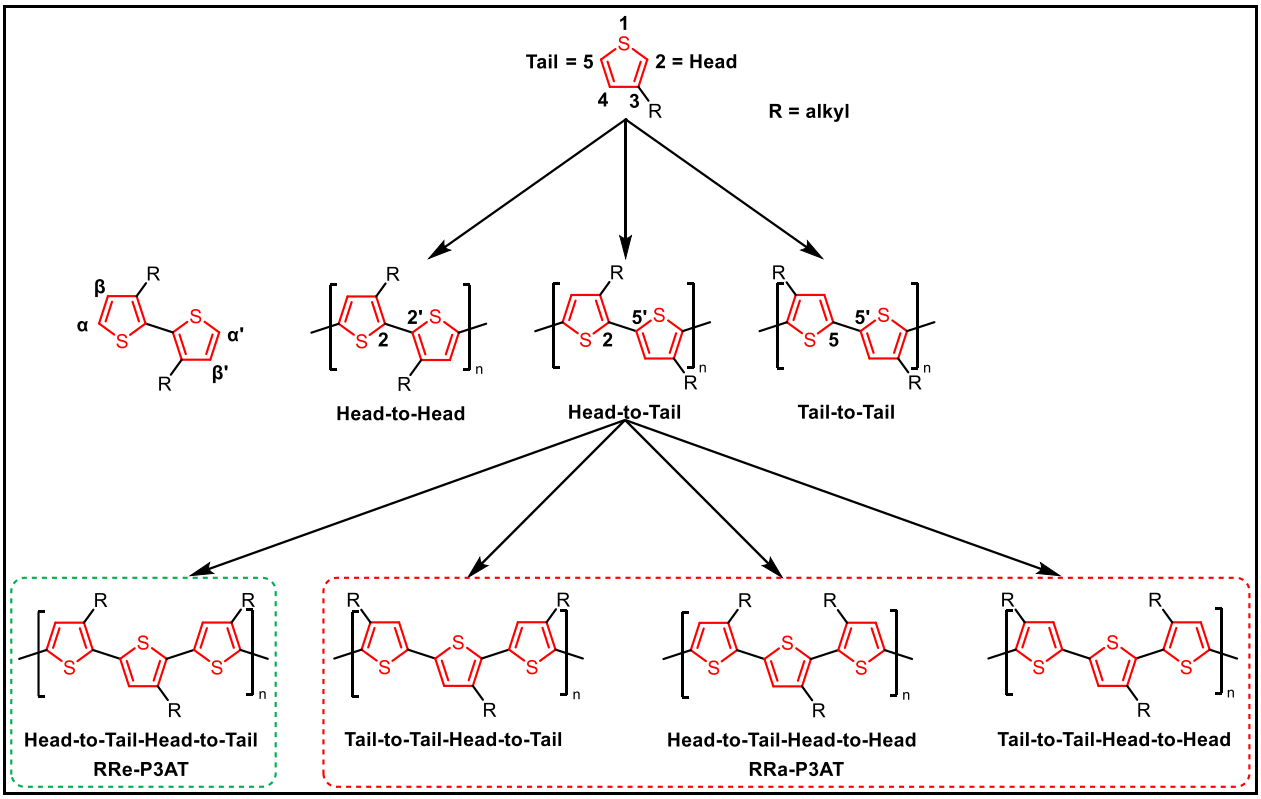


Figure 3: α-Coupling Motifs of Poly-3-Alkylated Thiophenes[38]

It was in 1992 that the first truly RRe-P3AT was synthesized by the McCullough group using an enhanced synthetic process to produce poly-3-dodecylthiophene (P3DDT).[39] The reported conductivity of this RRe-P3DDT doped with I_2 was on average 600 S/cm, which is a 50- to 60-fold increase when compared to RRa-P3DDT, with some samples reaching 1000 S/cm.[39] The presence of regularly positioned alkyl chains provided multiple benefits (**Figure 4**). It improved backbone planarity as it forced the thiophene rings to adopt a *trans*-conformation (**1**) in order to accommodate the alkyl chains[37] which increases conjugation length. The *trans*-conformer is favored due to steric repulsion present in the *cis*-conformer (**2**). RRa-P3AT with HH couplings experience steric strain in both the *trans*-conformation (**3**) and the *cis*-conformation (**4**). The steric repulsion between alkyl chains pushes RRe-P3AT into a *trans*-conformation throughout the whole polymer. This, in turn, gives the polymers the ability to self-assemble into more tightly stacked microstructures[40] (**5**). The result is improved molecular ordering, leading to improved response to doping and improved charge carrier mobility, with all of these qualities culminating in better semiconducting performance.[37,41–44] The introduction of alkyl chains solved issues that were at the time not addressed and simultaneously provided multiple and varied benefits for PTs to be

used as OSCs. From here, considerable interest was shifted towards poly-3-hexylthiophene (P3HT).

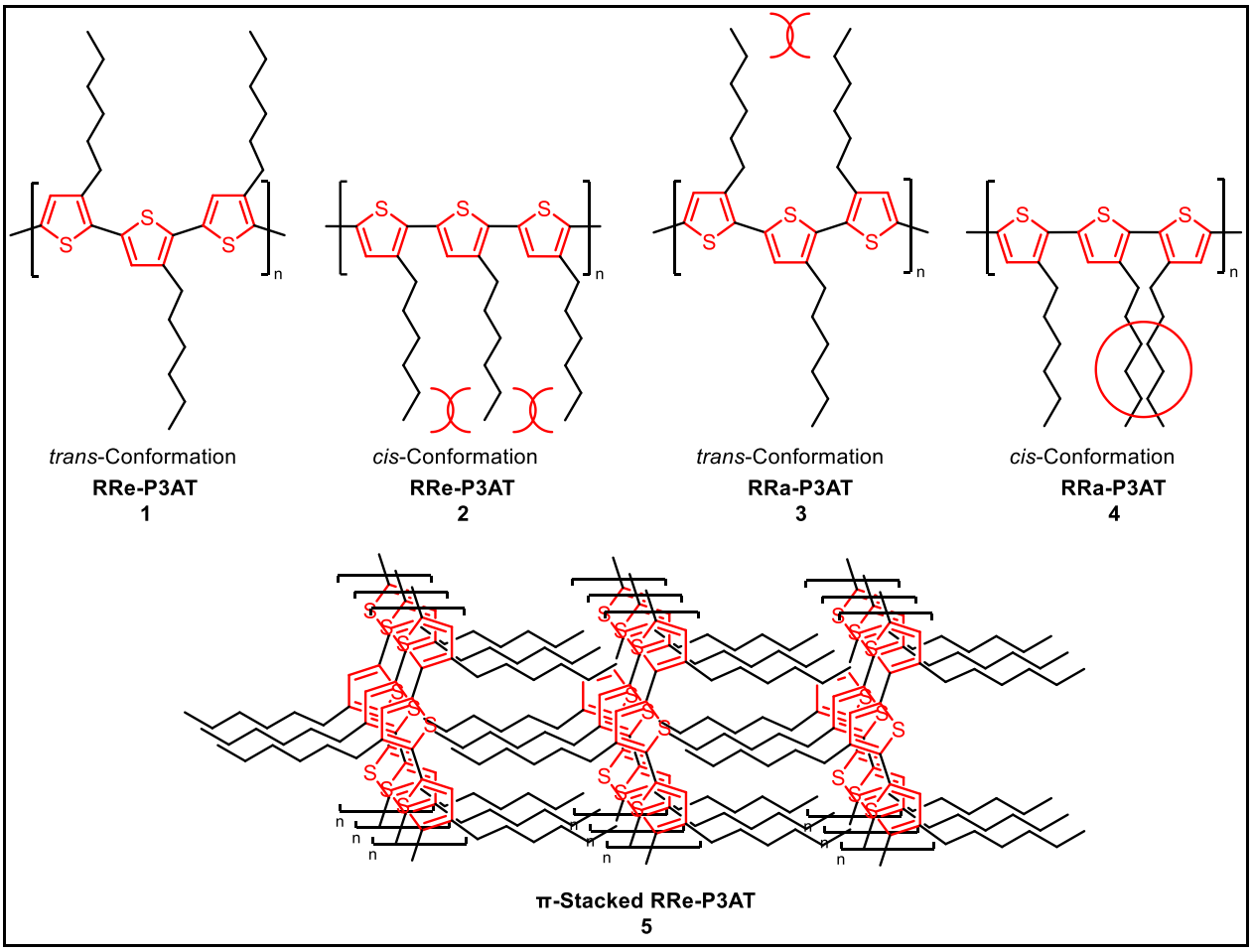


Figure 4: Steric Repulsion in *cis-trans* Conformers of RRe and RRa-P3AT[45]

The synthesis of RRe-P3HT was reported within the same year as the synthesis of RRe-P3DDT by the McCollough group.[46] This synthesis was revolutionary at the time, and subsequent modifications made the synthesis of RRe-P3HT exceptionally convenient. This, in turn, is partially the reason P3HT has become the benchmark polymer against which all other polymers are compared.[47] Countless studies, reviews and books have been devoted to the study of P3HT, in both its RRe and RRa forms, as such, it has become the "workhorse" of OSCP research.[48] The reasons for this being the case are varied and nuanced, but overall are mainly due to the convenient combination of properties that P3HT possesses. When compared to other P3ATs in the alkyl series, hole mobility has been shown to increase by several orders of magnitude from P3BT to P3HT and subsequently decrease by two orders of magnitude to poly-3-octylthiophene (P3OT) and then decrease exponentially to P3DDT.[49] This better charge carrier mobility has been

shown to be due to better self-organization in P3HT when compared to other P3ATs.[14,49] Additionally, longer alkyl chains have an overwhelming insulating effect on the thin-film matrix, which is also a contributing factor to lower charge-carrier mobilities.[50] In comparison, shorter alkyl chains will lead to solubility issues, making the PT harder to cast into thin films and resulting once again in poorer performance.[50] Bulky, polar and branching sidechains have also been shown to be detrimental to polymer performance. Groups with branching alkyl chains or H-bond capable groups, such as carboxylic acids, show diminished performance compared to P3HT, with the most likely cause being larger π-π stacking distances and a higher barrier for the formation of ordered/crystalline films.[51] P3HT also benefits from good processability as it can be cast into thin-films using a variety of casting methods, which can produce different micro/macro structures.[52] It can even be used in large-scale roll-to-roll printing of bulk heterojunction OSCs.[53] Furthermore, thanks to McCollough's method and subsequent improvements, P3HT benefits from a considerable ease of synthesis, which makes it an overall better choice when compared to PTs in general.[54]

All of these characteristics have culminated in P3HT becoming the most widely studied and well-understood PT, and as a result, it has become a model for studying different PT systems. However, being a polymer, P3HT suffers from one issue common to all polymers: the reproducibility of polymer samples. Since polymerization reactions generate a mixture of polymer chains of varied lengths (polydisperse), two samples made the same way can't be truly identical, even with modern techniques. This issue of reproducibility has led to oligothiophenes (monodisperse) becoming increasingly prevalent in PT research, in an attempt to compensate for the shortcomings of the polymerization synthetic procedures.

1.1.1.1 Oligothiophenes

Oligothiophenes are a subset of polythiophenes that are usually considerably shorter and have well-defined structures. According to IUPAC, an oligomer is defined as a molecule with intermediate molecular mass whose properties would vary significantly should one or a few of its units be removed.[55] This definition reveals one of the key differences between polymers and oligomers, which is their size. Polymers are long molecules and are generally made up of mixtures of varied unit-length chains as well as chains with minor imperfections[56] which makes accurate elucidation of structure-property relationships in polymers impossible.[57] The cause of this difference lies in the synthetic methods used to synthesize polymers, which are reactions that produce mixtures of products regardless of the degree of control over their conditions.[56] On the contrary, oligomers tend to be synthesized by iterative/sequential elongation of the conjugated

backbone, yielding well-defined products with consistent properties, which results in repeatability and predictability of their behaviors and experimental results.[56] Modern applications of oligothiophenes include OPVC[58,59], organic light-emitting transistors (OLET)[60] and OFET.[61] Additionally, their well-defined structures enable them to serve another significant role, namely as models for studying PTs.

In their role as model systems, OTs have yielded a variety of insights into the structure-property relationships of PTs. These model systems have yielded a precise correlation between physical properties and the length of the conjugated chain or the number of monomer units.[57] These investigations have made it possible to extrapolate the physical properties of finite oligomers to those of an analogous polymer of theoretical infinite length.[31] The higher degree of molecular uniformity of OTs results in better ordering, subsequently leading to highly defined optoelectronic properties. This makes them suitable as both theoretical and practical models for studying functional group substitution and its effects, as well as the energies of charged and neutral states.[31]

Recent research on the subject of OTs has focused on the doping behavior of symmetric OTs in contrast to P3HT using 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) (**6**) as dopant (**Figure 5**). In recent years, F_4TCNQ has become a desirable p-dopant for PTs for several reasons, primarily because inorganic dopants are unsuitable for device applications due to their tendency to diffuse.[62] F_4TCNQ also has another advantage thanks to its LUMO energy of -5.2 eV which is slightly lower than the HOMO energy of P3HT and other PTs at ~ -5.0 eV (**Figure 5-*A***) and that makes it particularly well-suited to oxidize P3HT.[63] In 2015, the Salzmann group investigated the doping mechanism of F_4TCNQ in P3HT by using unsubstituted quaterthiophene (QT) oligomers as model compounds. Surprisingly, they discovered a striking difference in its doping mechanism when compared to P3HT.[62] When P3HT is doped with F_4TCNQ, the HOMO electrons of P3HT simply cross over into the LUMO of F_4TCNQ, generating a positive charge carrier (hole) in the P3HT matrix.[62] This process is known as integer charge transfer (ICT) and it leads to the formation of an ion-pair (**Figure 5-*A***).[62] Ion-pair formation can easily be observed by measuring the CN stretch vibration of F_4TCNQ through FTIR spectroscopy, which varies in cm^{-1} depending on the charge of F_4TCNQ.[62] In contrast, when QT is doped with F_4TCNQ, a charge-transfer complex (CPX) is formed where the QT HOMO and F_4TCNQ LUMO hybridize to form a pair of bonding and antibonding orbitals (**Figure 5-*B***).[62]

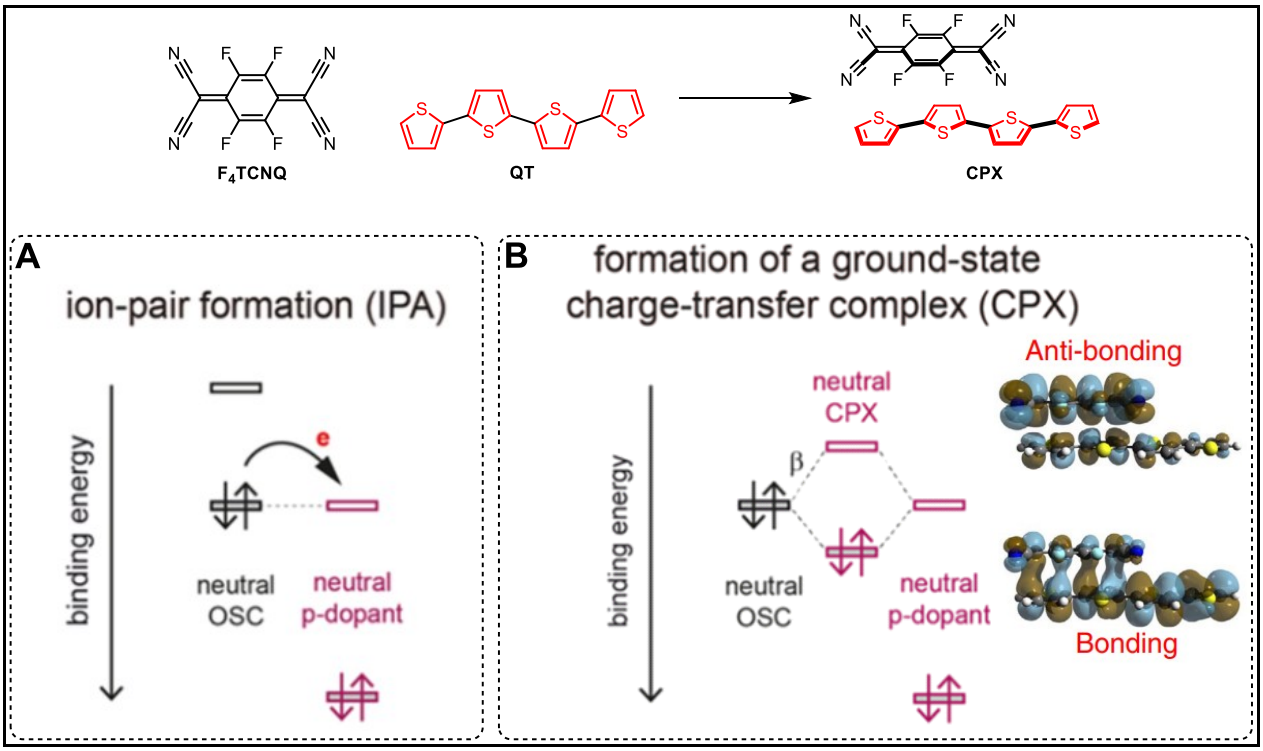


Figure 5: Doping Mechanism of QT and F_4TCNQ[62,64] (Image credits to *Nat. Commun.* **2015**, *6,* 8560 and *Acc. Chem. Res.* **2016**, *49,* 370)

Unfortunately, CPX formation is not favorable for device applications. In the hybridized orbital, electrons need a lot more energy in order to be excited and generate holes.[62] This results in fractional charge transfer (FCT) instead of complete ionization. The research which is a direct precursor to the present work aimed to identify the thiophene-unit length at which CPX formation stops and only ICT is observed.[65] Symmetric OTs with even numbers of thiophene units were synthesized and doped with F_4TCNQ. The oligomers in question had 4, 6, 8 and 10 thiophene units (**4T**, **6T**, **8T** and **10T**). It was found that **10T** formed both a CPX and ion-pairs, as evidenced by peaks observed in FTIR spectra.[65] One of the goals of the present work is to continue this investigation by synthesizing the odd-numbered sequence of symmetric OTs, namely 3, 5, 7 and 9 thiophene units (**3T**, **5T**, **7T** and **9T**) as well as the next oligomers in both sequences after **10T** which have 11 and 12 thiophene units (**11T** and **12T**). Through collaboration with Dr. Salzmann's group, these samples will then be doped with F_4TCNQ and their doping behavior determined. The results of F_4TCNQ doping of these OTs will be presented in a different work as the present work will focus solely on the synthesis of the OTs in question.

1.2 Synthesis of Oligo- and Polythiophenes

As previously mentioned, thiophenes were excellent choices as building blocks for polymers due to several qualities that they possess, however here the focus will shift on one of these qualities. Specifically, thiophenes respond exceptionally well to transition-metal catalyzed cross-coupling (CC) conditions as evidenced by the plethora of works on this subject.[66–68] While it is true that there are other methods for polymerization (such as oxidative radical coupling[54]), cross-coupling reactions have become by far the most common method for the synthesis of long thiophene-based molecules.[69,70] A variety of transition metals can be used as catalysts in CC reactions; however, this work will focus on palladium-catalyzed CC reactions, with nickel-based CC reactions being discussed in the subsequent section (Section 1.2.1).

In 1968, Heck reported the coupling of in-situ generated aryl-palladium halides with olefins at room temperature.[71] However, this reaction was not catalytic as it generated Pd(0) as a byproduct. Shortly after, Heck published another paper in which he reported that the addition of $CuCl_2$ rendered the reaction catalytic with respect to palladium, as $CuCl_2$ is able to re-oxidize Pd(0) to Pd(II).[72] The aryl coupling partners were provided as mercury salts, making the reactants toxic, difficult to prepare, and necessitating the handling of thick slurries.[73] Almost simultaneously and independently, both Mizoroki and Heck reported palladium-catalyzed cross-coupling conditions that did not require aryl-mercury salts or an oxidant additive, but instead used aryl-halides.[73,74] These publications were crucial steps in the development of the Pd-catalyzed CC reaction methodology, as they eliminated the need for metalation of the electrophilic aryl coupling partners, making the reaction self-sustaining without the need for oxidant additives. Following this major discovery, a multitude of different reactions were published based on the same concept, where now an aryl halide was the electrophilic partner and an organometallic compound was the nucleophilic partner. In order, Corriu[75] and Kumada[76] independently reported Grignards as coupling partners (1972, using Nickel), Sonogashira[77] reported the coupling of alkynes (1975), Negishi[78] reported organozinc compounds as coupling partners (1977), Migita[79] and Stille[80] independently reported the coupling of organotin with organohalides (1977-1978), Suzuki and Miyaura[81] reporting the coupling of organoboron compounds (1979), Hiyama[82] reporting the coupling of organosilicon compounds (1988) and Buchwald[83] and Hartwig[84] independently reporting the coupling of amines with aryl halides (1995). In 2010, Richard F. Heck, Ei-ichi Negishi and Akira Suzuki were awarded the Nobel Prize in chemistry for “palladium-catalyzed cross couplings in organic synthesis”.[85] Thanks to their contributions, works like this one are possible

today. The field of Pd-catalyzed CC reactions has kept progressing since then, with novel methods being developed which will be covered later (Section 1.2.3).

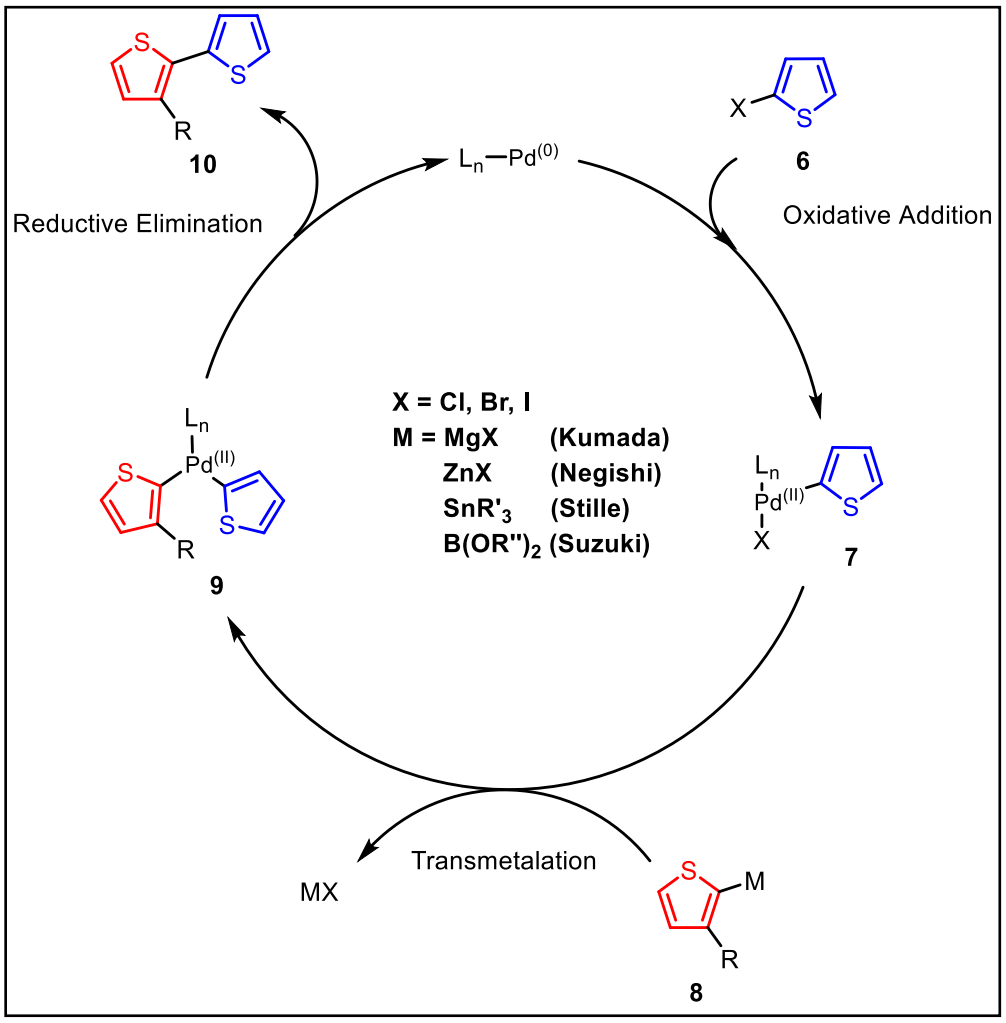


Figure 6: General Mechanism of Palladium-Catalyzed Cross-Coupling Reactions

The general concept of the Pd-catalyzed CC reaction has been thoroughly studied and can be generally illustrated by a cycle of 3 consecutive steps[86] (**Figure 6**). Initially, a source of Pd is introduced; this source can be Pd(II), which is reduced to Pd(0) or it can be Pd(0) directly.[86] In the first step, called the oxidative addition, the Pd(0) inserts between an ArX or generally C(sp^2)-X bond of the electrophilic coupling partner **6** to create the $Ar_1Pd(II)X$ species **7**. It is this crucial step, introduced by the work of Heck and Mizoroki mentioned previously, that is responsible for the self-sustaining character of these reactions. It is the first step of the cycle but also a way of re-oxidizing Pd(0) without the need for oxidant additives. Next, the $Ar_1Pd(II)X$ species **7** goes through the second step, called transmetalation, where it reacts with the nucleophilic coupling partner **8** to generate the $Ar_1Pd(II)Ar_2$ species **9** and produces MX (metal salts) as a byproduct.

The generation of MX at this step is stoichiometric, and depending on the nature of the two coupling partners, this step could be a considerable weakness in terms of the sustainability and safety of the reaction (particularly for Stille CC). Finally, the last step, known as reductive elimination, produces the Ar_1-Ar_2 product **10** and regenerates Pd(0) allowing the cycle to start again. The different types of this reaction involve additional steps at various points, including side processes that are crucial. The relevant mechanisms will be covered in more detail later (see Sections 1.2.2.3, 1.2.3.1 and 1.2.3.2).

With all the different variations of this process that have been reported, there are many options for synthesizing conjugated molecules. Although, some processes do dominate certain fields more than others. In the upcoming sections, the synthetic processes of P3HT as well as symmetric OTs will be covered and common synthetic patterns to both will become apparent.

1.2.1 *Poly-3-Hexylthiophene Synthesis*

Poly-3-hexylthiophenes are primarily synthesized through transition-metal-catalyzed polymerization reactions. Other methods[87] for P3HT synthesis have been reported, including oxidative radical polymerization, which was initially popular but has largely been supplanted by CC-based approaches. The simplicity, efficiency, and scalability of transition-metal-catalyzed methods have made them the dominant choice. Moreover, when factors such as regioregularity in P3HT (RRe-P3HT) are considered, these methods become virtually indispensable.

1.2.1.1 Kumada and Negishi Cross-Coupling Methods

By far, the most common methods for synthesizing RRe-P3HT today are transition-metal catalyzed CC reactions.[70] As previously mentioned, the first example of such a synthesis was by McCullough[39], however, around the same time, Rieke independently published a similar yet distinct approach that proved equally effective[88] (**Figure 7**). The McCullough process is based on a Kumada-type coupling. It begins with 2-bromo-3-hexylthiophene (**11**), which is lithiated at C5 followed by addition of $MgBr_2$ to generate 2-bromo-5-bromomagnesium-3-hexylthiophene (**12**).[46] This monomer is then polymerized using Ni(dppp)Cl_2 as the catalyst, yielding P3HT with a regioregularity of 98%. The Rieke method, by contrast, employs a Negishi-type coupling. It starts with 2,5-dibromo-3-hexylthiophene (**13**), which is treated with activated zinc to form 2-bromo-5-bromozinc-3-hexylthiophene (**14**).[44] This reaction proceeds with high selectivity, favoring the 5-ZnBr isomer in a 97:3 ratio over the 2-ZnBr isomer, and with no bis(bromozinco)thiophene side product being observed. Subsequent polymerization with Ni(dppe)Cl_2 affords P3HT with a regioregularity of 98.5%[44]. Interestingly, Rieke also reported that replacing the nickel catalyst with

$Pd(PPh_3)_4$ resulted in the formation of completely RRa-P3HT, highlighting the critical influence of the catalyst on the polymer's regioregularity.

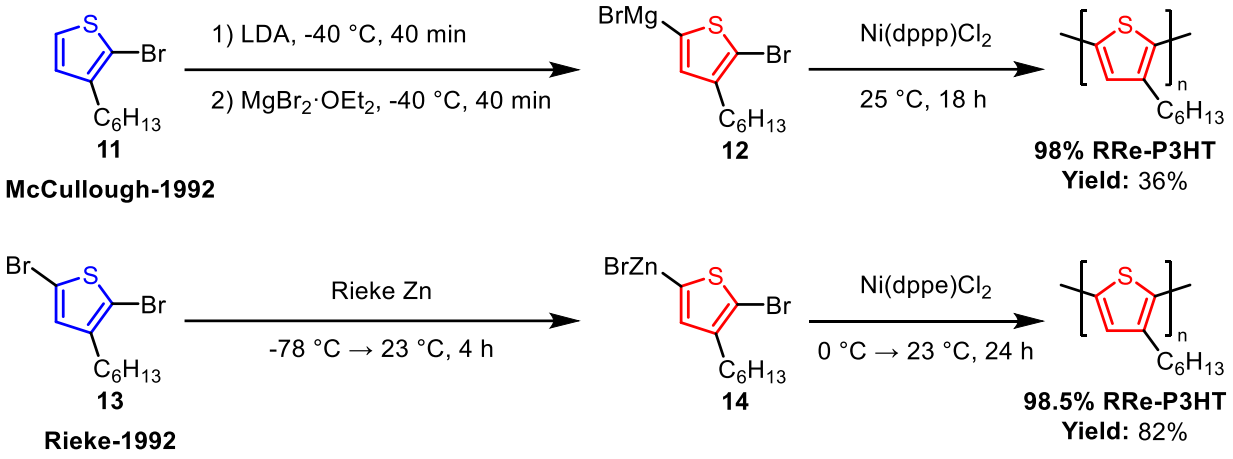


Figure 7: General Reaction Scheme of Original McCullough and Rieke Methods[44,46]

At the time, these syntheses were considered groundbreaking advances in the field. However, both the McCullough and Rieke methods shared notable limitations: they required cryogenic temperatures (–78 °C) for the preparation of the active monomer and involved relatively long reaction times, making them impractical for large-scale applications. This changed in 1999 when McCullough reported the Grignard metathesis (GRIM) process, which remains widely used today.[89] The GRIM method quickly became the preferred route for synthesizing P3HT, as it eliminated the need for low-temperature conditions and significantly reduced reaction times[89] (**Figure 8**).

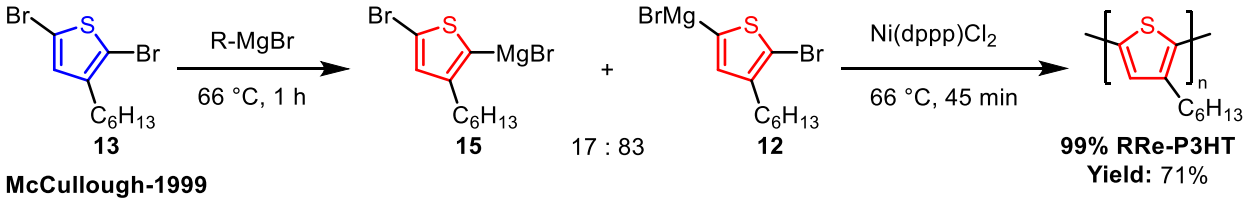


Figure 8: General Reaction Scheme of GRIM Polymerization[90]

The reaction of 2,5-dibromo-3-hexylthiophene (**13**) with magnesium yields a mixture of Grignard isomers (**12**, **15**). However, due to steric hindrance, only the 5-bromomagnesium isomer (**12**) is selectively consumed in the subsequent polymerization.[37] This process proceeds via a quasi-living chain-growth mechanism, meaning that polymerization continues as long as monomer remains in solution and the nickel catalyst stays bound to the growing polymer chain.[91] This quasi-living nature offers several valuable advantages. Most notably, the molecular weight of the

resulting polymer can be controlled by adjusting the ratio of nickel catalyst to monomer.[91] Furthermore, because the nickel catalyst remains at the chain end, block copolymers can be synthesized by sequential addition of different thiophene monomers.[91] The process also enables convenient end-capping with a variety of functional groups, greatly expanding the structural diversity of P3HT derivatives.[92] Despite its efficiency in producing highly RRe, low-polydispersity P3HTs, the method is not without flaws. Due to the reactive nature of zerovalent[93] Ni, the catalyst is provided as Ni(II). In order to be reduced to the active Ni(0), the first step in the process is the TT homocoupling of the active monomer, meaning that every polymer has at least one defect.[91] Modern iterations of this process make use of specific Ni-complex initiators to yield defect-free, 100% RRe-P3HT polymers, although with larger polydispersities.[94]

1.2.2 *Oligothiophene Synthesis*

OT synthesis follows the same general methodology as P3HT as they are also synthesized by transition-metal catalyzed CC reactions. Unlike P3HT though, the reactions are under strict control and iterative, meaning that instead of polymerizations, OTs are synthesized sequentially. Although there is a rich variety of OT motifs and aromatic monomer combinations (**Figure 9**), this work will be focused explicitly on OTs that are part of the C_{2v} point group, meaning they have two planes of symmetry, one for the π-system and one perpendicular to the π-plane across the middle of the molecule (**3T**, **4T**, **3O-DiA-8T**).

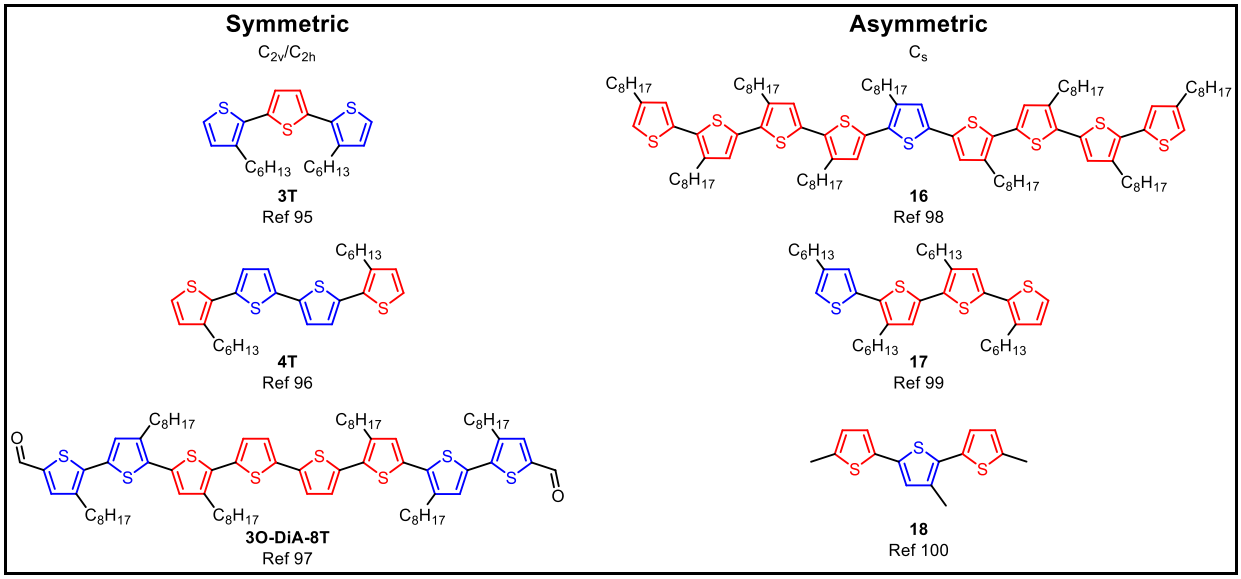


Figure 9: Examples of Symmetric and Asymmetric Oligothiophenes[95–100]

Asymmetric OT refers to oligomers that have only one plane of symmetry for the π-system (**16**, **17**, **18**), putting them in the C_s point group. From here on, the focus will shift to symmetric

oligomers containing 3-alkylthiophene (3AT) monomers with a non-functionalized core and in the C_{2v}/C_{2h} point groups, similar to those in the *Symmetric* group.

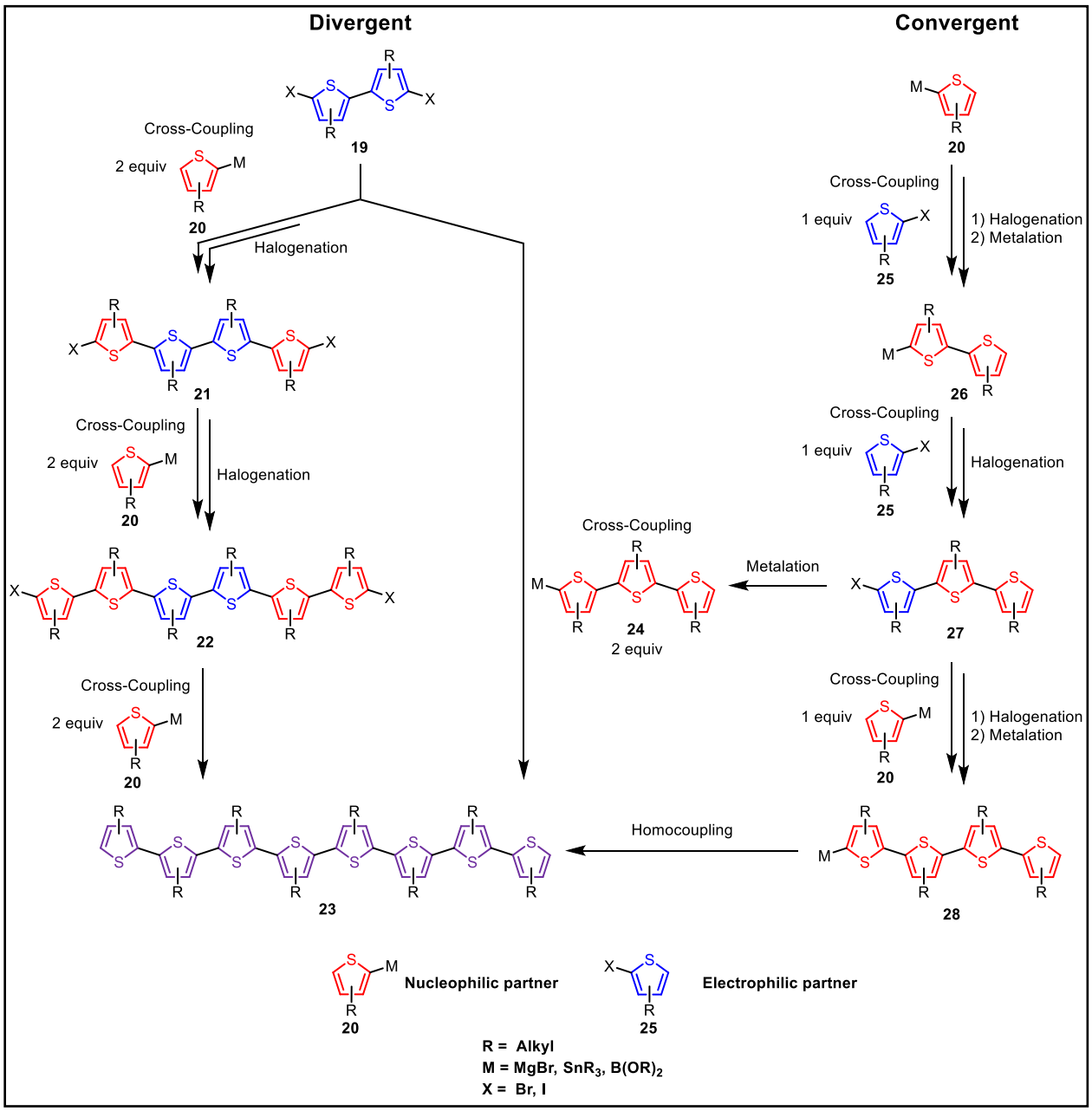


Figure 10: Overview of Oligothiophene Synthetic Strategies

There are two general categories of OT synthesis: divergent and convergent synthesis[70] (**Figure 10**). The divergent route starts with a central, di-functionalized monomer (or often dimer) (**19**), which is reacted with 2 equivalents of the appropriate monomer (**20**) to extend the OT from both sides through a double CC reaction. It is called divergent since it diverges away from the central core thiophene(s) in two directions. This method has two variants, the first one being a process

where the oligomer is elongated by 1 monomer on each side, adding a total of 2 monomers per reaction, followed by dibromination (**21**, **22**) to finally produce a longer oligomer (**23**). To our knowledge, not many procedures of this type have been reported and those that have often report 3 or less products of the respective sequence.[101–104] A good example of a process using this method to synthesize 4 members of a sequence is the work directly preceding the present one. It reports the synthesis of 4 sequential OTs with an even number of thiophene monomers.[65]

The second variant of the divergent process elongates the oligomer by adding 2 equivalents of a short, pre-functionalized asymmetric OT (**24**) to the di-functionalized core (**19**), thereby synthesizing a much longer OT (**23**). This process is much more common as it allows for the instantaneous synthesis of an extended oligomer, provided the pre-functionalized asymmetric OT coupling partner (**24**) is prepared first.[105–108] Since longer oligomers can be obtained in one step, there are examples where 5 OTs of a given sequence are reported.[108] However, there is a potential disadvantage to this synthetic methodology. Depending on the particular combination of coupling partners, there is a possibility that the short asymmetric OT starting materials participate in a homocoupling, in turn generating a byproduct that is very similar to the desired product.[103] Consequently, the purification of the product will be considerably more difficult even if the homocoupling product is present in small quantities.

In contrast, the convergent synthetic process involves elongation by a single monomer (**25**) which is coupled with a mono-metalated partner (**20**) to synthesize an asymmetric OT which is then halogenated and mono-metalated (**26**). This process is repeated in order to extend the oligomer by one monomer (**24**). It is also possible to change the coupling partners by halogenating the oligomer (**27**) and reacting it with a nucleophilic coupling partner instead (**20**), leading to a longer oligomer (**28**). These asymmetric oligomers can also be homocoupled in order to double the length of the oligomer (**23**).[109,110] This method is called convergent because the elongation proceeds in a single direction. Very often, the products of this process are used as starting materials for the divergent method, in other words the elongation is converging towards the di-functionalized core with which they will be coupled. Another common scenario for this process is when an end-cap group is needed on one end of the asymmetric OTs while the other end is elongated sequentially.[111]

Regarding the specific cross-couplings used to synthesize OTs, they are slightly more varied than those commonly employed for P3HT. There are examples of Kumada, Stille, and Suzuki-based syntheses, which are the most common, with CH-arylation procedures also being reported. More

recently, decarboxylative cross-couplings (DCC) have been published as well. These will be covered in the following sections.

1.2.2.1 Kumada Cross-Coupling for Symmetric Oligothiophene Synthesis

Similarly to the GRIM process used for P3HT, the Kumada-based methods (**Figure 11**) begin with the metalation of 2-Br-3AT (**29**) to yield 3-alkyl-2-thienylmagnesium bromide (**30**). Subsequently, this starting material is added dropwise to an ether solution of Nickel catalyst and the di-halogenated coupling partner (**31**).[102,107] The reaction is refluxed between 20 to 24 hours and the resulting product (**3O-4T**) is obtained in yields between 71 to 83%.[102,107] Unfortunately, due to the nature of the nucleophilic coupling partner, these reactions are incompatible with base-sensitive functional groups and degrade in presence of water. This limits their use-cases and makes handling of the Grignard reagent cumbersome.

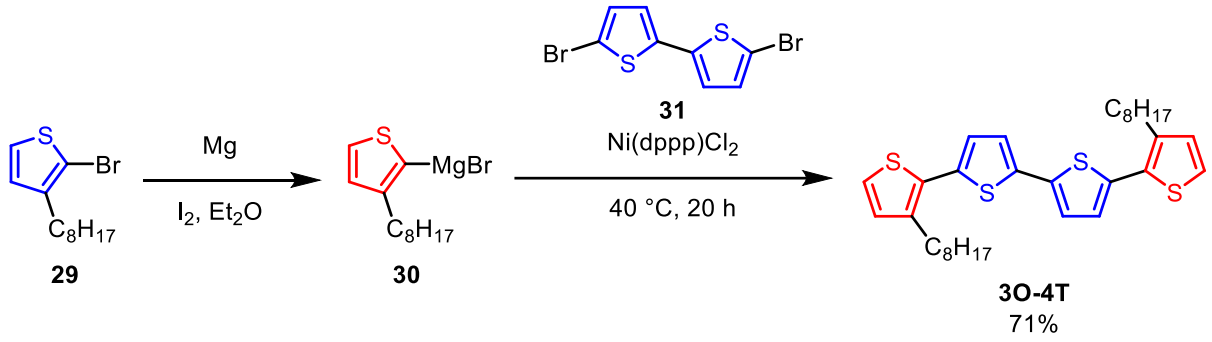


Figure 11: Kumada-Based Synthesis of Symmetric OT[107]

1.2.2.2 Stille Cross-Coupling for Symmetric Oligothiophene Synthesis

The Stille cross-coupling has become a very popular method of Ar-Ar bond formation. It is extremely common in the synthesis of OTs and the most common in the synthesis of polymers from short oligomer building-blocks.[112,113] The Stille CC conditions involve an organotin-functionalized partner and of course a halogenated partner. A common synthetic strategy seen in Stille conditions for the synthesis of OTs is the use of short oligomers that are reacted with a di-stannylated core.[95,105,107,108]

The preparation of the electrophilic coupling partner (**Figure 12**) involves the functionalization of 3HT (**32**) into a 5-stannylated monomer (**33**), which is then coupled with 2-Br-3HT (**11**) to give a dimer (**34**).[114] The dimer is then brominated with NBS to yield the functionalized electrophilic coupling partner (**35**).

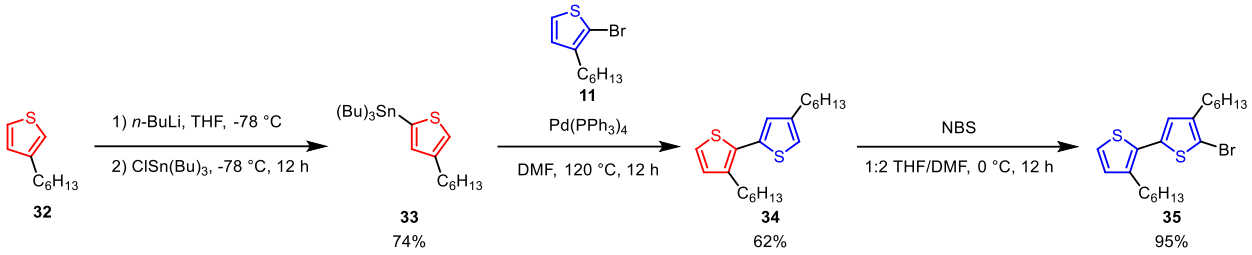


Figure 12: Preparation of Electrophilic Coupling Partner for Stille CC[114]

The next step (**Figure 13**) involves functionalizing the core (**36**) to yield a di-stannylated dimer (**37**) which is subsequently reacted with the bromo-dimer (**35**) to produce a symmetric hexamer (**6T**)[108] at a yield of 67%. This exact methodology has been used to synthesize the symmetric sequence of **4T**, **6T**, **8T**, **10T** and **12T**.[108]

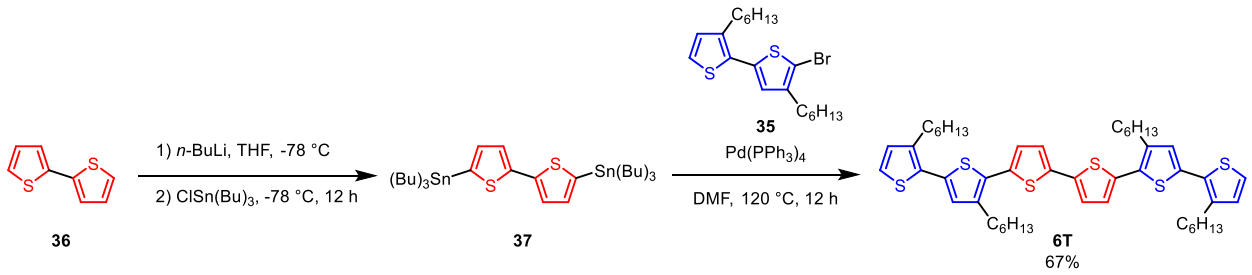


Figure 13: Symmetric OT Stille Synthesis Using Dimers as Coupling Partners[108]

The Stille CC has several advantages when compared to the Kumada CC, mainly the organotin coupling partner can be isolated.[115] They are stable to moisture and air, can be stored for long periods, are compatible with a wide range of functional groups, and require no additives other than the catalyst.[115] Although organotin reagents can indeed be isolated, that does not mean all of them can be. Isolation can prove to be a considerable challenge for some of them, as they are reported to be too unstable to be purified by column chromatography.[115] Another considerable drawback of the Stille CC is that it produces stochiometric quantities of organotin salts, which are toxic to living organisms as they target multiple organs.[116–118] Furthermore, salts such as XSn(*n*-Bu)$_3$ are often difficult to remove from the product due to their solubility in most organic solvents, and they tend to smear during column chromatography, further complicating separation.[119] A method of addressing this is by washing the organic phase with an aqueous solution of KF which should precipitate most organotin byproducts so they could then be filtered off. However, even after this, the product could still contain as much as 5% by weight of tin.[120] This in turn could have a disastrous impact on OSC device performance.

1.2.2.3 Suzuki Cross-Coupling for Symmetric Oligothiophene Synthesis

The Suzuki CC reaction has become the most widely known and well-established reaction among all Pd-catalyzed CC reactions.[121,122] There is a large amount of literature on the subject, and it is a method commonly used in industrial settings too.[121] Several factors can be credited for this trend, and one of the most important factors is the nucleophilic coupling partner involved in Suzuki CC reactions. These reactions utilize organoboron derivatives, which distinguishes the Suzuki reaction from the previously mentioned Kumada, Negishi, and Stille methods, as the active functional group is not a real metal but rather a metalloid.[123] Boron's interesting set of properties stem from the fact that it behaves like a Lewis acid. This is a result of the empty p-orbital of boron (due to it having only 3 valence electrons) and its electronegativity.[123,124] The use of organoboron derivatives makes it possible to carry out the reaction in aqueous media. This leads to the other way the Suzuki CC stands out, which is by its mechanism and reaction conditions (**Figure 14**).

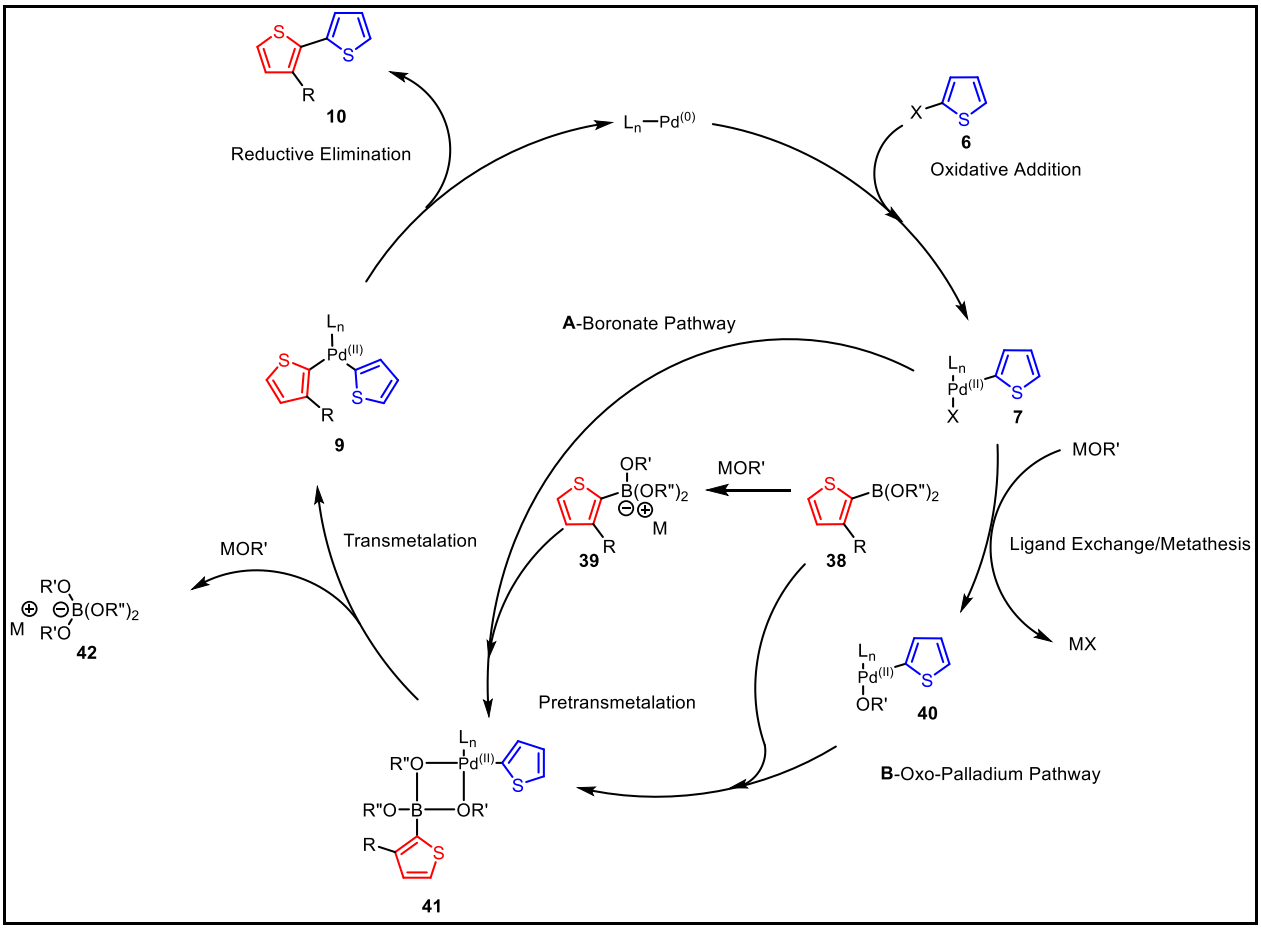


Figure 14: Suzuki CC Proposed Mechanism[125]

The key characteristics of this reaction are that it requires a base and is often carried out in biphasic conditions, where one of the phases is water, thereby eliminating the issue of moisture as a negative factor entirely. In fact, water can play such an important role that recent work reported up to a 7-fold increase in reaction rate when the proportion of water in the biphasic system is increased while keeping the volume constant.[126] Currently, the exact mechanism of the Suzuki CC has not been fully elucidated, particularly with regard to the role of the base.[127] Two major pathways are proposed, with *Path A* being the boronate pathway and *Path B* being the oxo-Palladium pathway[127]. Both pathways start the same way as previously shown CC reactions with a halogenated coupling partner (**6**) participating in oxidative addition to generate a Pd (II) intermediate (**7**). From here, the mechanism can diverge into *Path A* or *B*. *Path A* begins with the borylated coupling partner (**38**) being attacked by an alkoxide or hydroxide to generate the $Ar_2(OR)_3B^-$ species **39** which then reacts with the Ar_1PdX complex **7** formed after oxidative addition. At the same time, *Path B* proposes that Ar_1PdX complex **7** instead undergoes ligand exchange with a hydroxide or alkoxide to generate Ar_1PdOR complex **40** which then reacts directly with the organoboron coupling partner **38**.[128] Both of these pathways lead to the formation of pretransmetalation complex **41** where the organoboron and the Pd(II) species form a new complex. This complex then rearranges and undergoes transmetalation to produce stochiometric amounts of borate salts (**42**) and the final complex of the cycle (**9**).[125] The borate salts are reasonably safe and non-toxic to the environment[128] and can easily be removed with an aqueous extraction. This is one of Suzuki CC's biggest strengths and what makes it suitable for industrial applications.[129] The last step of the cycle is reductive elimination, which releases the cross-coupled product **10** and regenerates Pd(0). The unique mechanism and properties of the Suzuki CC make it stand out among the CC reactions, but this can also be a drawback. In contrast to the previously mentioned CC reactions, which only required the metal catalyst and solvent (if we assume the nucleophilic partner is already prepared), the Suzuki CC requires the presence of base, which not only increases the number of reagents used but also could make it incompatible with base-sensitive starting materials.

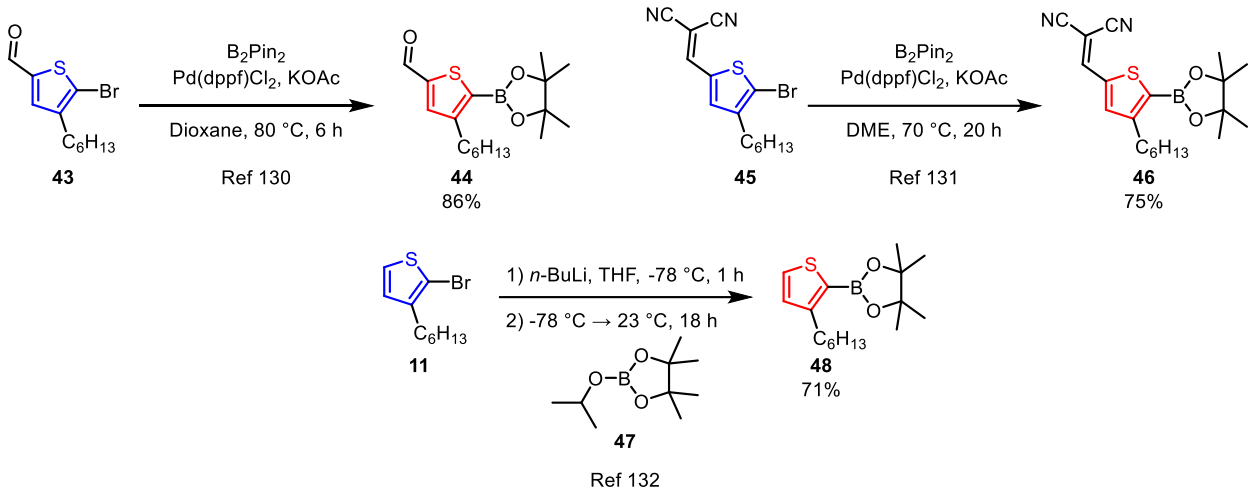


Figure 15: Synthesis of 2-Bpin Functionalized 3-Alkylthiophenes[130–132]

The Suzuki CC does have an advantage in terms of the preparation of its nucleophilic coupling partner since they can be prepared catalytically through a Miyaura borylation (**Figure 15**).[127] If the 2-Br-3AT monomer is functionalized with an electron-withdrawing group at C5 (such as 5-formyl-3-hexylthiophene (**43**) or 5-dicyanovinylene-3-hexylthiophene (**45**)), a catalytic Miyaura borylation can be carried out using bis(pinacolato)diboron (B_2Pin_2) to yield the C2 borylated product (**44**, **46**).[130,131] Unfortunately, this is not a viable option for 2-Br-3AT (**11**) that are not functionalized with a withdrawing group at C5. Consequently, for the synthesis of symmetric OTs without pre-installed C5 end-caps, the monomers are synthesized by lithiation followed by quenching with a source of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Bpin), which often is *i*-PrOBpin (**47**).[132] This produces a boronic ester (**48**), which is bench-stable, easy to handle, and possible to isolate using column chromatography, giving these monomers a significant advantage over the previous CC monomers.

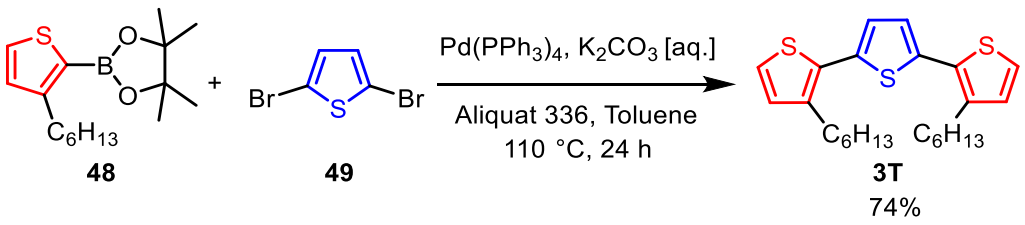


Figure 16: Symmetric OT Suzuki Synthesis Using Functionalized Monomers[133]

Finally, the OTs of interest usually synthesized by CC reactions are not water soluble and in fact quite hydrophobic (due to the alkyl chains). In theory, this does pose a challenge considering the reaction is carried out in aqueous media; however this obstacle can be overcome through the

addition of ethanol to the reaction mixture.[134,135] Another alternative is through the use of phase-transfer catalysts (PTC)[133] such as Aliquat 336 (tricaprylmethylammonium chloride). PTCs can shuttle reactants between the two phases and have even been shown to influence which pathway (*A* or *B*) the mechanism follows.[126] Using a biphasic system of toluene and water with Aliquat 336 as the PTC (**Figure 16**), the sequential synthesis of symmetric oligomers **3T**, **5T** and **7T** has been reported.[133] This Suzuki CC has 2-Bpin-3HT (**48**) as the nucleophilic coupling partner and dibromothiophene **49** as the difunctionalized core. The reaction produced **3T** at a yield of 74% after which it was di-brominated and subjected to another Suzuki CC producing **5T** with a yield of 81% over two steps.[133] This process is repeated to obtain **7T** at a yield of 62% over two steps.[133] This is an example of the uncommon divergent OT synthesis achieved through sequential monomer addition, a procedure particularly relevant to the present work, as it was adapted for part of its synthetic component.

1.2.2.4 Terminal Group Functionalization

Terminal groups, also known as end-caps, have a variety of reasons for being important in the context of OTs. Two major examples are that terminal groups can fine-tune the HOMO-LUMO gap as well as optical properties, and the other is the introduction of end-caps to serve as linkers.[70] Research into OT end-capping has shown that the HOMO and LUMO energies can be manipulated, and the gap between them can be tuned through the introduction of specific functional groups.

For example, introducing withdrawing tricyanovinyl (TCV) groups as end-caps on OTs has been shown to drastically lower the HOMO-LUMO gap and result in a red-shift of optical spectra.[70] With relation to chain growth, TCV was shown to stabilize the LUMO energy (at around -3.5 eV) while the HOMO energy is changed with increasing OT length.[139] This is possible because the electron density of the LUMO localizes on the electron-withdrawing end-caps while the HOMO localizes on the backbone, resulting in a change in HOMO energy and stabilization of LUMO energy with OT backbone growth.[139] Changing the HOMO-LUMO gap also has an effect on absorption and emission properties, making it possible to tune OTs for a specific color for use in OLEDs as well.[104,140] In terms of anchors, OTs have been modified with phosphine groups (PPh_2) and used as ligands for ruthenium and gold nanoparticles.[141] Thiophenes are indeed quite versatile in terms of the chemical reactions they can participate in. The resonance donation of sulfur into the ring generates a considerable difference in nucleophilicity at C2 and C5 compared to C3 and C4. The introduction of an alkyl group at C3 results in further segmentation of reactivity between C2 and C5. This nuanced reactivity enables a wide range of functionalization strategies for 3ATs,

leveraging the electronic and steric influence of the alkyl substituent. As a result, two main approaches to the functionalization of oligothiophenes (OTs) have emerged: pre-oligomer functionalization (*Pre-Functionalization*) and post-oligomer functionalization (*Post-Functionalization*) (**Figure 17**).

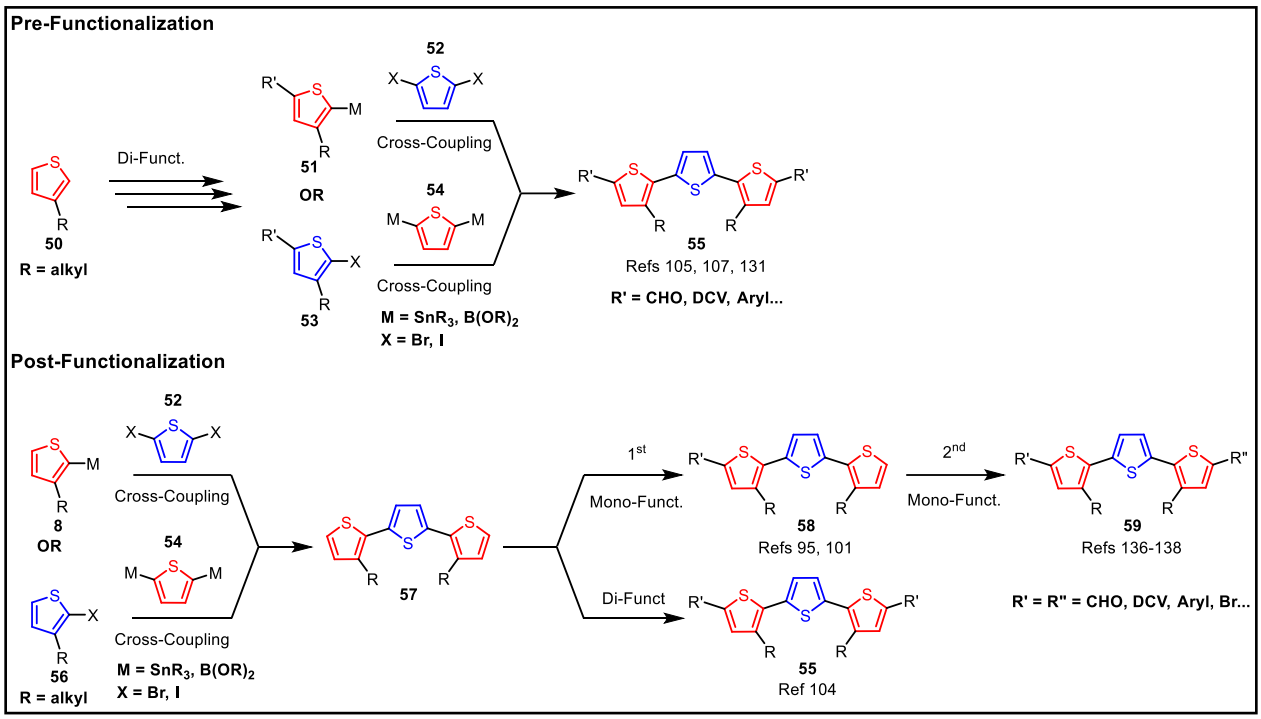


Figure 17: Synthetic Route for Pre- and Post-Functionalization[95,101,104,105,107,131,136–138]

These two methodologies enable OTs to be fine-tuned to a high degree of precision. In the *Pre-Functionalization* method, 3HT (**50**) is modified through the installation of a functional group at C5 of the terminal monomer (or dimer/trimer and so on) while a cross-coupling functional group is installed on C2 (**51**, **53**). The C5-capped partner is then coupled with a di-functionalized core (**52**, **54**) to produce a symmetric end-capped OT (**55**).[105,107,131] In the *Post-Functionalization* method, the OT is first synthesized by whichever cross-coupling method and is functionalized afterwards. Starting with a monomer functionalized for CC at C2 (**8**, **56**), cross-coupling is carried out with a di-functionalized core (**52**, **54**) to yield un-capped OT **57**. It is possible to di-functionalize the OT to keep it symmetrical[104] (**55**) or to mono-functionalize it[95,101] (**58**) or di-functionalize it with two different functional groups[136–138] (**59**). Generally, halogenation and formylation are the two most common and useful modifications, since halogenation opens the door to further cross-coupling while formylation provides a conjugated handle that can be modified to add different kinds conjugated end-caps.

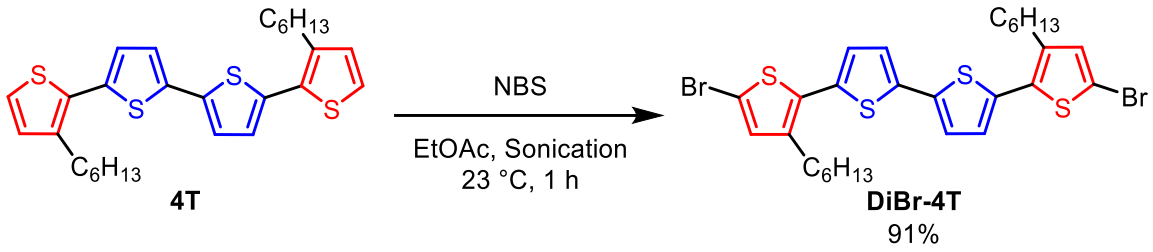


Figure 18: Dibromination of Symmetric OT Tetramer[65]

The functionalization of particular interest is the dibromination of OTs. Previously, a very efficient procedure has been published for the dibromination of thiophenes, particularly an unsubstituted 2,5-thiophene dimer and trimer.[142] This procedure reported rapid dibromination in 10 minutes using NBS in EtOAc and an ultrasonic bath, producing dibromo thiophene dimer and trimer with yields of 97% and 88%, respectively. That same procedure was adapted to the dibromination of **4T**, **6T** and **8T** in the work directly preceding this one (**Figure 18**) in order to synthesize **DiBr-4T**, **DiBr-6T** and **DiBr-8T** with yields of 91%, 85%, and 89% respectively.[65]

1.2.3 *Recent Advances in Cross-Coupling Chemistry*

Although it is true that the classic CC reactions have become widespread and have been proven to be robust and reliable, research into other CC routes has not been impeded. As demonstrated in Sections 1.2.1 and 1.2.2, the classic CC reactions necessitate the installation of an organometallic or metal-like functional group on the nucleophilic coupling partner. This in turn generates stochiometric quantities of waste based on this functional group after the transmetalation step. This issue can be addressed by changing the nature of the functional group on the nucleophilic coupling partner. Additionally, if the functional group has a lower molecular weight, this reduces the amount of waste generated. Furthermore, it often makes preparing the nucleophilic coupling partner and handling it much more convenient. In the two upcoming sections, two such methodologies will be covered. Section 1.2.3.1 will cover direct CH-arylation reactions while Section 1.2.3.2 will cover DCC reactions and their use for the synthesis of thiophene-based materials.

1.2.3.1 Palladium-Catalyzed CH-Arylation

A direct CH-arylation describes a cross-coupling reaction that occurs between an aryl-halide and another aryl that is not functionalized at the reactive position of interest (**Figure 19**). In such a reaction, a 5-membered aromatic heterocycle (**60**) is coupled to a bromobenzene (**61**) to yield the cross-coupled product (**62**). This process is highly enticing due to some of the advantages it has over other methods, such as the fact that a C-H group is the nucleophilic group,

which is in direct contrast to all the previous CC reactions where the nucleophilic coupling partner was functionalized with a metal or metalloid. However, this introduces issues of regioselectivity, since CH bonds are ubiquitous in aromatic molecules. Because of this, early work into CH-arylations relied heavily on intramolecular coordinating directing groups in order to improve selectivity for the position of interest.[143–145] These reactions were generally carried out between benzene derivatives, which is why directing groups were so vital. Although, through the effect that sulfur has on the π-system, a certain degree of regioselectivity is imparted to thiophenes.[144] This makes heterocycles like thiophene excellent candidates for direct CH-arylation reactions and this was demonstrated in 1990 by Ohta and coworkers when they published the first CH-arylation of thiophenes and furans with bromobenzene derivatives (**Figure 19**).[146]

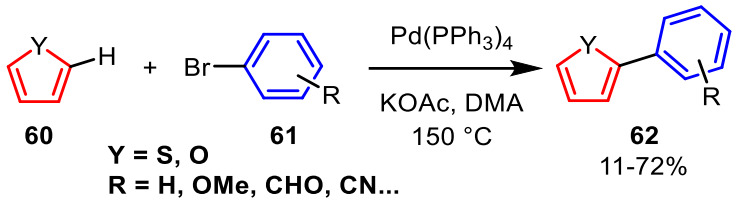


Figure 19: First CH-Arylation of Thiophenes and Furans[146]

Early into the development of CH-arylations, there was considerable disagreement about the exact mechanism of these reactions. Two proposals that garnered significant interest were the S_EAr (electrophilic aromatic substitution) and Heck-type mechanisms. The S_EAr mechanism proposed that the reaction proceeds through a Wheland intermediate while the Heck-type mechanism proposes an insertion into a π-bond followed by a β-hydride elimination.[145]

Interestingly, it was observed that the presence of carboxylic acids and their derivatives significantly aided these reactions, with Fagnou reporting pivalic acid (PivOH) as a very effective additive in 2006.[147] This pointed to the possibility of a third mechanism, its transition state having been proposed as early as 1985.[148] Subsequent work by several groups[149–151] culminated in the elucidation of the concerted-metalation-deprotonation (CMD) mechanism[152] by Fagnou in 2008 (**Figure 20**). It follows the same basic principle as other CC reactions, starting with the halogenated partner **6** which undergoes oxidative addition to yield intermediate **7** followed by a ligand exchange with **67** which creates the acid-ligated complex **63**. The nucleophilic coupling partner **50** then coordinates to the Pd center to form a 6-membered transition-state (TS) (**64**) which leads to the breaking of the C-H bond and formation of a C-Pd bond (**65**). Subsequently, the acid ligand **66** leaves with the abstracted proton, which is then removed by a base, generating H^+ in the form of protonated bases as stochiometric waste and regenerating the carboxylate anion

67. This leads to the final intermediate which undergoes reductive elimination to produce the cross-coupled product and regenerate the palladium catalyst.

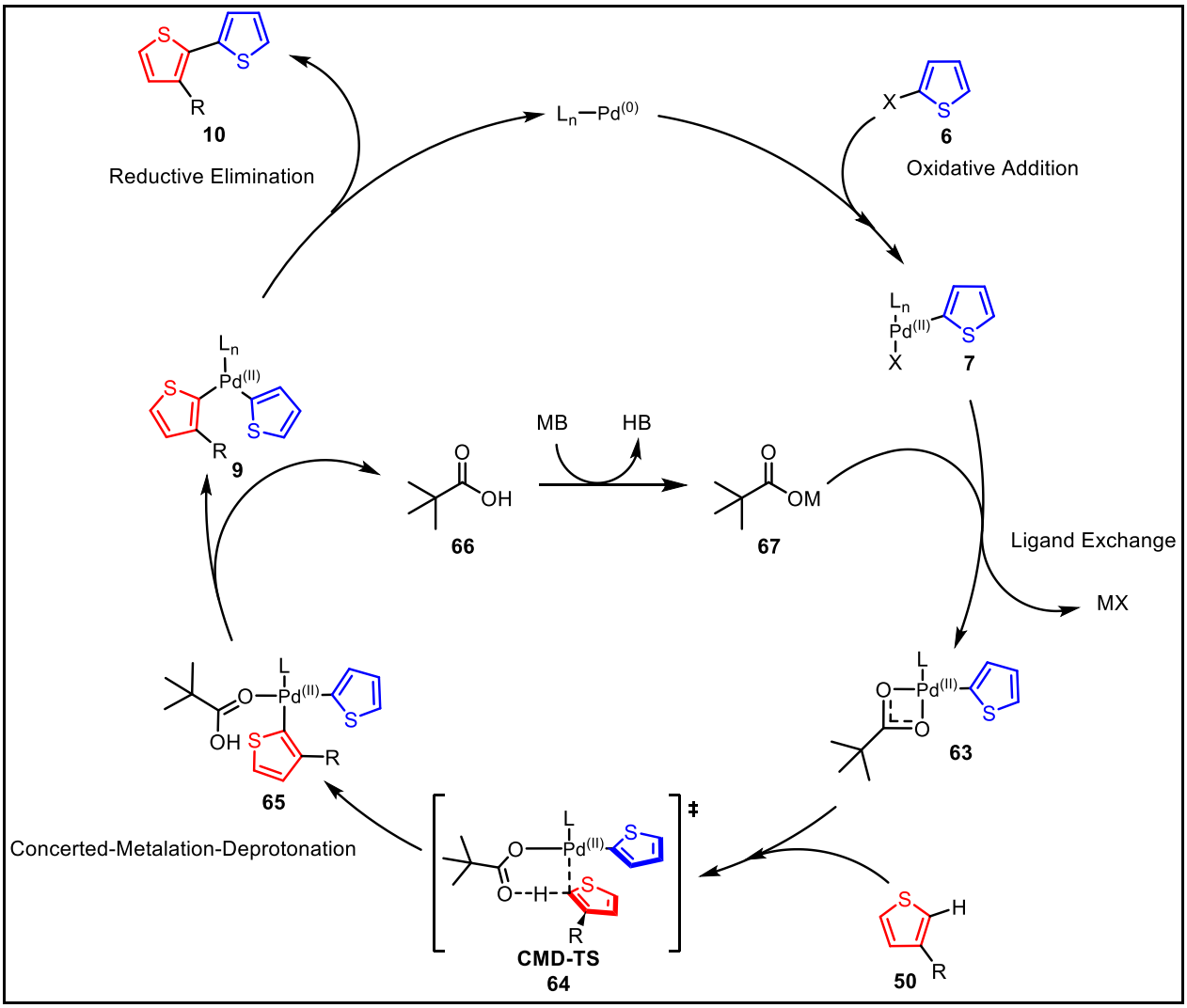


Figure 20: CMD Mechanism of CH Arylation Reactions[147,152]

Fagnou's contribution was particularly important because it provided further computational and experimental evidence for the 6-membered transition state, and he discovered the two major factors deciding the outcome of CH-arylations[152] (**Figure 21**). The two factors were E_{dist} and E_{int}. E_{dist} is the energy required for the C-H bond (**50** to **69**) and RCOO-Pd(Ar)L complex (**63** to **68**) to distort and elongate in order to accommodate the 6-membered transition state **64**.[152] E_{int} is the energy decrease through the formation of the 6-membered transition state **64**.[152] From there, different aromatics and heteroaromatics were analyzed and classified into 3 groups. In group 1 the determining factor is E_{dist} which usually means that the most acidic C-H should be most reactive, group 2 is governed by E_{int} which means that the most nucleophilic position should react,

and group 3 is governed by a combination of the two factors[145]. Thiophene is in group 3, meaning that both E_{dist} and E_{int} are important[145].

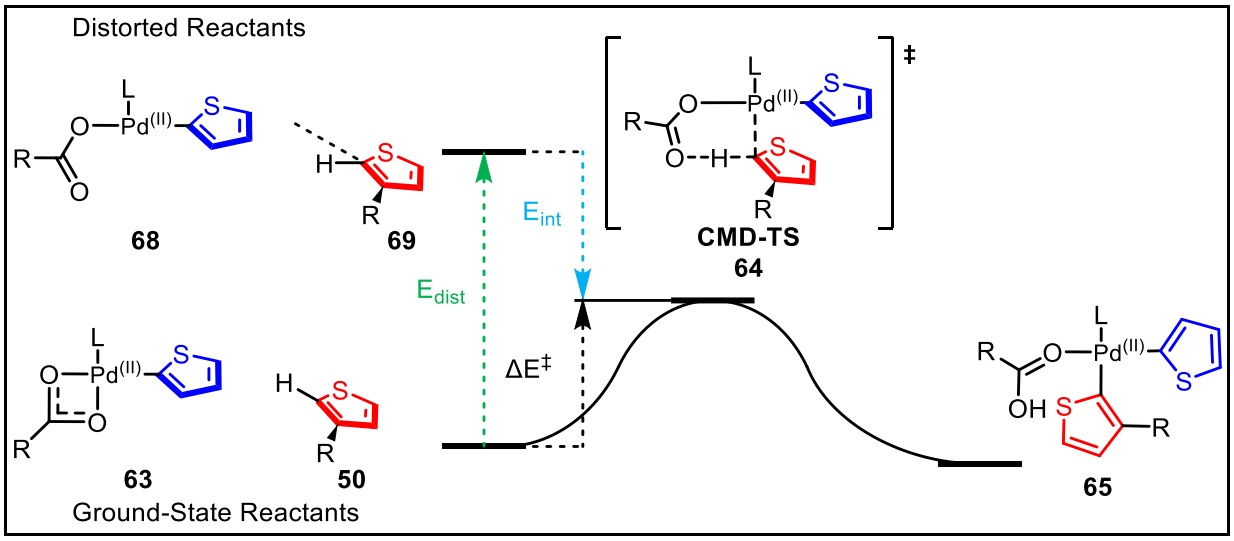


Figure 21: Energy Diagram of CMD TS Formation[145,152]

Concerning P3ATs, in 2010 Ozawa and colleagues reported the direct-arylation-polymerization (DArP) synthesis of P3HT which yielded 98% RRe-P3HT.[153] Using Hermann's catalyst along with substituted triphenylphosphine ligands, they synthesized P3HT from 2-Br-3HT with a Mw of 30 600 g/mol, polydispersity of 1.6 and yield of 99%.[153] This work resulted in a considerable rise in CH arylation papers and fueled interest in this process.[113] A very favorable particularity of CH-arylations is that they have been reported to work at extremely low catalyst loadings and without ligands.[154] In 2015, Thompson and colleagues published optimized conditions of their previously reported process[155] for the DArP synthesis of P3HT from 2-Br-3HT in an attempt to lower the amount of undesirable β-branching which was observed.[156] They introduced 3.75% of neodecanoic acid in place of PivOH and managed to optimize the conditions to a 0.0313% catalyst loading of $Pd(OAc)_2$ without any ligand.[156] They reported 96% RRe-P3HT with an average Mw of 25 200 g/mol, polydispersity of 3.3 and yield of 84%, repeated over 3 reactions.[156] This is indeed an exceptionally efficient and clean process although it does suffer from issues with polydispersity. Considering that CH-arylations only generate H^+ as byproducts, this makes them the most efficient and environmentally friendly process for P3HT synthesis.

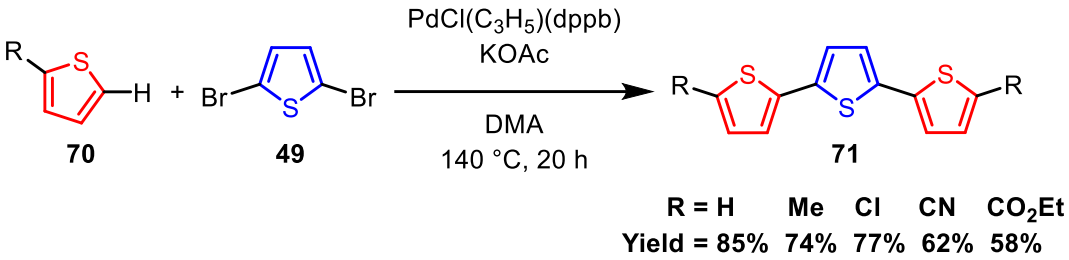


Figure 22: Synthesis of Symmetric OT Trimer by CH-Arylation[100]

In terms of OTs, CH-arylation has also been applied but not in the same way described previously. In 2006, Mori and colleagues reported the silver-assisted CH-homocoupling of mono-brominated thiophene dimers, trimers and tetramers to synthesize symmetric di-brominated Ots.[109] This does not quite fit into the same class as the CH-arylation described above since it needs silver salts to oxidize Pd(0) and keep the process going. Later in 2010, Mori reported the convergent synthesis of a C5-capped 3HT tetramer using 5-phenyl-2-iodo-3-hexylthiophene and 2-bromo-3-hexylthiophene which reacts at C5.[111] In terms of divergent CH-arylation of symmetric OTs, to our knowledge, Doucet makes the only such report[100] in 2014 (**Figure 22**).

The nucleophilic coupling partners were C5-substituted thiophenes (**70**) which were coupled with a dibrominated thiophene core (**49**).[100] Using $PdCl(C_3H_5)(dppb)$ at 2% loading, several C5-functionalized thiophenes were tested as well as non-functionalized thiophene to yield symmetric OTs without 3-alkyl functional groups (**71**). Some methylated coupling partners were reported as well, leading to symmetric oligomers similar to those of interest (**Figure 9** in Section 1.2.2) however the heterocycles were not thiophenes (4-methylthiazole, 3,5-dimethylisoxazole and 5-Cl-1,3-dimethylpyrazole). This leaves the divergent synthesis of symmetric OTs by CH-arylation largely unexplored.

1.2.3.2 Decarboxylative Cross-Coupling

Decarboxylative cross-coupling is another more environmentally friendly variation of the palladium-catalyzed CC reaction methodology. In this variation, the nucleophilic coupling partner is a carboxylic acid derivative while the electrophilic partner is an aryl halide, with triflates having been used as well. Similarly to CH-arylation, DCC benefits from the simplicity of its nucleophile since carboxylic acid functional groups are widespread, easy to handle and store, are not intrinsically toxic and their synthesis is well-documented. Additionally, carboxylic acids are commonly found in nature, allowing for biomass-derived heterocyclic acids to be used as starting materials in DCCs[157,158], further improving their environmental profile.

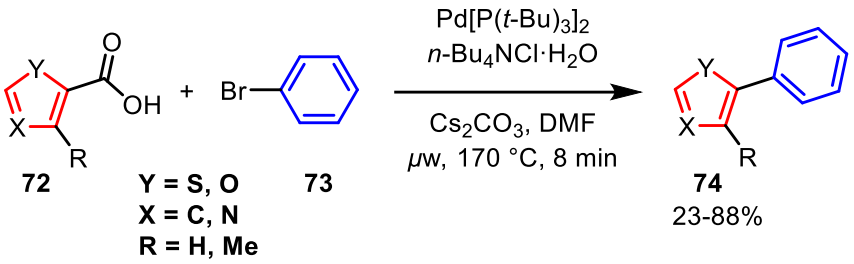


Figure 23: First DCC Using 5-Membered Heterocycles[159]

Modern DCCs are partially the result of work carried out in the 1960s by Nilsson, Cohen and Shepard where they investigated the protodecarboxylation of aromatic acids by copper.[160] In 2006, Gooßen and coworkers were the first to report a biphenyl synthesis from benzoic acid derivatives and phenyl bromides through DCC using a bimetallic system with catalytic amounts[161] of Pd and Cu. The role of the copper metal was to decarboxylate the acid derivative and form ArCu which would be the active nucleophilic coupling partner.[161] Unfortunately, this method suffered from scope limitations due to the crowding of the copper metal by halides released after oxidative addition.[162] This was addressed through the replacement of aryl halides with aryl triflates, broadening the scope of the reaction.[163] In terms of heterocycles, the first example of a DCC using a heterocyclic acid was an intramolecular reaction for the synthesis of a natural product.[164] The potential of heterocyclic acids would be demonstrated by the work of Forgione and colleagues published in the same year as Gooßen's biphenyl synthesis (**Figure 23**). This work reported the use of C2-carboxylated heterocycles (**72**) (including a 3AT) which were coupled with phenyl bromides (**73**) to yield the cross-coupled product (**74**).[159] The major difference in this work was that no Cu or Ag additives were required. Once again, the presence of a heteroatom in the 5-membered ring **72** is responsible for the intrinsic nucleophilicity of the α-carbons thanks to electron delocalization.[165] They reported good yields for β-methylated starting materials (53% to 86%) which consisted of thiophene, furan, benzofuran, oxazole and thiazole. Interestingly, 5-membered heterocyclic-2-carboxylic acids without an alkyl substituent at C3 were observed to have lower yields which were 2 to 3 times smaller than their alkylated derivative.[159]

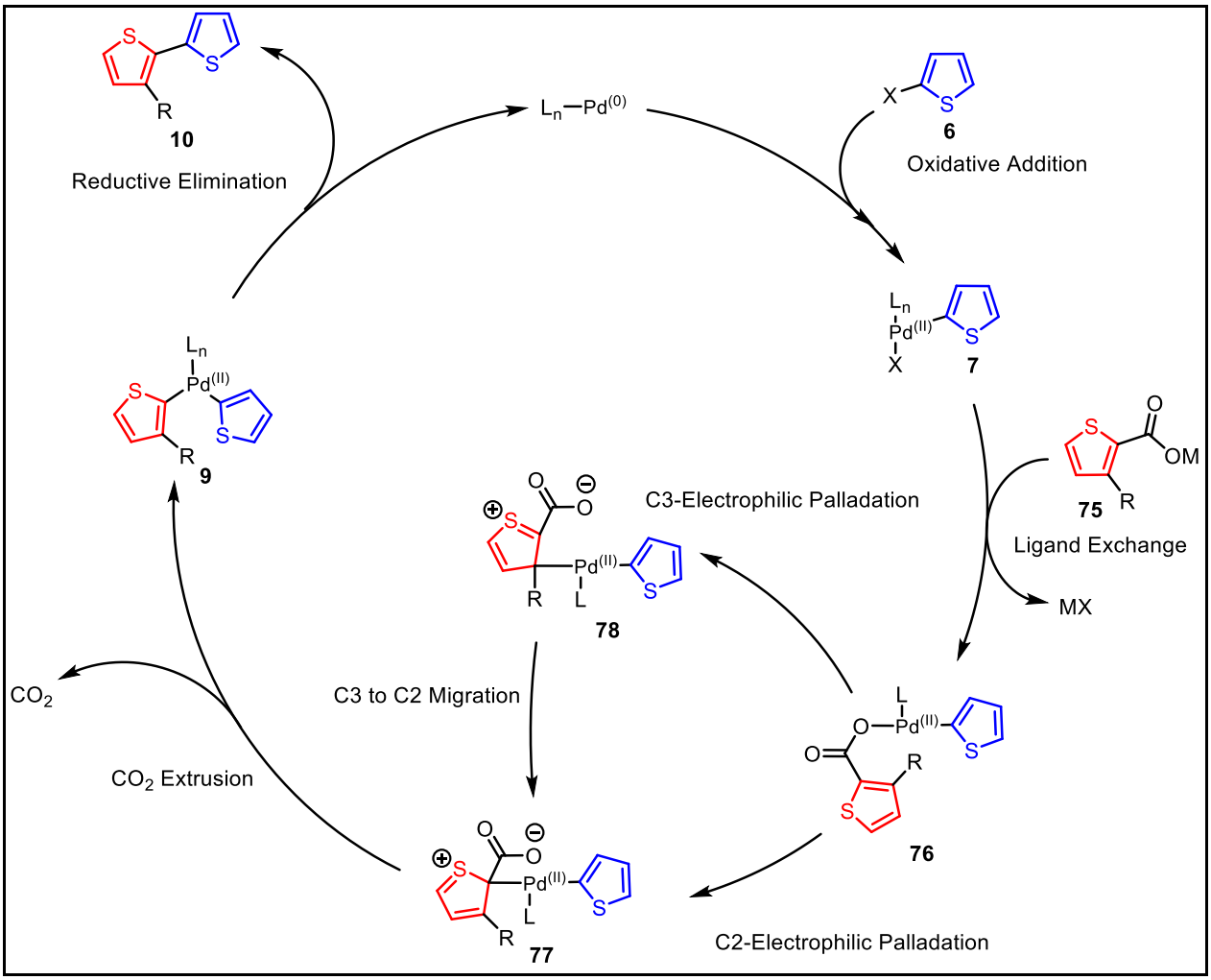


Figure 24: Proposed Mechanism of DCC Reactions With 3-Alkylthiophene-2-Carboxylic Acids[165]

The subpar yields of starting materials without an alkyl group at C3 are due to the particular mechanism that DCC reactions go through for this type of starting materials (**Figure 24**). Within the same general principle, the mechanism starts with the oxidative addition of **6** to produce the first intermediate **7,** which then undergoes a ligand exchange with the acid functional group of the starting material **75** to yield intermediate **76**. The carboxylate group acts as a directing group which can direct the Pd-complex in one of two ways, either at C2 or C3. When directed at C2, the next intermediate in the cycle is formed (**77**), but when directed at C3, a secondary intermediate is formed (**78**). If the heterocycle is not alkylated at C3 (not shown), cross-coupling occurs and this 3-arylated-2-carbyoxylate byproduct subsequently re-enters the cycle which leads to 2,3-diarylated byproducts.[159] This is the cause of lower yields in non-C3 alkylated starting materials. In contrast, when C3 is alkylated, the Pd-complex migrates to C2 (**78** to **77**) which is followed by

CO_2 extrusion to generate the final intermediate **9** that releases the C2 arylated product **10** and reforms Pd(0). The stochiometric byproduct generated here is CO_2 gas which simply dissipates into the atmosphere. The DCC is the only reaction that behaves this way out of those presented and results in less solid waste that is a direct product of the catalytic cycle.

The particularly attractive quality of these kinds of DCCs, aside from one partner being a carboxylic acid, is that Forgione's synthetic procedure made use of microwave irradiation (μw) at high temperatures but extremely short times (170 °C for 8 minutes) (**Figure 23**).[159] This is another quality of DCC that makes it considerably more convenient than other CCs. A subsequent publication was released where the impact of base, solvent, catalyst, aryl halide as well as the use of thermal conditions were investigated.[165] N-methyl pyrrole was the main substrate for that work, but it showed that the reaction responded well to several solvents as well to the use of aryl iodides, chlorides and triflates. Additionally, a 1:1 ratio of $PdCl_2$ to P(*t*-Bu)$_3$ had an essentially identical yield to conditions using a 1:2 ratio, implying that the active complex is a monophospine species.[165] Furthermore, the use of lithium bases led to a drastic decrease in yield, suggesting that the carboxylic acid does indeed coordinate to the Pd-complex after the oxidative addition step.[165]

Currently, the Forgione group is continuing to investigate the application of DCC for the synthesis of thiophene-based materials. Previously, Liu reported the synthesis of P3HT using a DCC process with 5-Br-2-COOH-3HT being the monomer.[166] The conditions were microwave irradiation at 190 °C for 8 minutes which produced P3HT with a Mw of 6499 g/mol, polydispersity of 1.93 and conversion of 90% (RRe not reported).

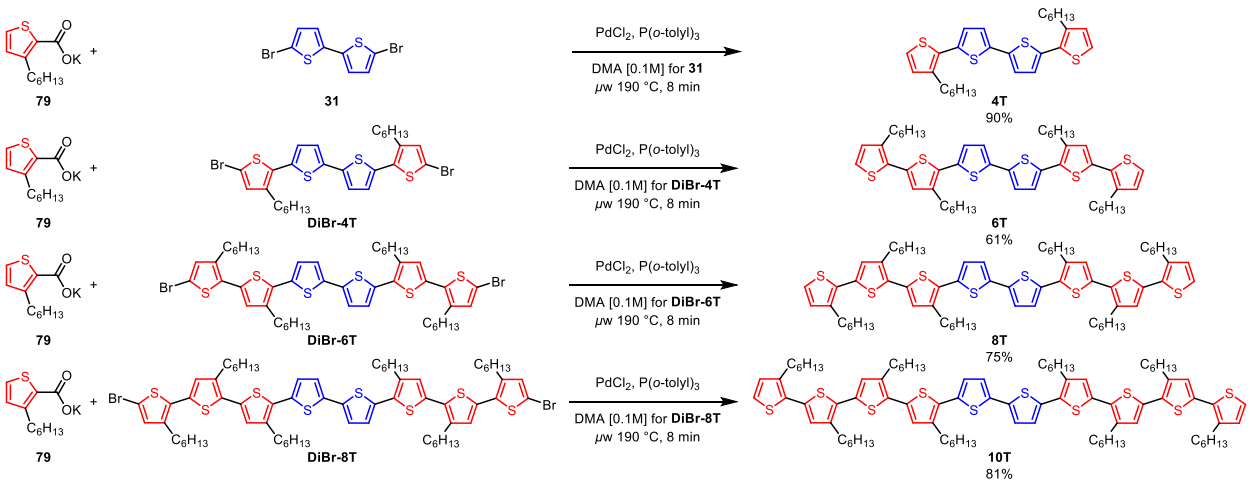


Figure 25: Liu's Synthesis of Symmetric OTs by DCC[65]

Additionally, DCC conditions were adapted by Liu[65] for the divergent synthesis of symmetric OTs (**Figure 25**). Previously, one of the requirements for DCCs was the addition of excess base such as Cs_2CO_3 in order to fully deprotonate the acid starting material and allow it to ligate the Pd metal. This requirement was removed in Liu's work and effective use of a potassium salt of 3HT carboxylate 2-COOK-3HT (**79**) was demonstrated for the synthesis of symmetric, even-numbered OTs.[65] Once again, the reactions were carried out using a microwave reactor and only required 8 minutes of reaction time. This further improved the profile of DCCs by getting rid of the excess base and quaternary ammonium salt additive, bringing the reaction closer to Kumada and Stille CCs in terms of reagent requirement. This work made use of a divergent DCC synthesis of symmetric OTs by adding two monomers per reaction, sequentially synthesizing 4 members of the even sequence[65] which are **4T**, **6T**, **8T** and **10T**.

Lui's work on the DCC synthesis of symmetric OTs is the precedent for the present work. DCC had not been used to synthesize the analogous odd-numbered symmetric OTs and this presented an opportunity to further expand the library of compounds synthesized by this methodology.

1.3 Research Goals and Thesis Organization

The objective of the present work was to investigate the synthesis of two sequences of symmetric OTs based on 3HT using a divergent, sequential methodology that makes use of palladium-catalyzed cross-coupling reactions, particularly Suzuki and Decarboxylative cross-couplings. Chapter 1 provides historical context and introduces the concept of organic semiconductors and P3HT as well as the importance of regioregularity and molecular ordering. Oligothiophenes are subsequently introduced as viable models to make up for the shortcomings of polymer sample variability. The research, which serves as precedent for the present work, is also introduced along with the motivation behind the specific choice of symmetric oligomers, namely to continue the investigation into their doping mechanism. Finally, palladium-catalyzed cross-coupling methodology is presented along with the most common and relevant synthesis methods of P3HT and symmetric OTs.

Chapter 2 covers the synthesis of symmetric OTs based on 3HT using CH-arylation, DCC and Suzuki CC. Synthesis of thiophene monomers required for each cross-coupling is reported along with the outcomes of each cross-coupling process. Additionally, the dibromination of the resulting oligothiophenes is presented and an improvement of the previously used method is described.

Chapter 3 covers the conclusions of this work and provides directions for future work related to the synthesis of symmetric OTs through Pd-catalyzed CC reactions and their dibromination.

Chapter 2 – Synthesis of Symmetric Oligothiophenes

2.1 Introduction

The end-use of the library of symmetric OTs synthesized through this work would be to be doped with F_4TCNQ and their doping behavior to be studied. This would allow for the establishment of a relationship between oligomer length and doping mechanism. The syntheses used are based on palladium-catalyzed cross-couplings that are deemed as being more environmentally benign as well as not fully explored in literature. The Suzuki CC is widely used and studied, however for the particular OT sequences of interest, only scattered and incomplete literature exists. Additionally, DCC has been used previously for the synthesis of the even sequence of OTs[65] but the odd sequence remained unexplored. Finally, as previously mentioned, the literature on CH-arylations for the synthesis of these molecules using a double CC reaction is sparse, which motivated an investigation into possible conditions for a symmetric double CH-arylation.

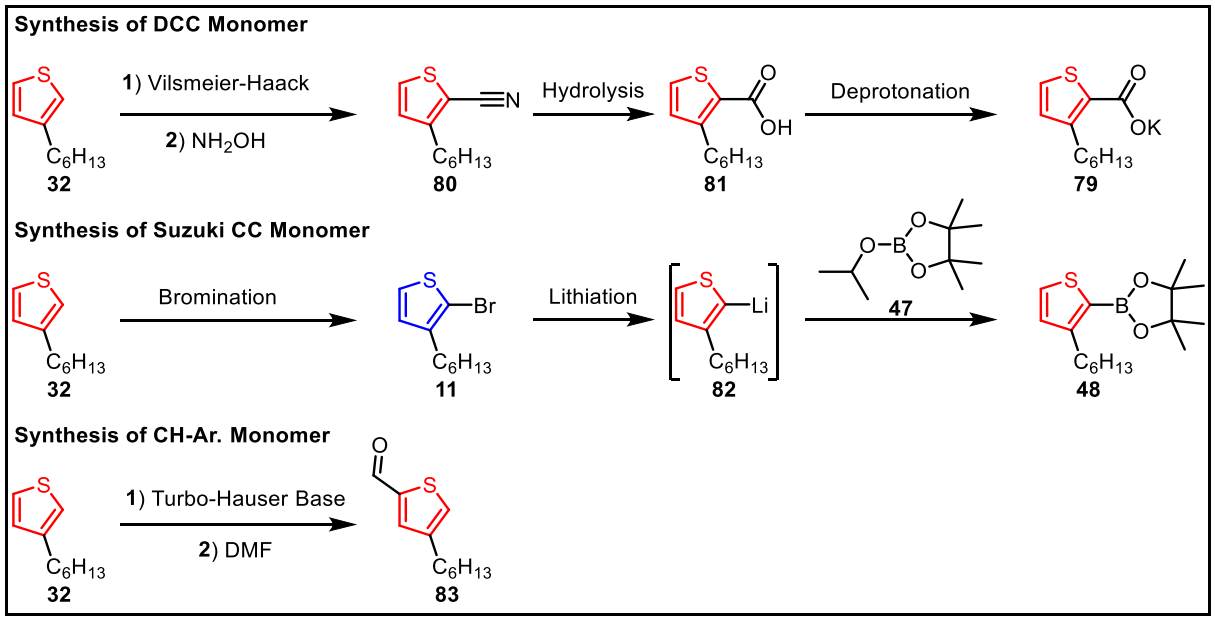


Figure 26: General Scheme of Nucleophilic Coupling Partners Synthesis

Figure 26 illustrates the synthesis of the major monomers required for each cross-coupling methodology. The preparation of the DCC coupling partner starts with **32** which is reacted under Vilsmeier-Haack conditions to generate the Vilsmeier intermediate. Instead of quenching with water, it is quenched with hydroxylamine which generates nitrile **80**. Next the nitrile is hydrolyzed under basic conditions to yield the acid product **81** which is finally deprotonated to generate the

potassium salt **79**. Similarly, the Suzuki coupling partner starts with **32** and is also functionalized at C2 but through a bromination instead to generate **11**. The next step involves lithiation with *n*-BuLi to generate the lithiated intermediate **82** which is subsequently quenched with **47** to yield the Suzuki coupling partner **48**. The preparation of the CH-arylation coupling partner is considerably simpler as it is a single step for **83**. The starting material **32** is reacted with a highly hindered Turbo-Hauser base. This base selectively deprotonates C5 and this nucleophilic intermediate is quenched with DMF to yield the desired product **83**. Overall, all processes start from **32** and rely on functionalization of C2 or C5, with both Suzuki CC and DCC requiring functionalization only at C2 while CH-arylation requires monomers functionalized only at C5.

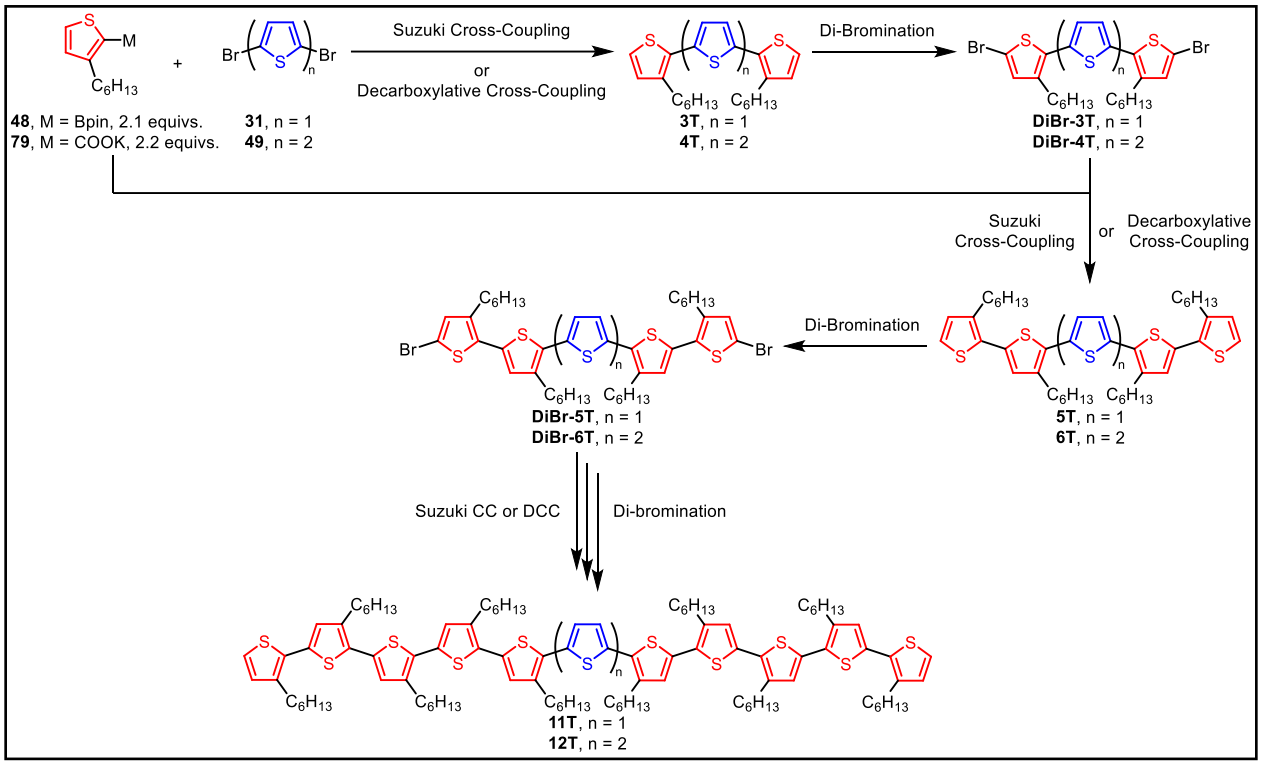


Figure 27: General Scheme of Stepwise Synthesis of Symmetric OTs

The synthetic concept for the sequential synthesis of symmetric OTs is based on alternating CC and bromination reactions. **Figure 27** shows this concept and how it applies to both the Suzuki CC and DCC methodologies. First, the nucleophilic coupling partner (**48** or **79**) is coupled twice to the di-functionalized core (**31** or **49**). This results in the first OT of the respective sequence which is either **3T** or **4T**. Next, this product needs to be functionalized in order to serve as the core for the next CC reaction, thus it is brominated, leading to the second compound of the synthesis which is the di-brominated intermediate **DiBr-3T** or **DiBr-4T**. This completes the first cycle of CC-bromination of the synthesis with the next step being another CC reaction which

elongates the OT by 2 monomers and yields the third compound of the synthesis which is also the second compound of the respective OT sequence (**5T** or **6T**). Bromination is repeated to yield the di-brominated intermediate **DiBr-5T** or **DiBr-6T** which ends the second cycle of CC-bromination. From there, these cycles are repeated until the desired product is obtained, which in this particular case was **11T** and **12T** for the odd and even-numbered sequences respectively.

This synthetic concept does not apply to the CH-arylation procedure since the expected product would have been already capped with aldehyde functional groups (**Figure 28**). The next sections will cover the outcomes of the CH-arylation (Section 2.2), DCC (Section 2.3), and Suzuki CC (Section 2.4) methodologies. The bromination procedure will not be discussed in those sections and will instead be covered separately in its own section (Section 2.5).

2.2 Palladium-Catalyzed Direct CH-Arylation

The following section will present attempts at carrying out a double CH-arylation for the synthesis of di-formylated **3T** (**DiA-3T**). The general concept of this process (**Figure 28**) involves coupling the core partner **49** with C5-formylated 3HT (**83**) to yield terminally di-formylated **DiA-3T** as the product. This method is part of the pre-functionalization methodology (**Figure 17**) mentioned in Section 1.2.2.4. For this CC methodology we tried adapting previously reported conditions for the CH-arylation of thiophenes and phenyl bromides.

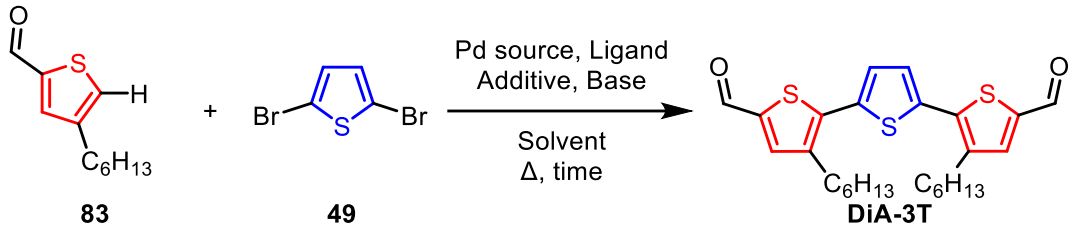


Figure 28: General Synthetic Concept of Double CH-Arylation

2.2.1 *Synthesis of 4-Hexylthiophene-2-Carbaldehyde Monomers*

Thiophenes are particularly amenable to modifications at C2 and C5. In the case of 3HT, the reactivity of C2 is different to that of C5 in a variety of situations. This can be exploited through the addition of strong bases, however if for example *n*-BuLi is used, the selectivity will be less than ideal. In order to ensure the highest level of selectivity for a C5-deprotonation, a sterically hindered base can be used. Following the method reported by Mori and coworkers (**Figure 29**), the highly hindered Turbo-Hauser base[167] 2,2,6,6-tetramethylpiperidinylmagnesium chloride

lithium chloride (TMPMgCl·LiCl) was used for the selective C5-deprotionation of 3HT (**32**). Using an excess (1.5 equivs.) of a 1.0 M solution of TMPMgCl·LiCl in THF/toluene, **32** was added directly dropwise without the addition of more THF. The benefits of this base are that aside from being highly hindered which results in complete selectivity, it can also be used at room temperature (~23 °C) and does not require cooling the reaction to -78 °C. This considerably improves the reaction's simplicity and convenience. The mixture was stirred for 3 hours which leads to the generation of a C5-lithiated 3HT. This intermediate is then quenched through the addition of excess DMF dissolved in THF and the mixture is stirred for 1 more hour.

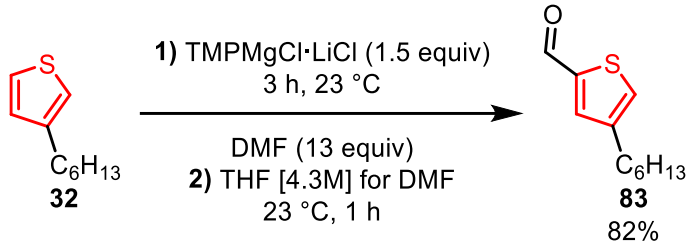


Figure 29: Synthesis of 4-Hexylthiophene-2-Carbaldehyde[167]

This procedure resulted in the desired product **83** isolated at a yield of 82% with no presence of the C2-formylated isomer. The originally reported yield of this reaction was 93% although it was reported for a scale of 0.50 mmol while the above reaction was carried out at a scale of 14.6 mmol, possibly justifying the decrease in yield.

2.2.2 *CH-Arylation for the Synthesis of Di-Formylated Oligomers*

With the desired 3HT monomer **83** synthesized, the double CH-arylation reaction could be investigated. The conditions that were chosen for optimization of this reaction were based on common CH-arylation conditions reported for thiophenes with ArX coupling partners. **Figure 30** illustrates 2 different sets of conditions that were repeated for optimization called *Conditions A*, and *B*. **Table 1** contains the optimization reaction data and ^{1}H NMR (nuclear magnetic resonance) yields of **83** and **DiA-3T** measured with 1,3,5-trimethoxybenzene (TMB) as the internal standard. *Conditions A* are based on the work of Schipper and Fagnou[168]. In this work they present CH-arylation reactions for the synthesis of phenyl-thiophene organic materials that were previously synthesized through Kumada, Stille and Suzuki CC reactions. With these conditions, monomers **83** and **49** are reacted at a 2:1 ratio. The loadings were 5 mol% to 10 mol% of Pd-catalyst to ligand with 30 mol% of PivOH as the additive and 2.0 equivs. of K_2CO_3 as the base. The solvent was anhydrous toluene heated at 110 °C for 24 hours. The factors being varied are the Pd source, ligand, and reaction time. *Conditions B* are based on the work of Doucet and colleagues where

they reported the ligand-less CH-arylations of thiophenes and ArX at low-catalyst loadings (as low as 0.001 mol%). For these conditions we set a 3:1 ratio of **83** to **49**, 3 equivs. of KOAc with anhydrous DMA and a temperature of 140 °C for 48 hours. For reactions using these conditions, both the Pd-catalyst and ligand as well as their loading are varied.

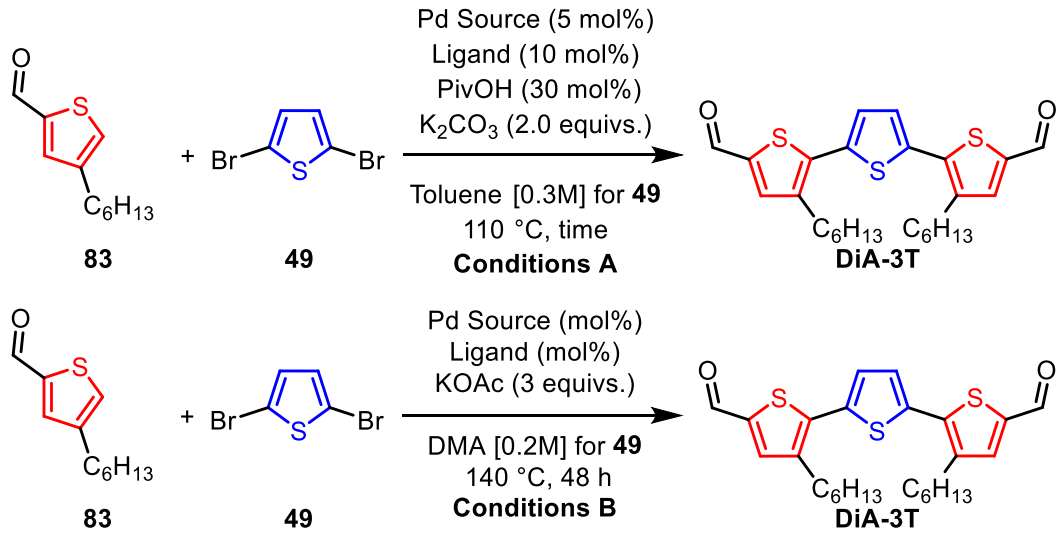


Figure 30: Double CH-Arylation Conditions for the Synthesis of DiA-3T

Table 1: Optimization Table of Double CH-Arylation Conditions for **DiA-3T** With ^{1}H NMR Yields

Entry	Cond.	Pd Source	Pd (mol%)	Lig.	Lig. (mol%)	Time (h)	NMR Y. 83 (%)[a]	NMR Y. DiA-3T (%)[a]
1	A	$(OAc)_2$	5	$PCy_3{\cdot}HBF_4$	10	24	80	0
2	A	$(OAc)_2$	5	$PCy_3{\cdot}HBF_4$	10	24	76	2
3	A	$(PPh_3)_4$	5			16	93	0
4	A	$[P(t\text{-}Bu)_3]_2$	5			16	93	0
5	A	$(OAc)_2$	5	$PCy_3{\cdot}HBF_4$	10	16	92	1
6	B	$(PPh_3)_4$	2			48	57	27
7	B	$[P(t\text{-}Bu)_3]_2$	2			48	55	24
8	B	$(OAc)_2$	0.5			48	60	24
9	B	$(OAc)_2$	2	$PCy_3{\cdot}HBF_4$	4	48	57	18
10	B	$PdCl_2$	2	$PCy_3{\cdot}HBF_4$	4	48	62	28

[*a*]: ^{1}H NMR yields were obtained through the addition of a known amount of 1,3,5-trimethoxybenzene to the reaction upon completion, mixed and subsequently analyzed by ^{1}H NMR, internal standard peak at 6.0 ppm was integrated to 3.0, all visible starting-material and product peaks were integrated and an average yield calculated.

Conditions A (entries 1 to 5) yielded almost no product, with entry 2 having a **DiA-3T** NMR yield of 2% which is the highest for this subset of reactions. The conversion of **83** was also calculated by its NMR signals and it became apparent that the reaction was not proceeding forward since all entries show that there is between 76% and 93% of **83** still unreacted. Staring material **49** was not used for NMR yield calculations as it was determined that a considerable amount evaporates

during workup. This subset of reactions did not work, most likely due to the choice of solvent, reaction temperature, and short reaction times as it was apparent that starting material **83** was not being consumed. To address this, we decided to use a more polar solvent and an increased reaction temperature. *Conditions B* (entries 6 to 10) resulted in considerably better results. In entry 6, we made use of 2 mol% of $Pd(PPh_3)_4$ as the catalyst and resulted in a product NMR yield of 27% and starting material NMR yield of 57%. Next, $Pd[P(t\text{-}Bu)_3]_2$ was used as the catalyst also at 2 mol% but resulted in a product NMR yield of 24% and starting material NMR yield of 55% (entry 7). In an attempt to emulate the original conditions for this reaction, we made use of 0.5 mol% of $Pd(OAc)_2$ without any ligand (entry 8). This reaction resulted in 24% NMR yield of **DiA-3T**, equivalent to entry 7 which used 4 times more catalyst in the presence of ligands. The NMR yield of **83** was also higher at 60%, meaning less starting material was consumed by side-reactions. Investigations into the behavior of $Pd(OAc)_2$ at high temperatures has revealed that soluble Pd(0) clusters form and CC reactions can take place on the surface of these soluble aggregates.[169] This would explain how this reaction performed as well as 4 times more $Pd(PPh_3)_4$. The increased ratio of ArX to Pd prevents the formation of inactive Pd black and allows reactions to proceed. Next, $Pd(OAc)_2$ was increased to 2 mol% and $PCy_3 \cdot HBF_4$ was added at 4 mol% (entry 9). This resulted in an NMR yield of 18%, which is a 6% decrease from the ligand-free reaction (entry 8) and starting material NMR yield of 57% making it overall the worst-performing reaction of this subset. Finally, the Pd source was replaced by $PdCl_2$ and loading and ligand kept the same (entry 10). This resulted in the highest recorded NMR yield for these reactions at 28% and the highest recorded starting material NMR yield of 62%. Overall, entry 10 performed the best out of all tested reactions, although it was still very far from being a viable set of CH-arylation conditions.

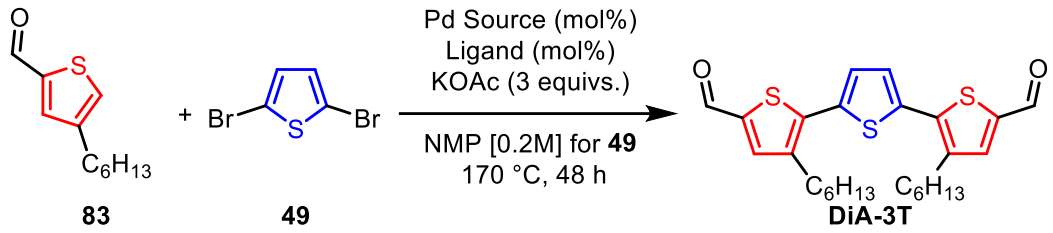


Figure 31: Optimization of *Conditions B* at 170 °C With NMP as Solvent

Table 2: Optimization Table of ***Conditions B*** at 170 °C With ^{1}H NMR Yields Using TMB as Internal Standard

Entry	Pd Source	Pd (mol%)	Lig.	Lig. (mol%)	NMR Y. DiA-3T (%)[a]
1	$(PPh_3)_4$	2			0
2	$[P(t\text{-}Bu)_3]_2$	2			0
3	$(OAc)_2$	0.5			0
4	$(OAc)_2$	2	PCy_3HBF_4	4	0
5	$PdCl_2$	2	PCy_3HBF_4	4	0

[*a*]: ^{1}H NMR yields were obtained through the addition of a known amount of 1,3,5-trimethoxybenzene to the reaction crude, mixed and subsequently analyzed by ^{1}H NMR, internal standard peak at 6.0 ppm was integrated to 3.0, all visible starting-material and product peaks were integrated and an average yield calculated.

Conditions B seemed to perform better but they still presented large quantities of unreacted starting material. This implies that the reaction could possibly still be forced towards a product. As such, we decided to increase the reaction temperature by changing the solvent to NMP. **Figure 31** and **Table 2** contain the data obtained from the use of NMP as solvent and reaction temperature increase to 170 °C. Elevated reaction temperature had the opposite effect of what was expected as ^{1}H NMR spectra of all reaction crudes (entries 1 to 5) presented no peaks that were associated with **DiA-3T**. Moreover, the spectra also did not contain any peaks that could be associated with starting material **83** either. These conditions seem to be so harsh that all reactants were likely broken down or converted into other byproducts. Since it was not possible to analyze these samples by GCMS (gas chromatography-mass spectrometry), TLC (thin-layer chromatography) was used instead to visualize the different compounds in the mixture.

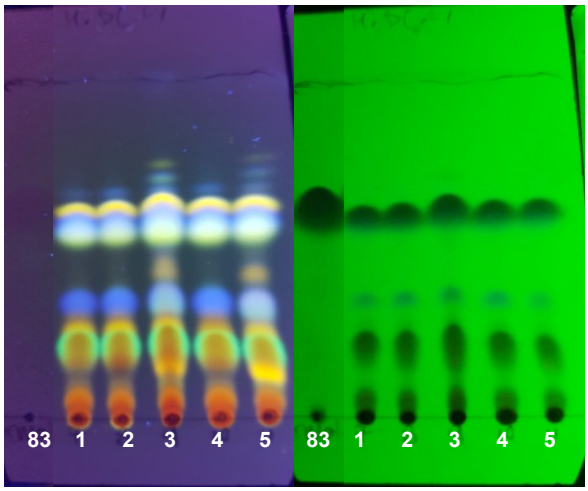


Image was cropped between **83** and **Spot 1** for simplicity as there were multiple other unrelated compounds spotted between them.

Figure 32: TLC of Entries 1 to 5 Crudes (Table 2) **Developed With 1:1 Hexanes/DCM and Visualized with 365 nm** (Left) **and 254 nm** (Right) **UV Light**

Figure 32 shows an image of a TLC done on the crudes of entries 1 to 5 from **Table 2**. The eluent was 1:1 hexanes/DCM and both the 365 nm and 254 nm UV illumination images are shown. The first spot is that of the starting material **83**. Spots 1 through 5 correspond to entries 1 through 5 in the previous table. It is clear from the 365 nm UV illumination that a large variety of conjugated products were formed (highly conjugated compounds tend to emit under 365 nm illumination). From the 254 nm UV illumination, it becomes apparent that there is indeed no more starting material but instead some other dark spot that is close to it in Rf but also seemingly luminescent under 365 nm UV illumination, which **83** is not. It is likely that **83** formed some kind of byproduct that is not too large but still conjugated, judging by the Rf and blue to yellow luminescence.

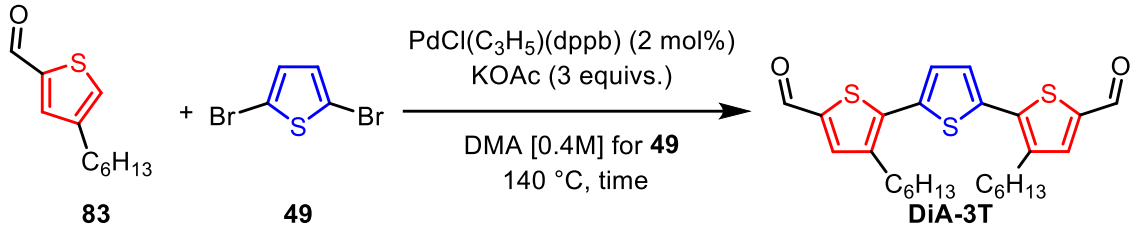


Figure 33: Double CH-Arylation for the Synthesis of DiA-3T Using $PdCl(C_3H_5)(dppb)$

Table 3: ^1H NMR Yield of Double CH-Arylation Reactions Using $PdCl(C_3H_5)(dppb)$ as Catalyst

Entry	Time (h)	NMR Y. DiA-3T (%)[a]
1	24	23
2	36	25

[*a*]: ^1H NMR yields were obtained through the addition of a known amount of 1,3,5-trimethoxybenzene to the reaction crude, mixed and subsequently analyzed by ^1H NMR, internal standard peak at 6.0 ppm was integrated to 3.0, all visible starting-material and product peaks were integrated and an average yield calculated.

Finally, two more reactions were attempted. Section 1.2.3.1 (**Figure 22**) mentioned reactions from literature that reported the double CH-arylation for the synthesis of C3-unsubstituted terthiophenes.[100] The catalyst used in this literature reference was $PdCl(C_3H_5)(dppb)$ which was not commercially available to us. Therefore, we followed the procedure reported for its preparation[100] and obtained the expected yellow solid at a yield of 99%. With this catalyst, we attempted two final reactions in order to confirm if this reaction could not be achieved with previously reported procedures and catalysts. **Figure 33** shows the reaction in question which uses *Conditions B* with the only difference being the catalyst and concentration of **49** while **Table 3** contains the NMR yields of the reactions heated for 24 hours and 36 hours.

Unfortunately, the NMR yields of **DiA-3T** remained low. Entry 1 shows the results for the reaction heated for 24 h which resulted in an NMR yield of 23%. Entry 2 is for a second reaction heated for 36 hours with an NMR yield of 25%. The best performing reaction with *Conditions B* (entry 10

in **Table 1**) was heated for 48 h and resulted in an NMR yield of 28%. The data collected from these reactions confirms that the double CH-arylation of **49** with **83** to yield **DiA-3T** is ineffective and cannot be achieved through widely accepted conditions used for CH-arylations.

2.2.1 *Conclusion*

The work presented in this subchapter focused on the application of direct CH-arylation for the synthesis of di-formylated symmetric terthiophene **DiA-3T**. The required monomer 2-formyl-4-hexylthiophene (**83**) was synthesized using reported procedures. This was achieved through the use of a hindered Turbo-Hauser base which selectively deprotonated C5 and quenched with DMF. The desired monomer was obtained at a yield of 82% which correlates with literature. The monomer was then used in several optimization reactions. Different conditions from literature were adapted for the synthesis of **DiA-3T** through a double CH-arylation. No conditions succeeded in achieving acceptable NMR yields, with the highest such yield being 28%. Considering these results, the most likely explanation for the failure of these reactions is due to the presence of an electron-withdrawing functional group and a long alkyl chain adjacent to the targeted C-H bond at C2. As mentioned in the introduction (Section 1.2.3.1), there are two governing factors that determine reactivity in CH-arylations (**Figure 21**) which are E_{dist} and E_{int}.[152] Thiophenes are part of group 3, meaning it depends on both factors[145], where E_{dist} should be low and E_{int} should be high. The hexyl group adjacent to C2 likely makes E_{dist} very high as it sterically hinders the surrounding space. Similarly, the formyl group at C5 withdraws electrons through resonance from C2, likely making E_{int} very low due to the decreased nucleophilicity at C2. Recently published work reporting the optimization of Miyaura borylations found that larger, more sterically hindered acetate bases, such as potassium 2-ethylhexanoate (2-KEH), perform orders of magnitude better than conventional acetates.[170] Future work could focus on attempting these reactions with similar bases as well as different solvents that would ensure proper solubility of said base. Different, non-conventional catalysts could also be explored.

2.3 Decarboxylative Cross-Coupling

The section that follows will present the outcomes of using DCC reaction conditions for the synthesis of symmetric, odd-numbered OTs. Work previously done in our group by Liu was the basis for this subsection. In his work, Liu modified the previously employed DCC conditions first published by Dr. Forgione by removing the need for a base additive.[65] This was achieved by preparing the potassium salt of the carboxylic acid monomer (**79**) that would be used in the reaction. In the same work, Liu reported the double DCC for the synthesis of the even-numbered

sequence consisting of **4T**, **6T**, **8T**, and **10T**. This leaves the synthesis of the odd-numbered sequence of **3T**, **5T**, **7T**, and **9T** unexplored by DCC. This motivated us to attempt to apply it to these compounds.

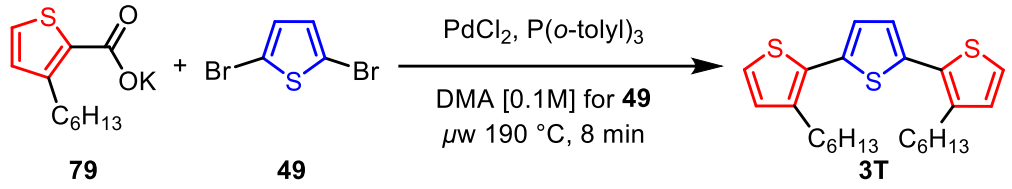


Figure 34: General Reaction Conditions of Double DCC

Figure 34 shows the general scheme of the reactions that will be presented in this section, which are identical to those reported by Liu. The potassium carboxylate salt **79** will act as the nucleophilic coupling partner which will be coupled with the di-brominated core **49**.

2.3.1 *Synthesis of 3-Hexylthiophene-2-Carboxylic Acid Monomer*

In order to carry out the double DCC for the synthesis of the odd sequence of OTs, the functionalized nucleophilic monomer must first be synthesized. There are a variety of ways to go about synthesizing this compound and we had the option of using the previously reported method for the synthesis of **79**. **Figure 35** illustrates this method along with a modified synthetic route that we developed.

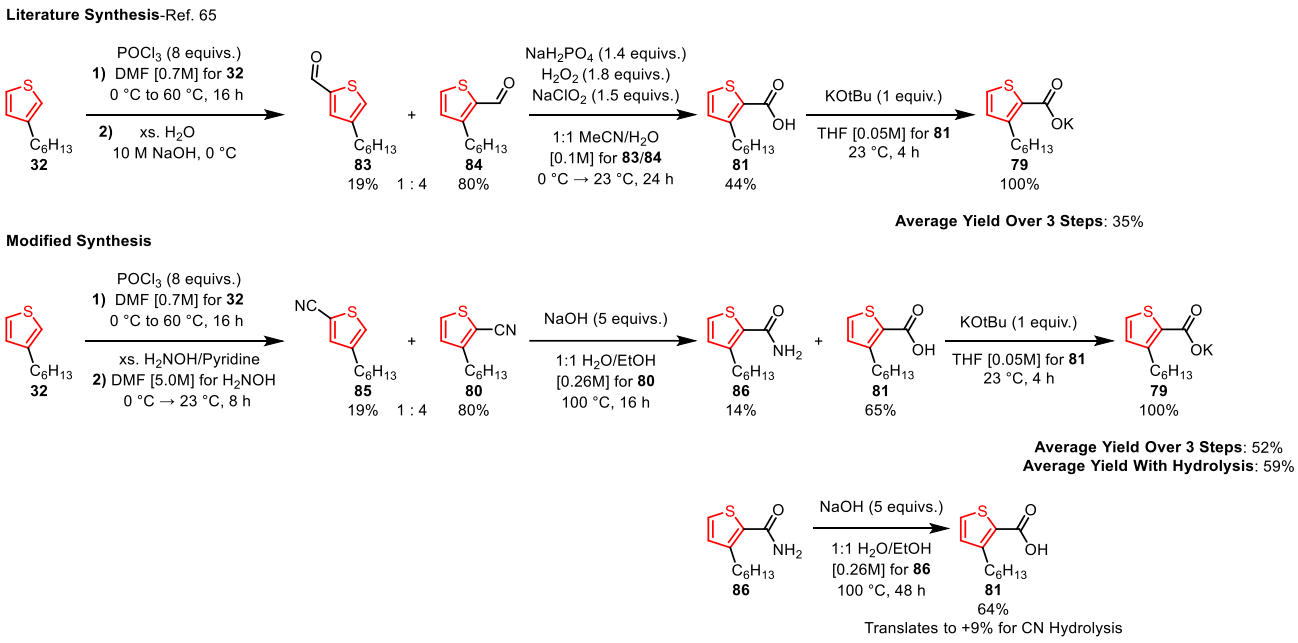


Figure 35: Synthesis Methods of Potassium 3-Hexylthiophene-2-Carboxylate

The *Literature Synthesis* begins with **32** reacted in a Vilsmeier-Haack formylation. The reaction starts with the slow addition of $POCl_3$ to a solution of **32** in DMF stirred on an ice-water bath. Once addition is complete, the mixture is heated at 60 °C overnight. This reaction creates a Vilsmeier reagent as a result of DMF reacting with $POCl_3$. The thiophene then reacts with the Vilsmeier reagent through S_EAr to form an iminium salt intermediate.[171] The next step involves quenching the mixture with water and NaOH, resulting in a 1:4 mixture of **83**:**84** at an overall average yield of 99% (19% for **83** and 80% for **84**, 36.6 mmol scale). When quenched in aqueous basic conditions, the iminium salt is converted into an aldehyde.[171] The major product of this reaction is **84** due to the increased nucleophilicity of C2 thanks to the adjacent alkyl group, which is donating through induction. However, the difference in nucleophilicity between C2 and C5 is not large enough to prevent formation of **83**. Additionally, with C5 being less sterically hindered, this reaction always results in a 1:4 ratio of isomers. The yield of individual isomers is determined by ^{1}H NMR as chromatographic purification is difficult and impractical. Thus, it is carried through to the next step, which is a Pinnick oxidation. This step requires the combination of NaH_2PO_4 (1.4 equivs.), H_2O_2 (1.8 equivs.), and $NaClO_2$ (1.5 equivs.) in a 1:1 mixture of MeCN/H_2O (0.26 M for the mixture of **83** and **84**) which is stirred in an ice-water bath. The Pinnick oxidation is a mild oxidation process that generates $HClO_2$ in situ, acting as the oxidant to convert aldehydes into acids.[172] However, a byproduct of this step is HOCl, which can oxidize ClO_2^- into ClO_2 and effectively stop the reaction.[172] For this reason, NaH_2PO_4 is added as an acidic buffer and H_2O_2 is added as a scavenger for HOCl, decomposing it into HCl, O_2 and H_2O.[172] This mixture is then allowed to warm to room temperature and stirred for 24 hours. The desired product **81** is subsequently isolated through column chromatography at an average yield of 44% (36.6 mmol scale for total mass of **83**:**84**) with yields ranging between 21% and 65% (standard deviation of 17%). Unfortunately, the average yield is quite low, with yield variability being quite high, and we suspect that it is likely due to the H_2O_2 used in the reactions. The highest recorded yield of 65% was achieved through an extreme excess (>2.2 equivs.) of H_2O_2. Unless stored very carefully, it tends to decompose, and we think that this might be the major obstacle to consistently reaching the reported yield of 62%.[65] The final step in this synthesis is the conversion of the acid **81** into its potassium salt **79** which is done with a stochiometric amount of KO*t*-Bu in THF. This step is very simple and practical as the workup only requires that the THF be evaporated, taking with it the *t*-BuOH byproduct. The yield of this reaction is always 99% to 100% (5.1 mmol scale). In summary, the *Literature Procedure* results in an overall yield of 35% of **79**. Considering the low average yield of the Pinnick oxidation and the high variability in its performance, we sought to develop an alternative route that was more consistent.

The *Modified Synthesis* in **Figure 35** illustrates the synthetic route that was developed in collaboration with Keegan McKibbon in the Forgione group. This process cleverly utilizes the first step to generate a distinct intermediate, which is subsequently converted into the desired product. The first step of the *Modified Synthesis* is identical to the *Literature Synthesis*, namely **32** is reacted in the same Vilsmeier-Haack conditions. However, the second step is where the processes diverge, with the reaction being quenched with H_2NOH instead of aqueous NaOH. Since H_2NOH is easier to handle and store as its hydrochloride salt, this step requires the neutralization of $H_2NOH{\cdot}HCl$ with pyridine. The neutralized mixture is then mixed with another volume of DMF and added dropwise to the Vilsmeier-Haack reaction while stirring in an ice-water bath. The mixture is stirred for 8 hours and worked up to yield the nitriles **85** and **80** in a ratio of 1:4, identical to the *Literature Synthesis* ratio of aldehydes. Literature examples exist of processes where an aldehyde is converted directly into a nitrile through the addition of a H_2NOH and a good electrophile[173] or a nitrogen source with a good leaving group.[174,175] In our process, we simply skip the isolation of the aldehyde and form the acetaldehyde oxime (**87**) directly in the same pot as the Vilsmeier-Haack reaction.

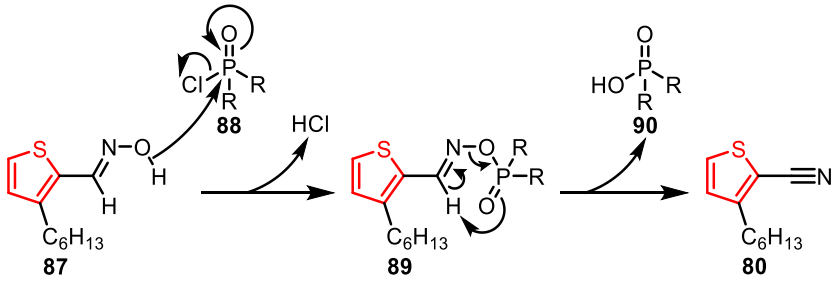


Figure 36: Suspected Mechanism for the Formation of 80

Figure 36 shows the proposed mechanism for this reaction starting from **87** which is formed from the reaction between the iminium salt intermediate and H_2NOH. Next, the hydroxyl attacks the P atom of a $POClR_2$ (**88**) byproduct formed as a result of the Vilsmeier-Haack reaction, yielding **89** and releasing HCl as a byproduct. The next step is theorized to be an electrocyclic rearrangement[175] resulting in the desired product **80** and releasing HO_2PR_2 (**90**). Similarly to the literature procedure, this reaction results in a 19% yield of the C5-nitrile **85** and 80% yield of the desired C2-nitrile **80** (30.0 mmol scale). The mixture of isomers is not chromatographically separated as in the *Literature Procedure* and is hydrolyzed in aqueous NaOH (5 equivs.) at 100 °C overnight for the next step (26.0 mmol scale for total mass of **85**:**80** starting material). The reaction mixture's volume is reduced under vacuum and the remaining water is washed with hexanes, which removes all amide byproducts from the crude, leaving behind only the acid

products (C2-COOH **81** and the isomer C5-COOH which is not shown). The desired product **81** is subsequently isolated through column chromatography at an average yield of 65% with yields ranging between 58% and 76% (standard deviation of 9%). Additionally, 14% of the C2-amide byproduct **86** is also recovered during the workup. Byproduct **86** can be collected over multiple reactions and resubmitted under the same conditions to generate **81** at an average yield of 64% (at an 8.0 mmol scale). Combining this yield with the yield of nitrile hydrolysis, the overall yield of **81** is increased to 74% (an increase of 9% over the nitrile hydrolysis alone). The final step is identical to that of the literature procedure, where **81** is converted to the potassium salt using KO*t*-Bu in THF for a complete conversion to **79**. The overall average yield of **79** from this process is 52% if amide **86** is ignored and 59% if amide **86** is collected and hydrolyzed. In the worst-case scenario, this procedure performs 17% better on average than the *Literature Procedure*, with the synthesis of **81** being considerably more consistent in its performance (standard deviation of 17% versus 9%). Having established a new viable route for the synthesis of **79**, the double DCC would be investigated next.

2.3.2 *DCC for the Synthesis of Symmetric Oligothiophenes*

The double DCC reaction was carried out following the same conditions in Liu's work[65]. The conditions make use of the previously discussed monomer **79,** which is reacted with di-brominated core **49**.

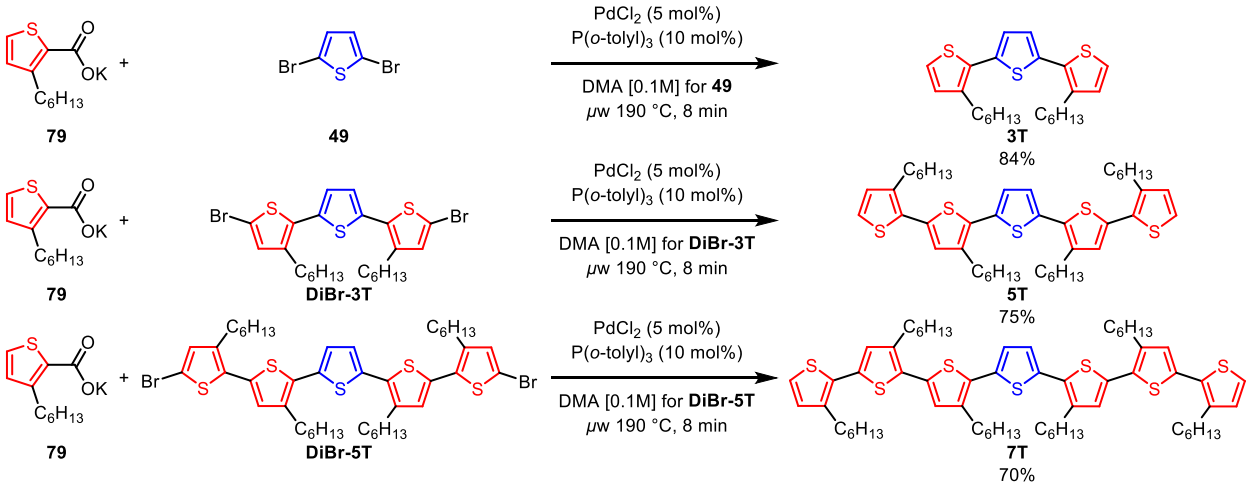
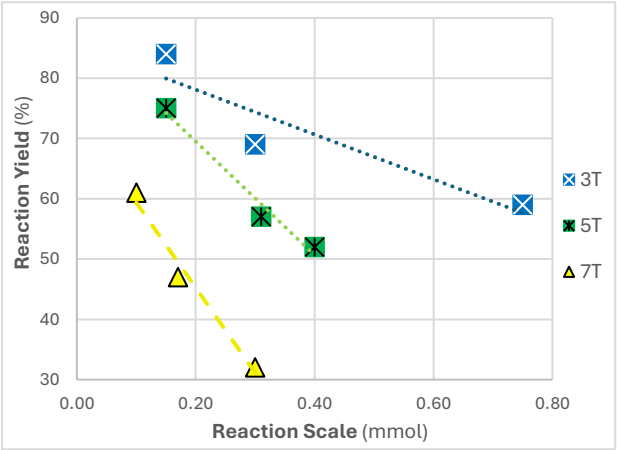


Figure 37: Summary of DCC Reactions for the Synthesis of Odd-Numbered OT Sequence

Table 4: Summary Plot of Double DCC Reaction Data for The Synthesis of Odd-OTs

Product	Scale (mmol)	Isolated Y. (%)[a]
3T	0.15	84
	0.30	69
	0.75	59
5T	0.15	75
	0.31	57
	0.40	52
7T	0.10	61
	0.17	47
	0.30	32

[*a*]: Products were isolated through column chromatography using silica as the solid phase and mixtures of hexanes and DCM as eluent.



The reaction conditions consist of 2.2 equivs. of **79** and 1 equiv. of **49** dissolved in DMA along with 5 mol% of $PdCl_2$ and 10 mol% of P(*o*-tolyl)$_3$ as the catalyst and ligand combination. The mixture is then heated in a microwave reactor at 190 °C for 8 minutes. Optimization of these conditions was previously done by Liu, here he specifically optimized the conditions using **3T** as the target compound. **Figure 37** shows successful reactions and their yields at the lowest attempted scale. **Table 4** showing a summary table along with a plot of the average yields of reactions carried out at different scales. All compounds were isolated through column chromatography with silica and hexanes or mixtures of hexanes and DCM. The synthesis of **3T** was quite favorable at scales of 0.15 mmol, resulting in isolated yields of 84%. Since this reaction consists of a double CC in one pot, the yield can be translated into a yield of 92% for two CC reactions ($\sqrt{0.84} = 0.92 \rightarrow 92\%$). However, when the reaction was scaled up by 2 and 5 times (0.30 and 0.75 mmol), the yields dropped considerably to 69% and 59% respectively (83% and 77% over two couplings). For **5T**, isolated yields were recorded at 75% (87% per coupling) for 0.15 mmol scale, while doubling the scale to 0.31 mmol resulted in a yield of 57% (75% per coupling). Further increasing the scale to 0.40 mmol resulted in yields of 52% (72% per coupling). **7T** behaved in a similar manner, resulting in a yield of 61% at 0.10 mmol (78% per coupling), 47% at 0.17 mmol (69% per coupling) and subsequently dropping to 32% when scale was increased by a factor of 3 from the first reaction to 0.30 mmol (63% per coupling). Overall, all synthesized oligomers using the double DCC performed from well to acceptable at scales between 0.10 mmol to 0.15 mmol but dropped in performance considerably with increases in scale. This is clearly illustrated by the plot of the data from **Table 4** which shows that yields tend to decrease with scale for these reactions. Moreover, yields seem to drop in relation to oligomer length as well when the scale is kept between 0.15 mmol to 0.10 mmol. Attempts were made to try and address this issue

by increasing reaction times to 16 minutes. However this resulted in the decomposition of products and starting materials (similar to what was discussed in Section 2.2.2, **Table 2** and **Figure 32**) and did not result in an improvement of yield. Moreover, the objective was to not only attempt DCC for the synthesis of the odd-numbered sequence of OTs but also to synthesize **9T**, **11T** and **12T** (**10T** had been previously synthesized by Liu). This was not achieved using this methodology, with the main cause being the solvent. The starting materials for these reactions are di-brominated oligomers, which must properly dissolve in the reaction solvent for a good yield to be achieved. Compound **49** as well as **DiBr-3T** and **DiBr-5T** can dissolve relatively well in DMA. However, **DiBr-7T**, which is the starting material for the synthesis of **9T** is impossible to dissolve in DMA at concentrations needed for the reaction. Even with increases in temperature, it remains as oily stains on the sides of reaction vials. Increasing the volume of solvent would also not be practical as we found that it would take concentrations below 0.01 M after attempting to dissolve a known amount of **DiBr-7T** in DMA. The counterpart from the even sequence to **9T** is **10T**, which was successfully synthesized using these conditions at a yield of 80% and scale of 0.10 mmol. The starting material for **10T** is **DiBr-8T** and we found that it was actually possible to get it dissolved in DMA when heated at small scales. This is also evidenced by the reported yield of **10T**. We hypothesize that this is due to the cores of even-numbered OTs which consist of unsubstituted bithiophene. These cores likely allow for better delocalization of electrons in the π-system which in turn makes them more polar than their equivalent counterpart. Additionally, they contain one extra, non-alkylated thiophene than their odd-sequence counterparts. This is most likely why **DiBr-8T** is more easily dissolved in DMA than **DiBr-7T** even though it is one thiophene shorter. Differences in reactivity between the two types of oligomers will be further demonstrated in the subsequent Section 2.4.2. Considering all of this, the DCC procedure still offers considerable advantages, regardless of its inability to synthesize **9T**. The extremely short reaction times of 8 minutes and good to acceptable yields (84% to 61% across all OTs at scales between 0.10 mmol and 0.15 mmol) makes it the process of choice if small reaction scales are targeted. In such a case, one could get up to 3 steps into the synthesis of either the even or odd-numbered sequence of OTs within a day. This translates to having either **5T** or **6T** in-hand after 1 day of work. We believe that this procedure is applicable for cases where small amounts of oligomers are needed quickly, which makes it particularly suitable for research in the early stages of materials development.

2.3.3 *Conclusion*

The work presented in this subchapter focused on the application of double DCC conditions for the synthesis of the odd-numbered sequence of OTs. The nucleophilic monomer 2-COOK-3HT (**79**) was synthesized using a modified method developed during this research. The previous method relied on the oxidation of an aldehyde through a Pinnick oxidation to yield the acid precursor (**81**). This process had low and inconsistent yields (average yield of 44% with standard deviation of 17%). The modified method makes use of a nitrile which is hydrolyzed to form precursor **81** at an average yield of 65% with a standard deviation of 9%. Overall, the new method has an average yield of 52% over 3 steps or 59% with an optional extra step, in contrast to the average yield of 35% of the previous method. With a reliable synthesis of **79** established, the double DCC of di-brominated thiophenes and OTs was investigated. Based on the method previously published by Liu, the synthesis of **3T**, **5T**, and **7T** was achieved on scales of 0.10 to 0.15 mmol (84% to 61%). Unfortunately, yields decreased consistently with increased reaction scale and **9T** was not synthesized through this method. However, this method has great potential for applications in the development of novel thiophene-based materials. The short reaction times of 8 minutes allow for the rapid synthesis of OTs, coupled with the improved bromination process (will be discussed in Section 2.5.2), several products could be obtained within a single day of work. Future work on this topic could investigate the use of different aromatic or heteroaromatic cores, as well as the use of different nucleophilic coupling partners for the synthesis of a variety of different oligomers.

2.4 Suzuki Cross-Coupling

The following section will discuss the results of Suzuki CC reaction conditions for the synthesis of symmetric, odd and even-numbered sequences of OTs. The reaction conditions are based on conditions found in literature that were used for the sequential synthesis of **3T**, **5T**, and **7T.**[133] However, to our knowledge, no synthesis of **9T** or **11T** has been reported. Moreover, no sequential synthesis using the same Suzuki CC conditions has been reported for the synthesis of **4T**, **6T**, **8T**, **10T** and **12T**. This motivated us to attempt the sequential synthesis of both sequences of odd and even-numbered OTs using the same Suzuki CC conditions. **Figure 38** illustrates the general reaction conditions which were adapted from literature. In this reaction, the C2-borylated compound **48** will act as the nucleophilic coupling partner and it will be coupled with **31** as well as **49** (not shown here).

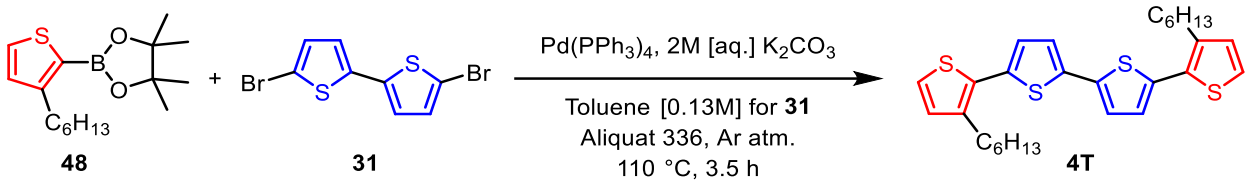


Figure 38: General Reaction Conditions of Double Suzuki CC

2.4.1 *Synthesis of 3-Hexylthiophene-2-Boronic Acid Pinacol Ester Monomer*

In order to carry out the double Suzuki CC reactions, a C2-functionalized boronic acid pinacol ester of 3HT had to be synthesized. Before this product could be synthesized though, a C2-brominated 3HT monomer had to be carried out first. **Figure 39** illustrates the reaction conditions used to synthesize the desired product **11**. This reaction was taken from a previously published procedure.[176]

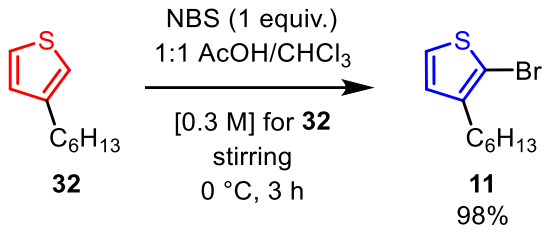


Figure 39: Synthesis of 2-Bromo-3-Hexylthiophene Monomer[176]

Like the syntheses of the other monomers, this reaction uses **32** as the starting material which is dissolved in a mixture of AcOH/$CHCl_3$ (1:1). The reaction flask is wrapped with aluminum foil and placed in an ice-water bath. A stochiometric amount of NBS (1 equiv.) is added and the mixture is stirred for 3 hours. The reaction is kept on an ice-water bath and wrapped in aluminum foil to prevent light from illuminating the contents and starting an undesirable radical reaction. Progress was followed by thin-layer chromatography (TLC) with hexanes as eluent until no more **32** is observed. Purification consists of dissolving the crude in hexanes and filtering it through a small silica plug. The average yield of **11** is 98% over multiple reactions at scales between 16.0 mmol and 18.8 mmol. This agrees with the published procedure which reports a yield of 96% for a scale of 16.0 mmol.[176]

One of the major benefits of Suzuki CC reactions is that the nucleophilic coupling partner can be synthesized through a catalytic Miyaura borylation. The general concept of this reaction (**Figure 40**) involves an ArBr (**11**) that is added to a mixture of Pd-catalyst, excess B_2Pin_2, excess base, and solvent which is then heated for a certain amount of time to yield the borylated product (**48**). To our knowledge, no peer-reviewed report exists of a successful C2-Miyaura borylation of 3HT,

with a single report of such a process being found in a patent using 2-bromo-3-methylthiophene being the starting material.[177]

The patent reported using $PdCl_2$(dppf) as the catalyst at 5 mol%, 1.5 equivs. of B_2Pin_2 and 2.5 equivs. of KOAc in 1,4-dioxane heated at 100 °C for 16 hours which is a pretty standard set of conditions. Using this as a starting point (**Figure 40**), several reactions were carried out to attempt the catalytic synthesis of **48**.

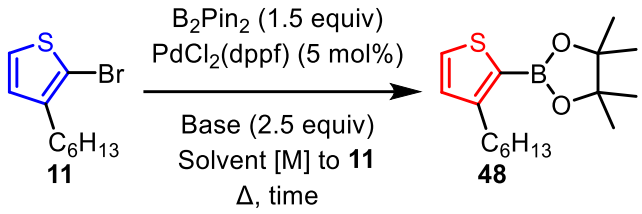


Figure 40: Synthesis of 2-Bpin-3HT (48) Using Miyaura Borylation Conditions

Table 5: Conditions of Miyaura Borylation Reactions for the Synthesis of 2-Bpin-3-HT (**48**)

Entry	**Base**	**Solvent**	**[11]** (M)	**Δ** (°C)	**Time** (h)	**Degas**
1	KOAc	1,4-Dioxane	0.25	100	16.0	Yes
2	KOPiv	2-MeTHF	0.16	80	3.5	No
3[a]	KOPiv	2-MeTHF	0.16	80→60	3.5→16.0	No
4[a]	KOAc	2-MeTHF	0.16	80→60	3.5→16.0	No
5[b]	KOPiv	2-MeTHF	0.16	100	4.0	No

[*a*]: Aliquots taken for TLC/GCMS every 0.5 h for 3.5 h which means the reaction went through multiple cooling and heating cycles. [*b*]: Aliquots taken for TLC/GCMS every 1 h for 4h which means the reaction went through multiple cooling and heating cycles.

Table 6: Comparison of ^{1}H NMR Peak Integrations of Starting Materials, Byproducts and Products of Miyaura Borylation Reactions

	Integration of Triplet Peak (2.87 to 2.48 ppm)[a]			
Entry	**2-Bpin-3HT (48)**	**3HT (32)**	**2-Br-3HT (11)**	**Estimated NMR Y. 48** (%)[b]
1	1.0	10.5		9
2	1.0	2.3	0.6	26
3	1.0	2.2	4.5	13
4	1.0	3.8	5.0	10
5	1.0	3.5	1.1	18

[*a*]: The triplet signals for 2-Bpin-3-Hexylthiophene, 3-Hexylthiophene and 2-Br-3-Hexylthiophene are all generated by the 2 hydrogens on the alkyl chain adjacent to thiophene and are located between 2.87 and 2.48 ppm. [*b*]: NMR yield was estimated by dividing the integration of **48** by the sum of all the signals, this provides an estimate of the maximal possible yield since it assumes there are only 3 compounds in the sample (**48**, **32**, **11**).

Table 5 contains the different conditions that were tested which included KOAc and KOPiv as the base, degassed 1,4-dioxane and non-degassed 2-methyltetrahydrofuran (2-MeTHF) as the solvent at varying concentrations of starting material and varying temperatures and reaction

times. The exact yield of these reactions was not determined, however **Table 6** reports ratios between the expected product, starting material, and protodebrominated byproduct (3HT-**11**) ^{1}H NMR signals which were used to gain insight into the outcome of the reactions. Using conditions identical to those reported in the patent led to a ratio between product and byproduct of 1:10.5 indicating that the major product of this reaction was by far 3HT (entry 1). According to recently published literature, the ligand dppf performs better in its mono-oxidized form dppfO[170]. Moreover, according to another similar source, more lipophilic solvents along with more sterically hindered and in turn lipophilic acetate bases result in better yields in Miyaura borylations[178]. Both of the previously mentioned sources observed a drastic increase in borylation rate when solvents such as *i*-PrOAc or 2-MeTHF were used along with bases such as KOPiv and 2-KEH. The temperatures were reported as being considerably lower and reaction times shorter (80 °C to 35 °C and 1 to 3 hours) for a variety of substrates. Their justification for this was the improved solubility of the base in the solvent along with an increase steric bulk around the Pd center, which likely inhibits the formation of inactive Pd ate-complex $[PdAr(OAc)_2L]^-$. As we only had access to 2-MeTHF and KOPiv at the time of experimentation, we decided to combine all of the outcomes of these reports and changed the conditions. As such, non-degassed 2-MeTHF and KOPiv were tested in a more dilute solution at lower temperature and shorter time (entry 2). This resulted in a ratio of 1:2.3:0.6 of **48**/**32**/**11** which is an estimated NMR yield of at most 26%. The next reactions (entries 3 and 4) were carried out in similar fashion except that aliquots were taken over regular time periods and analyzed by GCMS. No significant formation of product was observed so the reactions were left overnight at lower temperatures. This resulted in a significant increase in the ratio of starting material for the reaction using KOPiv as the base (entry 3) and a significant increase in both starting material and byproduct for the reaction using KOAc as the base (entry 4). The last conditions tested (entry 5) increased the temperature to 100 °C and kept the reaction time at 4.0 h. This resulted in a considerable decrease of the ratio of starting material and an increase of byproduct. Overall, none of the reactions performed at acceptable levels and we wanted to get an idea as to what was occurring in the reaction mixtures. As mentioned, entries 3 to 5 were followed by GCMS, with aliquots being taken at intervals of 0.5 h or 1 h for the first 3.5 h to 4 h of reaction time (**Appendix A**). The GCMS spectra reveal that a complex equilibrium between starting material, byproduct and product exists in these reactions. The spectra also reveal that the reaction forms another byproduct in large quantities which was identified as most likely being 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) ($OBpin_2$). This byproduct is not observed in the ^{1}H NMR or GCMS spectra of worked-up crude products. It is also unlikely that this byproduct is a result of fragment recombination in the GCMS as it is not always observed at the start of the

reaction. Additionally, the solvents used for these reactions were freshly dried over activated basic alumina and titrated with *n*-BuLi (for other uses), therefore water content was known to be very low. Similar conditions were used for other reactions to borylate less hindered thiophenes and their GCMS spectra did not reveal any $OBpin_2$. The monitored samples were also not degassed, which suggests that the most likely cause for the formation of $OBpin_2$ is a combination of steric hinderance in the brominated starting material coupled with the presence of oxygen. This pushes the reaction to form this byproduct due to its inability to consume starting materials to form the desired product. It should be noted though, that the non-degassed reactions led to better NMR signal ratios. Overall, the Miyaura borylation of 2-Br-3HT (**11**) was not successful, leading to mixtures of product, starting materials, and protodebrominated byproduct. The best performing conditions (entry 2) were with KOPiv, 2-MeTHF, heated at 80 °C for 3.5 hours. The present investigation into this process was small, therefore further investigation is warranted where different catalysts, bases, solvents, and temperatures are tested.

Due to the failure of the Miyaura borylation to yield large quantities of starting material, another method had to be adopted for the synthesis of 2-Bpin-3HT. The commonly reported procedure for the synthesis of 2-Bpin-3-HT (**Figure 41**) involves the use of 2-Br-3HT (**11**) which is lithiated through lithium-halogen exchange at C2 and quenched with a source of BPin. Similar conditions are reported in these procedures[132,179], specifically the dissolution of 2-Br-3-HT (**11**) in THF at -80 °C followed by the dropwise addition of *n*-BuLi after which the mixture is left stirring for 30 min to 1 h. After this point, a source of boron is added (*i*-PrOBpin or $B(OMe)_3$). The reported yields are high and purification is described as simple owing to the high purity of the crude product, therefore these conditions were attempted.

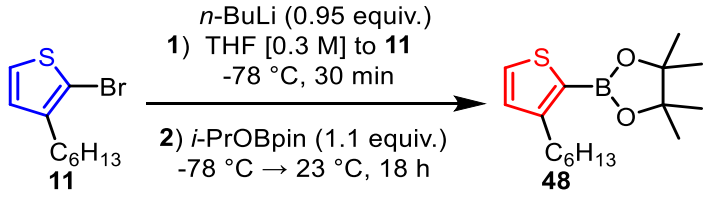


Figure 41: Literature Synthesis of 2-Bpin-3-Hexylthiophene Using n-BuLi

Surprisingly, the literature conditions were not as effective as expected, leading to mixtures of several compounds and yields of 30% to 44% (**Appendix B**). The THF and *n*-BuLi solutions were always titrated prior to use and addition volume adjusted to be between 1 and 0.95 equivalents of the starting material **11** so as to avoid lithiation at C5. The addition of *n*-BuLi was also very slow, taking upwards of 30 minutes to be complete. The crude mixture also contained several

byproducts (**Appendix B1/B3**). As this was not an effective synthetic process, a variation was investigated where the addition order was reversed, meaning that *n*-BuLi is added to THF at -78 °C first and 2-Br-3-HT (**11**) is added dropwise instead. This reaction was carried out at scales between 4.0 mmol and 12.1 mmol and yields between 72% to 90% were recorded. The crude product was also almost pure, with occasionally only a small contamination of the C5-isomer (**Appendix B2/B4**).

2.4.2 *Suzuki Cross-Coupling for the Synthesis of Symmetric Oligothiophenes*

With an effective method for the synthesis of the monomer required for Suzuki CC, the synthesis of the oligomers using this method was investigated next. Literature conditions were found reporting the synthesis of **3T**, **5T** and **7T** using Suzuki CC.[133] Suzuki conditions were found for **4T**[96,180], although without exact procedure or yield, and for **6T**[135] with detailed conditions and a yield of 97%. To our knowledge, no Suzuki CC conditions have been reported for **8T**, **10T** and **12T**. Additionally, we found no report of **9T** and **11T** regardless of conditions. As such, a detailed investigation into the Suzuki CC synthesis of both sequences of OTs was carried out.

Initially, two Suzuki conditions were tested for the synthesis of **4T** (**Figure 42**). Conditions **A** were adapted from the reported Suzuki synthesis of **3T** to **7T**[133] while Conditions **B** were directly repeated from a reported synthesis of **6T**.[135]

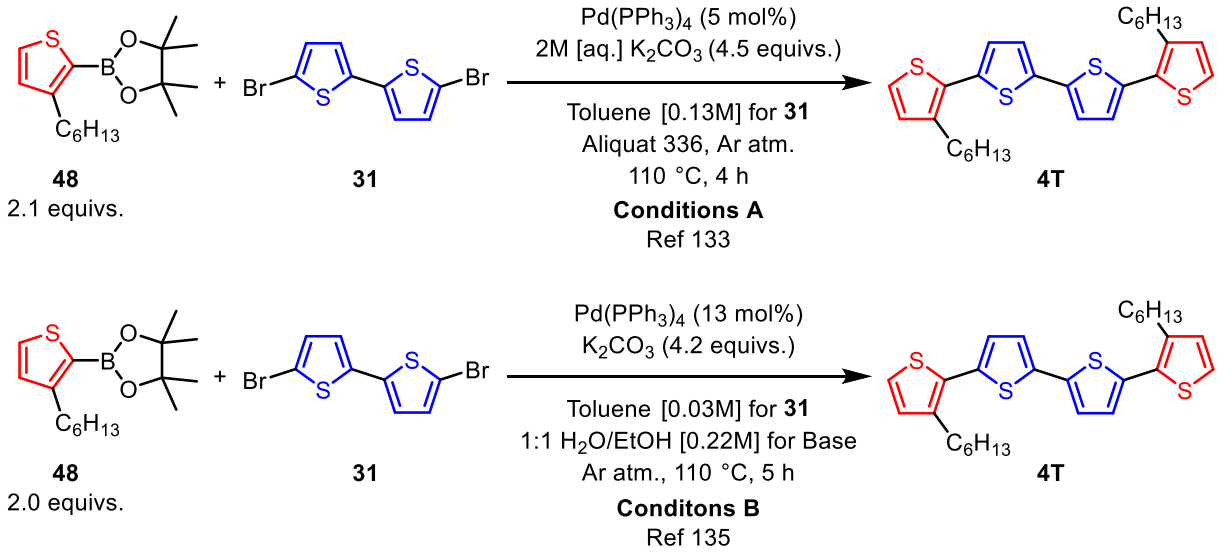


Figure 42: Suzuki CC Conditions for the Synthesis of 4T[133,135]

The major difference between the two conditions is the agent used to facilitate the mixture of polar salts and non-polar organics since both conditions are biphasic (water and toluene). *Conditions A* make use of the PTC Aliquat 336 while *Conditions B* use EtOH. *Conditions A* also call for a more concentrated solution and 5 mol% of $Pd(PPh_3)_4$ while *Conditions B* report a much more dilute solution with 13 mol% of the same catalyst. Both conditions were reported as using reflux for the heating at a temperature of 110 °C. This was modified for *Conditions A* and a microwave vial or pressure vessel that was flushed with argon and sealed was used instead. **Table 7** summarizes the outcomes of 5 reactions carried out using these conditions where the product **4T** was isolated by column chromatography. Entry 1 was true to the original procedure which called for a 24 h reaction time. Heating the reaction for 20.5 hours led to a dark mixture with a lot of black deposited material on the inside of the vessel and an isolated yield of 71%.

Table 7: NMR and Isolated Yields of **4T** Suzuki Reaction

Entry	**Conditions**	**Type**[a]	**Time** (h)	**Scale** (mmol **31**)	**Isolated Y.** (%)[c]
1	A	Vial	20.5	0.46	71
2[b]	A	Vial	4.0	0.31	75
3	B	Reflux	4.0	0.31	60
4	A	Vial	4.0	1.23	92
5	A	Vial	3.5	1.23	89

[*a*]: Vial means reaction was carried out in sealed microwave vial under Ar atm. with the seal being a rubber septum with a metal ring, reflux means the reaction was refluxed under Ar atm. [*b*]: Aliquots taken for TLC/GCMS every 1 h for 4 h which means the reaction went through several cooling and heating cycles and lost a certain amount of reaction mixture. [*c*]: **4T** was isolated through column chromatography using silica as the solid phase and hexanes as the mobile phase.

The initial hypothesis as to what caused the black deposits was the increased reactivity of the even-numbered OTs, as they have been observed to generally react faster than the odd-numbered OTs for which this procedure was developed. The theory was that the product had decomposed due to the extensive heating. To test this hypothesis, the same conditions were repeated (entry 2), although at a slightly smaller scale, and the reaction was followed by TLC (**Figure 43**) with aliquots taken each hour and the various byproducts subsequently identified by ^{1}H NMR and GCMS (**Appendix C**). TLC after 1 h of reaction time revealed a large spot of **4T** which validates the hypothesis of increased reactivity. Right above the product spot, two blue spots can be observed for the 1-hour aliquot. The lighter blue spot was identified (**Appendix C1**) as being the mono-coupled bromo-trimer intermediate (**91**) which is formed after one Suzuki CC takes place. This spot can be seen becoming fainter in the subsequent aliquots until it is no longer visible in the 4-hour aliquot. In its place remains a darker blue spot that was identified (**Appendix C2**) as being the mono-coupled protodehalogenated byproduct (**92**) of the mono-coupled bromo-

trimer intermediate **91**. Additionally, a yellow spot is observed in the first aliquot which persists until the last one. This spot has a lower Rf than the product, as such it must be a longer oligomer since this is the trend that is observed with this class of compounds (longer π-system results in increased polarity which leads to lower Rf). This compound (**93**) was identified by ^{1}H NMR only (**Appendix C3**) as being the homocoupling product of **91**.

There is a report in literature describing a similar case where a halogen-halogen homocoupling was observed during the Suzuki CC of thiophenes.[103] The authors suggest that this process takes place through a boron-halogen exchange, where Pd has gone through oxidative addition with the organoboron partner followed by metathesis with the organohalide. The end result is a nucleophilic trimer which cross-couples with its halogenated starting material **91** to generate **93**. Compounds suspected to be the products of these reactions were partially isolated from subsequent reactions but were not fully characterized, moreover they were present at yields of no more than approximately 2%. Finally, the isolated yield of this reaction (entry 2) from **Table 7** was only 75%, a negligible improvement compared to entry 1. We suspected that this was due to the multiple aliquots that were taken out during the reaction combined with the fact that the reaction went through heating and cooling cycles which might have negatively impacted the yield. Along with TLC, the reaction was monitored by GCMS (**Appendix C4**). Product **4T** is not observable by GCMS but the starting materials, intermediates and byproducts are. According to the spectra, the reaction had consumed both of the starting materials **48** and **31** within the first hour with no obvious change in composition after that.

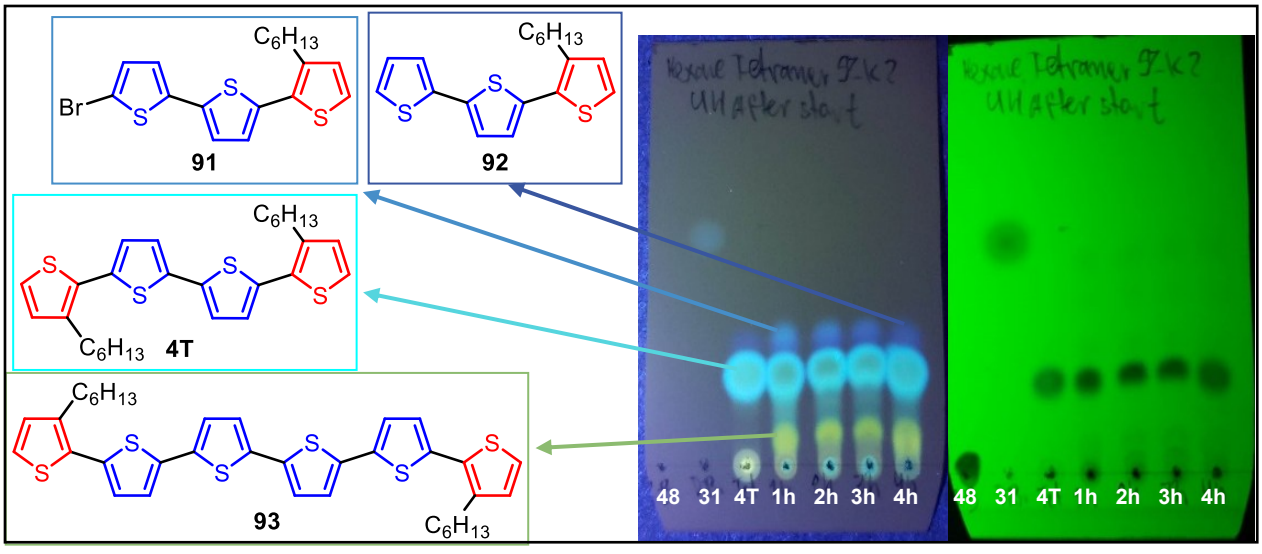


Figure 43: TLC of 4T Suzuki Reaction 2 (1-Hour Aliquots) **Developed With Hexanes and Visualized with 365 nm** (Left) **and 254 nm** (Right) **UV Light**

Entry 3 made use of *Conditions B*, where ethanol was used instead of the PTC Aliquat 336 and the mixture was refluxed. The reaction time and reaction scales were identical to entry 2, yet the isolated yield was only 60%. The original source for *Conditions B* reported a 5 h reaction time at a scale of 0.31 mmol which led to a yield of 97% of **6T**.[135] It was hypothesized that applying these conditions for the synthesis of the shorter **4T** precursor to **6T** should yield similar results but that was not what was observed even though the reaction conditions were identical. Returning to *Conditions A*, two more reactions were carried out (entries 4 and 5) with only a difference in reaction time. Entry 4 was a vial reaction that proceeded for 4 hours at a scale of 1.23 mmol and resulted in a yield of 92% while entry 5 was only heated for 3.5 hours to result in a yield of 89%. Statistically speaking, these yields could be considered identical and correspond to about a 95% yield per CC reaction ($\sqrt{0.91} = 0.95 \rightarrow 95\%$). At this point, we determined an adequate timeframe for the Suzuki CC conditions of the even-numbered oligomers. Even though GCMS and TLC indicate completion in less than 3 to 4 hours, we decided to keep reaction times in this time range to ensure consistency and to account for unexpected variations between reactions.

Having achieved acceptable results for the synthesis of **4T**, the sequence of even-numbered OTs was synthesized using the established Suzuki CC conditions discussed above (**Table 8**). The reactions were carried out at various scales in order to determine if the reaction behaves similarly when scaled up. **Table 8** contains the data of the reactions carried out at the highest scale for each OT. **Figure 44** contains the summary of all the Suzuki CC reactions shown in the table below. Conditions were identical for all OTs and reaction times were between 3.0 to 3.5 h. Yields would vary between 80% to 92% for each individual OT (not shown) but they did not correlate linearly with scale. We believe that yield variation is due to small differences in reaction preparation, workup and purification. The overall largest scale reaction was for **4T** with decreasing scales as OT unit-length increases (molar mass increases therefore less mmol are needed for the same mass of product). The goal of completing this sequence using Suzuki CC conditions was met since we were able to synthesize **8T**, **10T**, and **12T**, which to our knowledge, were previously not reported using Suzuki conditions. Furthermore, **12T** had only been reported using Stille conditions.[108] All compounds were obtained in yields above 85% in less than 4 hours and the conditions were shown to respond well to different reaction scales. This procedure adds another viable and convenient option to the existing repertoire of synthetic conditions for these compounds.

Table 8: Suzuki CC Yields of Largest Scale Reactions for the Synthesis of Even OT Sequence

Product	Scale (mmol)	Time (h)	Isolated Y. (%)[a]
4T	1.23	3.5	89
6T	0.50	3.5	89
8T	0.20	3.5	86
10T	0.16	3.0	85
12T	0.10	3.0	90

[*a*]: Products were isolated through column chromatography using silica as the solid phase and mixtures of hexanes and DCM.

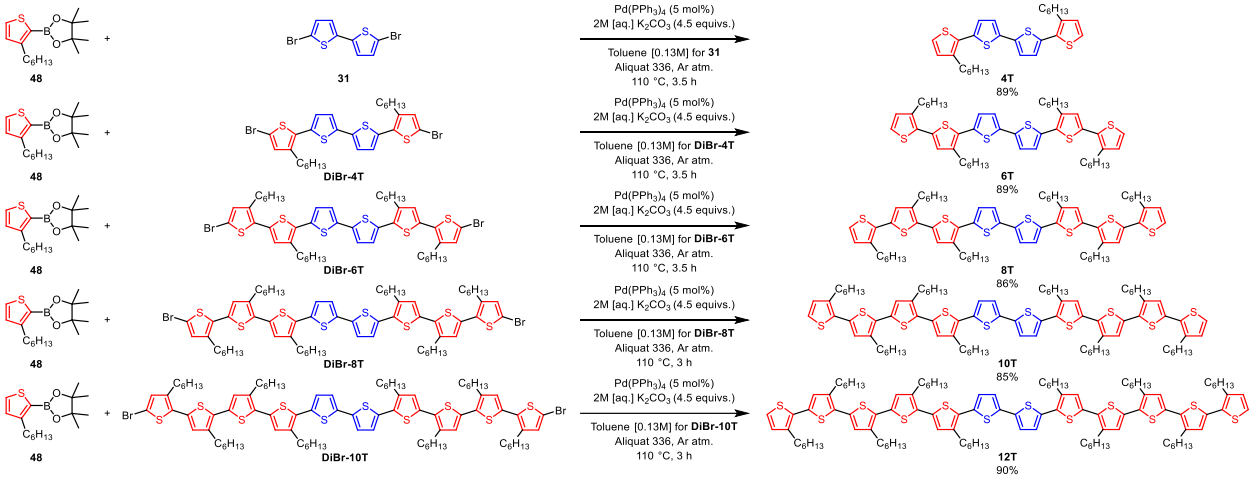


Figure 44: Summary of Suzuki CC Reactions for the Synthesis of Even-Numbered OT Sequence

Having completed the even-numbered sequence, the odd-numbered sequence was investigated next. As previously mentioned, the overall conditions used for the synthesis of the even-numbered sequence were adapted from literature with the major difference being that instead of reflux, the reactions were carried out in sealed vials/pressure vessels.[133] Using these conditions, a test reaction for **3T** was performed (**Figure 45**) at a scale of 1.37 mmol. The reaction resulted in an isolated yield of 81% of high purity **3T**.

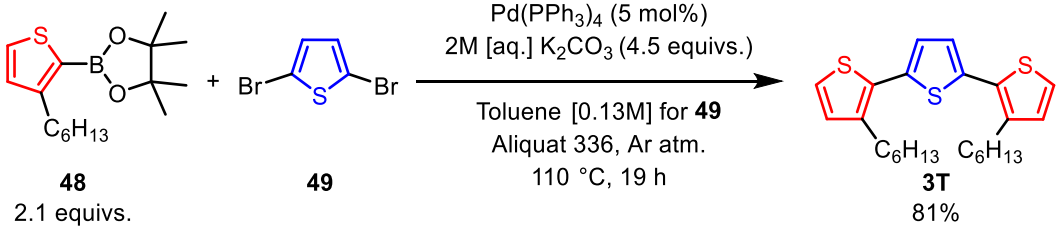


Figure 45: Synthesis of 3T Using Adapted Suzuki CC Conditions

However, TLC of the reaction mixture (**Figure 46**) revealed a peculiar spot which hinted at a process previously observed in the reactions of the even-numbered oligomers. Aside from the spot corresponding to **3T**, a cyan spot was observed right below it which visually resembled **4T** (refer to **Figure 43**). This compound was successfully isolated and confirmed as **4T** by ^{1}H NMR (**Appendix D1**). In this case, it was present at a yield of 5%, although this is the highest recorded yield of this class of byproduct. The same aliquot that was used for the TLC was also analyzed by GCMS along with the crude after work-up (**Appendix D2**).

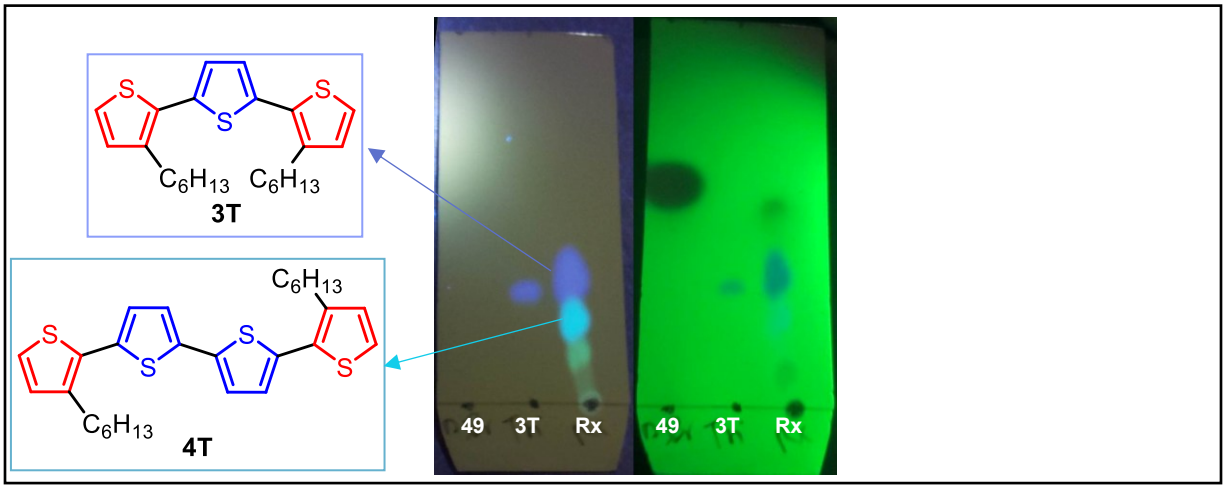
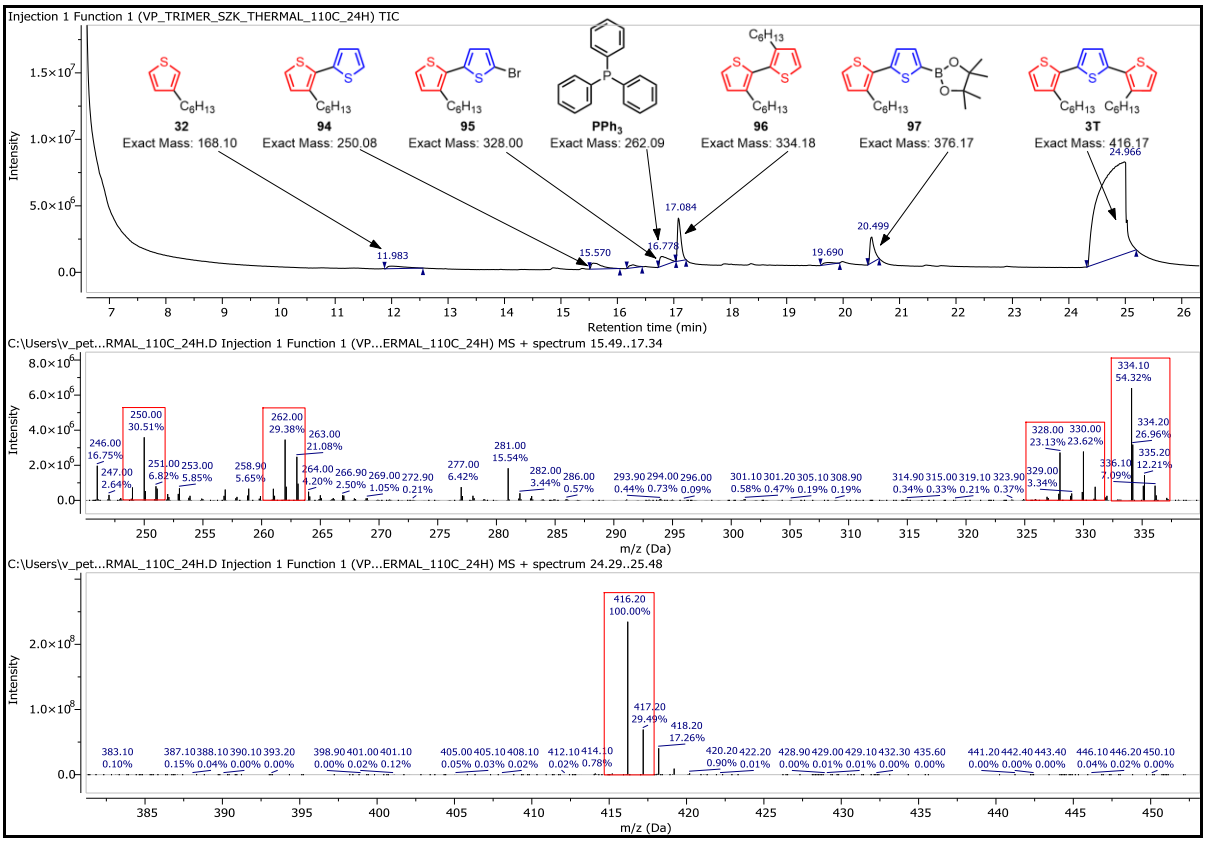


Figure 46: TLC of 3T Suzuki Reaction at 24 h Pre-Workup Developed with Hexanes and Visualized with 254 nm (Left) **and 365 nm** (Right) **UV Light**

The GCMS of the aliquot (**Figure 47**) revealed the presence of the protodeborylated monomer byproduct (**32**), mono-coupled protodeborylated dimer byproduct (**94**), mono-coupled bromo-dimer intermediate (**95**), the ligand (**PPh_3**), homo-coupled dimer byproduct (**96**) and what is suspected of being the mono-coupled borylated dimer byproduct (**97**) along with the product **3T**. GCMS of the crude mixture after work-up (**Appendix D2**) did not reveal any masses belonging to **97** which implies that it was removed during workup. The presence of this byproduct lends support to the hypothesis that the homocoupling of the mono-coupled bromo-intermediates (**91** for **4T** and **95** for **3T**) occurs through a boron-halogen exchange as mentioned previously. Unfortunately, since **97** was not present in the crude after the work-up (**Appendix D2**), there was no opportunity to isolate it and fully characterize it, therefore at present this still remains a hypothesis.



Top: TIC of analyzed sample with peaks associated to compounds. **Middle**: MS between 15.49 and 17.34 minutes. **Bottom**: MS between 24.29 and 25.48 minutes. Agilent 7890A GC system and Agilent 5975C VL MSD with Triple–Axis Detector MS with a HP–588 column coated with (5%–phenyl)–methylpolysiloxane were used to acquire this spectrum.

Figure 47: GCMS Spectrum of 3T Reaction After 24 h Pre-Work-Up (Agilent 7890A-5975C GCMS system)

Having confirmed that the reported conditions work as expected, the odd-numbered sequence of symmetric OTs was synthesized using the adapted procedure. Once again, different scales were tested (not shown) to confirm that the reaction is amenable to scale-up with yields varying between 79% to 92% and showing no evident correlation with scale. **Table 9** contains the data obtained for the reactions that were caried out at the highest scale for each respective OT while **Figure 48** contains the summary of the reactions shown in the table.

Table 9: Yields of Odd-Numbered Oligomers Synthesized by Suzuki CC

Product	**Scale** (mmol)	**Time** (h)	**Isolated Y.** (%)[a]
3T	1.37	19.0	81
5T	1.09	19.0	85
7T	0.58	17.5	91
9T	0.48	17.5	87
11T	0.10	14.5	87

[*a*]: Products were isolated through column chromatography using silica as the solid phase and mixtures of hexanes, DCM, and $CHCl_3$.

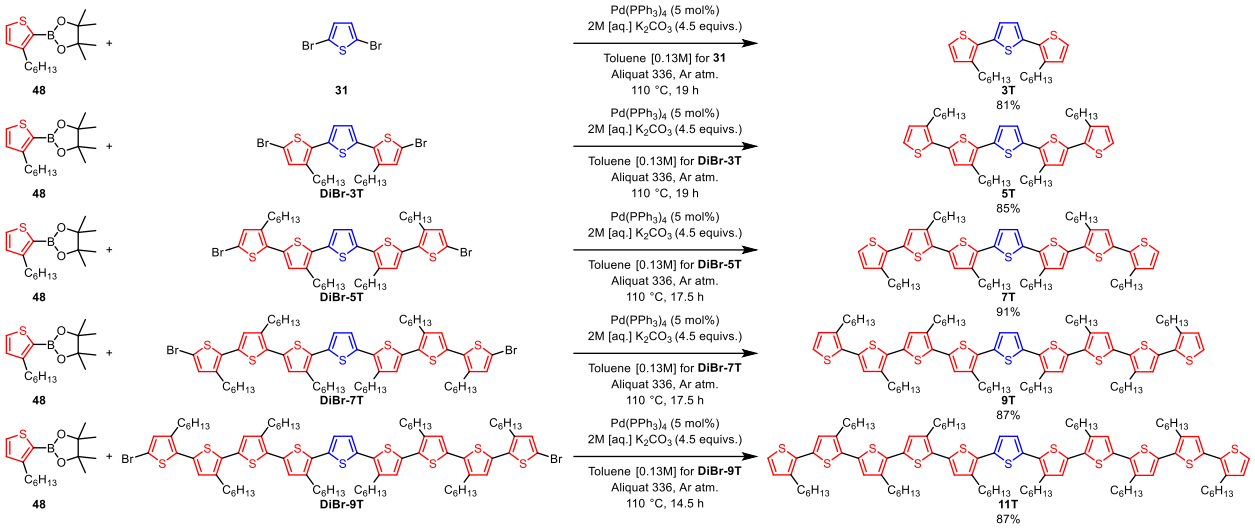


Figure 48: Summary of Suzuki CC Reactions for the Synthesis of Odd-Numbered OT Sequence

For this sequence of compounds, only **3T**, **5T**, and **7T** were previously reported using Stille[95] and Suzuki CC[133] procedures. To our knowledge, there has been no report of **9T** and **11T**. Once again, the shortest OT (**3T**) is synthesized at the largest scale with the longer OTs being synthesized at progressively smaller scales. Reaction yields were between 81% to 91% which is consistent with the even sequence yields. Moreover, our yields of **3T**, **5T**, and **7T** were consistently better than those reported for the original procedure (74%, 81%, and 70% respectively)[133], however it should be noted that our reactions were also carried out at smaller scales than those reported (13.2 mmol, 3.31 mmol, and 1.0 mmol respectively). Therefore, we can't conclude with certainty that the pressurized conditions perform better than reflux. In contrast to the reactions of the even sequence, the reactions of the odd sequence were heated for considerably longer periods of time as per the original procedure (3.0 h to 3.5 h vs 14.5 h to 19 h). It should be noted that an in-depth investigation into the exact reaction times was not carried out. Preliminary tests indicate that these reactions could likely be completed in shorter periods, but this will not be covered in the present work and will be investigated in the future. Finally, the adapted Suzuki CC procedure allowed us to synthesize **9T** and **11T** in sufficient quantities and good yields (87% for both). As a result, both compounds have been characterized by ^{1}H NMR and HRMS (high-resolution mass spectrometry) (Section 4.3), confirming their identities. Additionally, these compounds have been submitted to our collaborators at Dr. Ingo Salzmann's group and their optoelectronic properties will be studied in the future.

2.4.3 *Conclusion*

The work presented in this subchapter focused on the application of Suzuki CC for the synthesis of symmetric OTs based on 3HT containing a non-alkylated monomer or dimer thiophene core. Miyaura borylation conditions were tested for the synthesis of the nucleophilic coupling partner but did not produce desirable outcomes. The nucleophilic coupling partner was instead synthesized using lithiation at C2 of 2-Br-3HT (**11**) followed by quenching with *i*-PrOBpin which afforded the nucleophilic coupling partner 2-Bpin-3HT (**48**) with good to high yields (72% to 90% at scales up to 12.1 mmol). The Suzuki CC procedure was adapted from an existing literature process with the significant change being the use of sealed vials/pressure vessels instead of reflux, eliminating the need for circulating water. Reactions for both the even and odd-numbered sequences were carried out at various scales for each compound. Overall, yields were good (between 81% to 91%) for both sequences, with the major difference being the short reaction times needed for the even sequence and longer reaction times needed for the odd sequence (3 h vs 19 h). This work resulted in the successful synthesis of **8T**, **9T**, **10T**, **11T**, and **12T** in sufficient quantities, which are compounds not previously synthesized by this method. This has allowed us to confirm the reliability of this methodology for the synthesis of symmetric OTs over a range of reaction scales. Although it could be used at more minor scales, reaction times of at least 1 hour combined with the requirement of a biphasic solvent system, PTC and base make it a less convenient choice, and for such cases we still endorse the use of DCCs. Improvements could be achieved by adapting it for use in a microwave reactor which could reduce the reaction times considerably. Future work on this method would involve synthesizing even longer OTs, as well as testing a variety of di-functionalized cores and mixing and matching heterocycles within the rest of the OT structure, in order to synthesize them at large scales.

2.5 Bromination of Symmetric Oligothiophenes

The final section of the results will cover the bromination conditions used for the preparation of the di-brominated intermediates. Functionalization of the C2 and C5 positions of thiophenes can be achieved by a variety of methods as shown previously. A particularly important method is the dibromination of thiophene monomers and oligomers. In order for an OT to be elongated, it must first be di-brominated at the terminal C5 and C5” positions. One of the most convenient reagents for this transformation is NBS, which is the reagent of choice for this work. This section will cover the method that was used initially for this class of reactions as well as an improved method which results in similar yields but with drastically shorter reaction times.

2.5.1 *Initial Synthetic Method*

Arsenyan and colleagues made the first report of thiophene bromination using NBS and sonication in 2010 where they reported the efficient bromination of thiophene, bithiophene, terthiophene and furan among others in only 10 minutes.[142] This method was then applied by Liu for the synthesis of **DiBr-4T**, **DiBr-6T**, and **DiBr-8T** in the work which served as the precedent for the present research.[65]

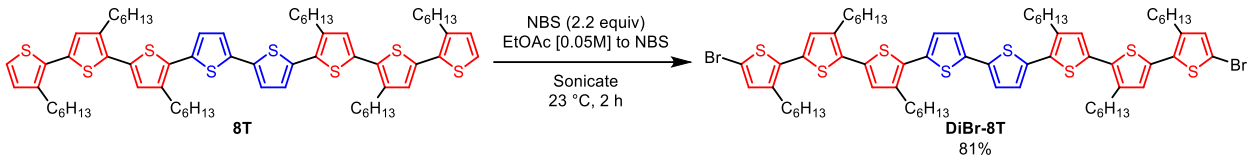


Figure 49: Reported Synthesis of DiBr-8T in Previous Work[65]

Figure 49 shows the reaction conditions in Liu's work for the preparation of **DiBr-8T** using an ultrasonic bath and these conditions were identical for all of the OTs. The conditions call for the dissolution of 0.1 mmol of **8T** in EtOAc (at a concentration of 0.023 M) followed by the addition of NBS (2.2 equivs. at a concentration of 0.05 M). The reaction flask is then wrapped in aluminum foil and sonicated for 1 to 2 hours after which it is worked-up and purified as needed. These conditions provide a convenient method for the efficient dibromination of the OTs so that they can be elongated by CC. As such, this reaction methodology was tentatively used for the synthesis of the needed di-bromo OT intermediates. **Figure 50** contains the reactions for oligomers from both sequences having between 3 and 8 thiophene monomers and **Table 10** contains the reaction data for all di-brominated OTs synthesized using EtOAc as the solvent. It's important to note that this table contains a column for both crude and isolated yields. This is because usually, these reactions are pure enough in their crude state to not require column chromatography. Additionally, all reactions eventually reach completion (confirmed by TLC), with only very small exceptions having yields below 99% while others have a crude yield above 100% which is indicative of byproducts being present. Finally, the last column of the table is a metric that measures the hours of reaction time required by mmol of reaction scale (reaction time divided by reaction scale). This metric was found to be relatively consistent between reactions of the same OT and an upward trend in its value was observed with increasing OT length. It is important to note that all of these reactions, regardless of scale, had a concentration of 0.023 M of OT starting material and 0.05 M of NBS.

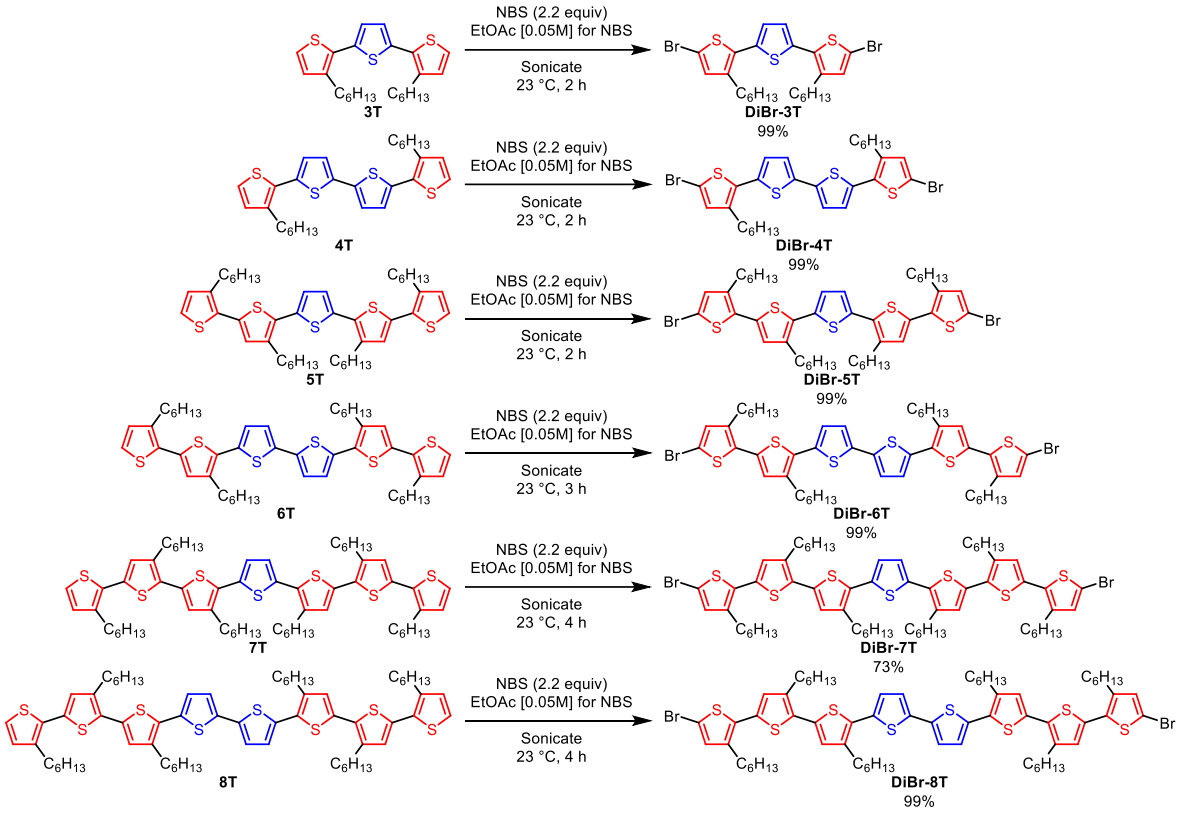
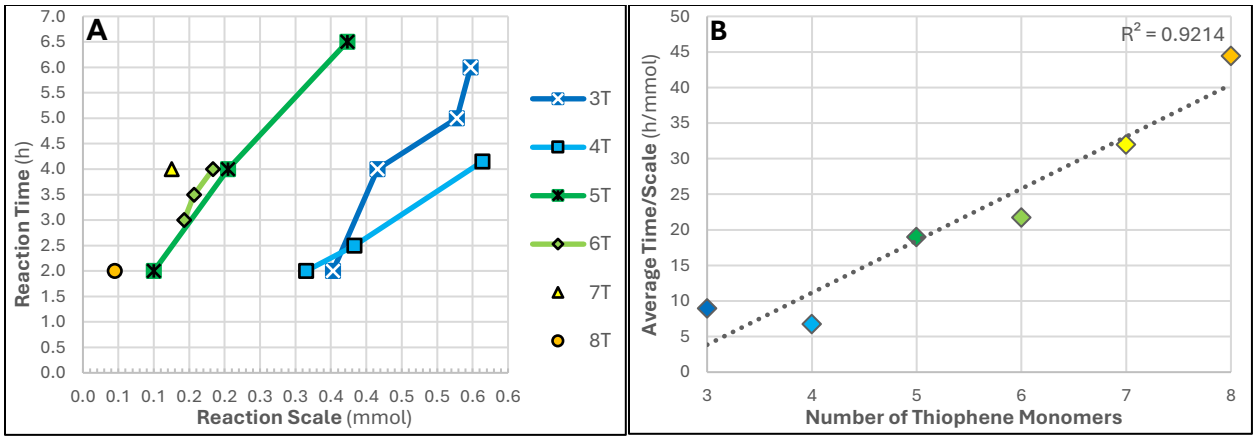


Figure 50: Synthesis of Di-brominated Symmetric OTs Using Sonication and EtOAc as Solvent

Table 10: Reaction Data from the Dibromination of Symmetric OTs Using EtOAc as Solvent at Concentrations of 0.023 M for OT and 0.05 M for NBS

Product	**Scale** (mmol)	**Time** (h)	**Crude Y.** (%)	**Isolated Y.** (%)[b]	**Time/Scale** (h/mmol)
DiBr-3T	0.35	2.0	95	95	5.7
	0.42	4.0	99	99	9.6
	0.53	5.0	100	100	9.5
	0.55	6.0	92	92	11.0
DiBr-4T	0.32	2.0	99	99	6.3
	0.39	2.5	101	81	6.5
	0.56	4.2	100	100	7.4
DiBr-5T	0.10	2.0	99	99	20.0
	0.20	4.0	100	100	19.5
	0.37	6.5	106	68	17.4
DiBr-6T	0.14	3.0	102	63	21.0
	0.16	3.5	105	62	22.3
	0.18	4.0	99	99	21.8
DiBr-7T[a]	0.13	4.0	110	73	32.0
DiBr-8T[a]	0.05	2.0	99	99	44.4

[*a*]: These reactions were carried out multiple times however only the replicates shown in the table had all of the relevant values recorded (time, crude yield, isolated yield) [*b*]: Most reaction have the same crude yield and isolated yield because most reaction crudes are pure enough to use in subsequent steps without purification.



A: Plot of the scale versus reaction time for each individual oligomer starting material. **B**: Reaction time was divided by reaction scale and the obtained ratios averaged and plotted versus the number of thiophene units in each oligomer, for n=7 and n=8 single value was used.

Figure 51: Effects of OT Length and Reaction Scale on Reaction Times at Concentrations of 0.023 M for OT and 0.05 M for NBS

Concerning **DiBr-3T**, its synthesis was carried out at scales between 0.35 mmol to 0.55 mmol. This resulted in a steady increase of reaction time from 2.0 hours to 6.0 hours. All reactions reached completion within the listed time. **DiBr-4T** was synthesized at 0.32 mmol to 0.56 mmol scales, with times also increasing from 2.0 hours to 4.2 hours. One reaction had a crude yield above 100% and ^{1}H NMR showed undesirable side products, therefore it was purified and afforded 81% of isolated yield. An unfortunate problem with these compounds is that a considerable amount of product will be lost if they are purified with too much silica. It is therefore crucial that the least amount of silica be used for their purification, or that the reaction conditions are such that they don't lead to columns being required in the first place. **DiBr-5T** was similarly synthesized between 0.10 mmol and 0.37 mmol scales with the largest scale reaction resulting in a crude yield of 106% and requiring purification which afforded 68% of isolated **DiBr-5T**. **DiBr-6T** was synthesized at a small range of scales between 0.14 mmol and 0.18 mmol. Reactions at 0.14 and 0.16 mmol scales had crude yields of 102% and 105% respectively which resulted in isolated yields of 63% and 62% respectively. **DiBr-7T** was carried out at a scale of 0.13 mmol which resulted in a crude yield of 110% and a purified yield of 73%. Finally, **DiBr-8T** was carried out a scale of 0.05 mmol which resulted in a crude yield of 99% which was pure and thus used without purification. The overall trend observed for these compounds is that whenever the crude mass is over 100% of the expected mass, the crude usually contains side products that can be observed by ^{1}H NMR. We were unable to fully characterize any of them, but we suspect that they are some variants of tri-brominated products.

At a glance, the general trend of these reactions can be observed by looking at the lowest-scale reactions for each oligomer. Looking at the reaction times for **DiBr-3T**, **DiBr-4T** and **DiBr-5T**, reactions requiring 2.0 h decrease in scale as oligomer monomer count increases. The same trend can be tentatively observed for the remaining oligomers as well with **Figure 51** visually illustrating said trend. **Figure 51** contains two plots, *Plot A* displays the individual scales versus reaction times in **Table 10** while *Plot B* contains the average values of the time/scale metrics from **Table 10** plotted versus the number of thiophene monomers. *Plot A* illustrates the seemingly positive correlation between reaction time and reaction scale, particularly for **DiBr-3T**, **DiBr-4T**, **DiBr-5T**, and **DiBr-6T**. Reactions for **DiBr-7T** and **DiBr-8T** were repeated in multiples as well, but precise reaction data was not recorded, therefore only one entry is shown for each. *Plot B* illustrates another trend, which is the seemingly positive correlation between reaction time and OT monomer count. As the OT starting materials get longer, the reaction times also seem to become longer. Another clear illustration of this would be to compare the 0.35 mmol reaction of **DiBr-3T** with the 0.05 mmol reaction of **DiBr-8T**. Both of these reactions took 2.0 hours to complete yet the scale difference is a factor of 7. The linear best-fit for this data has a coefficient of determination (R^2) of 0.92 which does seem to indicate that thiophene monomer count has an effect on the time/scale metric, however we cannot with certainty affirm that the monomer count is solely responsible for this observed trend at this time. As mentioned previously, the concentration of every reaction presented in **Table 10** is the same. Normally, reactions should have the same rates if they are carried out under the same conditions and concentrations at different scales. However, this is not always true and is clearly illustrated *Plot A* although the degree of variation between different reaction scales is considerable. Issues related to scale-up tend to arise when a lab-scale reaction is scaled-up to industrial scales, requiring considerable changes in reaction conditions and vessels/reactors.[181] In the present case, the reaction vessel and instrument (ultrasonic bath) were not changed between scale-ups and reaction scales were still reasonably within the margins of lab-scale procedures. Further investigation would be needed to fully understand the mechanism and kinetics at hand. Aside from the increasing reaction times, this process had another issue, which is that the compounds necessary for the synthesis of **11T** and **12T** were impossible to synthesize through this method. **DiBr-9T** and **DiBr-10T** were not observed even after sonicating **9T** and **10T** under the reaction conditions (2.2 equivs. of NBS in EtOAc at 0.05 M) for more than 7 hours each. This presented a major issue for the present work and the following section discusses how this procedure was modified to afford **DiBr-9T** and **DiBr-10T** as well as drastically decrease reaction times.

2.5.2 *Improved Synthetic Method*

In order to effectively synthesize **DiBr-9T** and **DiBr-10T**, we had to look into modifications of the reaction protocol. The correlation between reaction rate and solvent polarity in reactions involving NBS is well known.[182–184] Moreover, the only reference we found reporting the dibromination of **10T** used a very dilute solution of DMF and NBS stirred for 12 hours,[108] most likely so dilute due to the low solubility of **10T** in DMF. We had also previously made use of a highly polar solvent for the synthesis of the Suzuki nucleophilic partner precursor (refer to **Figure 39** in Section 2.4.1) which resulted in excellent yields. This motivated us to investigate a different solvent system for the bromination protocol.

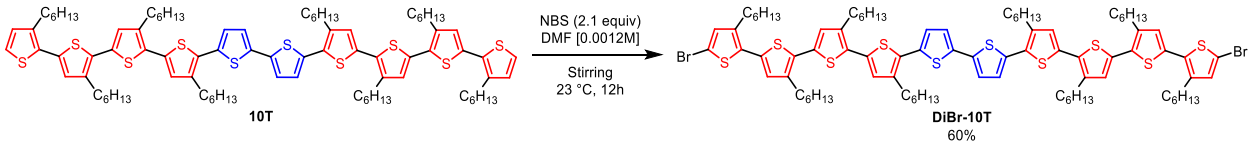


Figure 52: Dibromination of 10T with NBS Stirred in DMF[108]

Our first attempt was to determine if the bromination protocol of **10T** did indeed work as reported. **Figure 52** illustrates the reaction we tested according to the reported procedure.[108] The yield we obtained for **DiBr-10T** was 60% which is in agreement with the reported yield of 64%. Unfortunately, this protocol suffers from several drawbacks. The first issue is the large amount of DMF required to properly solubilize the starting material **10T**. The second issue is the long reaction time of 12 hours, and the final issue is the low yield of 60%. The previous starting materials could all be reacted to completion, which indicated that it should be possible to achieve completion for this reaction as well. Having confirmation that dibromination of **10T** was indeed possible with a more polar solvent, the next step was to find a solvent system that would be more polar than EtOAc but at the same time be able to solubilize the longer oligomers at reasonable concentrations. Initial tests consisted of finding mixtures of EtOAc and DMF that would be able to dissolve the OTs at concentrations of 0.025 M to 0.05 M. This would translate to a concentration of NBS between 0.05 M and 0.1 M which would not deviate too far from the original conditions and allow for a better comparison. **Figure 53** contains the reaction schemes for the synthesis of all the required di-brominated oligomers along with their yields at the largest reaction scale that was tested while **Table 11** contains reaction data for the same reactions. It was found that mixtures of approximately 1:3 of EtOAc/DMF were successful for the dissolution of **3T** to **8T**. For **3T** to **6T** a concentration of 0.05 M of OT was possible while for **7T** and **8T** a more dilute solution of 0.025 M was required. Testing this solvent system for **9T** and **10T** was not successful and resulted in incomplete reactions even after long periods of sonication. As such, the solvent system

was modified with the addition of $CHCl_3$ at a ratio of 1:1.6:0.4 of EtOAc/DMF/$CHCl_3$ which resulted in the dissolution of **9T** and **10T** at concentrations of 0.025 M. The use of these solvent systems resulted in a drastic reduction in reaction time with all reactions reaching completion. All recorded reactions in **Table 11** reached completion in 1.0 hour or less. The largest recorded scale was **DiBr-4T** with a scale of 1.13 mmol which required 0.75 h to complete in stark contrast to the reactions carried out in EtOAc only, which required 2.0 h for a scale of 0.32 mmol (2.6 times longer reaction time for 3.5 times smaller reaction scale). The same trend is observed for the rest of the oligomers, with drastically larger reaction scales requiring drastically less time to reach completion.

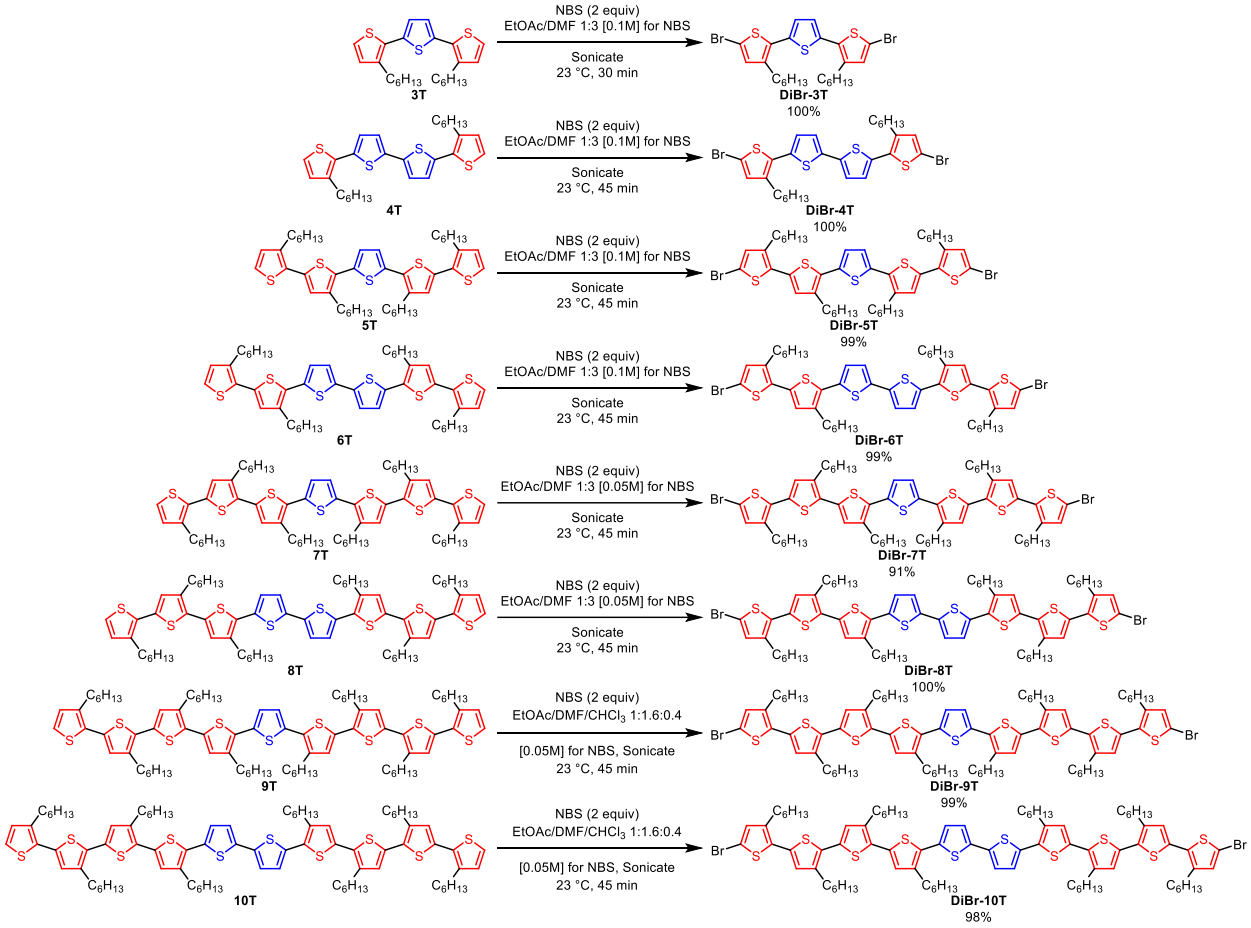


Figure 53: Synthesis of Di-brominated Symmetric OTs Using Sonication and Mixtures of EtOAc, DMF and $CHCl_3$ as Solvents

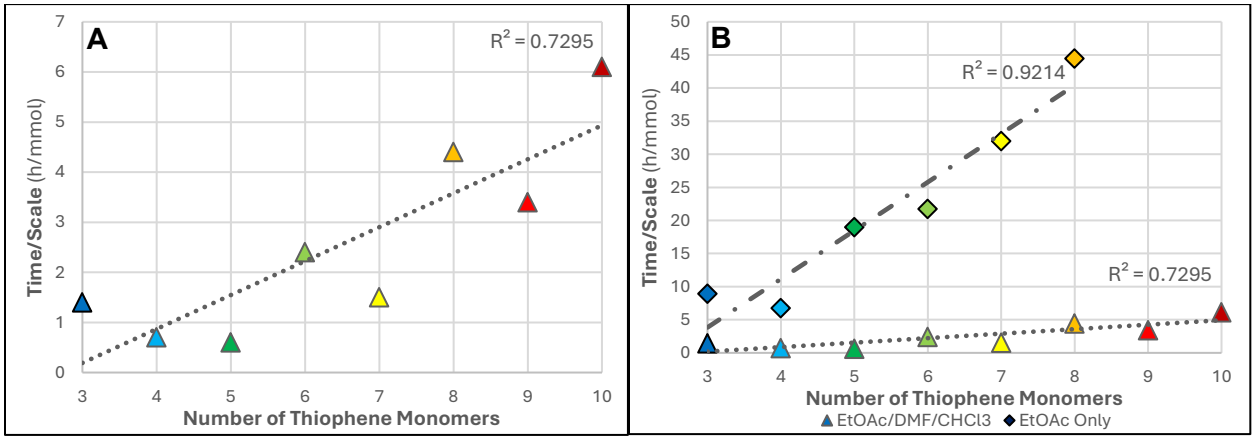
Table 11: Reaction Data from the Dibromination of Symmetric OTs Using EtOAc/DMF/$CHCl_3$ as Solvent

Product	Scale (mmol)	Solvent	Solvent Ratio	Time (h)	Crude Y. (%)[a]	Time/Scale (h/mmol)
DiBr-3T	0.67	EtOAc/DMF	1:3	1.00	100	1.4
DiBr-4T	1.13	EtOAc/DMF	1:3	0.75	100	0.7
DiBr-5T	0.82	EtOAc/DMF	1:3	0.50	99	0.6
DiBr-6T	0.31	EtOAc/DMF	1:3	0.75	99	2.4
DiBr-7T	0.53	EtOAc/DMF	1:3	0.80	91	1.5
DiBr-8T	0.17	EtOAc/DMF	1:3	0.75	100	4.4
DiBr-9T	0.22	EtOAc/DMF/$CHCl_3$	1:1.6:0.4	0.75	99	3.4
DiBr-10T	0.12	EtOAc/DMF/$CHCl_3$	1:1.6:0.4	0.75	98	6.1

[*a*]: Reaction crudes were pure enough to not require purification and they were used as is for CC reactions.

Figure 54 illustrates the trend between the oligomer length and the time/scale metric. *Plot A* shows the data from **Figure 54** for the reactions using mixtures of EtOAc/DMF/$CHCl_3$ as the solvent. *Plot B* contrasts the data from *Plot A* with the data from **Figure 51-*B*** (which contained the plot for the EtOAc solvent system) to serve as a visual comparison aid between the two solvent systems. The trend observed in *Plot A* once again appears to be positive, but the values are considerably more scattered. The values appear to be split up in 4 groups which overall increase in value but decrease within their groups. From n=3 to n=5, we see a downward trend with a jump to n=6 followed by a decrease to n=7 then another jump to n=8 and a slight decrease to n=9 with a final jump to n=10. The value of R^2 is also lower at 0.7295, indicating a much lower certainty in the linearity of this data set. It should be noted that unlike the data for the EtOAc solvent system, this plot is generated from single data points for each OT which makes it difficult to make confident assertions about the nature of this relationship. Additionally, the reactions of **3T** to **6T** were carried out at concentrations of 0.05 M while **7T** to **10T** were at 0.025 M. Furthermore, as evidenced in **Table 11**, the reactions of **9T** and **10T** used a 3-solvent system while all others used the same 2-solvent system. As of now, we can tentatively say that OT monomer count possibly displays the same positive linear correlation between reaction time and OT length for the EtOAc/DMF/$CHCl_3$ solvent system as it does for the EtOAc system. What we are most interested in is the drastic decrease in reaction times for all reactions as well as the efficient synthesis of **DiBr-9T** and **DiBr-10T** which are outcomes made obvious in *Plot B.* The main takeaway is that the reactions using the EtOAc/DMF/$CHCl_3$ solvent systems reach completion much faster than those carried out in only EtOAc. This remains true despite the uncertainty surrounding the nature of *Plot A* as we can just compare the difference between the Time/Scale value for each individual thiophene monomer value n. For n=3, 4, 5 the values in the two plots are separated by factors of 6, 10 and 32 respectively. For n=6, 7 the factors are 9 and 21 respectively and for n=8 the factor is 10. On

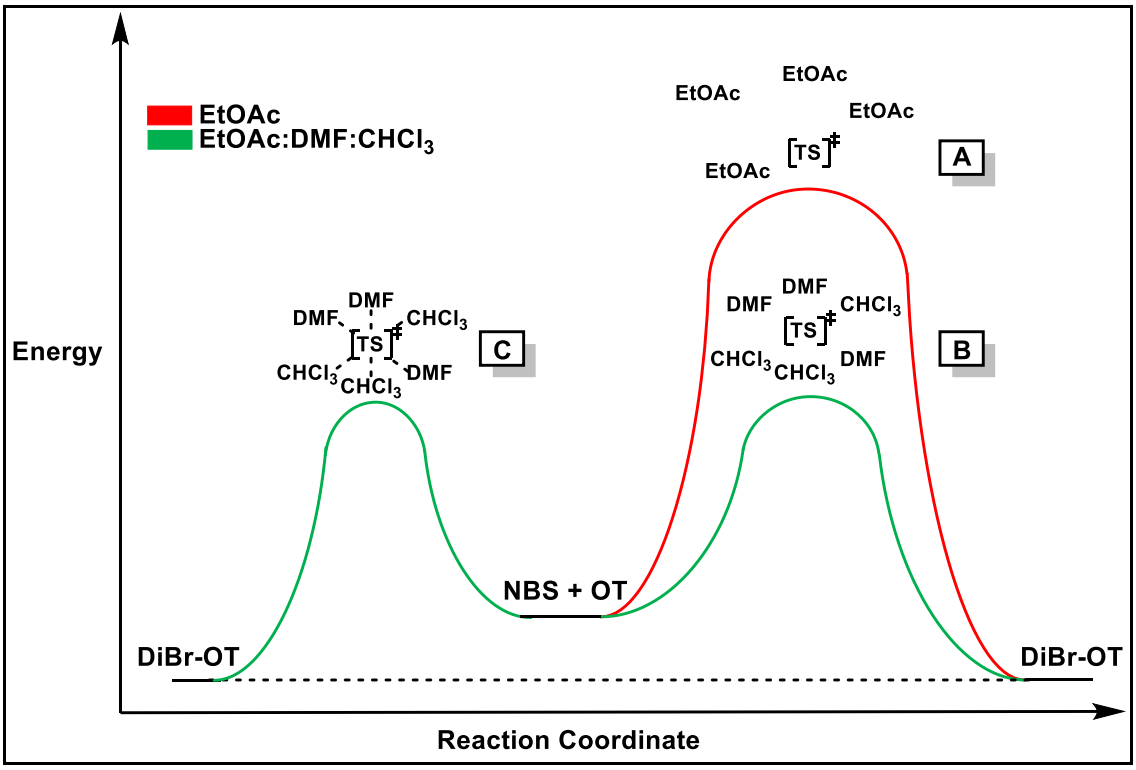
average, reactions carried out in the EtOAc/DMF/$CHCl_3$ solvent systems appear to have a Time/Scale metric that is lower by a factor of 15 which can be interpreted as reaction times being shortened by a factor of 15.



A: Plot of time/scale versus monomer count for each individual oligomer starting material using EtOAc/DMF/$CHCl_3$ mixtures as solvent. **B**: Plot comparing the time/scale vs monomer count of EtOAc/DMF/$CHCl_3$ solvent from **A** and EtOAc only solvent from **Figure 51-B**.

Figure 54: Effects of OT Length and Reaction Scale on Reaction Times Using EtOAc/DMF/$CHCl_3$ Mixtures as Solvents

Reactions involving NBS can occur through two mechanisms, with one process involving radicals and the other being the electrophilic bromination of aromatic compounds.[183] The mechanism involved in the bromination of the OTs is the electrophilic bromination process which proceeds through an S_EAr. The classic mechanism for S_EAr was proposed to proceed through an initial π-complex which rearranges into a σ-complex, also known as a Wheland intermediate. The σ-complex has a positive charge within in the aromatic ring as a result of the aromatic ring attacking the electrophilic species in the reaction media.[185,186] Generally, formation of the σ-complex is the rate-limiting step but sometimes it can also be the formation of the electrophilic species.[187–189] Concerning thiophenes, a DFT analysis of the mechanism of NBS dibromination of 3,4-ethylenedioxythiophene has been published recently as well.[190] Four possible mechanisms are presented with the most likely mechanism being an interaction between NBS and the thiophene while the minor process would incorporate Br_2 and HBr which would be generated in situ.[190] To our knowledge, no in-depth investigation on the effect increasing OT length has on bromination rates has been carried out, which leaves us to hypothesize on the probable causes of some of the observed reaction behaviors.



This graph represents a theoretical potential energy diagram for three possible scenarios of OT bromination. **A**: Theoretical energy profile of reaction with poorly dissolved TS. **B**: Theoretical energy profile of reaction with a well-dissolved TS. **C**: Theoretical energy profile of reaction where solvent directly participates in TS.

Figure 55: Theoretical Potential Energy Diagram of OT Bromination Reactions in Different Solvents

First, we will address the considerable decrease of reaction times when solvent polarity is increased. **Figure 55** illustrates a theoretical energy diagram of the bromination reaction in the two different solvent systems. Changes in reaction rate resulting from changes in reaction solvent are due to solvent effects.[191] Depending on the reaction, solvents can allow for better diffusion of reactants, or they can create a favorable electrostatic environment for the transition state which would lower the activation energy.[191] *Path A* in **Figure 55** illustrates the TS of the reaction carried out in EtOAc. The solvent does not properly dissolve the TS, resulting in higher activation energy. *Path B* on the other hand represents the result of the solvent properly dissolving the TS. Through favorable electrostatic interactions, the TS is stabilized, and the activation energy is lowered. Solvent molecules could also participate in the transition state, effectively modifying the reaction's mechanism and unlocking a different lower energy path towards products.[191] *Path C* represents this possibility. Since the solvent molecules directly participate in the mechanism, the reaction takes a different path. Once again, this results in a lower energy of activation compared to the solvent that does not participate in the mechanism or does not properly dissolve the TS (*Path A* in our case). In the case of electrophilic bromination of aromatic rings, solvent effects on reaction

rate and selectivity are well documented.[182–184,192,193] Recent research into the subject has determined that electrophilic halogenations using X_2/HX systems in non-polar media proceed through mechanisms that do not involve a σ-complex.[185,188,194] Instead, these reactions proceed through a concerted process or an addition-elimination process and a σ-complex becomes favorable only when solvent polarity is increased.[185,188,194] DFT calculations of phenyl σ-complexes in different solvents determined that $\Delta G^{\ddagger}_{\sigma\text{-cpx}}$ decreases with increasing dielectric constant ε of the reaction media.[188] With both solvent systems used for the bromination of OTs being relatively polar, it would be reasonable to conclude that the mechanism involves a σ-complex. Decrease in reaction time with increase in solvent polarity is also an indicator that the rate-limiting TS is more polar than the reactants, serving as further evidence for the involvement of a σ-complex.[195] The polar solvent molecules are able to stabilize the polar σ-complex through favorable electrostatic interactions and they could possibly even participate in the mechanism at some point. The increased polarity of the solvent could also have an effect on the reactivity of NBS by polarizing the N-Br bond and making it weaker, thus more prone to breaking.[183] This can be further exploited through the addition of acids which would protonate the oxygens and possibly even the nitrogen, drastically withdrawing electron density from the N-Br bond and promoting the buildup of positive charge on bromine.[196] However, for the bromination of the OTs, acids were not used so as to not risk degradation of the starting materials as we feared that sonication might promote unwanted side reactions. Overall, we think that the difference in reaction times between the two solvent systems used for OT dibromination is due to the favorable interactions that the polar solvent molecules have with the polar rate-limiting transition state.

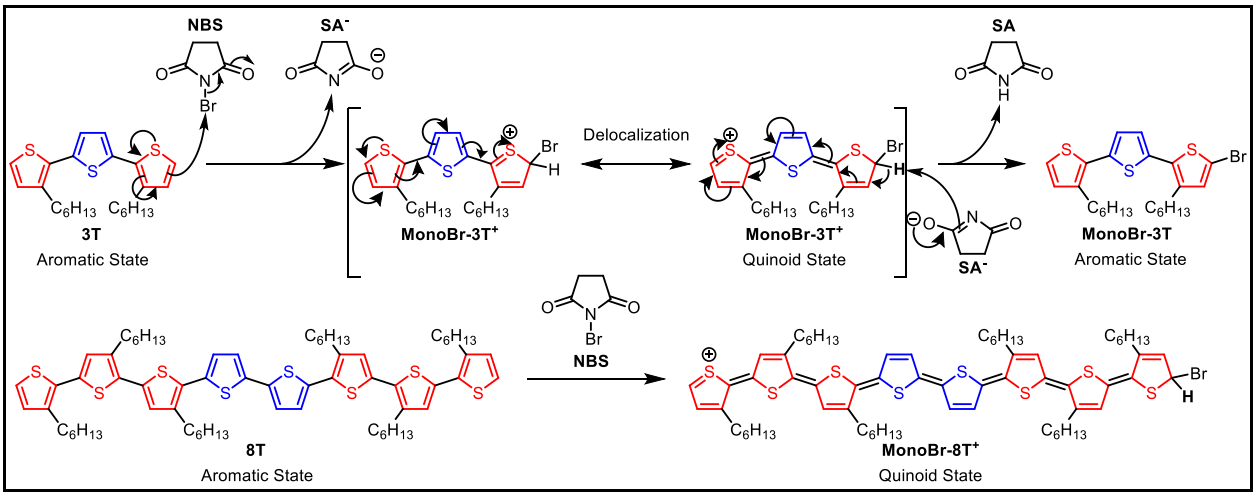


Figure 56: Mechanism of Mono-Bromination of OTs

Next, we will address the differences in reaction times between individual OTs in the same solvent. This difference is most likely a result of the increased conjugation of their backbones. Previous work on S_EAr reactions has established that the activation energy of the reaction decreases with increasing electron density at the reacting carbon.[197,198] The activation energy for the bromination by Br_2 of 3-methylthiophene is about half that of thiophene (4.8 kcal/mol vs 8.5 kcal/mol respectively) due to the inductive effect of the methyl adjacent to C2.[197] This is in agreement with our results for the C2-functionalization of 3-hexylthiophene (Section 2.3.1 and Section 2.4.1) where we observed higher nucleophilicity at C2. Considering this fact, it is possible that the electron density at the terminal positions of the OTs decreases as their length increases due to increased delocalization towards the center. Electron density from the terminal positions could be delocalized towards the center of the oligomer, resulting in a decrease of nucleophilicity at the reactive positions. If this is indeed the case, formation of the σ-complex would become more difficult as the π-system grows. Delocalization towards the center could also be slightly favored by the absence of C3/C4 substituents on the central thiophenes, making them slightly electron deficient relative to the 3-hexylated thiophenes. DFT calculations would be helpful in determining if such a trend does indeed exist as they could provide theoretical values for the electron densities across the oligomer. Another more likely explanation for the difference in reactivity would be obtained by applying the same theory to the σ-complex. **Figure 56** illustrates the proposed mechanism of mono-bromination of the OTs. The first step is the formation of the σ-complex **MonoBr-3T$^+$**. The step right after its formation is the deprotonation of the hydrogen at the reactive position which reforms the double bond, returning to neutrality and yielding **MonoBr-3T**. It is possible that once the σ-complex forms, the positive charge delocalizes throughout the π-system, making the σ-complex much more stable. When **3T** acquires a positive charge, it adopts a quinoid state, making it highly planar and restricting rotation between individual thiophene monomers. As the OT becomes longer (**8T** for example), the positive charge is delocalized even further (**MonoBr-8T$^+$**), decreasing the acidity of the hydrogen relative to shorter OTs. Polymers synthesized through oxidative polymerization have been observed to become considerably less reactive as they grow.[199,200] In these cases, a radical cation forms and chain growth occurs through a reaction at the terminal carbons. As the polymers grow, the cationic character at the terminal positions decreases due to it being delocalized throughout a large π-system.[199,200] Generally, the formation of the σ-complex is the rate-limiting step in S_EAr reactions and the deprotonation is a very quick step. However, as previously mentioned, DFT calculations on the mechanism of dibromination of 3,4-ethylenedioxythiophene suggest that the rate-limiting step is indeed the deprotonation.[190] This hypothesis could be tested by determining if these reactions exhibit a

kinetic isotope effect. OTs could be terminally deuterated and submitted through the dibromination reaction conditions. If deprotonation is indeed the rate-limiting step, then a variation in reaction rate will be observed for the deuterated starting material relative to the hydrogenated OT. To summarize, a possible cause for the difference in reaction times between oligomers within the same solvent system could be due to the increase in conjugation as the OTs get longer. Higher degrees of delocalization of electron density and positive charge could increase the energetic requirement for the formation of the σ-complex or the deprotonation. Further experiments would be required in order to determine the exact cause of the observed behaviors.

2.5.3 *Conclusion*

The present subchapter contained the outcomes the reactions carried out for the synthesis of the di-brominated OTs required for the CC reactions. Previously reported literature conditions were used for the synthesis of **DiBr-3T**, **DiBr-4T**, **DiBr-5T**, **DiBr-6T**, **DiBr-7T** and **DiBr-8T** (scales between 0.56 mmol and 0.05 mmol). These conditions consisted of sonicating a mixture of OT and 2.1 equivs. of NBS in EtOAc. Reactions generally reach completion and crude products can be used without purification with some exceptions requiring column chromatography which results in lower yields. However, reaction times would vary with reaction scale even though reactant concentrations were identical. A Time/Scale metric was used to compare the reactions by adjusting for scale and increasing reaction times were observed relative to OT length. Moreover, the literature method was unsuccessful at producing **DiBr-9T** and **DiBr-10T** which were crucial for the synthesis of the final products (**11T** and **12T**). To address this issue, the reaction was carried out in a more polar solvent system consisting of 1:3 EtOAc/DMF for oligomers **3T** to **8T** and 1:1.6:0.4 EtOAc/DMF/$CHCl_3$ for **9T** and **10T**. These more polar solvent systems resulted in complete conversions with reaction times decreased on average by a factor of 15. Dibrominations of **3T** to **8T** in these polar solvents were successfully carried out at much larger scales (1.13 mmol to 0.17 mmol) compared to those in the EtOAc solvent system. Additionally, **DiBr-9T** and **DiBr-10T** were synthesized successfully in excellent yields (99% and 98% respectively) and at scales of 0.22 mmol and 0.12 mmol respectively. The suspected cause of the reduced reaction times and successful synthesis of **DiBr-9T** and **DiBr-10T** is the polar nature of the rate-limiting transition state. Said transition state is either the formation of a σ-complex or the subsequent deprotonation. Further experimentation is required to establish the precise mechanism of this particular reaction. DFT calculations combined with carrying out the reactions with deuterated OTs would allow for a better understanding of the mechanism and the nature of the rate-limiting step.

Chapter 3 – General Conclusions and Future Work

The overarching objective of this project was to carry out the synthesis of two sequences of symmetric oligothiophenes based on 3-hexylthiophene so that they can be used to study the effect of oligothiophene length on their doping mechanism. The specific objective of this thesis was to carry out their synthesis using decarboxylative cross-coupling and Suzuki cross-coupling. The objective was achieved and two sequences of symmetric oligothiophenes were synthesized using the two methodologies. Comparing the two methodologies allowed us to determine the advantages and limitations of each method. Decarboxylative cross-couplings are favored when small scales and quick reaction times are desired as they are complete following 8 minutes of microware irradiation. Suzuki cross-couplings are favored when larger reaction scales are needed and long reaction times of multiple hours are not a deterrent. Moreover, an improved method for the dibromination of the relevant oligothiophenes was established which drastically reduced reaction times and resulted in the efficient synthesis of dibrominated oligomers that were impossible to synthesize using the literature procedure. To our knowledge, using the described methodologies, we were able to synthesize four previously unreported compounds (**DiBr-7T**, **DiBr-9T**, **9T**, **11T**).

Future work based on this project is multifaceted (**Figure 57**). Regarding the applications of decarboxylative cross-coupling, multi-solvent systems could be tested in an attempt to improve the yield of **7T**. If successful, the multi-solvent system could be used to synthesize the rest of the odd sequence using DCC (**A**). Furthermore, different aromatic or heteroaromatic cores could be used to quickly synthesize various short oligomers. Using electron-rich cores such as 3,4-ethylenedioxythiophene, A-D-A oligomers could be synthesized (**B**). Alternatively, cross-couplings using alternating nucleophilic coupling partners could be carried out to synthesize symmetric heterogeneous oligomers (**C**). A variety of heteroaromatics could be incorporated, such as thiazoles, oxazoles, furans and pyrroles (**98**). The effect of these different monomers on absorbance, emission, doping behavior and solubility could be studied. Based on these initial results, elongation of the desired oligomers could be done using Suzuki cross-couplings which excel at larger scales and longer oligomer structures. Additionally, using the oligothiophenes described in this thesis, push-pull systems could be synthesized through terminal group functionalization using electron poor and electron rich functional groups (**D**). These compounds would allow for the determination of the effects that whole-molecule dipoles would have on doping behavior. In terms of the Suzuki cross-coupling methodology, the process could be adapted for use in a microwave reactor. The solvent-free synthesis of oligothiophenes using microwave

irradiation has previously been reported[103] although only boronic acids of 3-methyl thiophene and thiophene were used with the longest oligomer having 8 monomers. Boronic esters do not react under microwave conditions, thus 3-hexylthiophene-2-boronic acid (**99**) could be used as the nucleophilic partner. This could result in a considerably faster Suzuki-based synthetic process for the synthesis of the relevant OTs. Another possible path to explore would be the application of desulfinative cross-coupling for the synthesis of the symmetric OTs (**F**). We could synthesize 2-SO_2Li-3HT (**100**) using 2-Li-3HT and quenching it with a source of SO_2 gas (such as DABSO). It could be used to determine adequate conditions for cross-coupling, resulting in a novel synthetic route towards symmetric OTs. Finally, the dibromination of the OTs could be studied in order to elucidate its exact mechanism. DFT calculations of the starting materials and products along with intermediates and transition states could serve as a starting point for this project. The exact rates, rate constants and reaction orders could be determined by measuring the absorbance of aliquots taken over time by UV-Vis spectrophotometry. Finally, deuterating the OT starting materials and measuring their bromination rate would determine if the deprotonation is indeed the rate-limiting step (**G**).

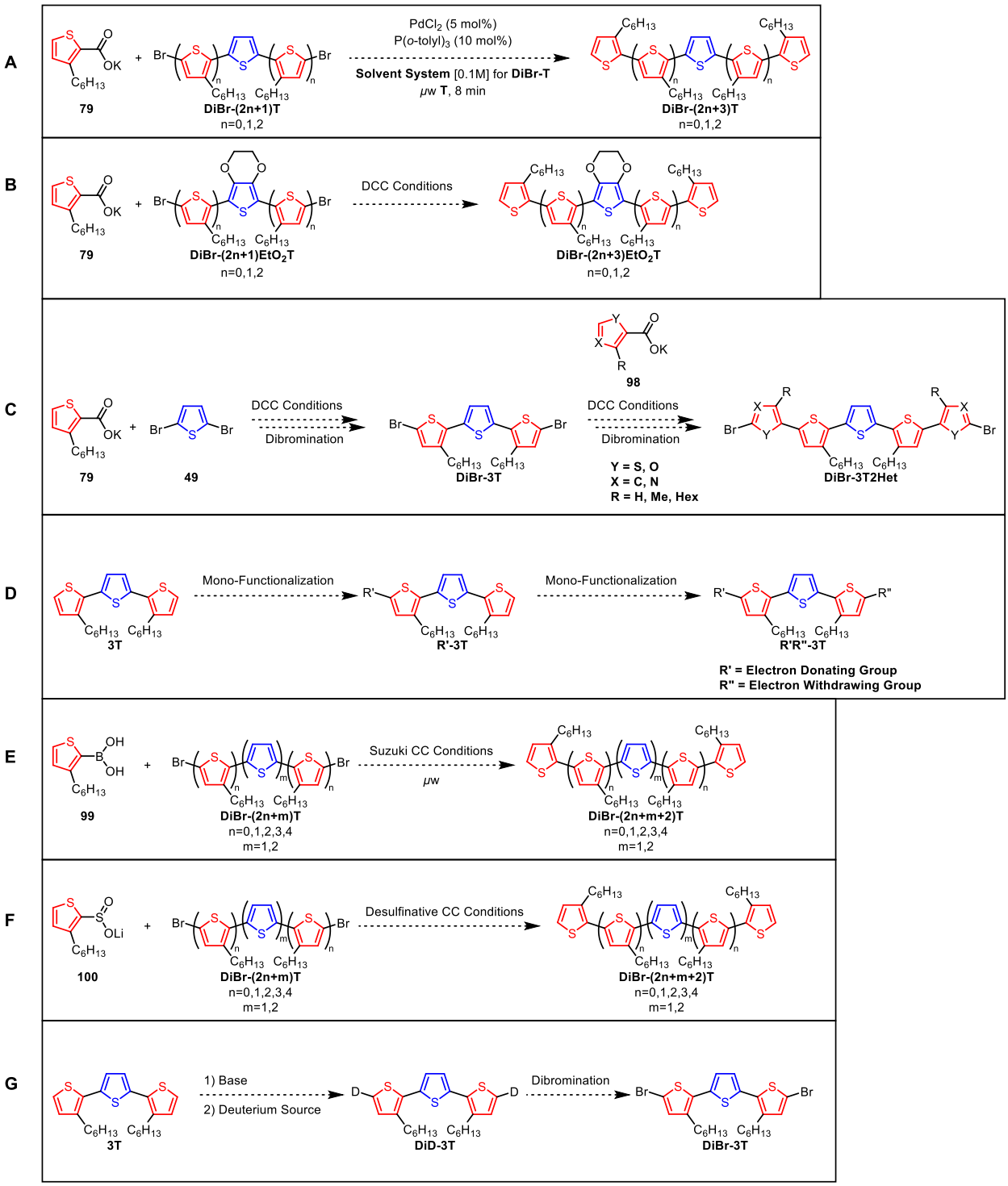


Figure 57: Reaction Schemes of Possible Future Work

Chapter 4 – Experimental

4.1 **Reagents and Instruments**

All reactions were carried out in 25 mL to 250 mL round-bottom glass flasks or 5.0 mL and 20 mL glass microwave vials along with 40 mL thick-walled glass pressure vessels. Whenever inert atmosphere was needed, argon was supplied directly into a flask before it is sealed from a tank or balloon when required during the rection process. All oligomer products were protected from prolonged exposure to light by wrapping their vials they were stored in with aluminium foil to prevent unwanted degradation. For long-term storage, samples were sealed under argon in their vials and stored in a closed box in -24 °C freezers.

The main starting materials 3-hexylthiophene (**32**) and 2,5-dibromothiophene (**49**) were purchased from AK Scientific, 5,5'-dibromo-2,2'-bithiophene (**31**) was purchased from Ark Pharma and their purities confirmed by ^{1}H NMR and GCMS prior to use. TMPMgCl·LiCl 1.0 M in THF/toluene and *n*-BuLi 2.5 M in THF were purchased from Sigma-Aldrich. All organic solvents were purchased from Sigma-Aldrich and Fisher ACP as ACS grade. Anhydrous THF and 2-MeTHF were prepared by flushing a volume of 500 mL through a column with a 1” radius filled to a height of 3” with activated basic alumina (Sigma-Aldrich, Brockmann I, pH 9.5±0.5, 150 mesh, 58Å) with argon directly into a flame-dried flask loaded with activated 3 Å molecular sieves (Sigma-Aldrich, 4-8 mesh). Titration using diphenylacetic acid was done prior to every reaction involving *n*-BuLi. Diphenylacetic acid was dissolved in the anhydrous THF and *n*-BuLi was added dropwise until solution turned light yellow. All other anhydrous solvents were prepared in oven-dried Schlenk flasks under argon by storing them over activated 3 Å molecular sieves for at least 4 days. Distilled water was obtained from an in-house distillery and saturated $NaHCO_3$ and NaCl solutions were prepared using the same distilled water. The sodium salts NaOH, NaCl, $NaClO_2$ and $NaHCO_3$ were purchased from Sigma-Aldrich and NaH_2PO_4 was purchased from American Chemicals. The potassium salts KOAc and K_2CO_3 were purchased from Sigma-Aldrich, KOPiv was purchased from AK Scientific and KO*t*-Bu was purchased from Honeywell Fluka. KOAc, KOPiv and KO*t*-Bu were stored in a desiccator under vacuum and dried in a vacuum oven prior to use. Hydrogen peroxide was purchased from Sigma-Aldrich as a 30% w/w solution in water and stored in a refrigerator at 4 °C. The catalysts $PdCl_2$, $Pd(OAc)_2$, $PdCl_2$(dppf) and $Pd(PPh_3)_4$ were purchased from AK Scientific, $Pd[P(t\text{-}Bu)_3]_2$ was purchased from Fischer Scientific and $[PdCl(C_3H_5)]_2$ was purchased from Sigma-Aldrich. The phosphine ligands dppb and $PCy_3{\cdot}HBF_4$ were purchased from Sigma-Aldrich and $P(o\text{-tolyl})_3$ was purchased from AK Scientific. The air-

stable catalysts and ligands $PdCl_2$, $Pd(OAc)_2$, $PdCl_2$(dppf), dppb, $PCy_3 \cdot HBF_4$ and P(*o*-tolyl)$_3$ were stored in a desiccator under vacuum at room temperature. The air/moisture sensitive catalysts $Pd(PPh_3)_4$, Pd[P(*t*-Bu)$_3$]$_2$ and $[PdCl(C_3H_5)]_2$ were stored in airtight desiccated bags in a -20 °C freezer with small quantities transferred to bottles which were used for reactions in order to avoid needless exposure of the original bottles to air and moisture. The catalyst $PdCl(C_3H_5)$(dppb) was prepared in-house from $[PdCl(C_3H_5)]_2$ and dppb following a previously published procedure.[100] The reagents $POCl_3$ and NBS were purchased from Sigma-Aldrich. Aliquat 336 (tricaprylmethylammonium chloride), B_2Pin_2 and *i*-PrOBpin were purchased from AK scientific and $H_2NOH \cdot HCl$ was purchased from Sigma-Aldrich.

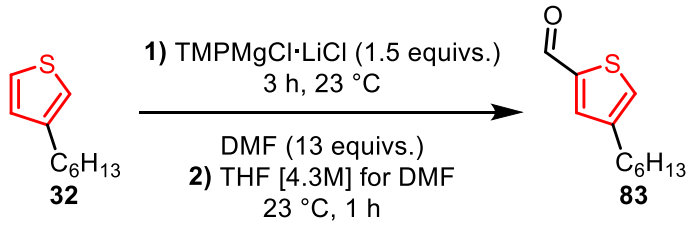
Thermal reactions were carried out using a silicon oil bath heated on a stirrer-hotplate with a temperature probe and separate standalone thermometer in order to accurately confirm temperature. Microwave-assisted reactions were carried out using the Biotage Initiator™ + with Robot Eight (400 W magnetron) with 5.0 mL and 20 mL microwave vials. Compounds were purified using column chromatography on silica gel (SiliCycle® SiliaFlash® F60, 40 – 63 μm, 60Å) combined with thin-layer chromatography (TLC) when noted (SiliCycle® SiliaPlate® TLC Plates, Aluminum-Backed, Silica, 200 μm, 20 x 20 cm). GCMS spectra were acquired on an Agilent 7890A GC system and Agilent 5975C VL MSD with Triple–Axis Detector MS with a HP–588 column coated with (5%–phenyl)–methylpolysiloxane and FID using helium as carrier gas. Samples were dissolved either in DCM or MeOH. ^{1}H NMR spectra were obtained on a Varian VNMRS-500 with a 500 MHz probe and Bruker-300 with a 300 MHz probe. ^{13}C NMR spectra were obtained on a Varian VNMRS-500 with a 125 MHz probe. Deuterated solvent $CDCl_3$+0.05% (v/v) TMS was purchased from Cambridge Istotope Laboratories and $CDCl_3$ without TMS was purchased from Sigma-Aldrich. ^{1}H NMR yields measured using trimethoxybenzene (TMB) as an internal standard. High resolution mass spectrometry (HRMS) data was collected using a LC-TOF ESI mass spectrometer operated in positive ion mode. Samples were dissolved in a solution of 2:1 DCM/MeOH at a concentration of 100 μM.

4.2 Experimental Procedures

4.2.1 *CH-Activation Reaction Procedures*

4.2.1.1 Monomer Reaction Procedures

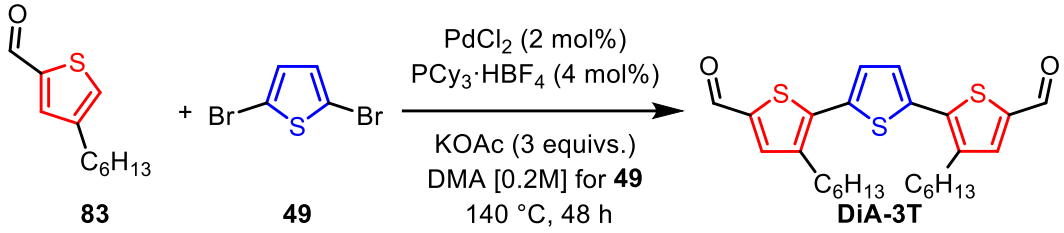
4-Hexylthiophene-2-Carbaldehyde (**83**)



To a flame-dried, 250 mL round-bottom flask with stirbar, TMPMgCl·LiCl in 1.0 M THF/toluene (21.9 mL, 21.9 mmol, 1.5 equivs.) is added first followed by dropwise addition of neat 3-hexylthiophene (**32**) (2.62 mL, 2.45 g, 14.6 mmol, 1.0 equiv.) under an argon atmosphere. The mixture is stirred at 23 °C for 3 h at which point a 4.3 M solution of DMF (66.6 mL, 62.9 mmol, 13 equivs.) in THF (44.1 mL) is added and the reaction stirred further for 1 h. Next, the reaction is quenched with 1.0 M HCl (29.2 mL, 2.0 equivs.) and poured into a mixture of Et_2O/H_2O and the phases separated. The aqueous phase is extracted with 2x Et_2O, the combined organic phases washed with brine, dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure to yield a reddish oil. The crude is purified using column chromatography using silica with a solvent ratio of 95:5 hexanes/EtOAc (Rf=0.32) to afford 4-hexylthiophene-2-carbaldehyde (**83**) as a light-yellow oil Yield=2.35 g (**82%**). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.87 (d, *J* = 1.2 Hz, 1H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.37 (s, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.62 (p, *J* = 8.0 Hz, 2H), 1.38 – 1.26 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.01, 144.74, 143.55, 137.15, 130.40, 31.55, 30.34, 30.10, 28.79, 22.53, 14.03. **HRMS** (TOF ESI+) Calcd. for C11H17OS $[M+H]^+$: 197.0995; found m/z 197.0994.

4.2.1.2 Di-Formyl Trimer General Reaction Procedure

3,3''-Dihexyl-[2,2':5',2''-Terthiophene]-5,5''-Dicarbaldehyde (**DiA-3T**)



83 **49** **DiA-3T**

KOAc (3 equivs.), $PdCl_2$ (2 mol%), $PCy_3{\cdot}HBF_4$ (4 mol%), 2,5-dibromothiophene (**49**) (1 equiv.) and 4-hexylthiophene-2-carbaldehyde (**83**) (3 equivs.) and DMF ([0.2M] for 2,5-dibromothiophene) are added to an oven-dried microwave vial with stirbar. The vial is flushed with argon, sealed and heated in a silicon-oil bath at 140 °C for 48 h with vigorous stirring. Once time has elapsed, the vial is allowed to cool to room temperature, after which a known mass of TMB is added to it after which it is poured into a mixture of EtOAc/water. The organic phase is separated and washed with 2x sat. $NaHCO_3$, 2x brine, 2x dH_2O and 1x brine. The organic phase is separated and dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. An ^1H NMR spectrum is then recorded in $CDCl_3$. The yield was calculated using the TMB peak at 6.09 ppm integrated to 3.00 and all defined product peaks integrated, and an average yield calculated based on their values. Average ^1H NMR yield for this reaction was calculated at 28%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.85 (s, 2H), 7.62 (s, 2H), 7.28 (s, 2H), 2.83 (t, *J* = 7.7 Hz, 4H), 1.75 – 1.66 (m, 4H), 1.46 – 1.37 (m, 4H), 1.37 – 1.30 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 6H). ^1H NMR of this compound was only recorded at 300 MHz. The spectrum was compared to reported values in the references listed below to confirm its identity, as such no ^{13}C NMR or HRMS were recorded either.

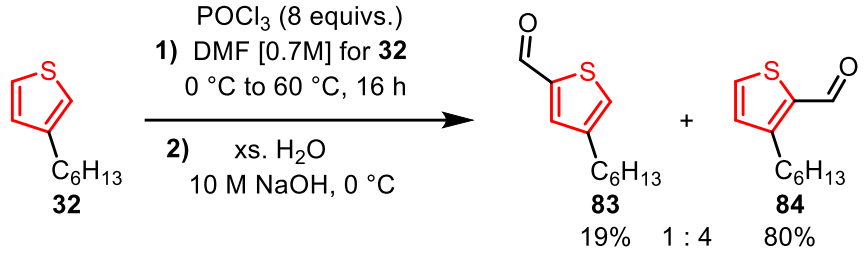
Olinga, T.; Destri, S.; Porzio, W.; Selva, A. *Macromol. Chem. Phys.* **1997**, *198*, 1091–1107. DOI:10.1002/macp.1997.021980413.

Pasini, M.; Vercelli, B.; Zotti, G.; Berlin, A. *Electrochim. Acta* **2016**, *193*, 261–267. DOI:10.1016/j.electacta.2016.02.035.

4.2.2 *DCC Reaction Procedures*

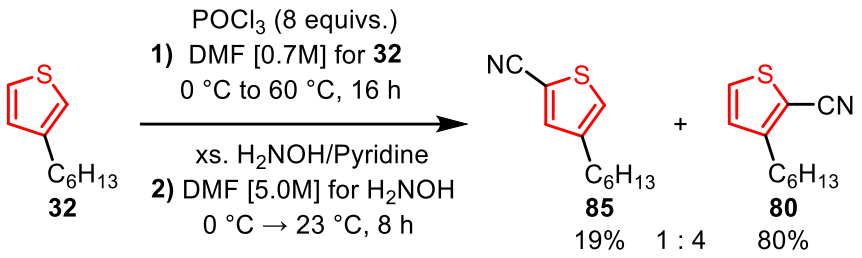
4.2.2.1 Monomer Reaction Procedures

3-Hexylthiophene-2-Carbaldehyde (**84**)



To a flame-dried 250 mL round-bottom flask with stir-bar, 3-hexylthiophene (6.58 mL, 6.156 g, 36.6 mmol, 1 equiv.) is added followed by DMF (51 mL, 18.1 equivs., [0.7 M] to 3-hexylthiophene). The mixture is stirred in an ice-water bath and an addition funnel is clamped above the mouth of the flask, leaving a small opening for gas to escape. The addition funnel is loaded with $POCl_3$ (16.4 mL, 292. 6 mmol, 8 equivs.) and added dropwise to DMF solution with strong stirring. A white cloud forms and dissipates at which point the addition is sped up. Once addition is complete, the mixture is stirred for 5 minutes, removed from the ice-water bath, sealed with a septum and heated at 60 °C in an oil bath overnight (18 h). A large beaker (500 mL) with ice and distilled water (200 mL) is prepared, once the reaction is done, it is very slowly poured into the beaker along with the stir-bar. The mixture is stirred at slow to medium rate and more ice is added slowly to prevent vigorous boiling. Next, 2M NaOH is very slowly added (great care should be taken here as the mixture could easily boil over) followed by 10M NaOH until pH reaches 7. During addition of NaOH, the mixture sometimes coagulates and becomes difficult to stir, this is remedied by adding more distilled water. The neutralized mixture is then poured in a 1 L separatory funnel and is extracted with 3x Et_2O, organics are combined and washed with 1x dH_2O then 1x brine. Organics are separated and dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude oil is filtered through a silica plug using ethyl acetate, evaporated again and left overnight under high vacuum. Product is used as is without further purification. Yield=7.135 g (**99%**), dark red/brown oil. The product should be a mixture of 1:4 3-hexylthiophene-4-carbaldehyde (**83**-C5 isomer) to 3-hexylthiophene-2-carbaldehyde (**84**-C2 isomer). They can easily be differentiated by NMR using the signals of the hydrogens of the methylene carbon adjacent to the thiophene (2.96 ppm for **84** and 2.64 ppm for **83**).

3-Hexylthiophene-2-Carbonitrile (**80**)

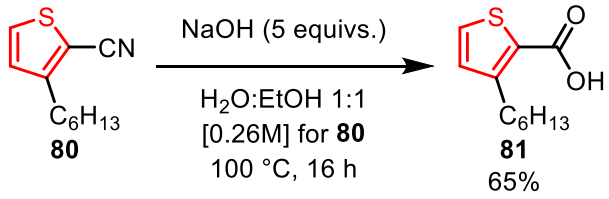


1) To a flame dried, two-neck, 250 mL round bottom flask with stir-bar, 3-hexylthiophene (5.34 mL, 5.00 g, 29.7 mmol, 1 equiv.) is added followed by DMF (42.4 mL, 18.5 equivs., [0.7 M] to 3-hexylthiophene). The mixture is stirred in an ice-water bath and a bubbler filled with silicon oil is attached to the secondary neck. Next, an addition funnel is clamped to the main neck and loaded with $POCl_3$ (22.2 mL, 8 equivs.) which is added dropwise slowly with strong stirring. A white cloud forms and dissipates at which point the addition is sped up. Once addition is completed, the mixture is stirred for 5 minutes, removed from the ice-water bath, both necks are sealed with septa and heated at 60 °C in an oil bath overnight (18 h). Once heating is done, the flask is taken off the oil bath and allowed to cool to room temperature (24 °C). In the meantime, an ice-water bath is prepared on top of a stir plate.

2) Once the flask reaches room temperature, it is placed in the ice-water bath and stirred. In a dried 50 mL round-bottom flask, $H_2NOH{\cdot}HCl$ (20.6 g, 297 mmol, 10 equivs.) is added, the flask is flushed with argon and sealed with a septum. Next, pyridine (24.0 mL, 297 mmol, 10 equivs.) is added slowly stirring by hand and sonicating, followed by DMF (66.7 mL, [4.5 M] to hydroxylamine). The solution is mixed and sonicated until all solids are dissolved. A bubbler is attached to the secondary neck of the reaction flask and the hydroxylamine solution is added very slowly (take great care to add slowly) dropwise using a syringe and needle. Once addition is done, the flask is taken out of the ice-water bath and stirred at room temperature for 8 h. Following that, the reaction mixture is transferred to a bigger flask or beaker (500 mL) and stirred. Ice is slowly added to the mixture while stirring vigorously. Next, sat. $NaHCO_3$ is added very slowly added until bubbling stops and pH is 7 (addition is done really slowly to prevent the solution from boiling over). The mixture is then poured in a separatory funnel and extracted with 3x EtOAc. Organics are combined, washed with 1x dH_2O, 3x 1M HCl and 2x brine. Organics are dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude oil is filtered through a silica plug using ethyl acetate, evaporated again and dried overnight under high vacuum. Product is used as is without further purification. Yield=5.67 g (**99%**), yellow to brown oil.

The product should be a mixture of 1:4 4-hexylthiophene-2-carbonitrile (**85**-C5 isomer) to 3-hexylthiophene-2-carbonitrile (**80**-C2 isomer). They can easily be differentiated by NMR using the signals of the hydrogens of the methylene carbon adjacent to the thiophene (2.79 ppm for **80** and 2.61 ppm for **85**).

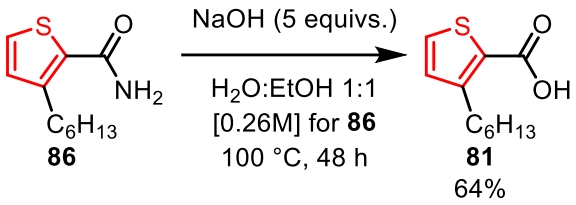
3-Hexylthiophene-2-Carboxylic Acid (**81**)



To a 250 mL round-bottom flask with stir-bar containing 1:1 H_2O:EtOH (98 mL), NaOH (5.17 g, 13 mmol, 5 equivs.) is added and dissolved while stirring. The mixture of nitrile starting material (1:4 **85:80**, 5.0 g, 26.0 mmol, 1 equiv.) is added to the solution and refluxed in an oil bath at 100 °C for 16 h. Once the heating period is done, the majority of the solvent is evaporated under reduced pressure. Enough water should remain to keep everything dissolved after which the contents of the flask are transferred to a separatory funnel (if too much water evaporates, a small amount can be added to dissolve the contents). The aqueous solution was then rinsed with hexanes. The hexanes was dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure to yield byproduct **86** (average yield of 14%) which is stored for future use. The remaining aqueous solution was acidified to pH 2 with 1M HCl. This aqueous solution was then extracted with 3x EtOAc, the organics were combined and washed with 1x brine then dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude mixture should be a yellow oil which is then purified using column chromatography on silica gel using a solvent gradient increase from hexanes to 95:5 hexanes/EtOAc. The 2-carboxylic acid (**81**) and 5-carboxylic acid (not shown) byproduct elute very close to each other with an Rf between 0.1 to 0.15 in 9:1 hexanes/EtOAc. Therefore, the gradient should be very gradual, a 2" diameter column with 500 mL reservoir is recommended and very gentle pressure should be applied. First 2 CV of hexane should be eluted, followed by 4 CV of 99:1 hexanes/EtOAc, 3 CV of 98:2 hexanes/EtOAc, 3 CV 97:3 hexanes/EtOAc and 2 CV of each subsequent increment until the product is eluted. The desired product **81** should elute first followed by some coelution with the 5-carboxylic acid byproduct. Pure product **81** appears as a clear to light yellow oil that slowly solidifies over time into a white solid. Yield=3.46 g (**60%**, average yield of 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 5.0 Hz, 1H), 6.99 (d, *J* = 5.0 Hz, 1H), 3.02 (t, *J* = 7.9 Hz, 2H), 1.63 (p,

J = 7.5 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.34 – 1.25 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.32, 153.22, 131.80, 130.99, 125.84, 31.63, 30.39, 29.72, 29.15, 22.58, 14.08. **HRMS** (TOF ESI+) Calcd. for $C_{11}H_{17}O_2S$ $[M+H]^+$: 213.0944; found m/z 213.0941.

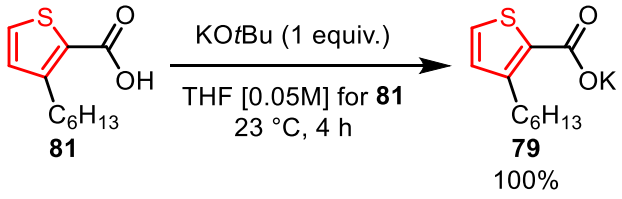
This reaction also produces 3-hexylthiophene-2-carboxamide (**86**) as a byproduct. This product is easily isolated in hexanes during workup and can be pooled over multiple reactions. It can then be subjected to the same reaction conditions but for 48 h to obtain some more of the desired product **81**. All steps for this reaction are identical as described above.



Analytical data for compound **86**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 5.0 Hz, 1H), 6.96 (d, *J* = 5.0 Hz, 1H), 5.59 (s, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.38 – 1.28 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 130.95, 127.14, 31.64, 30.53, 29.55, 29.18, 22.59, 14.07. **HRMS** (TOF ESI+) Calcd. for $C_{11}H_{18}NOS$ $[M+H]^+$: 212.1104; found m/z 212.1103.

Potassium 3-Hexylthiophene-2-Carboxylate (**79**)

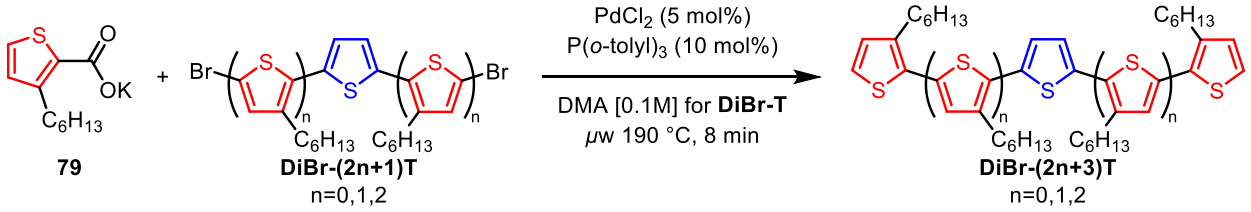


To a flame-dried, 250 mL round-bottom flask with a stirbar, 3-hexylthiophene-2-carboxylic acid (**81**) (1.5 g, 7.07 mmol, 1 equiv.) is added under a gentle stream of argon. The flask is sealed with a septum and anhydrous THF (141 mL, [0.05M] to thiophene) is added followed by dropwise KO*t*Bu (7.07 mL, 0.79 g, 7.07 mmol, 1 equiv., 1M solution in THF). The mixture was stirred at 23 °C for 4 hours. Once done, the stirbar is removed and the solvent is evaporated under reduced pressure until a white solid appears. The flask can be left to dry under high vacuum overnight. If the contents appear like an oil or transparent solid-like mass, anhydrous acetone can be added to it and it can be evaporated under reduced pressure again (this helps get rid of any residual

*t*BuOH). The product should be a white solid. Store under argon in anhydrous conditions, product is highly hygroscopic. Yield=1.763 g (**100%**)

4.2.2.2 Oligothiophene Reaction Procedures

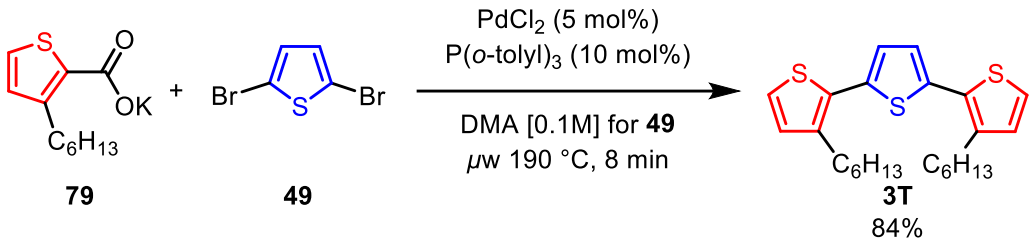
Decarboxylative Cross-Coupling General Reaction Procedure



Each individual oligomer has a solvent system that should be used for column chromatography with silica gel. The solvent system is set such that the target compound has an Rf of ~0.3. A 1.5" diameter, 10" length column filled at about 80% with dry silica is recommended at the reported scales. The difficulty/simplicity of separation depends on the byproduct profile of each individual reaction which tends to vary depending on starting material purity, reaction time and temperature. The products are also light sensitive, so avoid exposing them unnecessarily to light for prolonged periods.

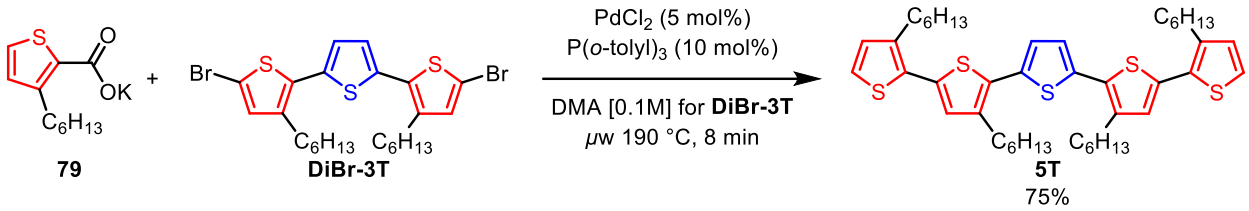
To a flame-dried, 5 mL microwave vial with a stirbar, potassium 3-hexylthiophene-2-carboxylate (**79**) (2.2 equivs.), dibrominated thiophene (1 equiv.), palladium (II) chloride (0.05 equiv.), Tri(o-tolyl)phosphine (0.1 equiv.) and anhydrous DMA ([0.1M] to dibrominated starting material) were added in that order. The vial was capped with a septum and the mixture was pre-stirred for 45 seconds at 23 °C and submitted to microwave heating at 190 °C for 8 min with stirring at the very high absorption setting. Once complete, mixture was allowed to cool to 23 °C and diluted with EtOAc then poured into separatory funnel. Organic layer was washed with 3x brine, 1x saturated $NaHCO_3$, 3x dH_2O and 1x brine. The aqueous phases were combined and extracted with EtOAc. The organic phases were combined and dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel and respective solvent system depending on which product is being synthesized.

3,3”-Dihexyl-2,2’:5’,2”-Terthiophene (**3T**)



The Decarboxylative Cross-Coupling General Reaction Procedure was followed using potassium 3-hexylthiophene-2-carboxylate (**79**) (82.0 mg, 0.33 mmol, 2.2 equivs.), 2,5-dibromothiophene (**49**) (16.8 µL, 36.0 mg, 0.15 mmol, 1 equiv.), $PdCl_2$ (1.3 mg, 0.0074 mmol, 0.05 equiv.), Tri(o-tolyl)phosphine (4.5 mg, 0.015 mmol, 0.1 equiv.) and DMA (1.5 mL, [0.1M] to dibrominated starting material) to give **3T** as a light yellow oil. Yield=52.1 mg (**84%**) Column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.2 Hz, 2H), 7.05 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.78 (t, *J* = 7.9 Hz, 4H), 1.65 (p, *J* = 7.4 Hz, 4H), 1.42 – 1.34 (m, 4H), 1.34 – 1.27 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.69, 136.02, 130.37, 130.05, 126.04, 123.72, 31.67, 30.72, 29.28, 29.24, 22.62, 14.08. **HRMS** (TOF ESI+) Calcd. for $C_{24}H_{33}S_3$ $[M+H]^+$: 417.1739; found m/z 417.1736.

3,3’”,3””,4’-Tetrahexyl-2,2’:5’,2”:5”,2”’:5”’,2””-Quinquethiophene (**5T**)



The Decarboxylative Cross-Coupling General Reaction Procedure was followed using potassium 3-hexylthiophene-2-carboxylate (**79**) (82.6 mg, 0.33 mmol, 2.2 equivs.), **DiBr-3T** (86.1 mg, 0.15 mmol, 1 equiv.), $PdCl_2$ (1.3 mg, 0.007 mmol, 0.05 equiv.), Tri(o-tolyl)phosphine (4.6 mg, 0.015 mmol, 0.1 equiv.) and DMA (1.5 mL, [0.1M] to dibrominated starting material) to give **5T** as a golden oil. Yield=84.2 mg (**75%**). Column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.09 (s, 2H), 6.95 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.83 – 2.75 (m, 8H), 1.73 – 1.62 (m, 8H), 1.46 – 1.36 (m, 8H), 1.36 – 1.29 (m, 16H), 0.94 – 0.83 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.86, 139.66, 135.72, 134.25, 130.44, 130.22, 130.09, 128.75, 125.90, 123.62, 31.69, 31.66, 30.65, 30.58, 29.45, 29.28, 29.26, 29.22, 22.63, 22.62, 14.10. **HRMS** (TOF ESI+) Calcd. for $C_{44}H_{60}S_5$ $[M]^+$: 748.3293; found m/z 748.3286.

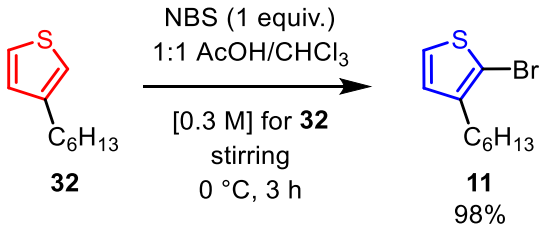
3,3"",3"""",3""""",4',4"-Hexahexyl-2,2':5',2":5",2"':5"',2"":5"",2""':5""',2""":5""",2"""-Septithiophene (**7T**)

The Decarboxylative Cross-Coupling General Reaction Procedure was followed using potassium 3-hexylthiophene-2-carboxylate (**79**) (55.1 mg, 0.22 mmol, 2.2 equivs.), **DiBr-5T** (90.7 mg, 0.10 mmol, 1 equiv.), $PdCl_2$ (0.9 mg, 0.005 mmol, 0.05 equiv.), Tri(o-tolyl)phosphine (3.0 mg, 0.01 mmol, 0.1 equiv.) and DMA (1.0 mL, [0.1M] to dibrominated starting material) to give **7T** as an orange oil that eventually solidifies. Yield=65.9 mg (**61%**). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 5.2 Hz, 2H), 7.10 (s, 2H), 6.98 (s, 2H), 6.94 (s, 2H), 6.93 (d, *J* = 5.2 Hz, 2H), 2.83 – 2.75 (m, 12H), 1.74 – 1.62 (m, 12H), 1.46 – 1.37 (m, 12H), 1.37 – 1.30 (m, 24H), 0.93 – 0.86 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.94, 139.83, 139.63, 135.73, 134.11, 133.94, 130.49, 130.29, 130.26, 130.10, 128.76, 128.57, 125.91, 123.59, 31.69, 31.67, 31.67, 30.64, 30.58, 30.52, 29.47, 29.43, 29.28, 29.24, 29.22, 22.63, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{64}H_{88}S_7$ $[M]^+$: 1080.4925; found m/z 1080.4914.

4.2.3 *Suzuki Reaction Procedures*

4.2.3.1 Monomer Reaction Procedures

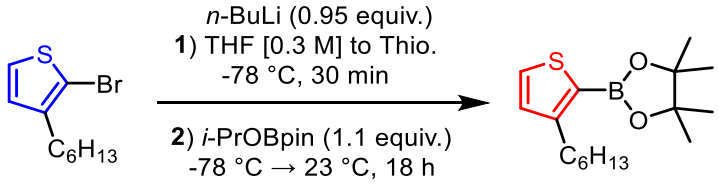
2-Bromo-3-Hexylthiophene (**11**)



To a 100 mL round-bottom flask with stir-bar, 3-hexylthiophene (3.16 mL, 3.160 g, 18.8 mmol, 1 equiv.) and a mixture of AcOH:$CHCl_3$ (1:1, 58.6 mL, [0.3 M] to 3-hexylthiophene). The flask is wrapped in aluminum foil, cooled on an ice-water bath and NBS (3.342 g, 18.8 mmol, 1 equiv.) is added slowly after which the flask is sealed with a septum. The mixture was stirred for 3 hours and progress was followed by TLC using hexanes as elution solvent (Rf=0.88). Once no more starting material is observed, the mixture is poured in a 125 mL separatory funnel and extracted with 3x hexanes. Organics are combined and washed with 3x distilled water, sat. $NaHCO_3$ and brine. The organic phase was then dried over anhydrous Na_2SO_4, filtered through a cotton plug

and evaporated under reduced pressure to yield a yellow/red oil. This oil was purified through a small silica plug using hexanes as elution solvent. The red colored contaminants should remain at the top and after eluting a small amount of hexanes, subsequent eluent is spotted on a TLC plate and illuminated with a short-wave (254 nm) lamp to determine the presence of product. Once eluent no longer spots on TLC, collection is stopped, hexanes is evaporated to dryness and the product left overnight under high vacuum. The product is a clear to light-yellow oil. Yield=4.51 g (**97%**). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.6 Hz, 1H), 6.79 (d, *J* = 5.6 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.57 (p, *J* = 8.1 Hz, 2H), 1.37 – 1.27 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.96, 128.22, 125.11, 108.77, 31.61, 29.69, 29.38, 28.88, 22.59, 14.08. **HRMS** (TOF ESI+) Calcd. for $C_{10}H_{15}{}^{79}BrS$ $[M]^+$: 246.0072; mass not detected.

2-(3-Hexylthiophen-2-yl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane (**48**)



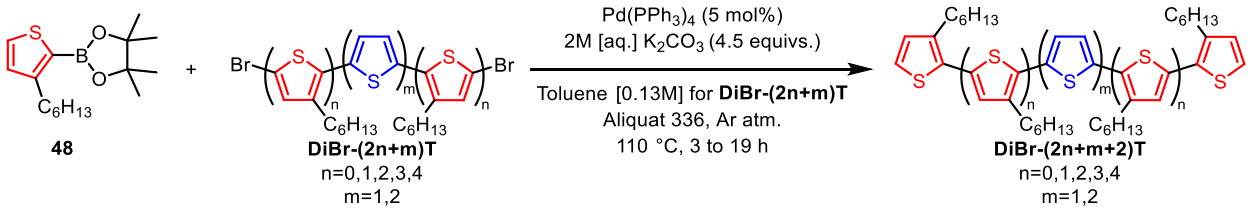
Anhydrous THF is prepared in-house by running THF through a short column of activated basic alumina (Brockmann I) and flushing with argon into a container full of freshly activated 3Å sieves. Before the reaction is started, the THF and *n*-BuLi solution are titrated using diphenylacetic acid to confirm *n*-BuLi concentration and account for water content in THF. Depending on the scale, this reaction is carried out in microwave vials or round-bottom flasks.

A flame-dried 100 mL round bottom flask with stir-bar, flushed with Argon and sealed with septum is filled with THF (33 mL, [0.3 M] to 2-bromo-3-hexylthiophene). The flask is cooled to -78 °C using an acetone/dry-ice bath. Once cooled, a freshly titrated 2.5 M *n*-BuLi (3.66 mL, 9.6 mmol, 0.95 equiv.) is added dropwise to the THF while stirring and the mixture is allowed to cool once again. Once the mixture reaches -78 °C (the acetone stops bubbling vigorously), 2-bromo-3-hexylthiophene (2.00 mL, 2.50 g, 10.1 mmol, 1 equiv.) is added dropwise very slowly over the course of 30 minutes while vigorously stirring. The mixture is stirred for 30 min to 1 hour at -78 °C after which, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.27 mL, 2.07 g, 11.1 mmol, 1.1 equiv.) is added dropwise. The mixture is allowed to heat up to room temperature while stirring overnight (18 h). Once complete, the reaction is quenched using distilled water, poured into a 250 mL separatory funnel and extracted with 2x EtOAc. Organics are pooled and washed with distilled water, followed by brine, dried over anhydrous Na_2SO_4 and filtered through a cotton plug. The

organic phase is evaporated under reduced pressure to yield a light brown oil. The crude was purified using column chromatography on silica gel with a solvent system of 6:4 Hexane:DCM (Rf=0.4) using a 1.5" diameter column with 400 mL of dry silica (14" height). This procedure yielded 2.69 g (**90%**) of clear to faint yellow oil which is the product. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 4.7 Hz, 1H), 7.01 (d, *J* = 4.7 Hz, 1H), 2.88 (t, *J* = 7.7 Hz, 2H), 1.58 (p, *J* = 7.6 Hz, 2H), 1.33 (s, 12H), 1.32 – 1.27 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.69, 131.25, 130.27, 83.49, 31.74, 31.64, 30.08, 28.93, 24.76, 22.60, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{16}H_{28}BO_2S$ $[M+H]^+$: 295.1898; found m/z 295.1896.

4.2.3.2 Oligothiophene Reaction Procedures

Suzuki Cross-Coupling General Reaction Procedure

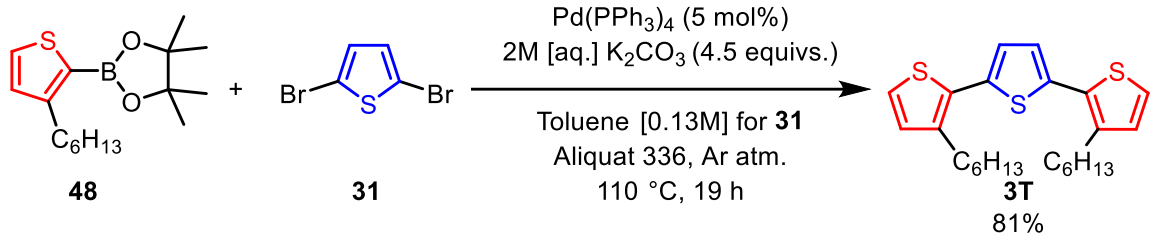


Reaction progress can be monitored using TLC (read note below for information about solvent) although this is limited by the presence of the septum. Therefore, TLC aliquots should be taken only near the listed reaction times for each oligomer. Refer to **Figure 43** and **Figure 46** for examples of expected TLC appearance. Each individual oligomer has a solvent system that should be used for column chromatography with silica gel. The solvent system is set such that the target compound has an Rf of ~0.3. A 1.5" diameter, 12" length column filled at about 80% with dry silica is recommended at the reported scales. The difficulty/simplicity of separation depends on the byproduct profile of each individual reaction which tends to vary depending on starting material purity, reaction time and temperature. The products are also light sensitive, so avoid exposing them unnecessarily to light for prolonged periods.

To a 5-20 mL microwave vial or 40 mL pressure vessel with a stirbar, K_2CO_3 (4.5 equivs.) was added followed by distilled H_2O ([2.0M] to K_2CO_3) and stirred until all solids were dissolved. This was followed by the addition of 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (2.1 equivs.), dibrominated starting material (1.0 equiv.), toluene ([0.13M] to dibrominated starting material) and 1 drop of Aliquat 336. The mixture was degassed using an argon balloon and needle while being sonicated for 5-10 minutes. Once degassed, $Pd(PPh_3)_4$ (0.05 equiv.) was added quickly, taking care to expose it to air as little as possible. The flask was flushed with argon, sealed and heated in an oil bath at 110 °C for 3.0-19.0 h depending on substrate. Reaction

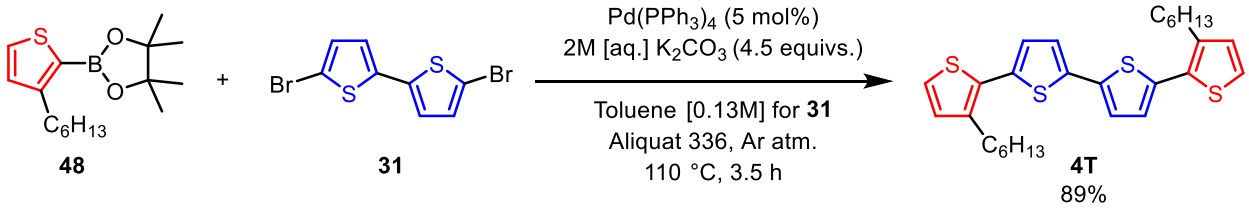
progress was followed by TLC if using a septum with the appropriate solvent system according to substrate. Once complete, mixture was allowed to cool to 23 °C and diluted with H_2O. Mixture was poured into separatory funnel, and aqueous phase was extracted with 2x DCM. Combined organic phases were washed with 1x dH_2O, 1x brine then dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel and respective solvent system depending on which product is being synthesized.

3,3''-Dihexyl-2,2':5',2''-Terthiophene (**3T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (863 µL, 848.0 mg, 2.88 mmol, 2.1 equivs.), 2,5-dibromothiophene (155 µL, 332.0 mg, 1.37 mmol, 1 equiv.), K_2CO_3 (853.5 mg, 6.18 mmol, 4.5 equivs), dH_2O (3.09 mL, [2.0M] to K_2CO_3), toluene (10.6 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (79.3 mg, 0.08 mmol, 0.05 equiv.) to give **3T** as a light yellow oil. Yield=463.4 mg (**81%**). Column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.2 Hz, 2H), 7.05 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.78 (t, *J* = 7.9 Hz, 4H), 1.65 (p, *J* = 7.4 Hz, 4H), 1.42 – 1.34 (m, 4H), 1.34 – 1.27 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.69, 136.02, 130.37, 130.05, 126.04, 123.72, 31.67, 30.72, 29.28, 29.24, 22.62, 14.08. **HRMS** (TOF ESI+) Calcd. for $C_{24}H_{33}S_3$ $[M+H]^+$: 417.1739; found m/z 417.1736.

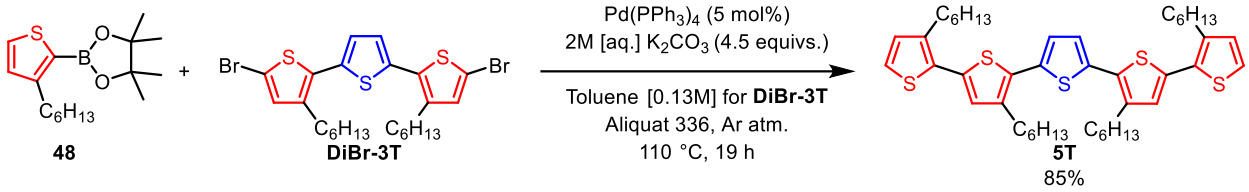
3,3'''-Dihexyl-2,2':5',2'':5'',2'''-Quaterthiophene (**4T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (776 µL, 762.8 mg, 2.59 mmol, 2.1 equivs.),

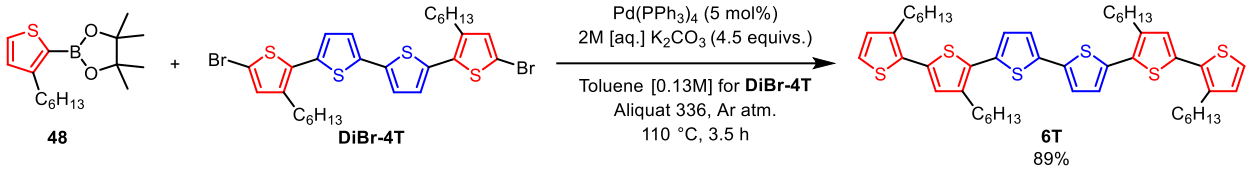
5,5'-dibromo-2,2'-bithiophene (400.0 mg, 1.23 mmol, 1 equiv.), K_2CO_3 (767.7 mg, 5.55 mmol, 4.5 equivs), dH_2O (2.78 mL, [2.0M] to K_2CO_3), toluene (9.5 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (71.3 mg, 0.06 mmol, 0.05 equiv.) to give **4T** as a gold/faint green oil that quickly solidifies but melts again upon handling. Yield=546.4 mg (**89%**). Column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.1 Hz, 2H), 7.13 (d, *J* = 3.7 Hz, 2H), 7.02 (d, *J* = 3.8 Hz, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 4H), 1.65 (p, *J* = 7.6 Hz, 4H), 1.38 (p, *J* = 7.1 Hz, 4H), 1.35 – 1.27 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.85, 136.76, 135.28, 130.28, 130.08, 126.50, 123.84, 123.80, 31.65, 30.63, 29.27, 29.20, 22.61, 14.09. **HRMS** (TOF ESI+) Calcd. for $C_{28}H_{34}S_4$ $[M]^+$: 498.1538; found m/z 498.1535.

3,3‴,3⁗,4'-Tetrahexyl-2,2':5',2":5",2‴:5‴,2⁗-Quinquethiophene (**5T**)



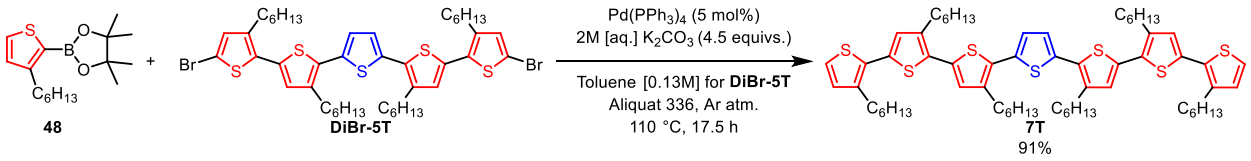
The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (683 µL, 671.4 mg, 2.28 mmol, 2.1 equivs.), **DiBr-3T** (624.2 mg, 1.09 mmol, 1 equiv.), K_2CO_3 (675.8 mg, 4.89 mmol, 4.5 equivs), dH_2O (2.44 mL, [2.0M] to K_2CO_3), toluene (8.4 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (62.8 mg, 0.05 mmol, 0.05 equiv.) to give **5T** as a golden oil. Yield=694.2 mg (**85%**). Column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.09 (s, 2H), 6.95 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.83 – 2.75 (m, 8H), 1.73 – 1.62 (m, 8H), 1.46 – 1.36 (m, 8H), 1.36 – 1.29 (m, 16H), 0.94 – 0.83 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.86, 139.66, 135.72, 134.25, 130.44, 130.22, 130.09, 128.75, 125.90, 123.62, 31.69, 31.66, 30.65, 30.58, 29.45, 29.28, 29.26, 29.22, 22.63, 22.62, 14.10. **HRMS** (TOF ESI+) Calcd. for $C_{44}H_{60}S_5$ $[M]^+$: 748.3293; found m/z 748.3286.

3,3'''',3''''',4'-Tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-Sexithiophene (**6T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (316 µL, 310.6 mg, 1.06 mmol, 2.1 equivs.), **DiBr-4T** (330.0 mg, 0.5 mmol, 1 equiv.), K_2CO_3 (312.6 mg, 2.26 mmol, 4.5 equivs), dH_2O (1.13 mL, [2.0M] to K_2CO_3), toluene (3.9 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (29.0 mg, 0.03 mmol, 0.05 equiv.) to give **6T** as a red/orange oil that solidifies over a long time. Yield=370.0 mg (**89%**). Column chromatography solvent: 94:6 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.15 (d, *J* = 3.7 Hz, 2H), 7.05 (d, *J* = 3.8 Hz, 2H), 6.95 (s, 2H), 6.93 (d, *J* = 5.2 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 8H), 1.73 – 1.61 (m, 8H), 1.45 – 1.36 (m, 8H), 1.36 – 1.30 (m, 16H), 0.93 – 0.86 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.00, 139.70, 136.70, 135.01, 134.34, 130.39, 130.13, 130.11, 128.74, 126.31, 123.88, 123.66, 31.66, 30.65, 30.49, 29.42, 29.29, 29.22, 22.62, 14.10. **HRMS** (TOF ESI+) Calcd. for $C_{48}H_{62}S_6$ $[M]^+$: 830.3170; found m/z 830.3163.

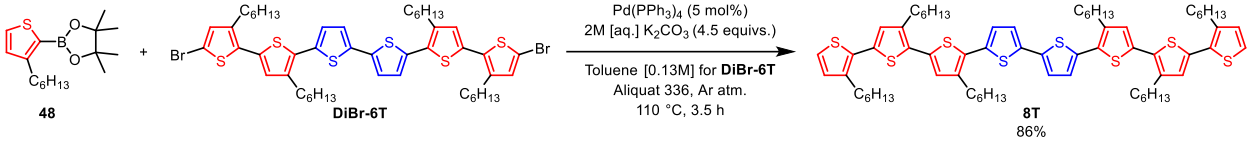
3,3'''',3''''',3'''''',4',4''-Hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-Septithiophene (**7T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (366 µL, 359.5 mg, 1.22 mmol, 2.1 equivs.), **DiBr-5T** (527.7 mg, 0.58 mmol, 1 equiv.), K_2CO_3 (361.8 mg, 2.62 mmol, 4.5 equivs), dH_2O (1.31 mL, [2.0M] to K_2CO_3), toluene (4.5 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (33.6 mg, 0.03 mmol, 0.05 equiv.) to give **7T** as a red/orange oil that quickly solidifies over time. Yield=572.0 mg (**91%**). Column chromatography solvent: 95:5 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 5.2 Hz, 2H), 7.10 (s, 2H), 6.98 (s, 2H), 6.94 (s, 2H), 6.93 (d, *J* = 5.2 Hz, 2H), 2.83 – 2.75 (m, 12H), 1.74 – 1.62 (m, 12H), 1.46 – 1.37 (m, 12H), 1.37 – 1.30 (m, 24H), 0.93 – 0.86 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.94, 139.83, 139.63, 135.73, 134.11, 133.94, 130.49, 130.29, 130.26, 130.10, 128.76, 128.57, 125.91, 123.59, 31.69, 31.67,

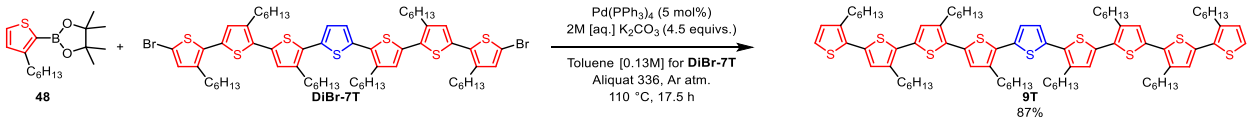
31.67, 30.64, 30.58, 30.52, 29.47, 29.43, 29.28, 29.24, 29.22, 22.63, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{64}H_{88}S_7$ $[M]^+$: 1080.4925; found m/z 1080.4914.

3,3''',3''''',3''''''',4',4''-Hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5''''''-Octithiophene (**8T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (124 µL, 122.2 mg, 0.42 mmol, 2.1 equivs.), **DiBr-6T** (195.0 mg, 0.20 mmol, 1 equiv.), K_2CO_3 (123.0 mg, 0.89 mmol, 4.5 equivs), dH_2O (0.44 mL, [2.0M] to K_2CO_3), toluene (1.5 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (11.4 mg, 0.01 mmol, 0.05 equiv.) to give **8T** as a bright red oil that quickly solidifies over time. Yield=197.3 mg (**86%**). Column chromatography solvent: 94:6 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 4H), 7.06 (d, *J* = 3.7 Hz, 2H), 6.97 (s, 2H), 6.94 (s, 2H), 6.93 (d, *J* = 5.2 Hz, 2H), 2.83 – 2.75 (m, 12H), 1.74 – 1.62 (m, 12H), 1.47 – 1.37 (m, 13H), 1.37 – 1.30 (m, 24H), 0.94 – 0.87 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.07, 139.87, 139.65, 136.71, 135.01, 134.15, 134.02, 130.47, 130.23, 130.18, 130.11, 128.77, 128.55, 126.32, 123.91, 123.61, 31.68, 31.67, 30.64, 30.51, 30.49, 29.44, 29.29, 29.24, 29.22, 22.63, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{68}H_{90}S_8$ $[M]^+$: 1162.4803; found m/z 1162.4792.

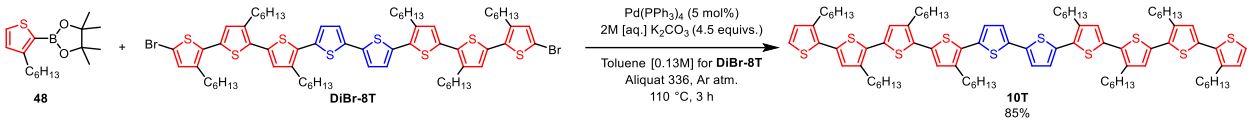
3,3''',3''''',3''''''',3'''''''',4',4'',4'''-Octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5''''''',2'''''''-Novithiophene (**9T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (302 µL, 296.7 mg, 1.01 mmol, 2.1 equivs.), **DiBr-7T** (595.2 mg, 0.48 mmol, 1 equiv.), K_2CO_3 (298.6 mg, 2.16 mmol, 4.5 equivs), dH_2O (1.08 mL, [2.0M] to K_2CO_3), toluene (3.7 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (27.7 mg, 0.02 mmol, 0.05 equiv.) to give **9T** as a dark red oil that quickly solidifies over time. Yield=593.0 mg (**87%**). Column chromatography solvent: 94:6 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.12 (s, 2H), 7.00 (s, 2H), 6.98 (s, 2H), 6.95 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.86 – 2.75 (m, 16H), 1.75 – 1.63 (m, 16H), 1.48 – 1.38 (m, 16H),

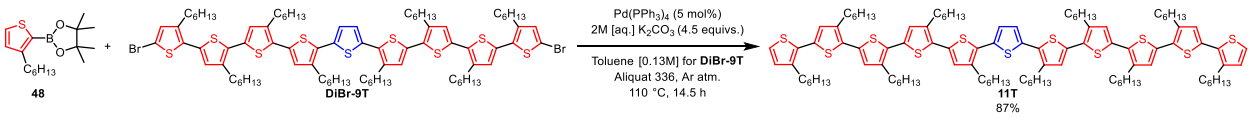
1.38 – 1.32 (m, 32H), 0.94 – 0.88 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.99, 139.93, 139.82, 139.64, 135.76, 134.10, 133.94, 133.81, 130.53, 130.36, 130.32, 130.13, 128.79, 128.59, 125.95, 123.61, 31.73, 31.71, 30.67, 30.61, 30.54, 30.53, 29.51, 29.48, 29.46, 29.32, 29.28, 29.27, 29.25, 22.67, 14.14. **HRMS** (TOF ESI+) Calcd. for $C_{84}H_{116}S_9$ $[M]^+$: 1412.6558; found m/z 1412.6542.

3,3''''',3''''',3''''''',3''''''',4',4'',4'''-Octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''':5''''''',2''''''':5''''''',2''''''':5''''''',2'''''''-Decithiophene (**10T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (98 µL, 96.3 mg, 0.33 mmol, 2.1 equivs.), **DiBr-8T** (206.0 mg, 0.16 mmol, 1 equiv.), K_2CO_3 (96.9 mg, 0.70 mmol, 4.5 equivs), dH_2O (0.35 mL, [2.0M] to K_2CO_3), toluene (1.2 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (9.0 mg, 0.008 mmol, 0.05 equiv.) to give **10T** as a bright red oil. Yield=199.4 mg (**85%**). Column chromatography solvent: 93:7 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 4H), 7.07 (d, *J* = 3.8 Hz, 2H), 6.99 (s, 2H), 6.97 (s, 2H), 6.94 (s, 2H), 6.93 (d, *J* = 5.1 Hz, 2H), 2.83 – 2.76 (m, 16H), 1.75 – 1.62 (m, 16H), 1.47 – 1.38 (m, 16H), 1.37 – 1.31 (m, 32H), 0.94 – 0.88 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.08, 139.94, 139.81, 139.62, 136.72, 135.00, 134.08, 133.99, 133.82, 130.49, 130.31, 130.27, 130.21, 130.10, 128.76, 128.57, 128.54, 126.32, 123.92, 123.59, 31.68, 31.67, 30.64, 30.51, 30.50, 29.45, 29.43, 29.28, 29.25, 29.23, 29.22, 22.64, 22.63, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{88}H_{118}S_{10}$ $[M]^+$: 1494.6435; found m/z 1494.6415.

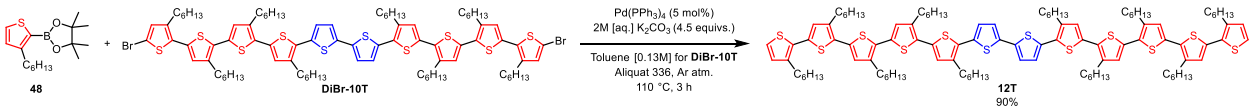
3,3''''',3''''',3''''''',3''''''',3''''''''',4',4'',4''',4''''-Decahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''':5''''''',2''''''':5''''''',2''''''':5''''''',2''''''''-Undecithiophene (**11T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (66 µL, 64.8 mg, 0.22 mmol, 2.1 equivs.), **DiBr-9T** (164.8 mg, 0.10 mmol, 1 equiv.), K_2CO_3 (65.2 mg, 0.47 mmol, 4.5 equivs), dH_2O (0.24 mL, [2.0M] to K_2CO_3), toluene (0.8 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat

336 and $Pd(PPh_3)_4$ (6.1 mg, 0.005 mmol, 0.05 equiv.) to give **11T** as a dark red/brown oil that solidifies into a red/brown solid with metallic green highlights when directly illuminated. Yield=158.4 mg (**87%**). Column chromatography solvent: 9:1 Hexanes:$CHCl_3$. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.12 (s, 2H), 7.00 (s, 2H), 6.99 (s, 2H), 6.98 (s, 2H), 6.95 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.86 – 2.75 (m, 20H), 1.75 – 1.62 (m, 20H), 1.47 – 1.38 (m, 20H), 1.38 – 1.31 (m, 40H), 0.94 – 0.89 (m, 30H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.96, 139.92, 139.85, 139.77, 139.60, 135.73, 134.06, 133.90, 133.74, 130.50, 130.36, 130.34, 130.31, 130.10, 128.75, 128.56, 125.92, 123.57, 31.70, 31.68, 30.64, 30.58, 30.51, 30.50, 29.48, 29.45, 29.43, 29.29, 29.26, 29.25, 29.24, 29.22, 22.64, 14.12, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{104}H_{144}S_{11}$ $[M]^+$: 1744.8190; found m/z 1744.8197.

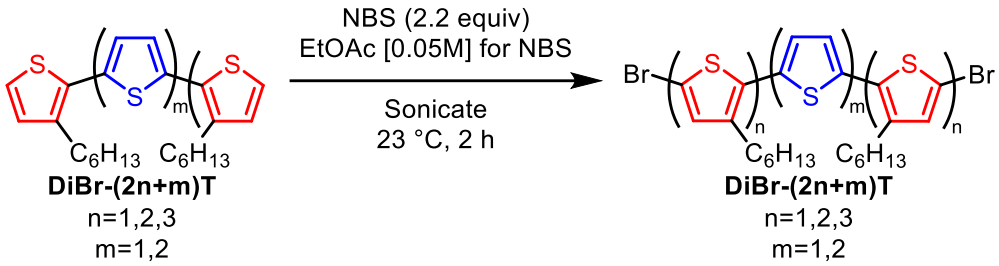
3,3''''',3''''''',3'''''''',3''''''''',3''''''''',4',4'',4''',4''''-Decahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''':5''''''',2'''''''':5'''''''',2''''''''':5''''''''',2'''''''''':5'''''''''-Dodecithiophene (**12T**)



The Suzuki Cross-Coupling General Reaction Procedure was followed using 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**48**) (61 µL, 60.3 mg, 0.22 mmol, 2.1 equivs.), **DiBr-10T** (161.5 mg, 0.10 mmol, 1 equiv.), K_2CO_3 (60.7 mg, 0.44 mmol, 4.5 equivs), dH_2O (0.22 mL, [2.0M] to K_2CO_3), toluene (0.8 mL, [0.13M] to dibrominated starting material), 1 drop of Aliquat 336 and $Pd(PPh_3)_4$ (5.6 mg, 0.005 mmol, 0.05 equiv.) to give **12T** as a bright red oil that solidifies quickly over time. Yield=160.5 mg (**90%**). Column chromatography solvent: 88:12 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 4H), 7.07 (d, *J* = 3.7 Hz, 2H), 6.99 (s, 2H), 6.98 (s, 2H), 6.97 (s, 2H), 6.94 (s, 2H), 6.93 (d, *J* = 5.3 Hz, 2H), 2.84 – 2.75 (m, 20H), 1.74 – 1.62 (m, 20H), 1.47 – 1.38 (m, 20H), 1.38 – 1.31 (m, 40H), 0.94 – 0.87 (m, 30H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.10, 139.96, 139.88, 139.79, 139.62, 136.73, 135.01, 134.07, 133.98, 133.79, 133.76, 130.49, 130.35, 130.34, 130.31, 130.23, 130.11, 128.77, 128.57, 126.33, 123.93, 123.58, 31.68, 31.68, 30.64, 30.50, 29.46, 29.43, 29.29, 29.25, 29.22, 22.64, 14.12, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{108}H_{146}S_{12}$ $[M]^+$: 1826.8068; found m/z 1826.8047.

4.2.4 *DiBromination Reaction Procedures*

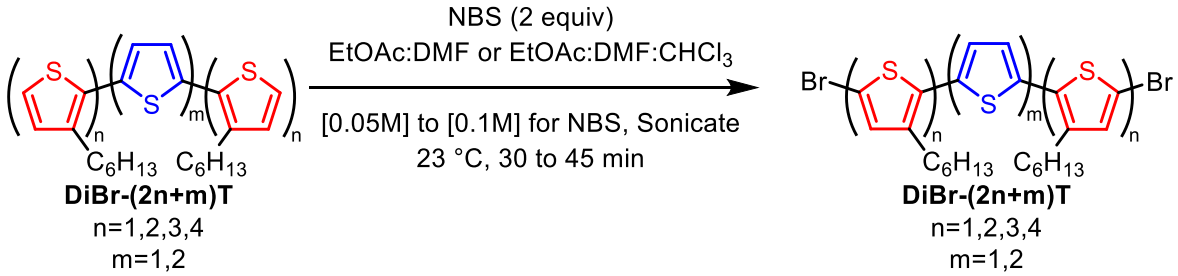
Dibromination General Literature Reaction Procedure



The procedure for this reaction is reported in reference 65. It can be applied up to the dibromination of **8T**. Individual data for each oligomer will not be reported for this procedure, refer to the Dibromination General Modified Reaction Procedure below for individual conditions.

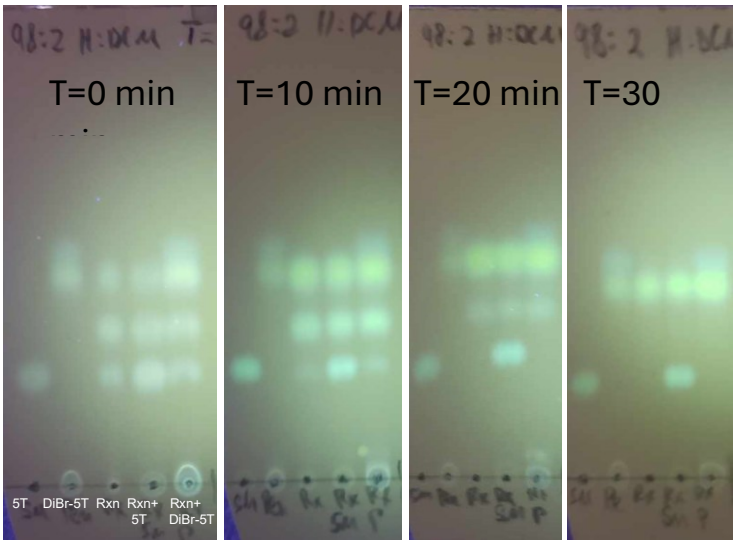
A flame-dried 5-20 mL microwave vial or 100 mL round-bottom flask was wrapped with aluminium foil. Oligothiophene (1 equiv.) and EtOAc ([0.05M] to oligothiophene starting material) were added first. NBS (2.2 equiv.) was added next and dissolved by gentle swirling of the vial/flask. The vial/flask was sealed with a septum and immersed in an ultrasonic bath without added heating for 2 to 6.5 hours depending on substrate. The reaction was followed by TLC and considered complete when only one spot appears with a considerably higher Rf than the starting material. Once complete, the solution was diluted with EtOAc and washed with 2x dH_2O, and 2x brine. The aqueous phases were combined extracted with EtOAc. Combined organic phases were dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude mixture is analyzed by ^1H NMR and used without purification if determined to be pure enough. Otherwise, the crude mixture is purified by column chromatography using silica gel and an appropriate solvent system.

Dibromination General Modified Reaction Procedure



This is the modified reaction procedure that can be applied for the dibromination of all oligothiophenes up to **9T** and **10T**. Solvent system, NBS concentration and reaction times vary

according to starting material. The reaction is followed using TLC with a solvent system slightly more polar than the one used to purify the oligothiophene starting material. The starting material should have the lowest Rf with the mono-brominated intermediate having a higher Rf and the desired product having the highest Rf. The reaction is complete when only the lowest Rf spot is visible under 254 nm UV-lamp illumination (as shown in **Figure 58** below).



From left to right, spots are: 5T (SM), DiBr-5T (Product), Reaction, Reaction+5T, Reaction+DiBr-5T. Note that the DiBr-5T sample is slightly degraded which is why it has a light blue colored spot above the green spot of interest.

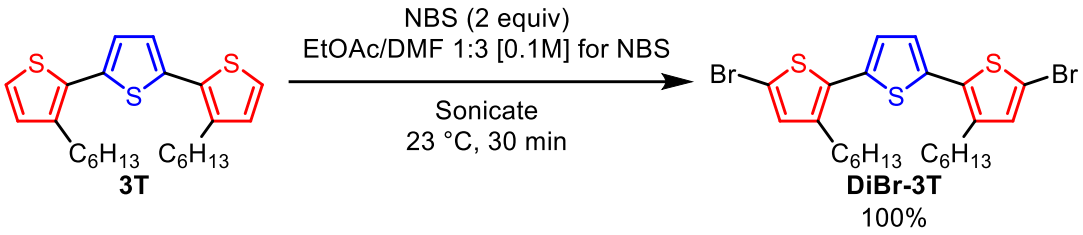
<u>Figure 58</u>: 365 nm Illumination of DiBr-5T Reaction at 0, 10, 20, and 30 min on TLC Plates Using 98:2 Hex:DCM

Each individual oligomer has a solvent system that should be used for column chromatography with silica gel. The solvent system is set such that the product has an Rf of ~0.3. A 1.5" diameter, 10" length column filled at about 75% with dry silica is recommended at the reported scales. For this reaction, the products should be pure enough to use without further purification. If too much NBS is added or the reaction is left to sonicate for too long, considerable quantities of byproducts will be generated. If that is the case, the crude mixtures can be purified using the solvent systems listed for each dibrominated oligomer.

A flame-dried 5-20 mL microwave vial or 100 mL round-bottom flask was wrapped with aluminium foil. Oligothiophene (1 equiv.) in EtOAc ([0.07M] to [0.20M] solution) was transferred to the reaction flask. DMF (1.6x to 3x the volume of EtOAc) and $CHCl_3$ (0.4x the volume of EtOAc) are added next depending on oligothiophene starting material (1:3 EtOAc:DMF from **3T** to **8T**, 1:1.6:0.4 EtOAc:DMF:$CHCl_3$ for **9T** and **10T**). and the solution is swirled until homogeneous. If the solution is not homogenous, a small amount of EtOAc is added until it is. NBS (2.2 equiv.)

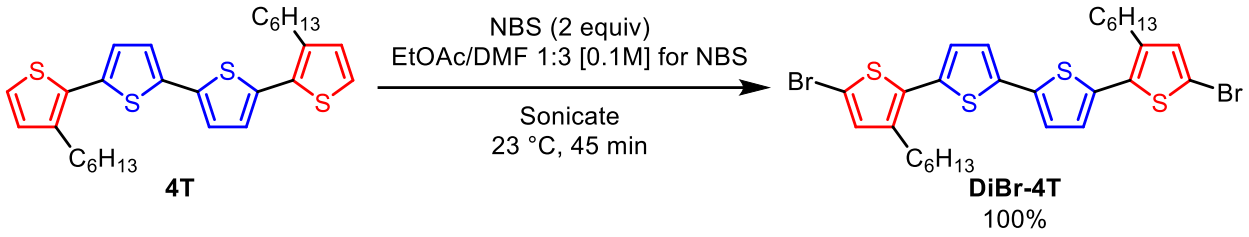
was added next and dissolved by gentle swirling of the vial/flask. The vial/flask was sealed with a septum and immersed in an ultrasonic bath without added heating for 2 to 6.5 hours depending on substrate. The reaction was followed by TLC and considered complete when only one spot appears with a considerably higher Rf than the starting material. Once complete, the solution was diluted with EtOAc and washed with 2x dH_2O, and 2x brine. The aqueous phases were combined extracted with EtOAc. Combined organic phases were dried over anhydrous Na_2SO_4, filtered through a cotton plug and evaporated under reduced pressure. The crude mixture is analyzed by ^1H NMR and used without purification if determined to be pure enough. Otherwise, the crude mixture is purified by column chromatography using silica gel and an appropriate solvent system.

5,5''-Dibromo-3,3''-Dihexyl-2,2':5',2''-Terthiophene (**DiBr-3T**)



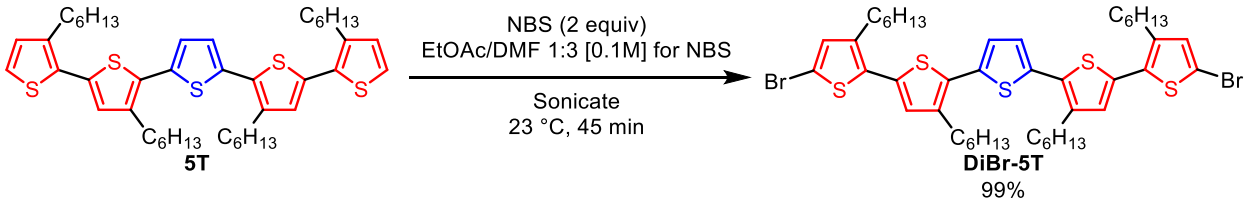
The Dibromination General Modified Reaction Procedure was followed using **3T** (292.1 mg, 0.70 mmol, 1.0 equiv.), NBS (247.7 mg, 1.39 mmol, 2.0 equivs.), EtOAc (3.5 mL) and DMF (10.4 mL) to give **DiBr-3T** as a transparent light green oil that solidifies quickly over time. Yield=401.0 mg (**100%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 6.90 (s, 2H), 2.70 (t, *J* = 7.8 Hz, 4H), 1.64 – 1.58 (m, 4H), 1.38 – 1.32 (m, 4H), 1.32 – 1.27 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.48, 135.15, 132.69, 131.57, 126.45, 110.65, 31.60, 30.55, 29.20, 29.10, 22.58, 14.07. **HRMS** (TOF ESI+) Calcd. for $C_{24}H_{30}{}^{79}Br_2S_3$ $[M]^+$: 571.98707; found m/z 571.9866.

5,5‴-Dibromo-3,3‴-Dihexyl-2,2′:5′,2″:5″,2‴-Quaterthiophene (**DiBr-4T**)



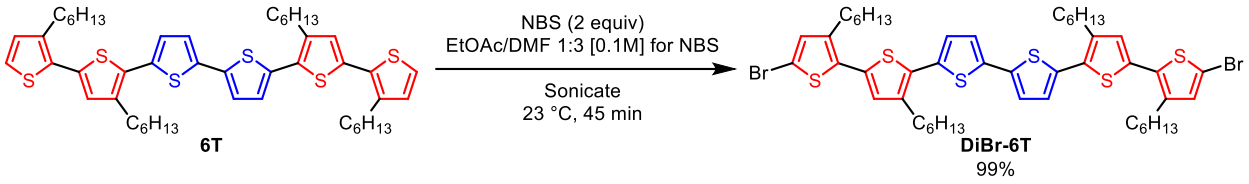
The Dibromination General Modified Reaction Procedure was followed using **4T** (562.6 mg, 1.13 mmol, 1.0 equiv.), NBS (401.5 mg, 2.26 mmol, 2.0 equivs.), EtOAc (5.6 mL) and DMF (16.9 mL) to give **DiBr-4T** as a lightly green tinted, golden solid. Yield=741.1 mg (**100%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: Hexanes. **^{1}H NMR** 1H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 3.7 Hz, 2H), 6.96 (d, J = 3.8 Hz, 2H), 6.90 (s, 2H), 2.71 (t, J = 7.8 Hz, 4H), 1.61 (p, J = 7.2 Hz, 4H), 1.39 – 1.33 (m, 4H), 1.33 – 1.28 (m, 8H), 0.88 (t, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.51, 137.01, 134.04, 132.69, 131.67, 126.96, 123.99, 110.64, 31.59, 30.49, 29.19, 29.08, 22.57, 14.08. **HRMS** (TOF ESI+) Calcd. for $C_{28}H_{32}{}^{79}Br_2S_4$ $[M]^+$: 653.9747; found m/z 653.9748.

5,5‴″-Dibromo-3,3‴,3‴″,4′-Tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2‴″-Quinquethiophene (**DiBr-5T**)



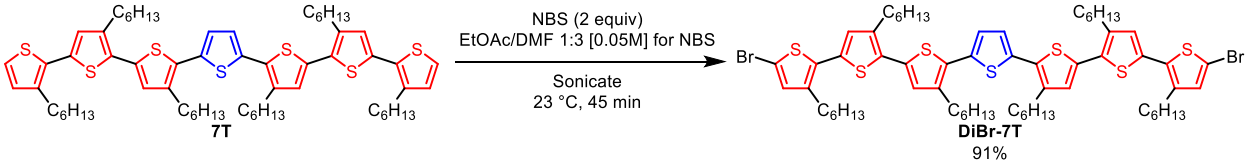
The Dibromination General Modified Reaction Procedure was followed using **5T** (614.4 mg, 0.82 mmol, 1.0 equiv.), NBS (291.9 mg, 1.64 mmol, 2.0 equivs.), EtOAc (4.1 mL) and DMF (12.3 mL) to give **DiBr-5T** as a transparent honey colored oil. Yield=739.8 mg (**100%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: Hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (s, 2H), 6.90 (s, 4H), 2.78 (t, *J* = 7.9 Hz, 4H), 2.73 (t, *J* = 7.8 Hz, 4H), 1.72 – 1.65 (m, 4H), 1.65 – 1.59 (m, 4H), 1.46 – 1.36 (m, 8H), 1.36 – 1.29 (m, 16H), 0.90 (t, *J* = 6.4 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.25, 139.97, 135.64, 132.92, 132.71, 131.92, 130.68, 129.11, 126.09, 110.34, 31.66, 31.60, 30.55, 30.51, 29.40, 29.24, 29.21, 29.10, 22.62, 22.59, 14.09. **HRMS** (TOF ESI+) Calcd. for $C_{44}H_{58}{}^{79}Br_2S_5$ $[M]^+$: 904.1503; found m/z 904.1497.

5,5''''-Dibromo-3,3'''',3''''',4'-Tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-Sexithiophene (**DiBr-6T**)



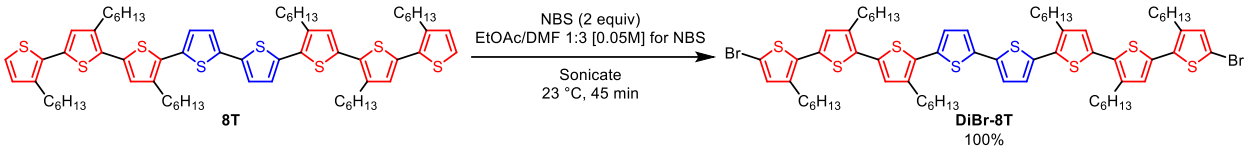
The Dibromination General Modified Reaction Procedure was followed using **6T** (260.0 mg, 0.31 mmol, 1.0 equiv.), NBS (111.3 mg, 0.63 mmol, 2.0 equivs.), EtOAc (3.1 mL) and DMF (9.4 mL) to give **DiBr-6T** as a red oil that quickly solidifies into a blood-red solid. Yield=307.0 mg (**99%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: 99:1 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.8 Hz, 2H), 7.05 (d, *J* = 3.7 Hz, 2H), 6.89 (s, 2H), 6.89 (s, 2H), 2.77 (t, *J* = 7.8 Hz, 4H), 2.71 (t, *J* = 7.7 Hz, 4H), 1.68 (p, *J* = 7.8 Hz, 4H), 1.61 (p, *J* = 7.9 Hz, 4H), 1.44 – 1.35 (m, 8H), 1.35 – 1.28 (m, 16H), 0.94 – 0.86 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.27, 140.05, 136.83, 134.77, 132.94, 132.72, 131.89, 130.66, 129.09, 126.50, 123.96, 110.36, 31.64, 31.61, 30.51, 30.46, 29.37, 29.22, 29.20, 29.10, 22.61, 22.59, 14.09. **HRMS** (TOF ESI+) Calcd. for $C_{48}H_{60}{}^{79}Br_2S_6$ $[M]^+$: 986.1380; found m/z 986.1375.

5,5''''''-Dibromo-3,3'''',3''''',3''''''',4',4''-Hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''-Septithiophene (**DiBr-7T**)



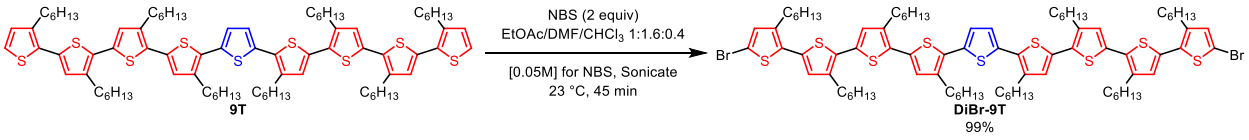
The Dibromination General Modified Reaction Procedure was followed using **7T** (572.7 mg, 0.53 mmol, 1.0 equiv.), NBS (188.4 mg, 1.06 mmol, 2.0 equivs.), EtOAc (2.6 mL) and DMF (7.9 mL) to give **DiBr-7T** as an orange oil that quickly solidifies into an orange-red solid. Yield=595.2 mg (**91%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: 97:3 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.98 (s, 2H), 6.89 (s, 2H), 6.89 (s, 2H), 2.84 – 2.75 (m, 8H), 2.72 (t, *J* = 7.9 Hz, 4H), 1.74 – 1.65 (m, 8H), 1.62 (p, *J* = 7.9 Hz, 4H), 1.47 – 1.37 (m, 12H), 1.37 – 1.31 (m, 24H), 0.93 – 0.88 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.17, 139.97, 139.85, 135.70, 133.64, 132.70, 132.68, 132.00, 130.83, 130.46, 129.10, 128.71, 125.96, 110.27, 31.68, 31.65, 31.61, 30.57, 30.50, 30.49, 29.70, 29.46, 29.37, 29.27, 29.21, 29.10, 22.64, 22.62, 22.59, 14.10. **HRMS** (TOF ESI+) Calcd. for $C_{64}H_{86}{}^{79}Br_2S_7$ $[M]^+$: 1236.3135; found m/z 1236.3127.

5,5''''''-Dibromo-3,3'''',3''''',3''''''',4',4''-Hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''-Octithiophene (**DiBr-8T**)



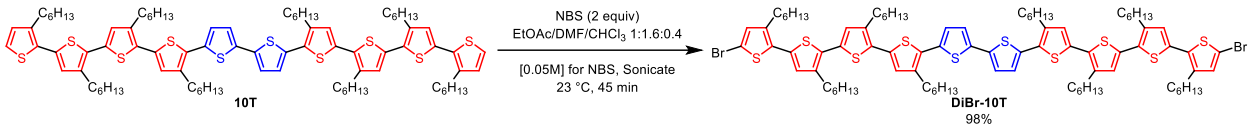
The Dibromination General Modified Reaction Procedure was followed using **8T** (197.3 mg, 0.17 mmol, 1.0 equiv.), NBS (60.3 mg, 0.34 mmol, 2.0 equivs.), EtOAc (0.8 mL) and DMF (2.5 mL) to give **DiBr-8T** as an orange oil that solidifies into a dark red solid. Yield=223.6 mg (**100%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: 97:3 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 3.8 Hz, 2H), 7.06 (d, *J* = 3.8 Hz, 2H), 6.97 (s, 2H), 6.89 (s, 2H), 6.88 (s, 2H), 2.83 – 2.73 (m, 8H), 2.72 (t, *J* = 7.9 Hz, 4H), 1.72 – 1.65 (m, 8H), 1.65 – 1.60 (m, 4H), 1.44 – 1.35 (m, 12H), 1.35 – 1.30 (m, 24H), 0.92 – 0.88 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.21, 140.11, 139.91, 136.76, 134.93, 133.71, 132.71, 131.98, 130.41, 129.13, 128.72, 126.39, 123.94, 110.29, 31.66, 31.61, 30.50, 30.49, 29.43, 29.38, 29.23, 29.22, 29.09, 22.62, 22.59, 14.10, 14.10. **HRMS** (TOF ESI+) Calcd. for $C_{68}H_{88}{}^{79}Br_2S_8$ $[M]^+$: 1318.3012; found m/z 1318.3009.

5,5''''''-Dibromo-3,3'''',3''''',3''''''',3'''''''',4',4'',4'''-Octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''':5''''''',2'''''''-Novithiophene (**DiBr-9T**)



The Dibromination General Modified Reaction Procedure was followed using **9T** (310.0 mg, 0.22 mmol, 1.0 equiv.), NBS (78.0 mg, 0.44 mmol, 2.0 equivs.), EtOAc (3.0 mL), DMF (4.8 mL) and $CHCl_3$ (1.3 mL) to give **DiBr-9T** as a red solid. Yield=341.5 mg (**99%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: 97:3 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.99 (s, 2H), 6.96 (s, 2H), 6.89 (s, 2H), 6.88 (s, 2H), 2.84 – 2.74 (m, 12H), 2.72 (t, *J* = 7.7 Hz, 4H), 1.74 – 1.64 (m, 12H), 1.64 – 1.58 (m, 4H), 1.46 – 1.36 (m, 16H), 1.36 – 1.30 (m, 32H), 0.93 – 0.88 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.18, 139.99, 139.93, 139.82, 135.73, 133.82, 133.46, 132.71, 132.65, 132.02, 130.90, 130.57, 130.37, 129.12, 128.74, 128.63, 125.95, 110.26, 31.69, 31.67, 31.66, 31.61, 30.58, 30.51, 30.48, 29.48, 29.44, 29.37, 29.28, 29.24, 29.21, 29.10, 22.63, 22.60, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{84}H_{115}{}^{79}Br_2S_9$ $[M+H]^+$: 1569.4846; found m/z 1569.4821.

5,5''''''''-Dibromo-3,3'''',3''''',3''''''',3''''''''',4',4'',4'''-Octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2''''''''-Decithiophene (**DiBr-10T**)

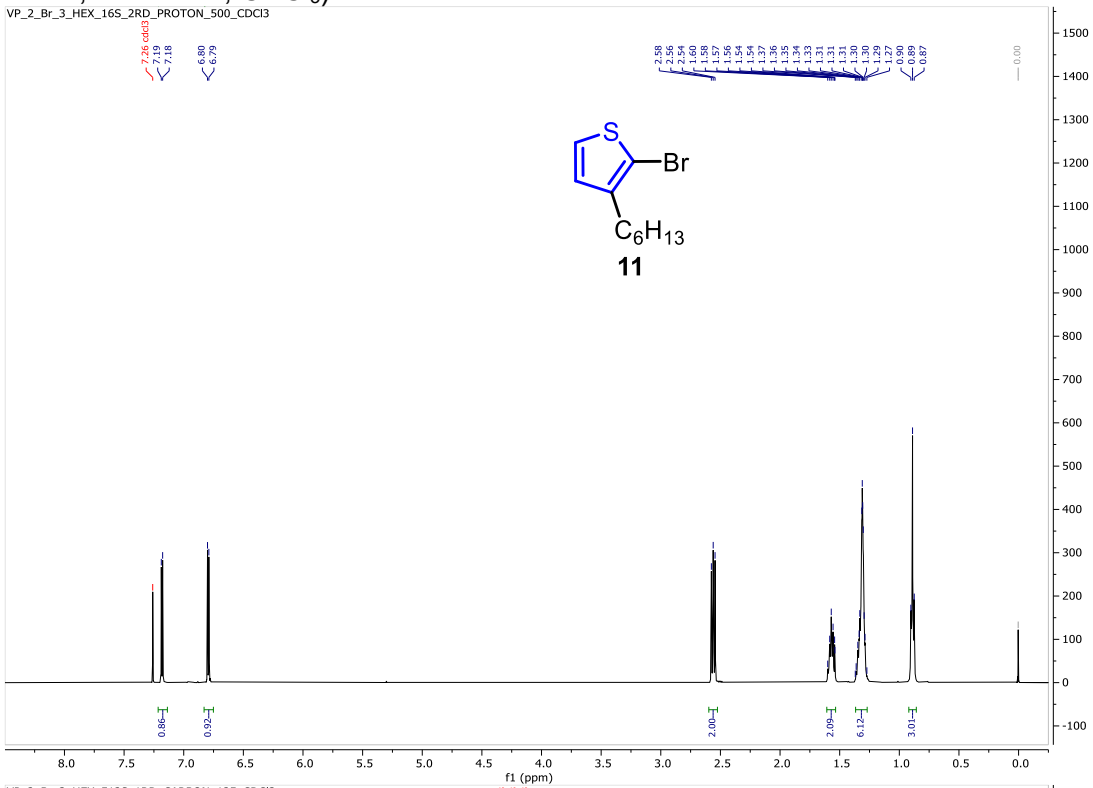


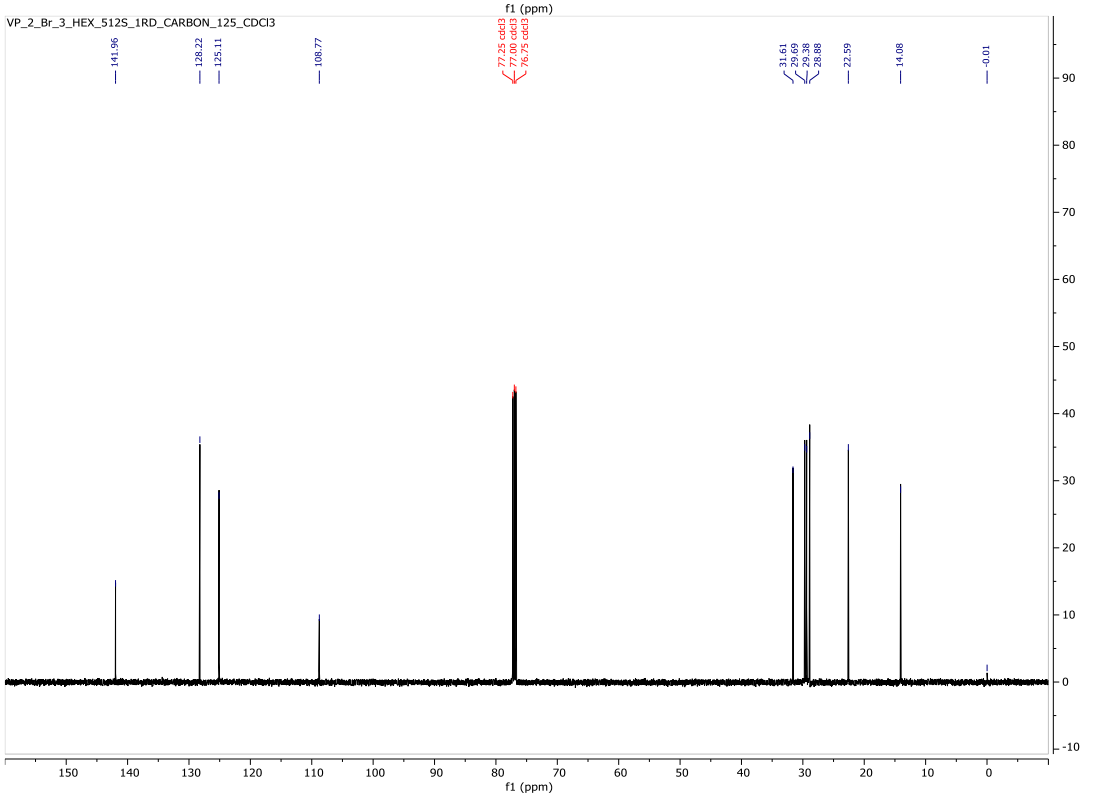
The Dibromination General Modified Reaction Procedure was followed using **10T** (183.6 mg, 0.12 mmol, 1.0 equiv.), NBS (43.7 mg, 0.25 mmol, 2.0 equivs.), EtOAc (1.6 mL), DMF (2.6 mL) and $CHCl_3$ (0.7 mL) to give **DiBr-10T** as dark red oil. Yield=198.1 mg (**98%**). Crude should be pure enough to use without purification, otherwise, column chromatography solvent: 93:7 Hexanes:DCM. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 2H), 6.98 (s, 2H), 6.96 (s, 2H), 6.89 (s, 2H), 6.88 (s, 2H), 2.87 – 2.74 (m, 12H), 2.72 (t, *J* = 7.8 Hz, 4H), 1.73 – 1.64 (m, 12H), 1.64 – 1.58 (m, 4H), 1.46 – 1.36 (m, 16H), 1.36 – 1.30 (m, 32H), 0.93 – 0.87 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.18, 140.10, 139.96, 139.83, 134.97, 133.89, 132.71, 132.66, 132.01, 130.87, 130.52, 129.12, 128.74, 128.60, 126.34, 123.93, 110.26, 31.67, 31.66, 31.61, 30.50, 30.47, 29.44, 29.37, 29.24, 29.21, 29.09, 22.63, 22.59, 14.11. **HRMS** (TOF ESI+) Calcd. for $C_{88}H_{117}{}^{79}Br^{81}BrS_{10}$ $[M+H]^+$: 1653.4703; found m/z 1653.4699.

4.3 ^{1}H NMR and ^{13}C NMR Spectra

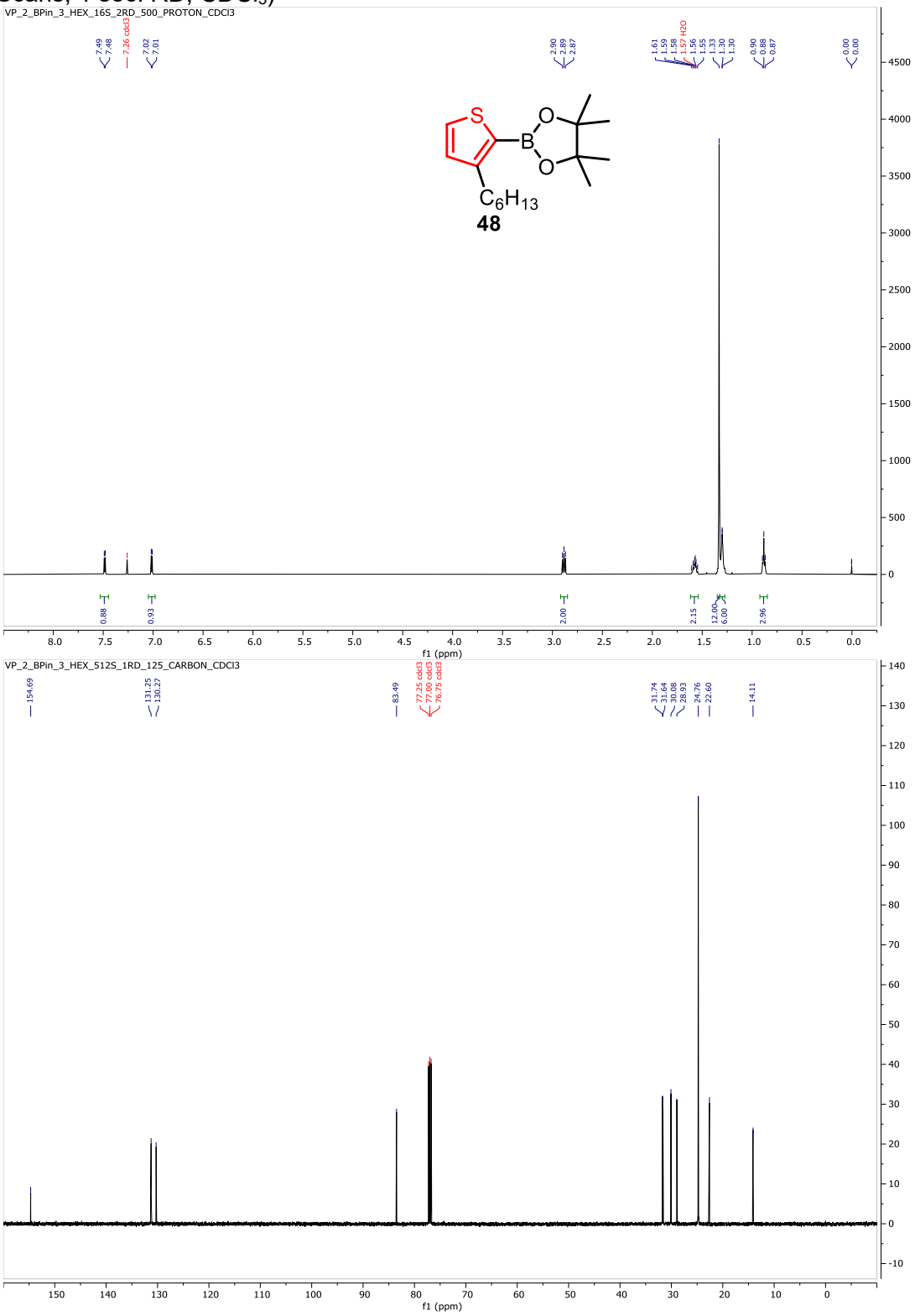
2-bromo-3-hexylthiophene **(11)**

^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

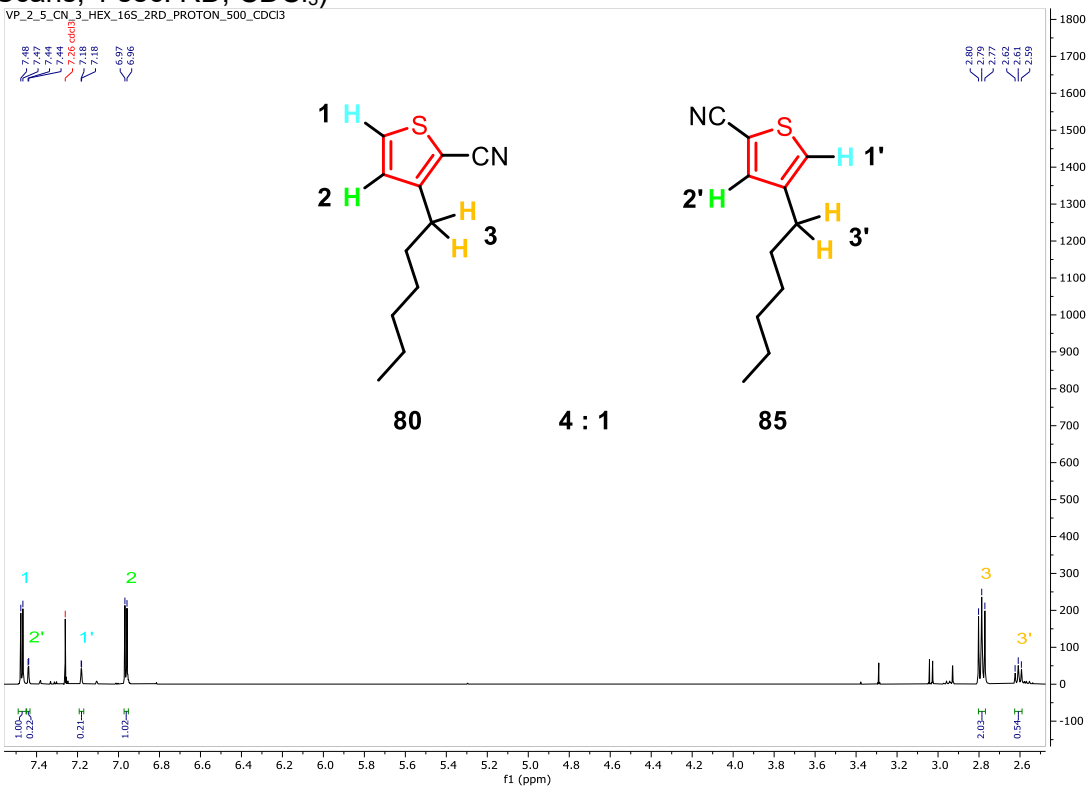


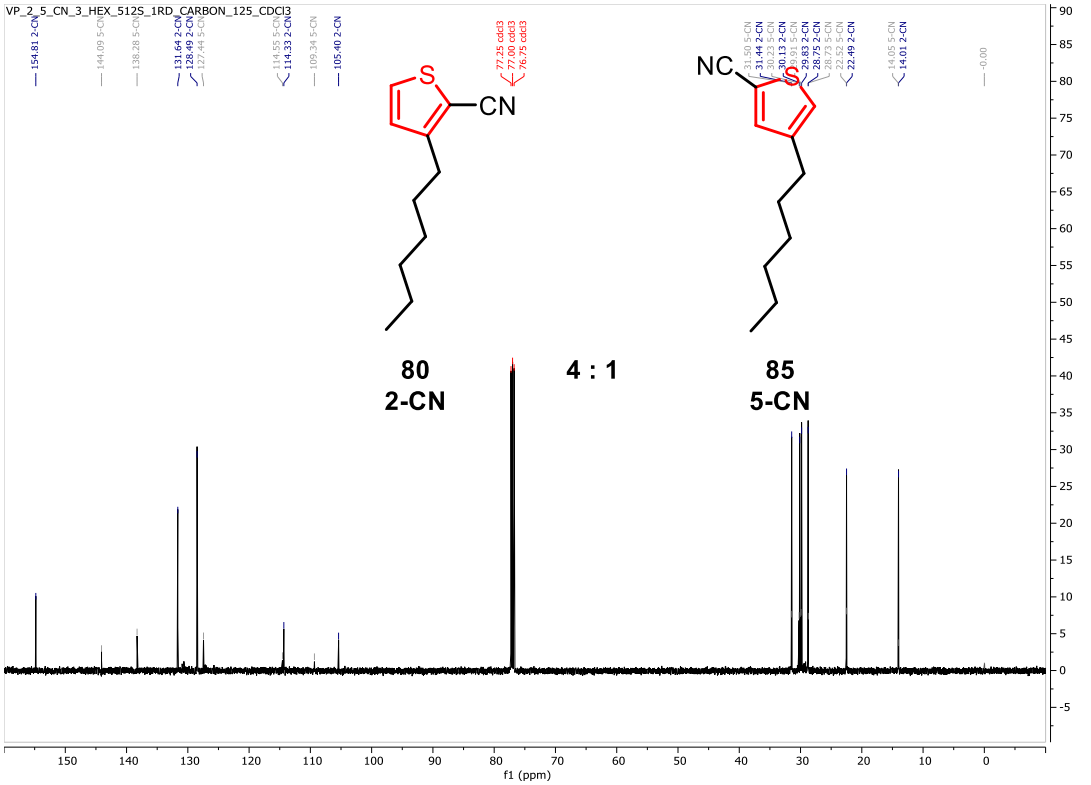


2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(48)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



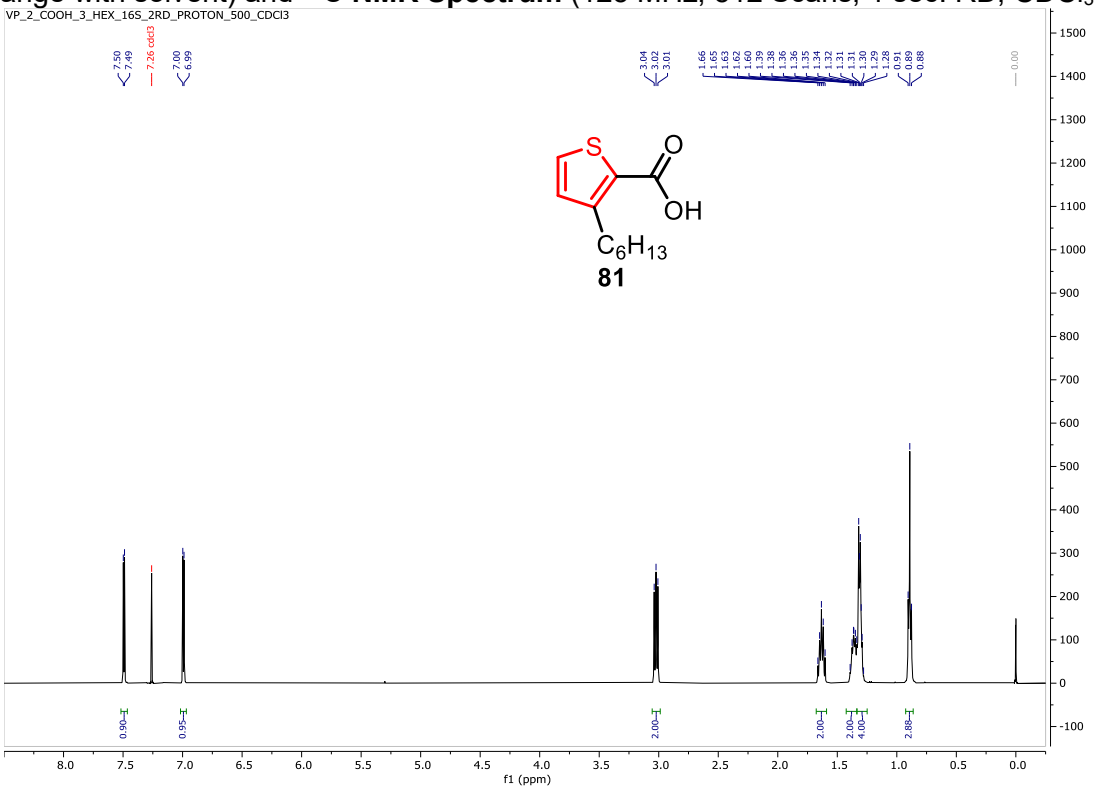
3-hexylthiophene-2-carbonitrile **(80)** and 4-hexylthiophene-2-carbonitrile **(85) 4:1**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

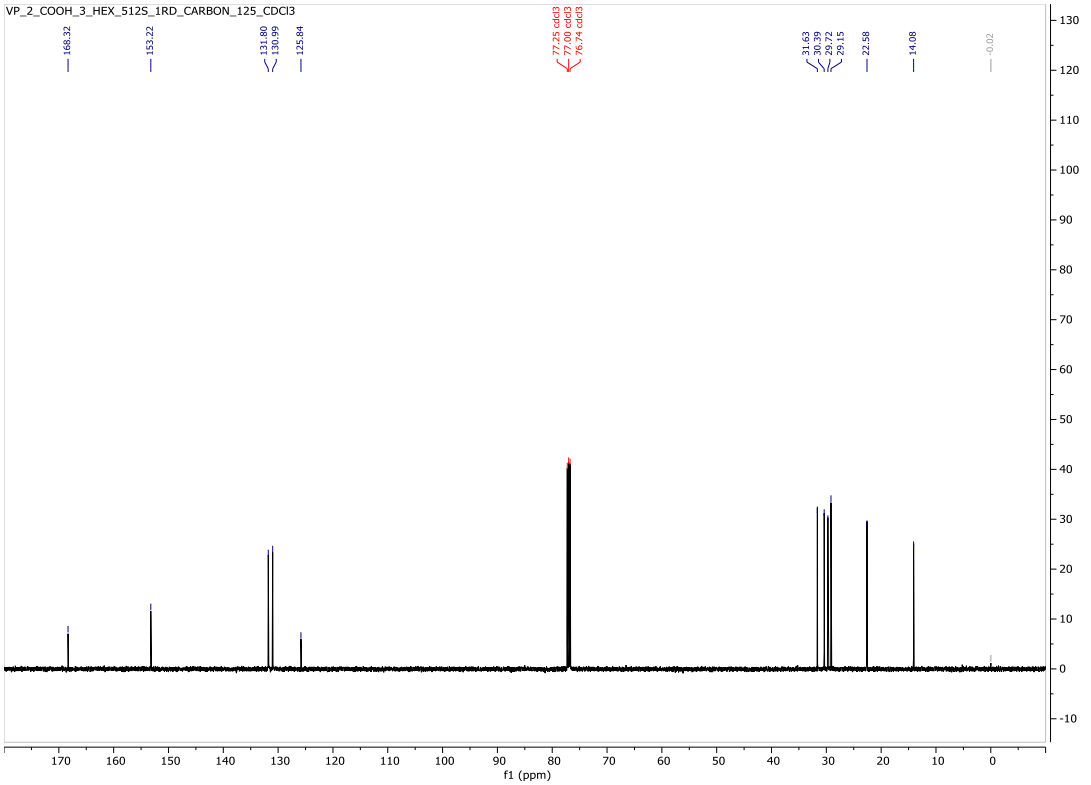




3-hexylthiophene-2-carboxylic acid **(81)**

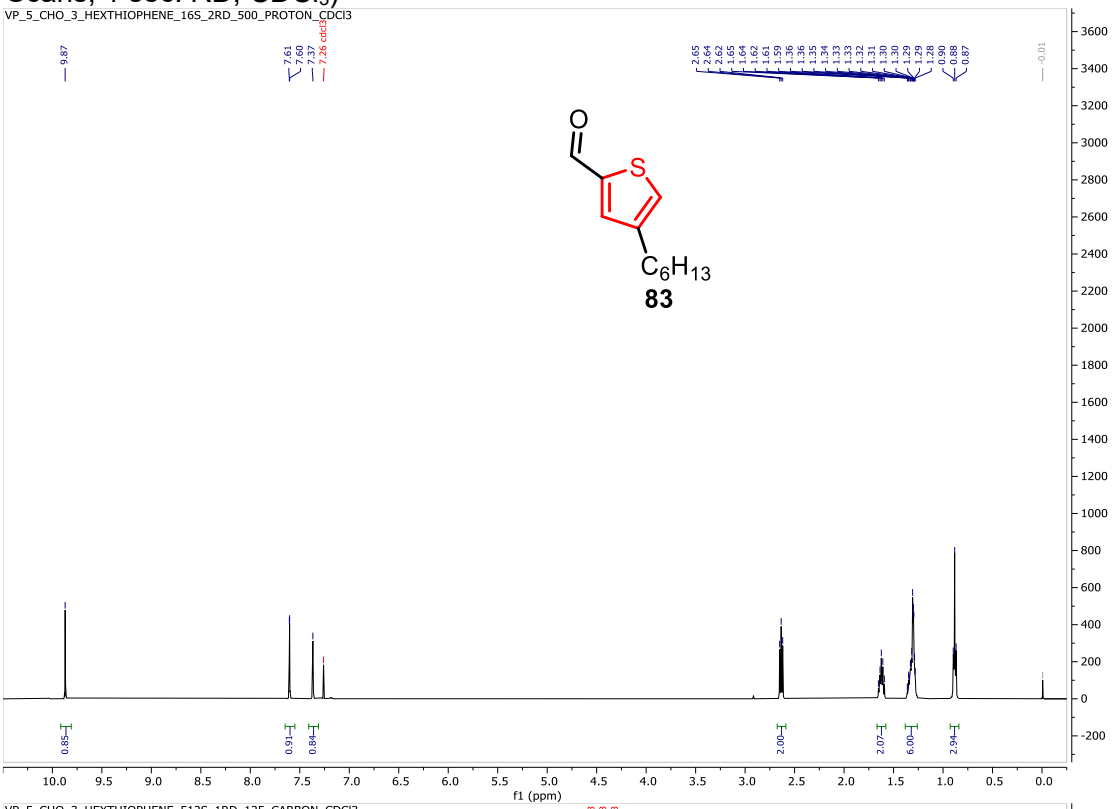
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) (Acid proton not visible due to H/D exchange with solvent) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

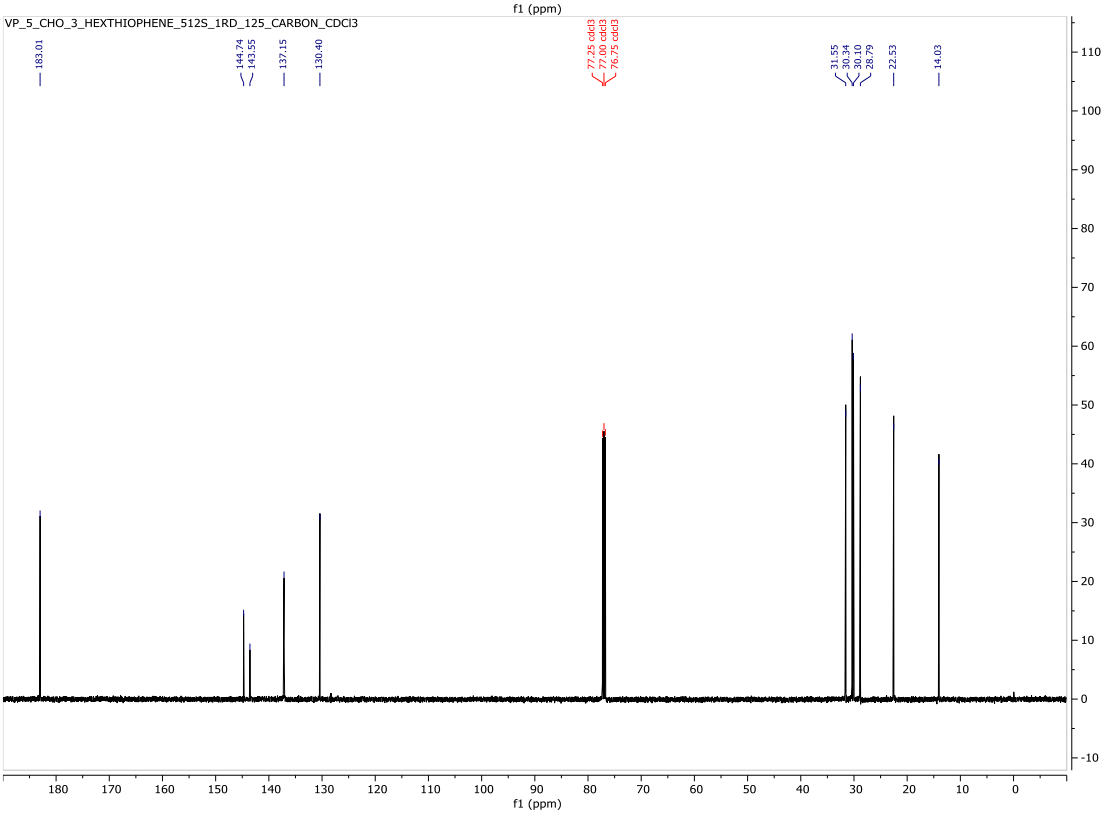




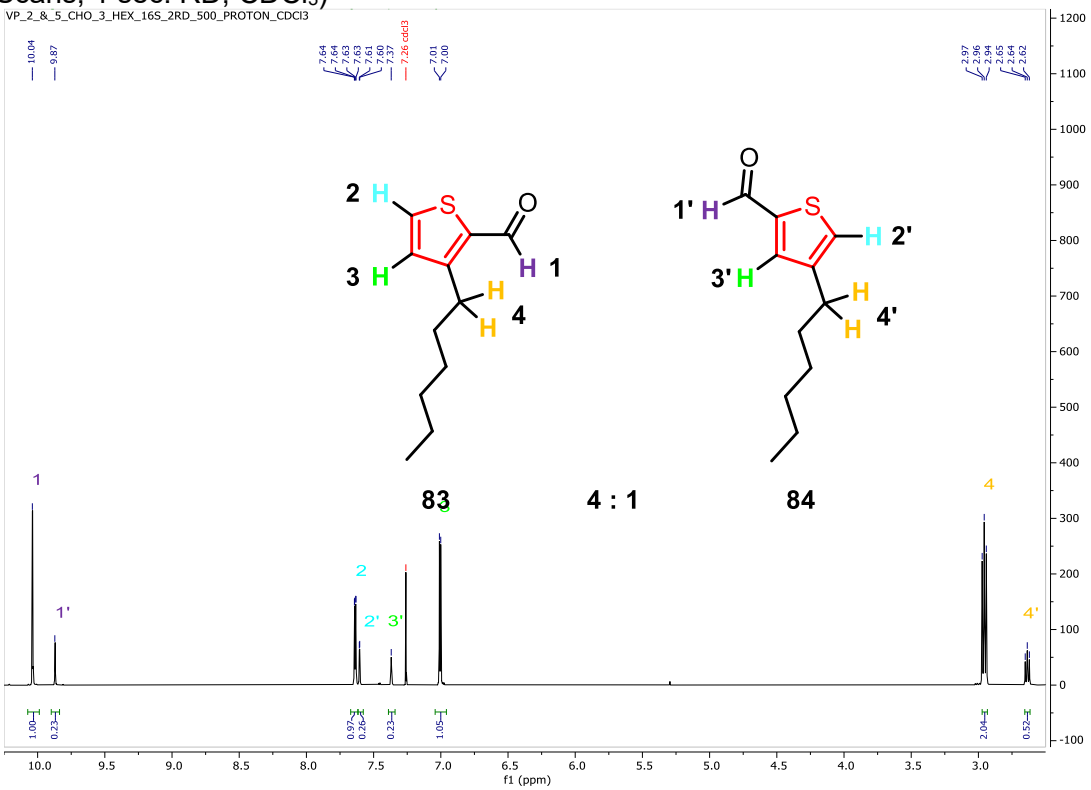
4-hexylthiophene-2-carbaldehyde **(83)**

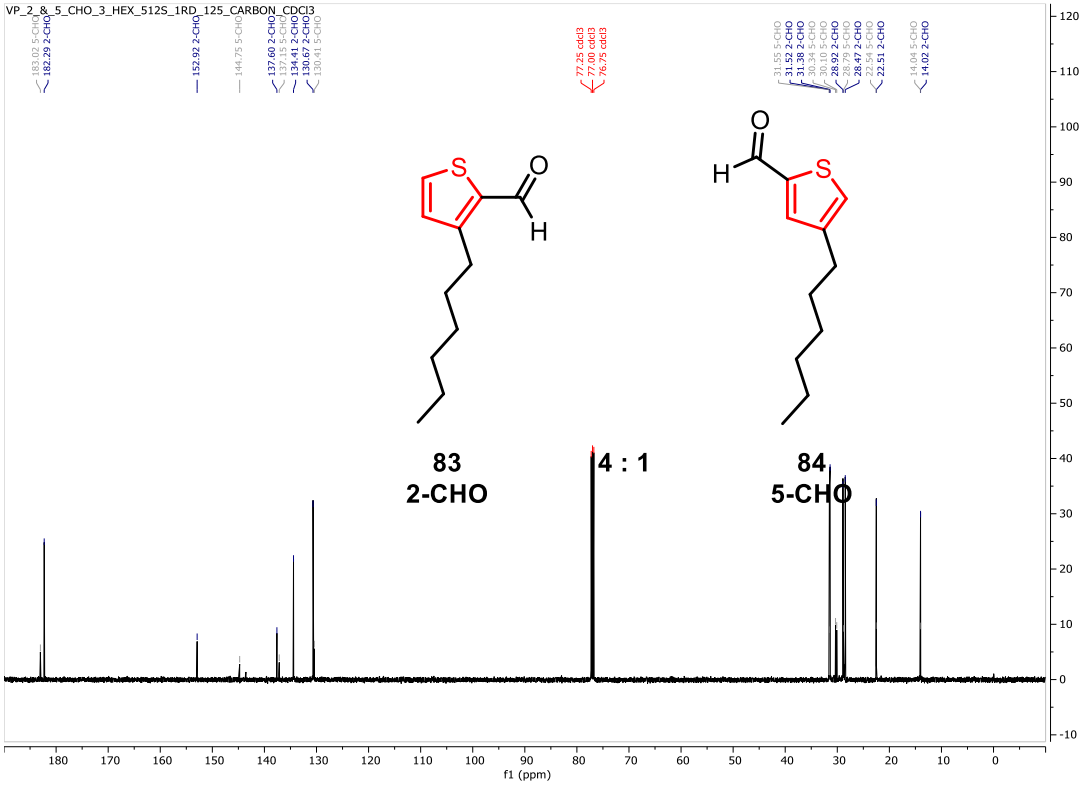
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)





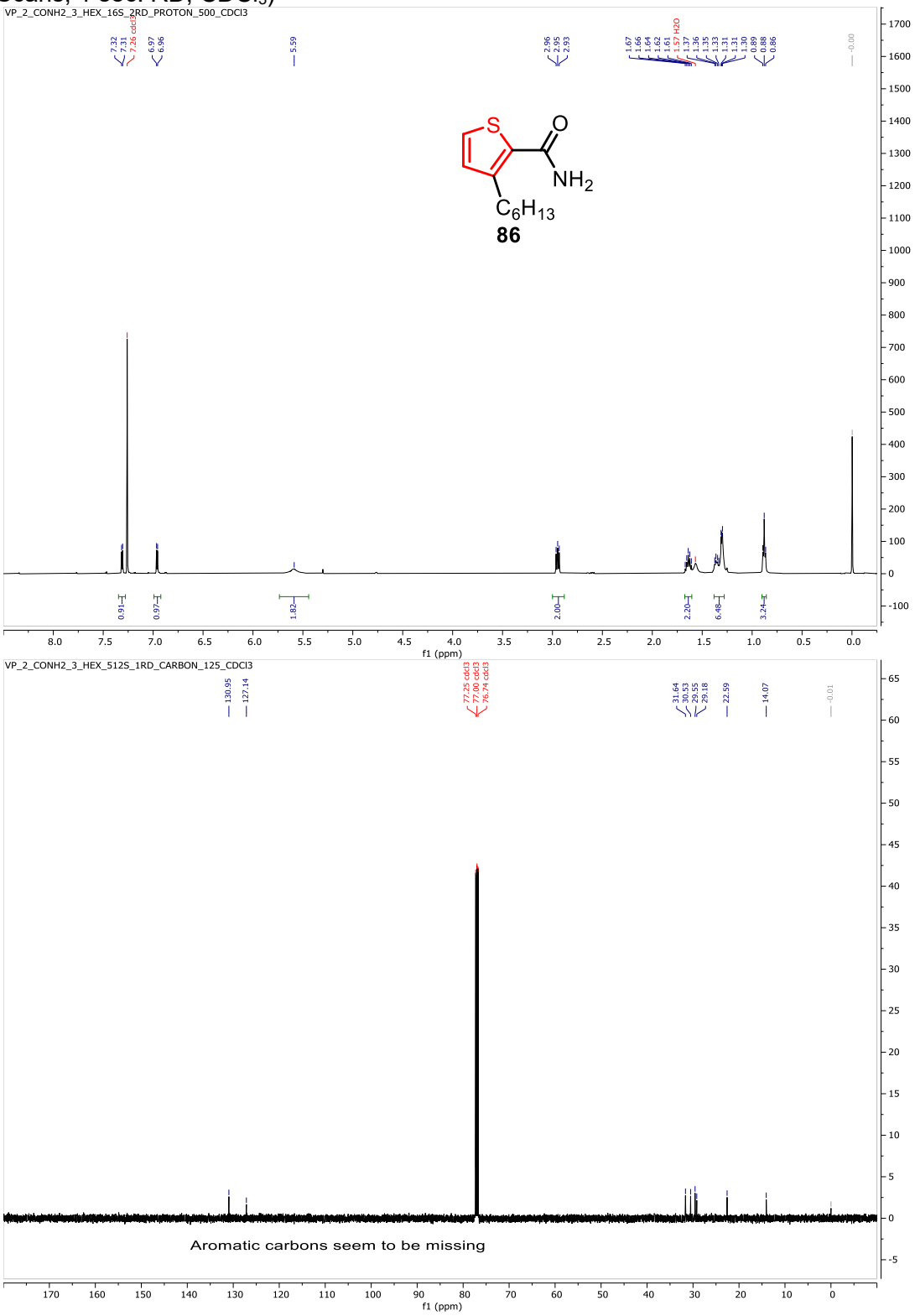
3-hexylthiophene-2-carbaldehyde **(83)** and 4-hexylthiophene-2-carbaldehyde **(84) 4:1**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)





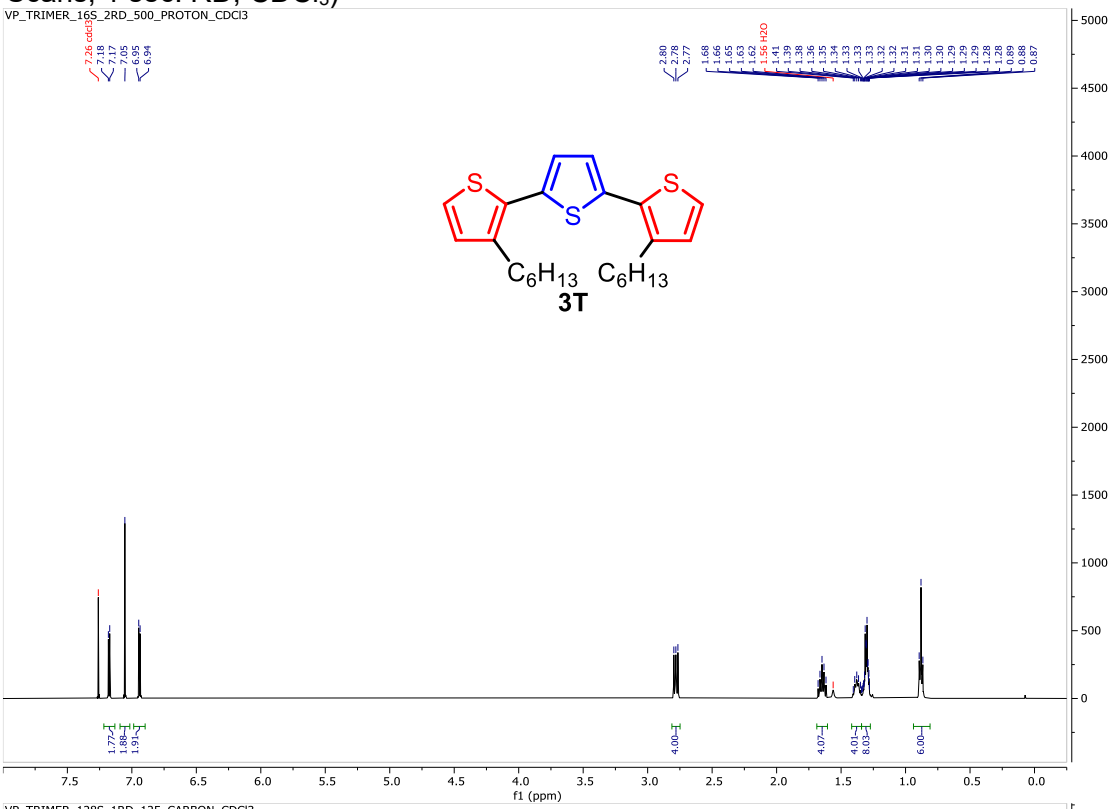
3-hexylthiophene-2-carboxamide **(86)**

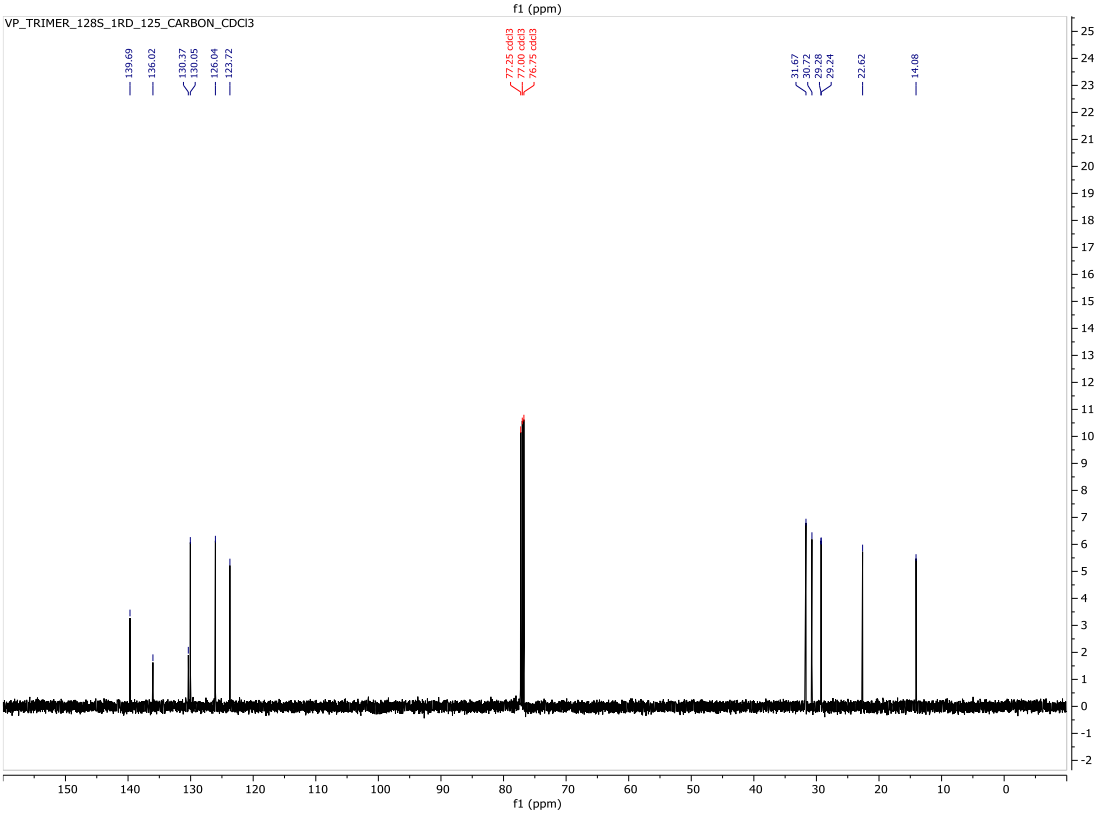
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



3,3''-dihexyl-2,2':5',2''-terthiophene **(3T)**

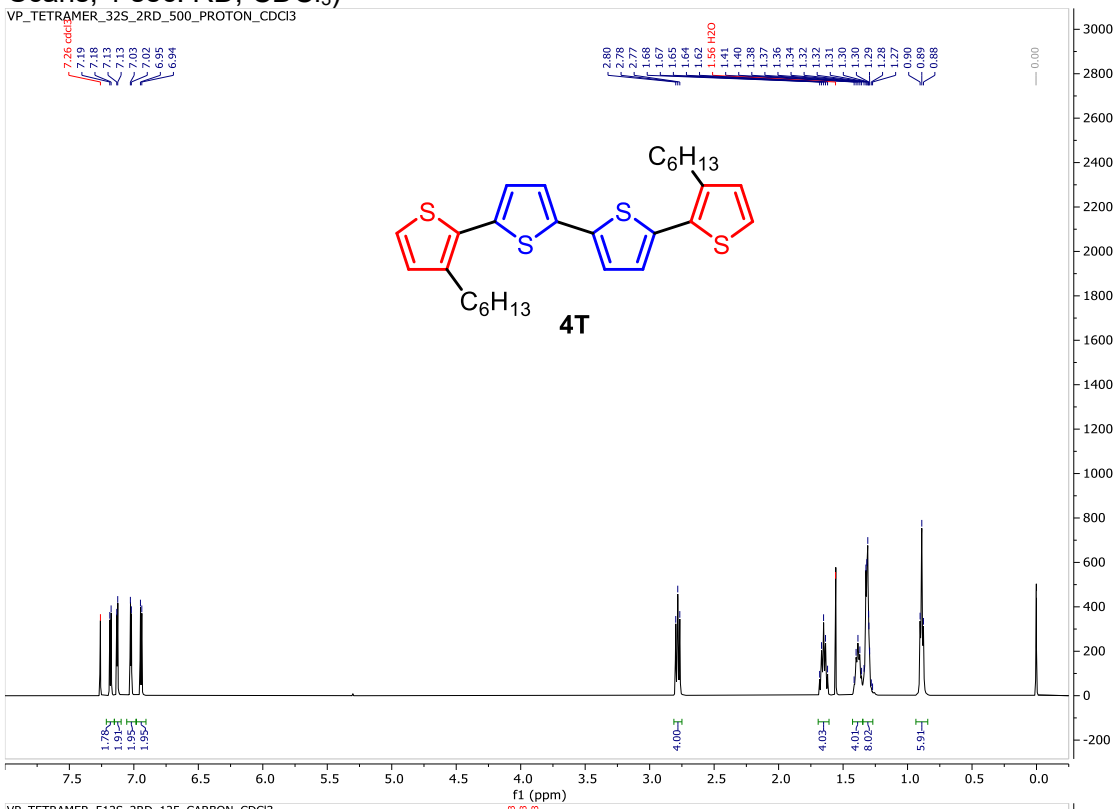
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 128 Scans, 1 sec. RD, $CDCl_3$)

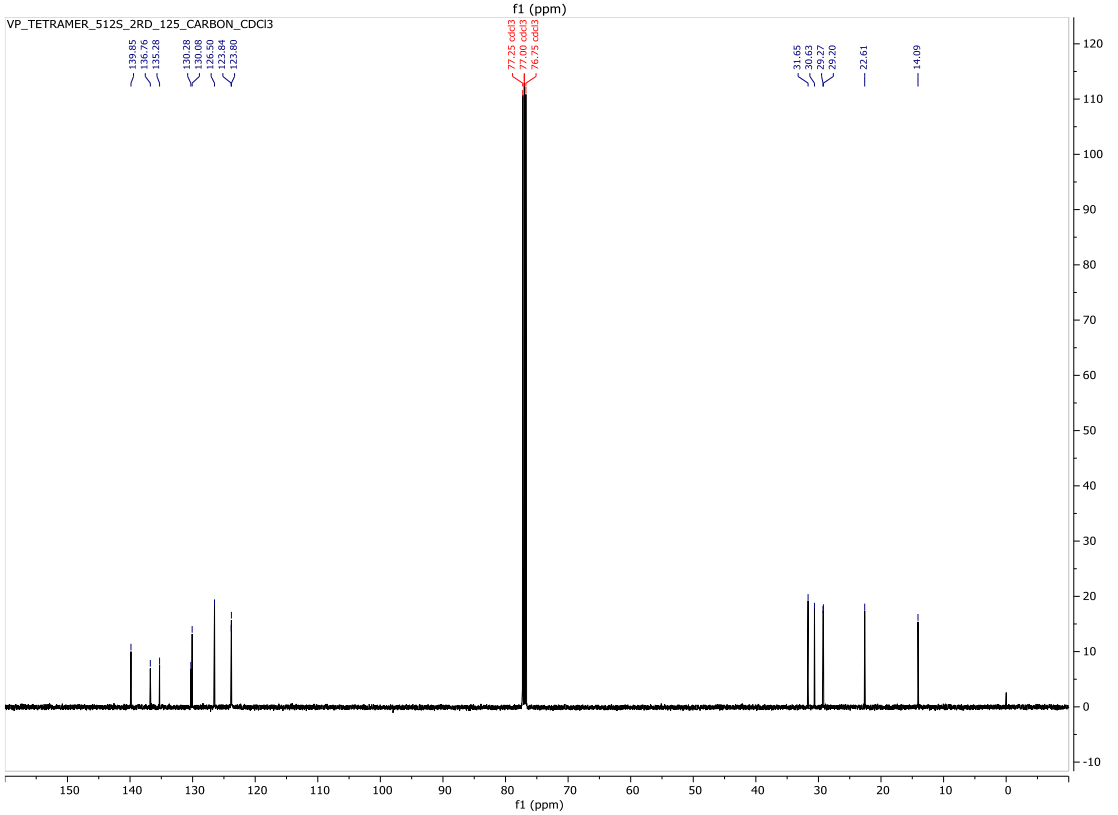




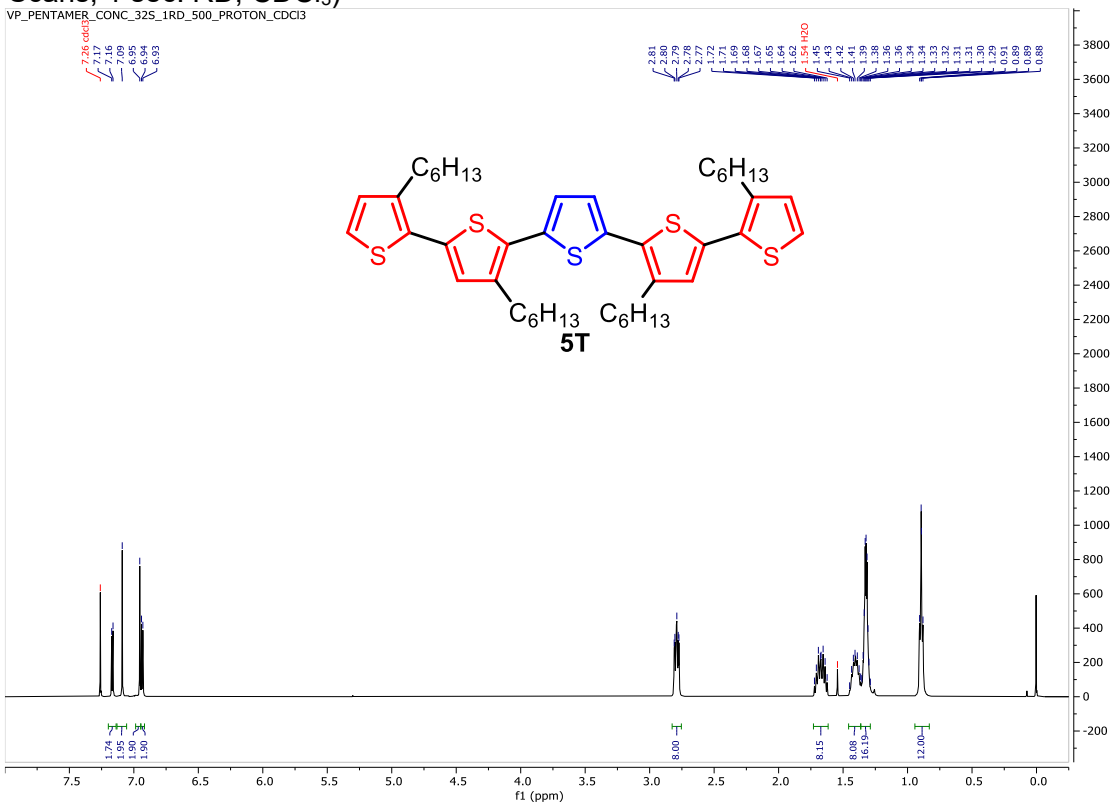
3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene **(4T)**

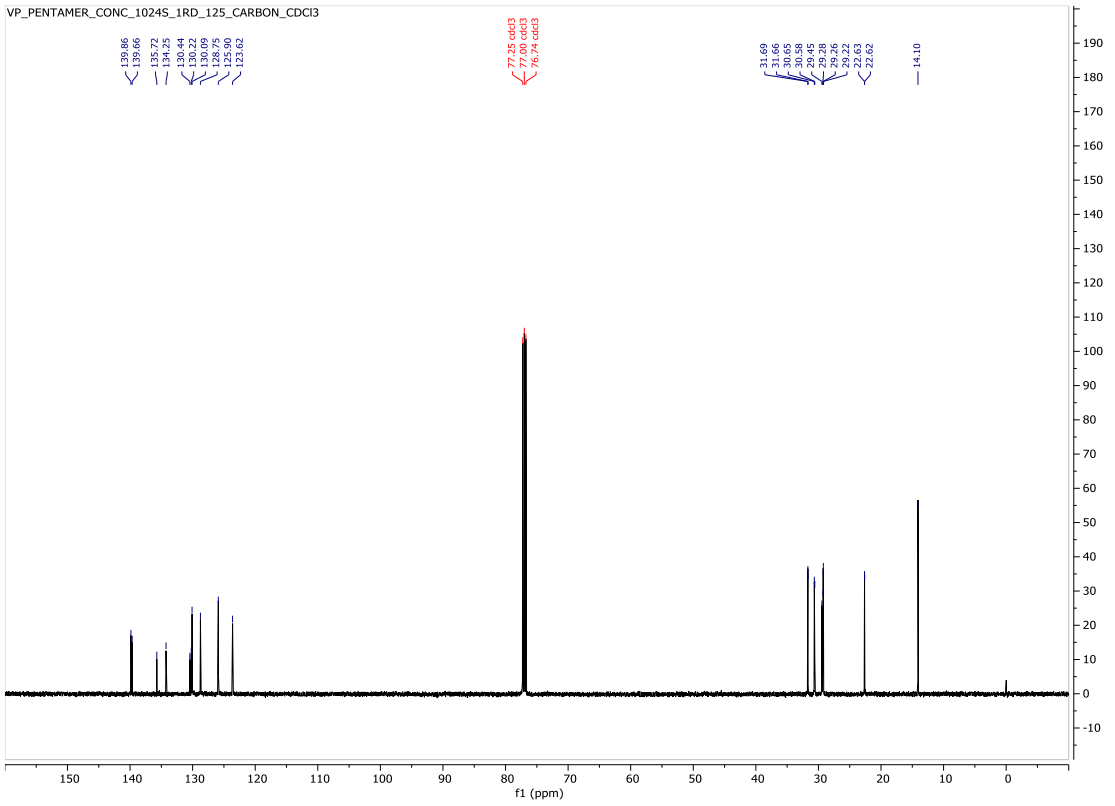
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



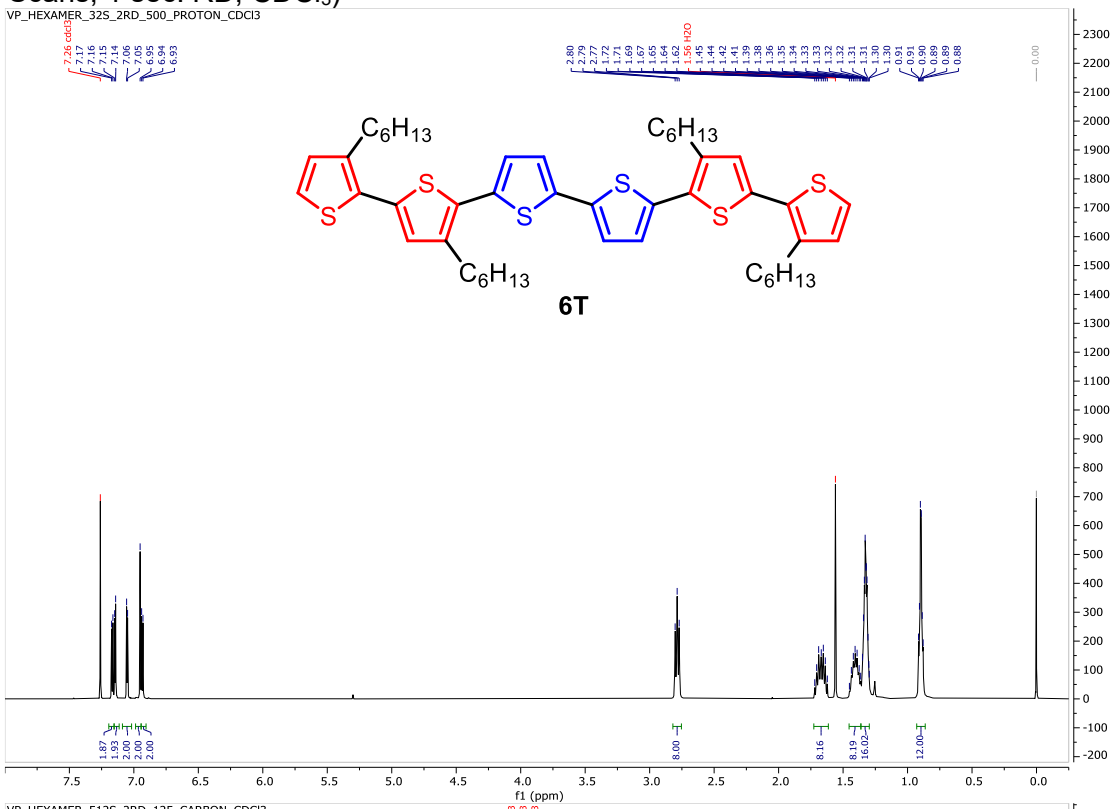


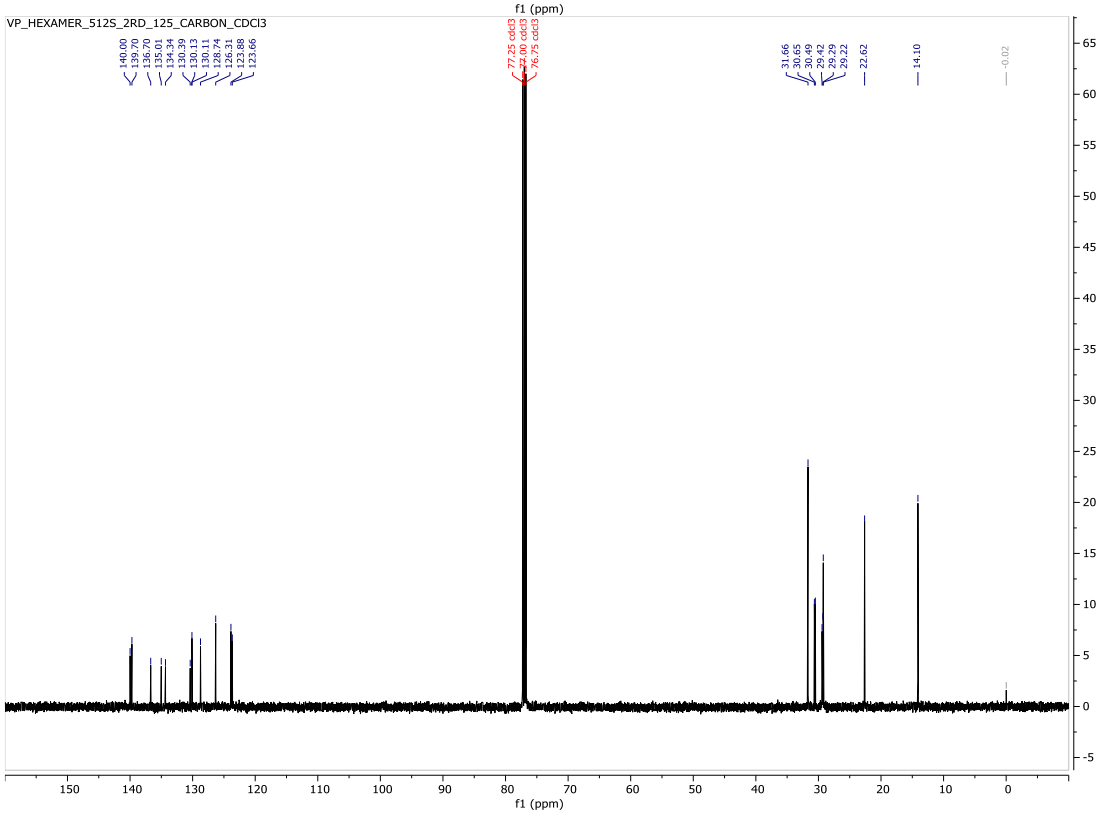
3,3‴,3⁗,4'-tetrahexyl-2,2':5',2'':5'',2‴:5‴,2⁗-quinquethiophene **(5T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



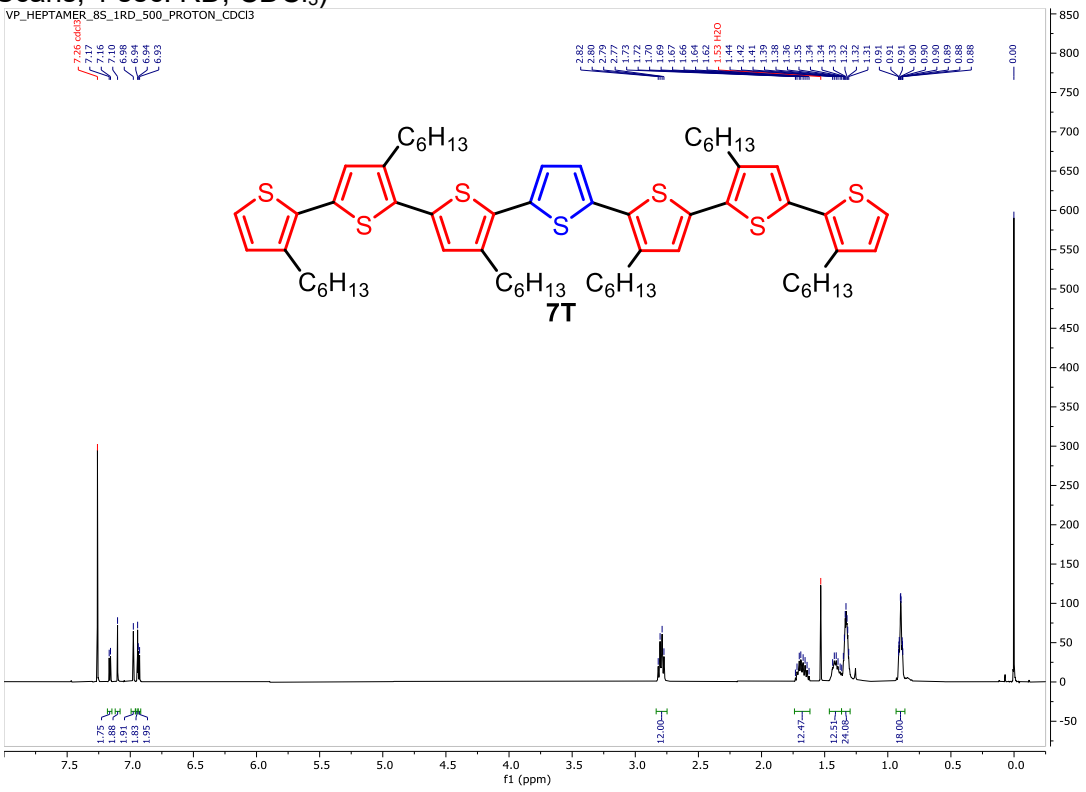


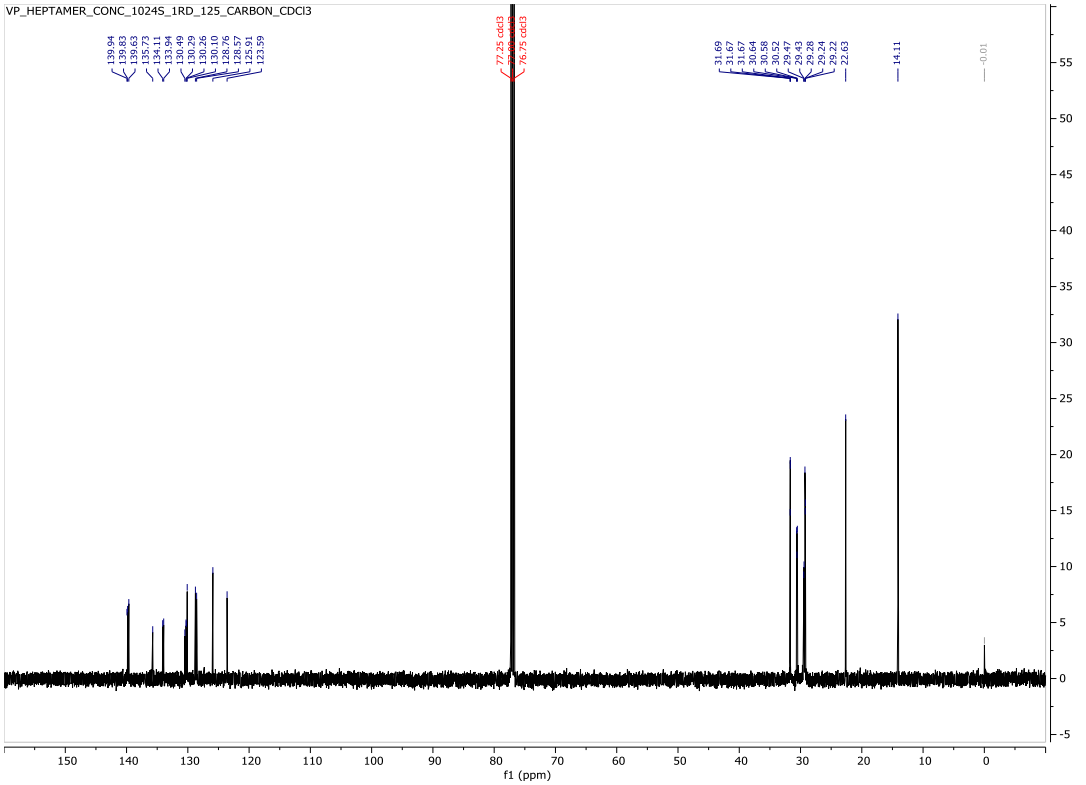
3,3"",3"",4'-tetrahexyl-2,2':5',2":5",2"':5"',2"":5"",2""'-sexithiophene **(6T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)





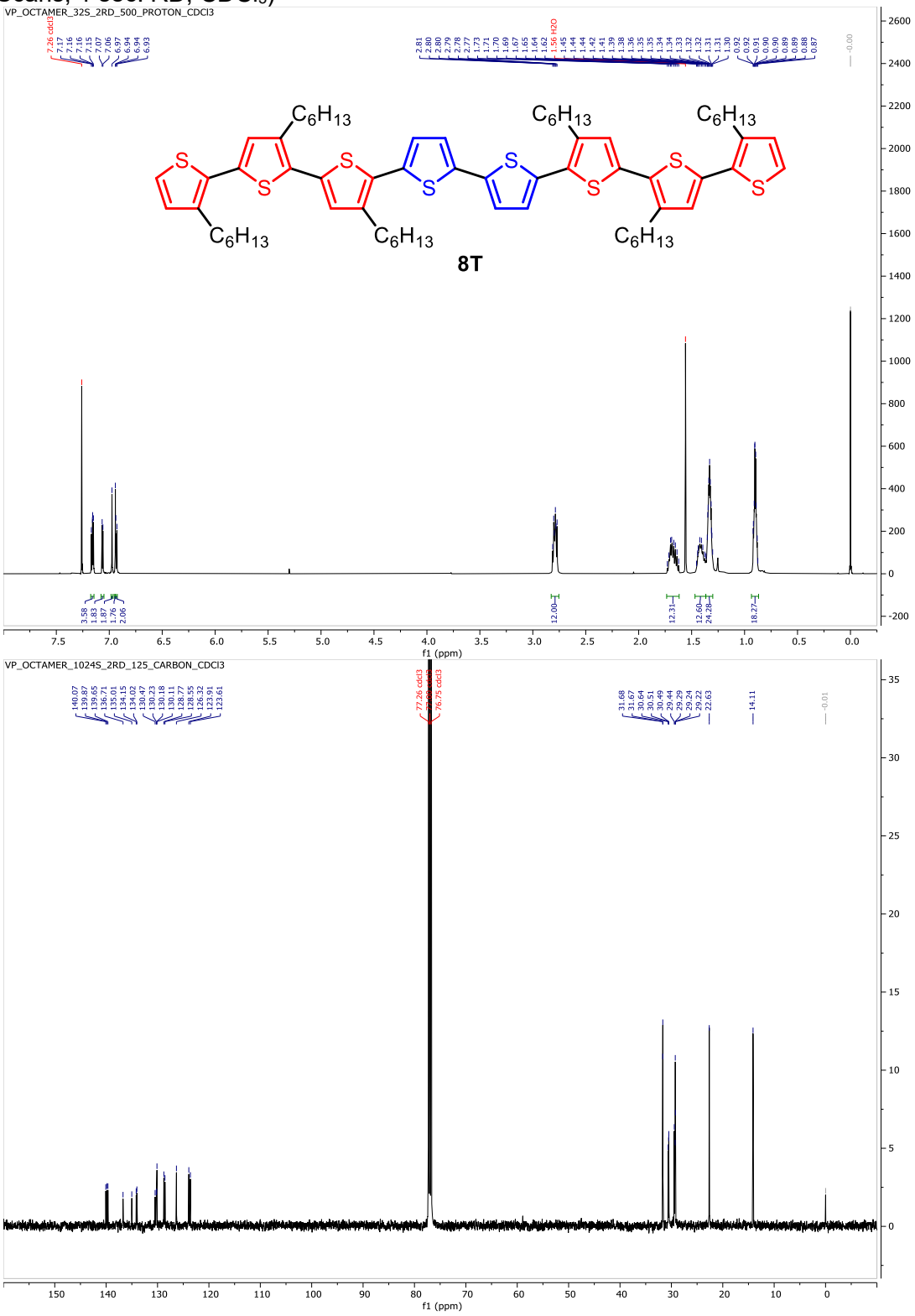
3,3"",3"",3"",4',4"-hexahexyl-2,2':5',2":5",2"':5"',2"":5"",2"":5"",2"":5"",2"""-septithiophene **(7T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



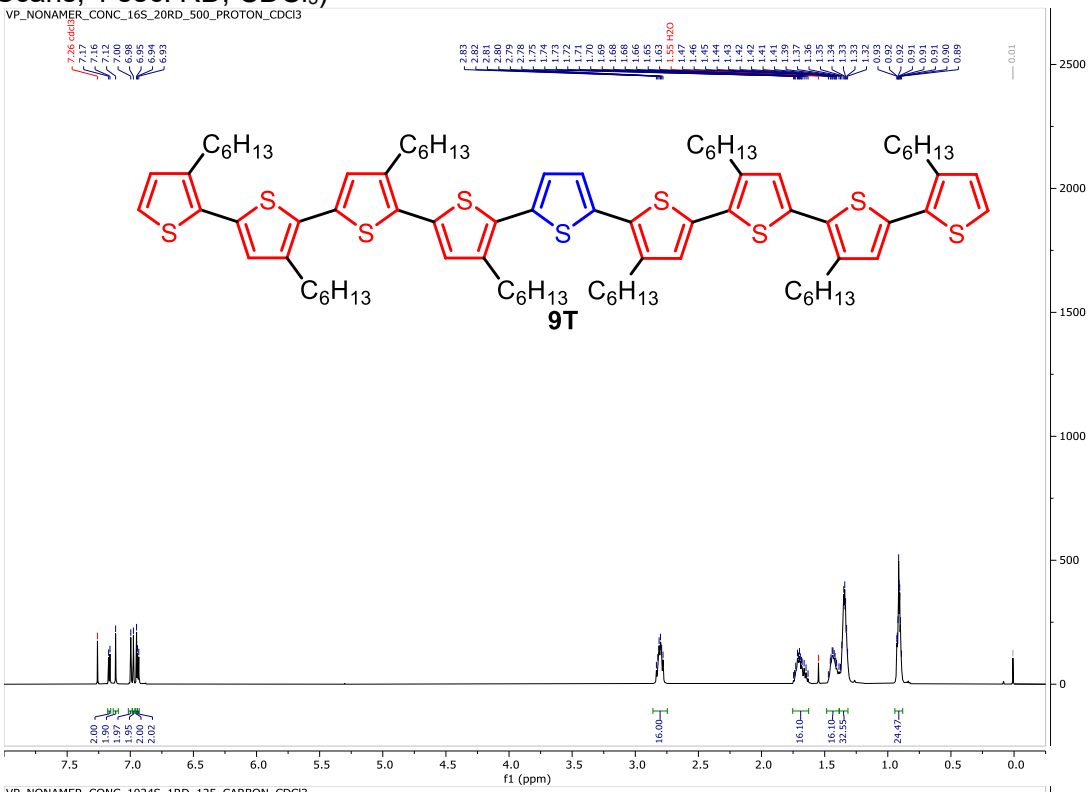


3,3'''',3''''',3''''''',4',4''-hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5''''''-octithiophene **(8T)**

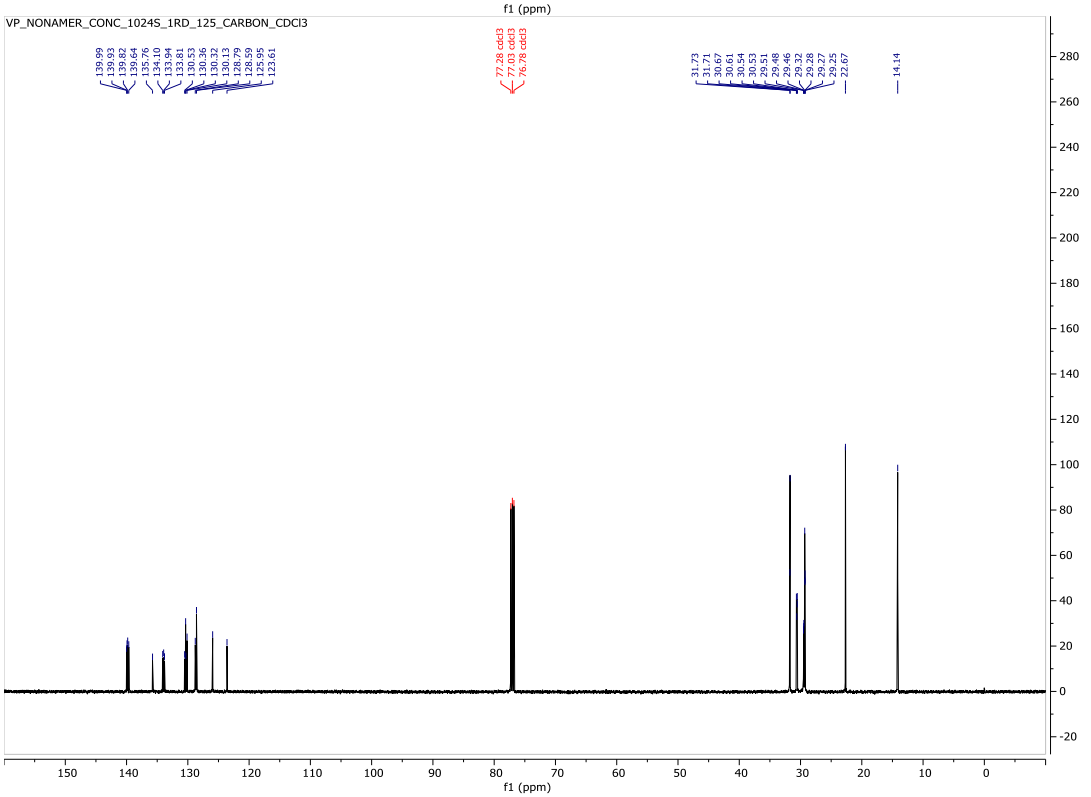
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



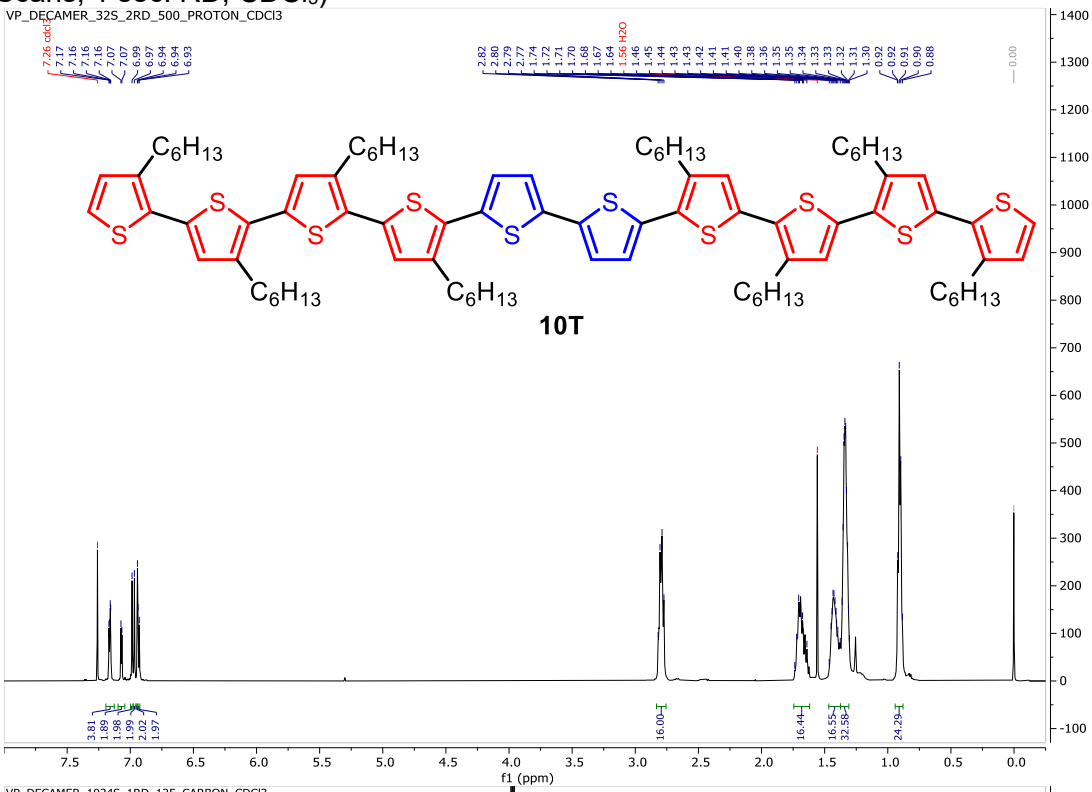
3,3'''',3''''',3'''''',3''''''',4',4'',4'''-octahexyl-
2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2'''''''-novithiophene **(9T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

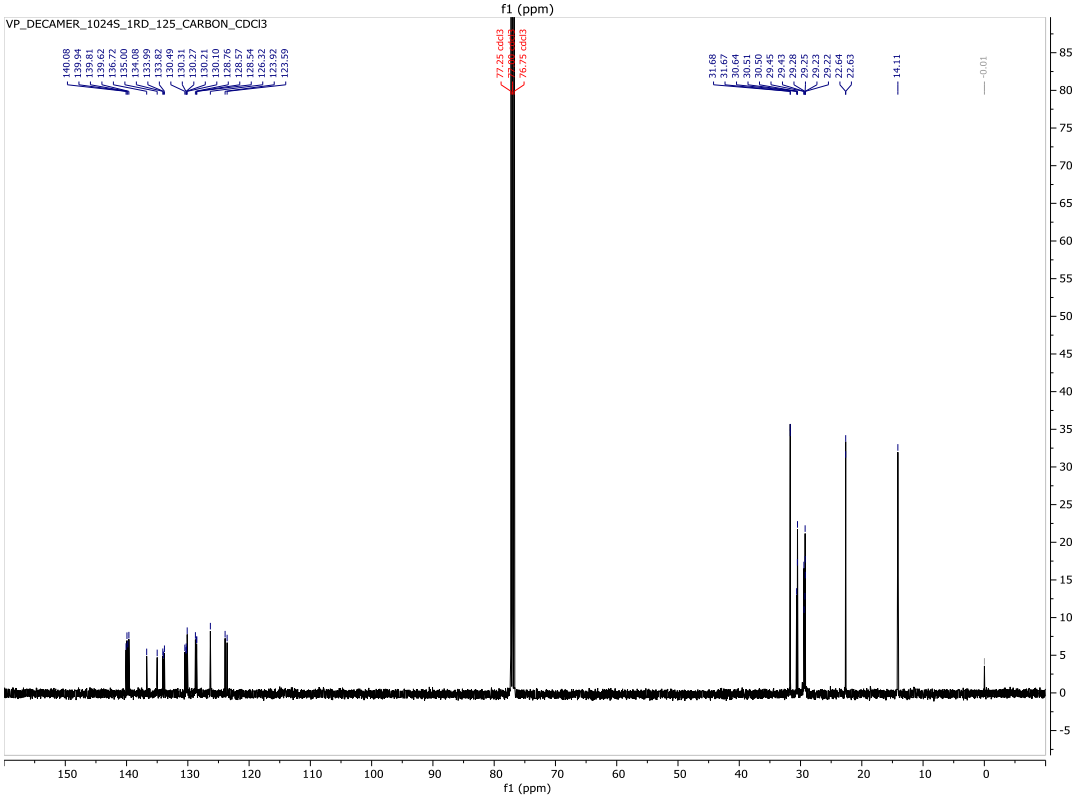


9T



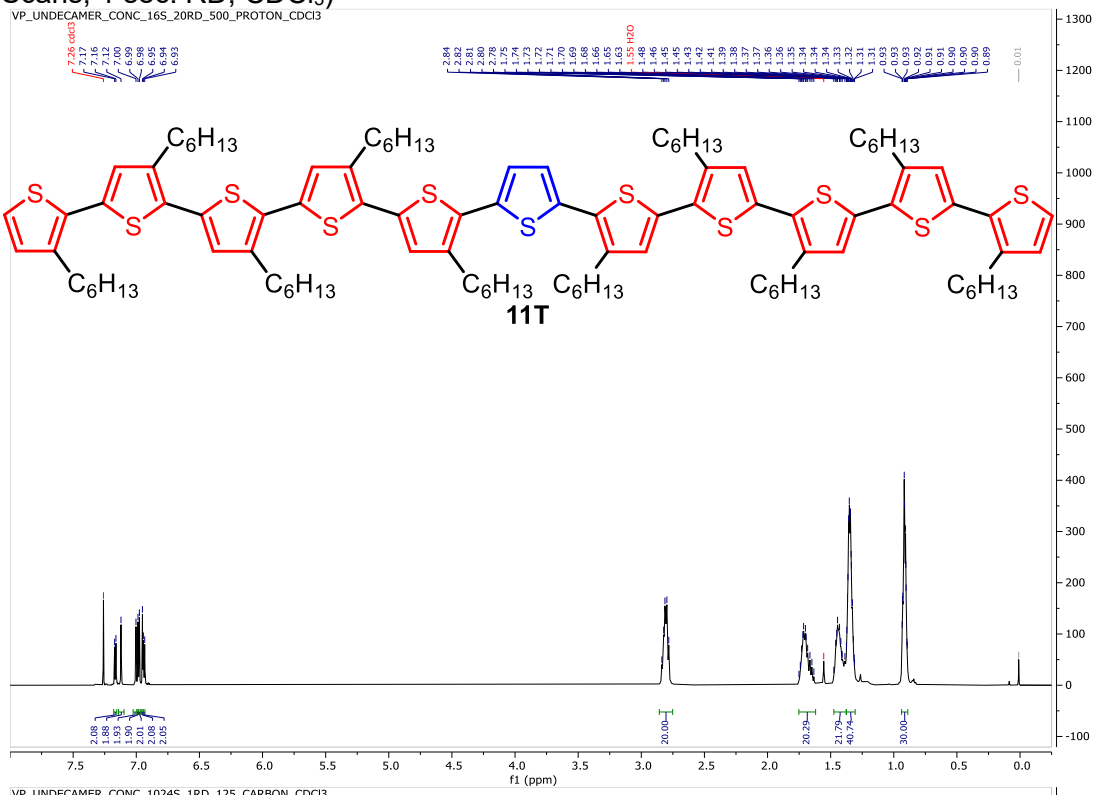
3,3''''',3''''',3'''''',3''''''',4',4'',4'''-octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2'''''''-decithiophene **(10T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

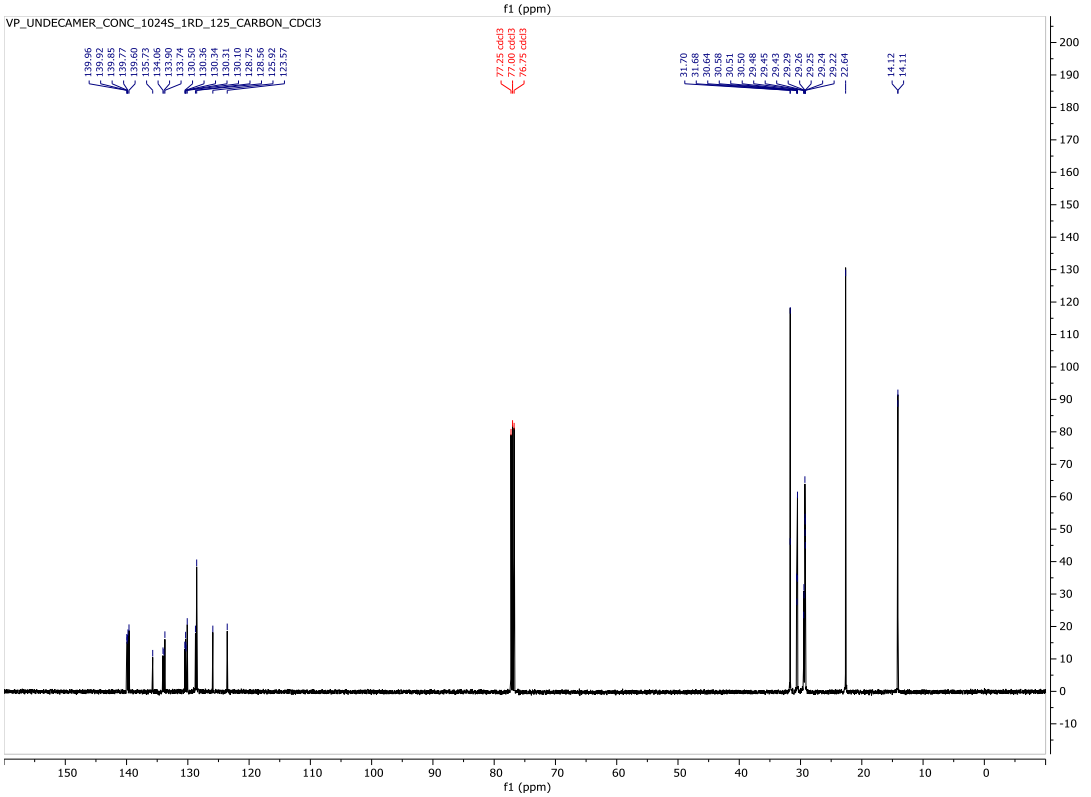




3,3''''',3''''',3''''''',3''''''',3''''''',4',4'',4''',4''''-decahexyl-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5''''',2''''':5''''',2''''':5''''',2''''':5''''',2''''''':5'''''''-undecithiophene **(11T)**

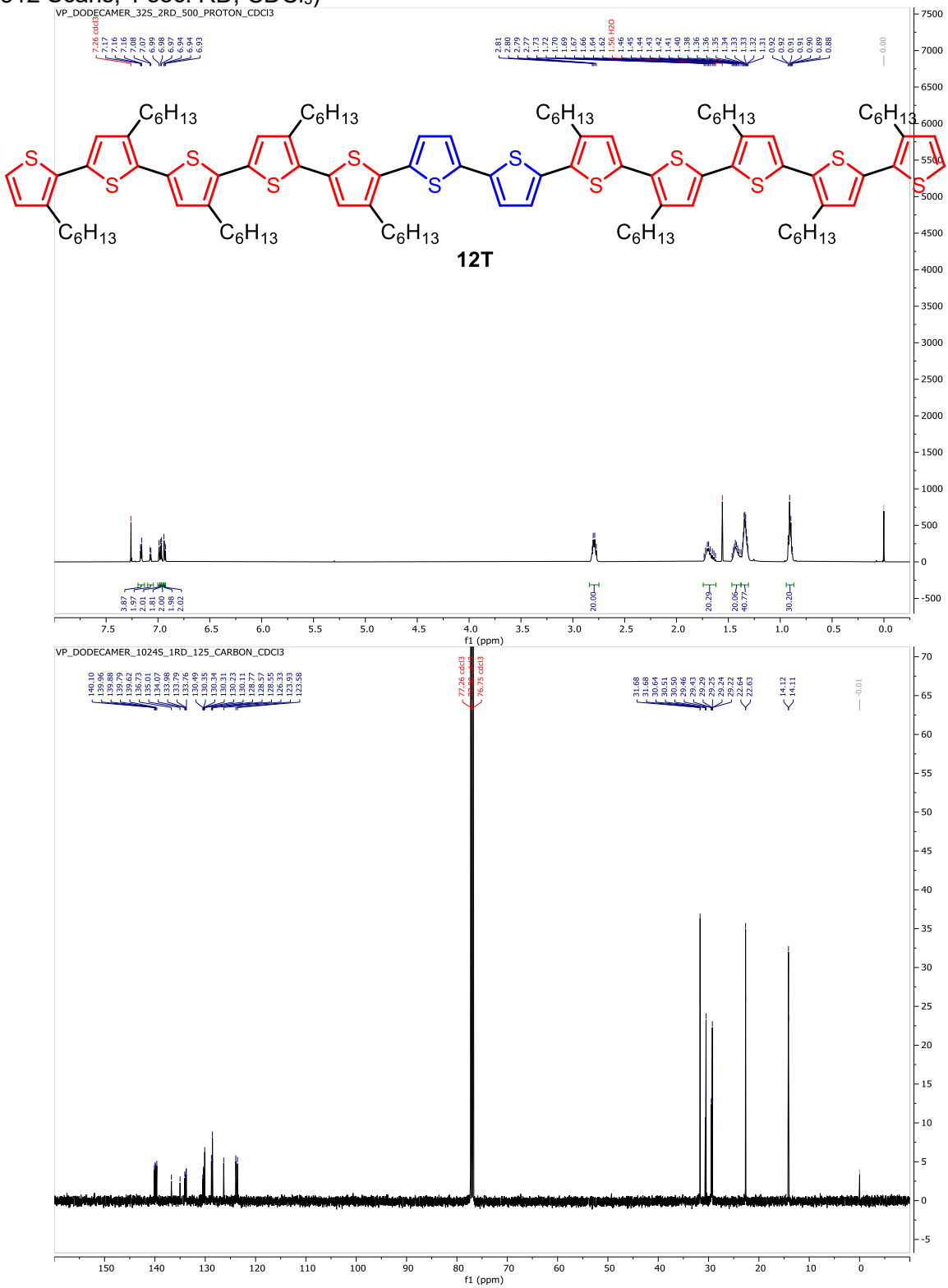
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



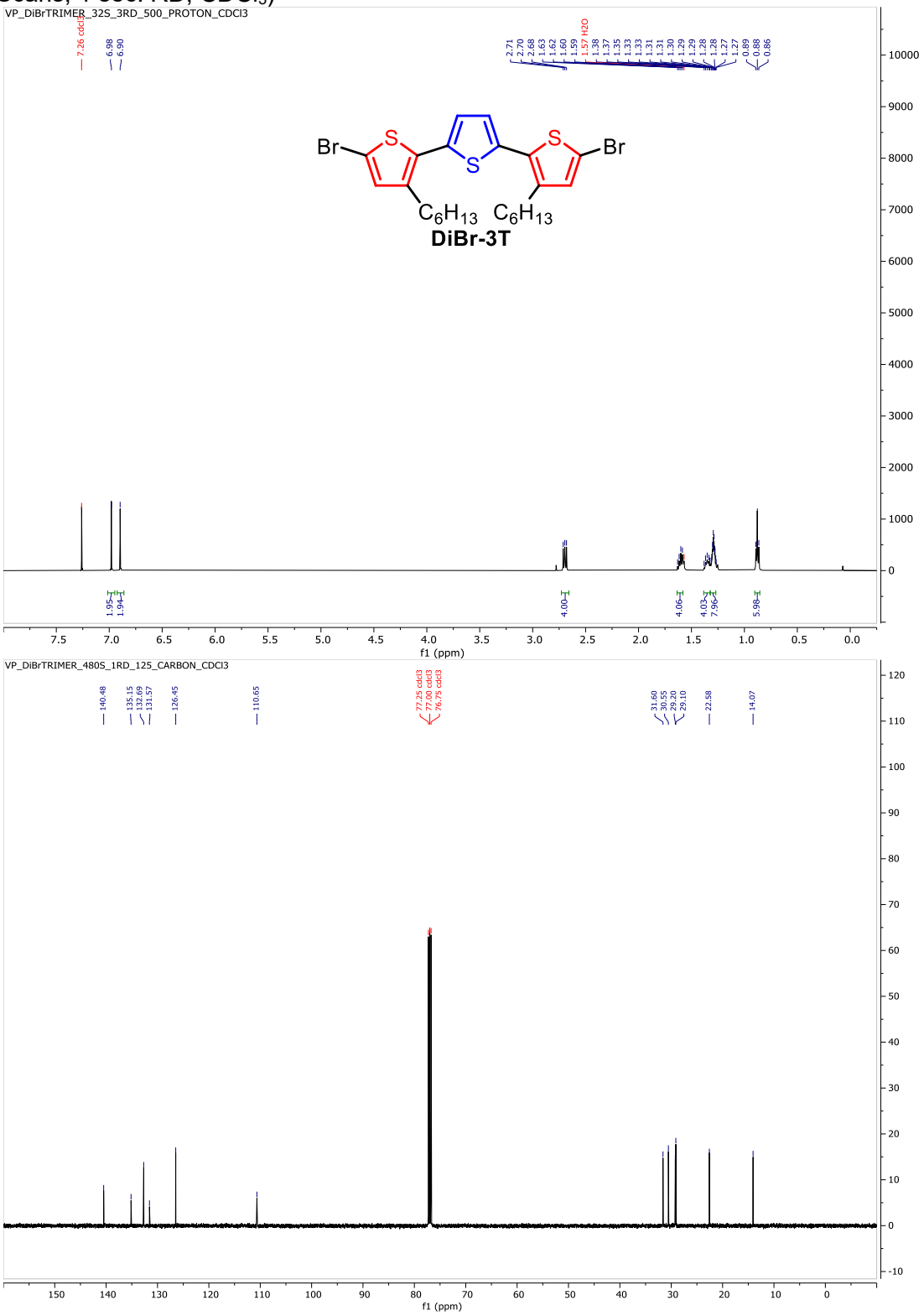


3,3''''',3''''''',3''''''',3'''''''',3'''''''',4',4'',4''',4''''-decahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2'''''''':5''''''',2''''''''-dodecithiophene **(12T)**

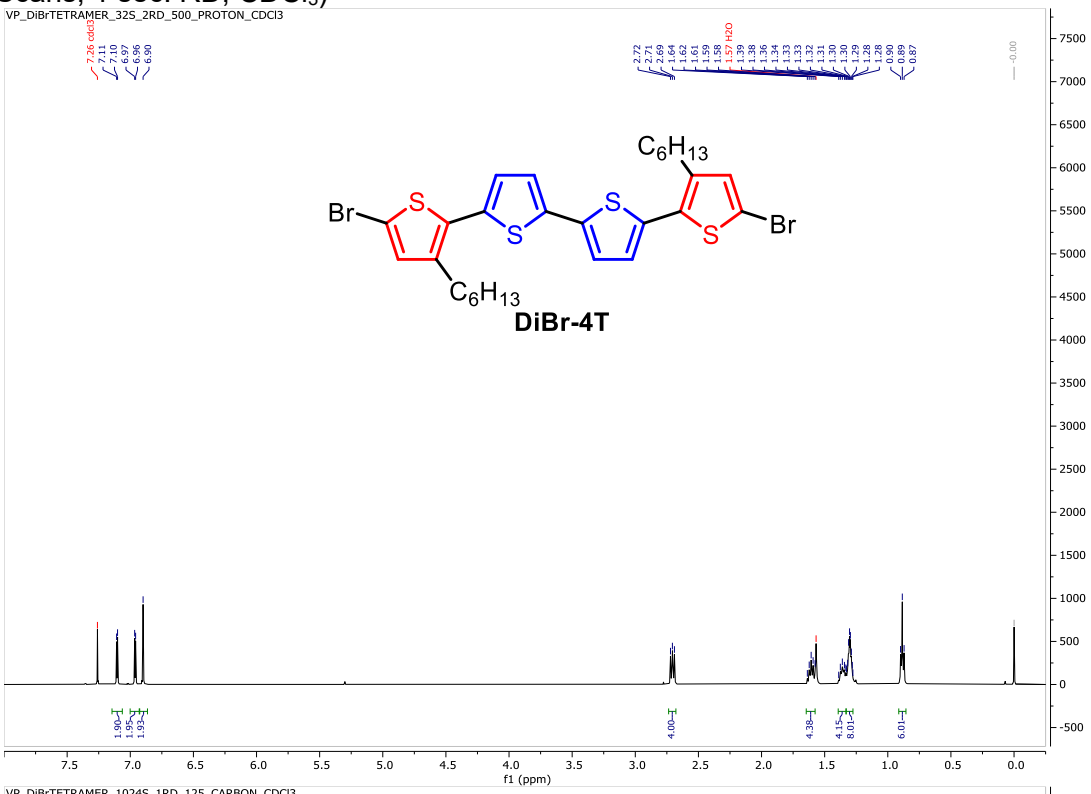
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

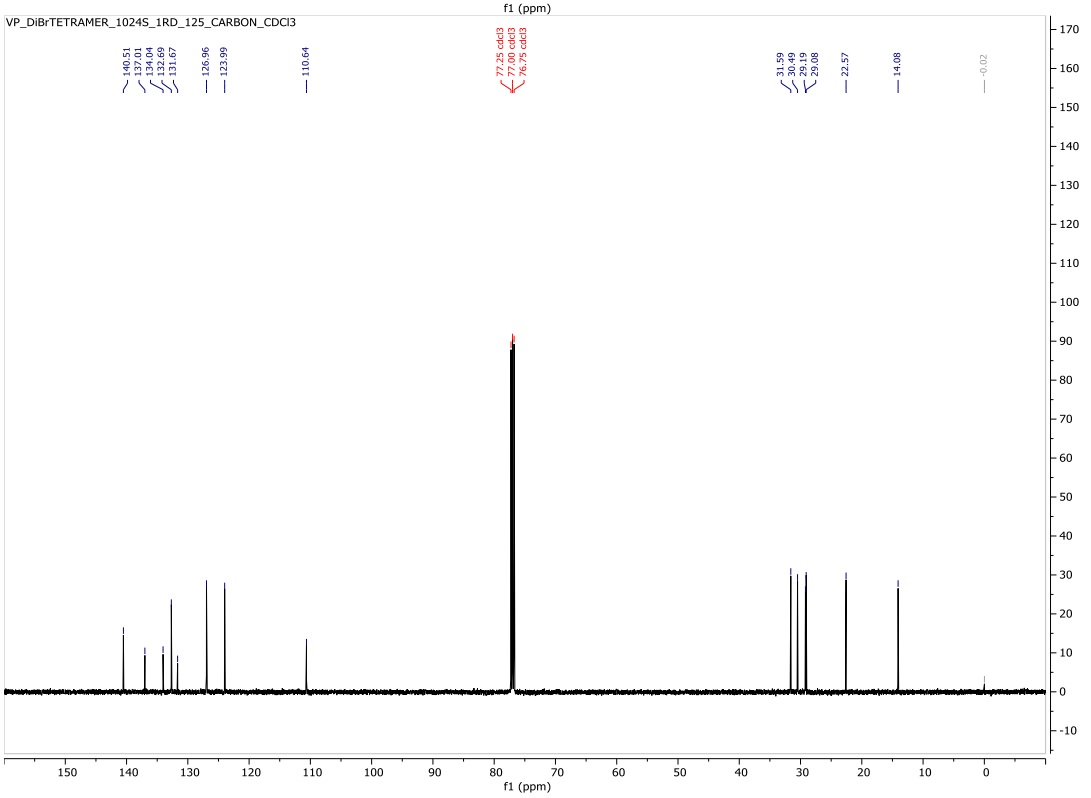


5,5''-dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene **(DiBr-3T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

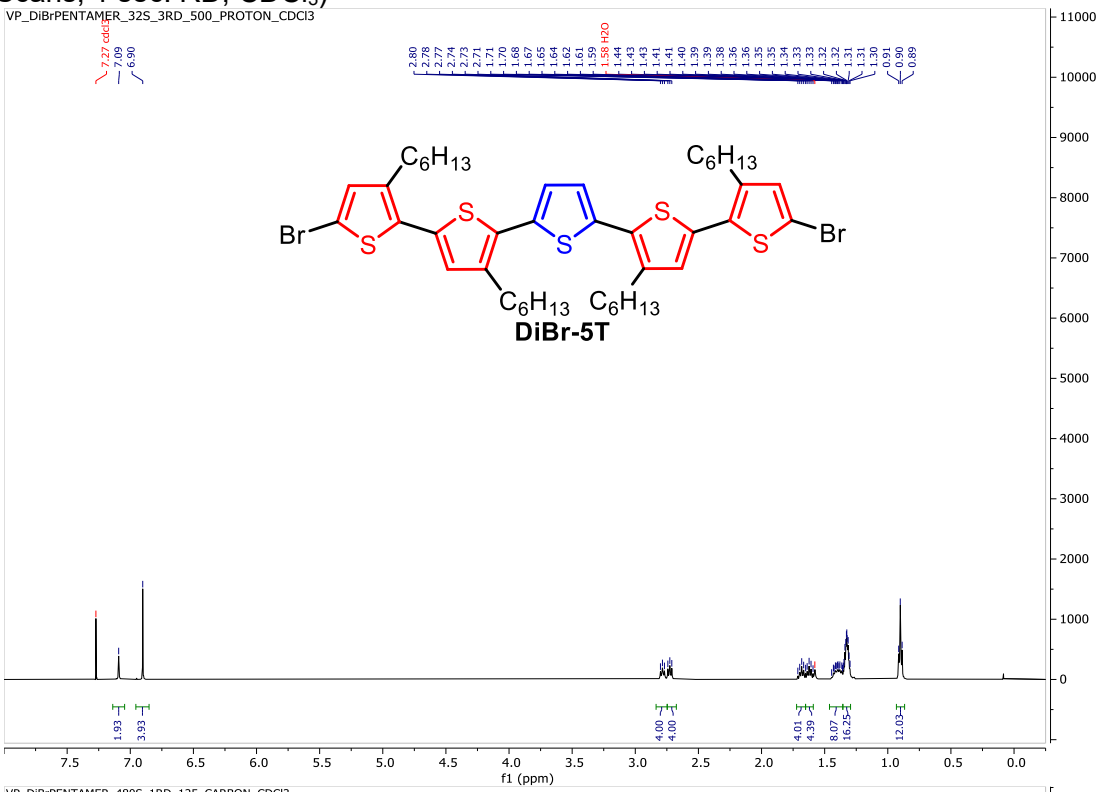


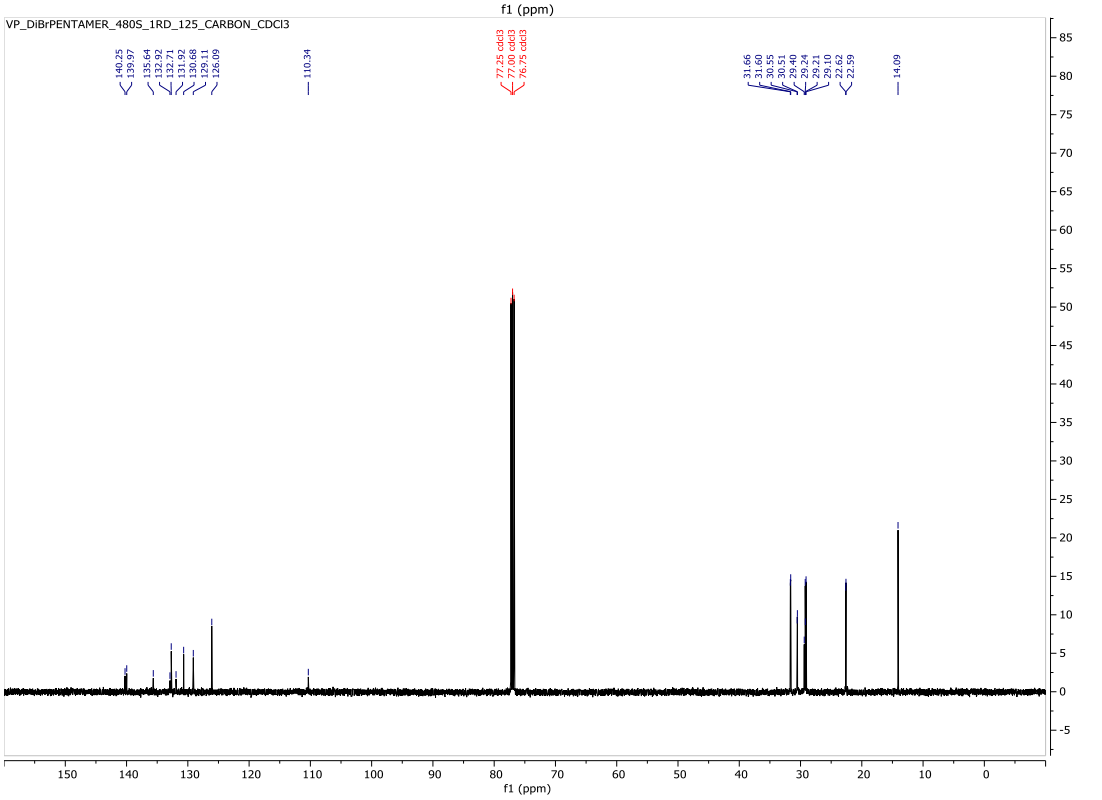
5,5'''-dibromo-3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene **(DiBr-4T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



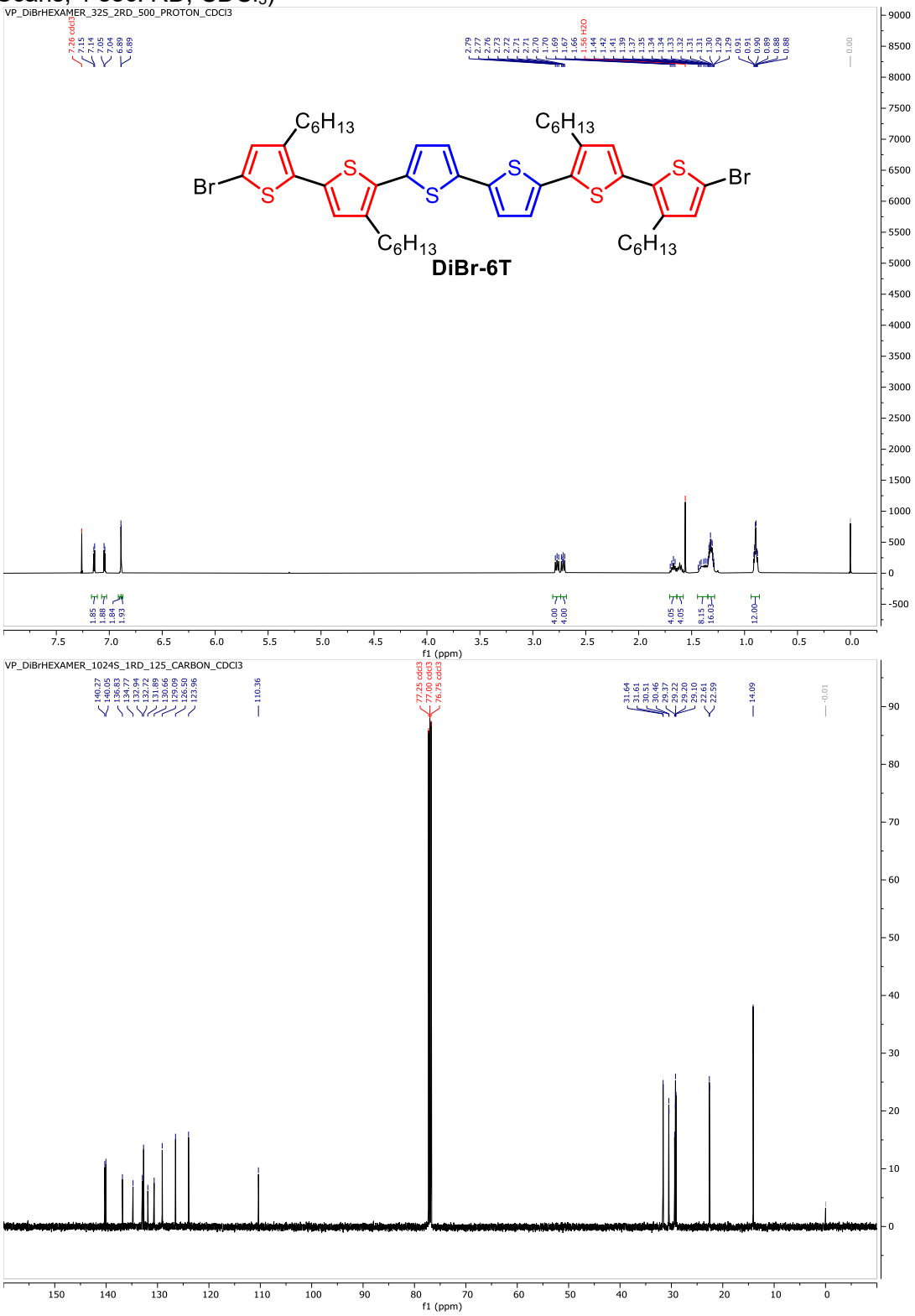


5,5""-dibromo-3,3"',3"",4'-tetrahexyl-2,2':5',2":5",2"':5"',2""-quinquethiophene **(DiBr-5T)**
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



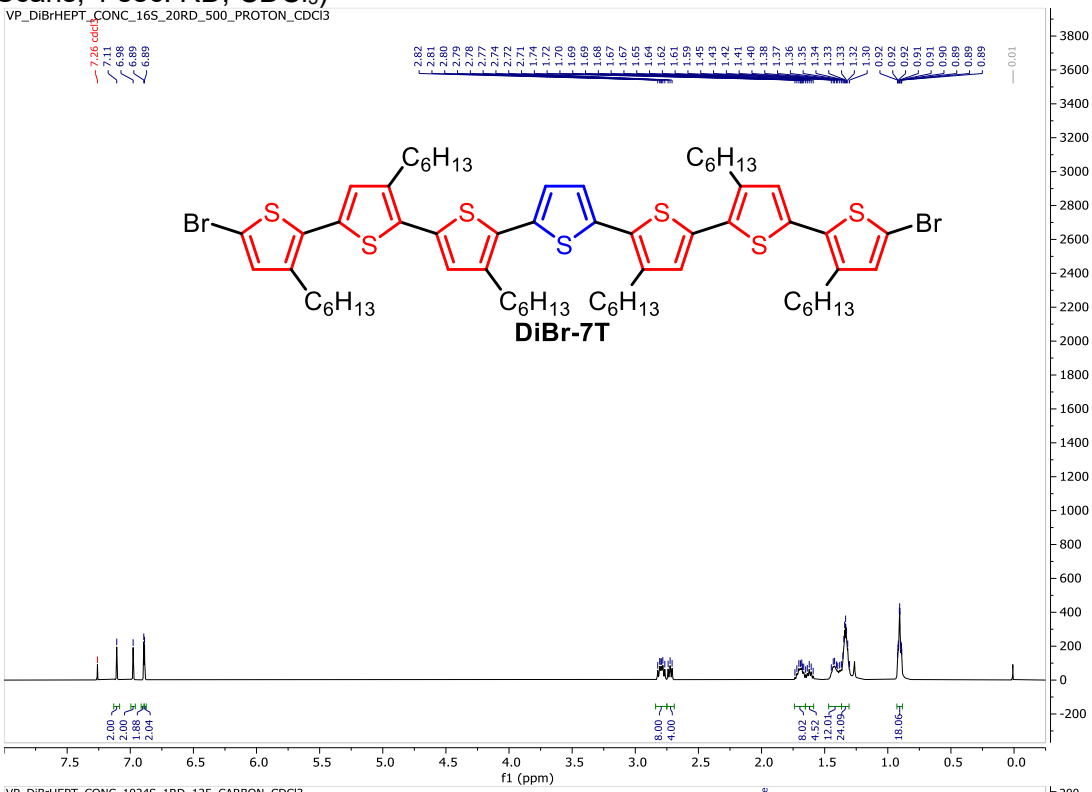


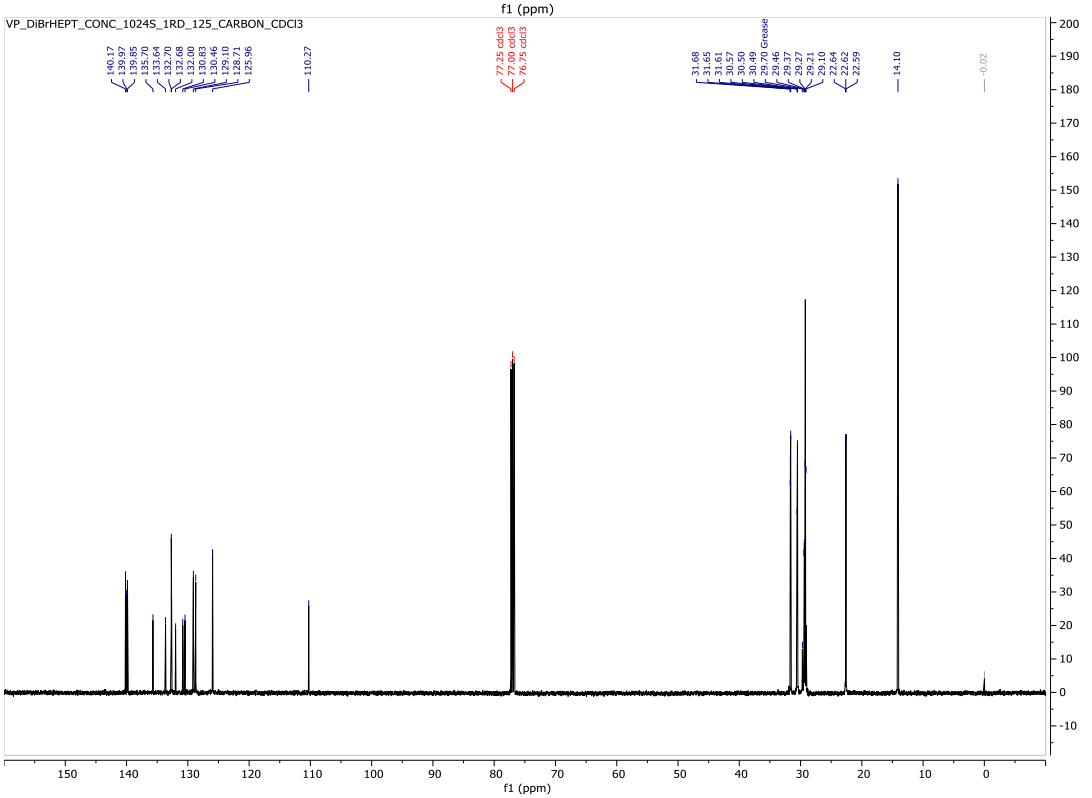
5,5''''-dibromo-3,3'''',3''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene **(DiBr-6T)** **^{1}H NMR Spectrum** (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



5,5''''-dibromo-3,3'''',3''''',3''''',4',4''-hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''-septithiophene **(DiBr-7T)**

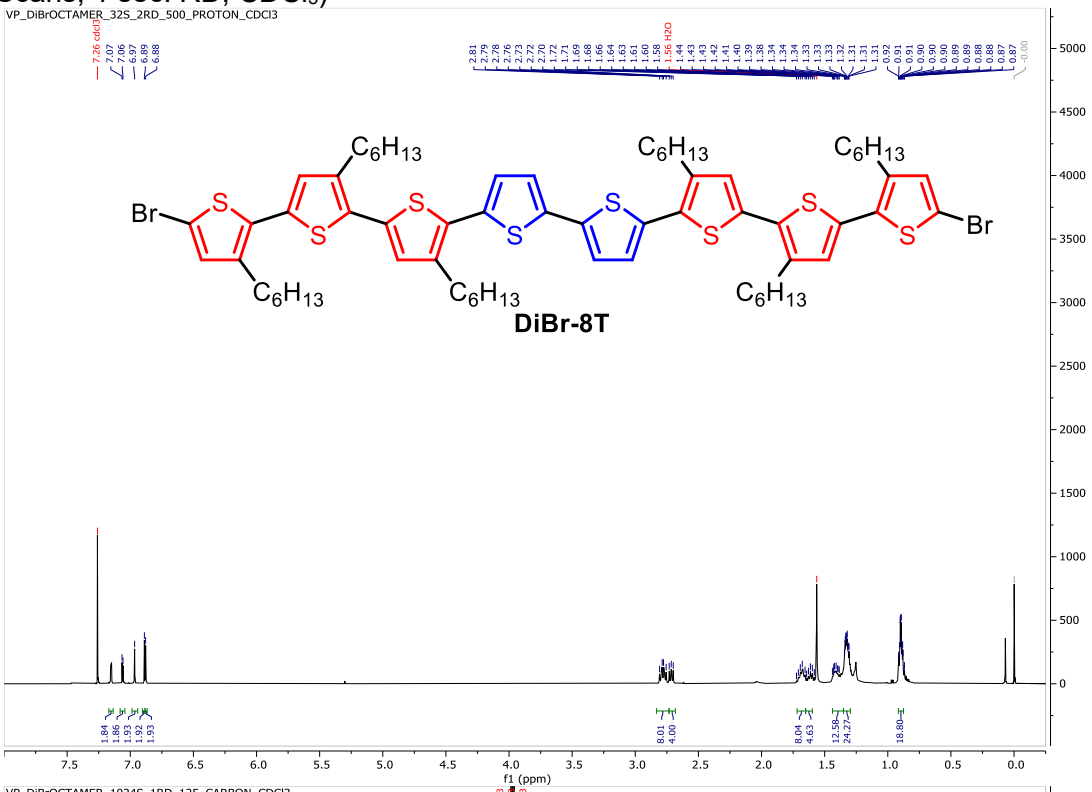
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)

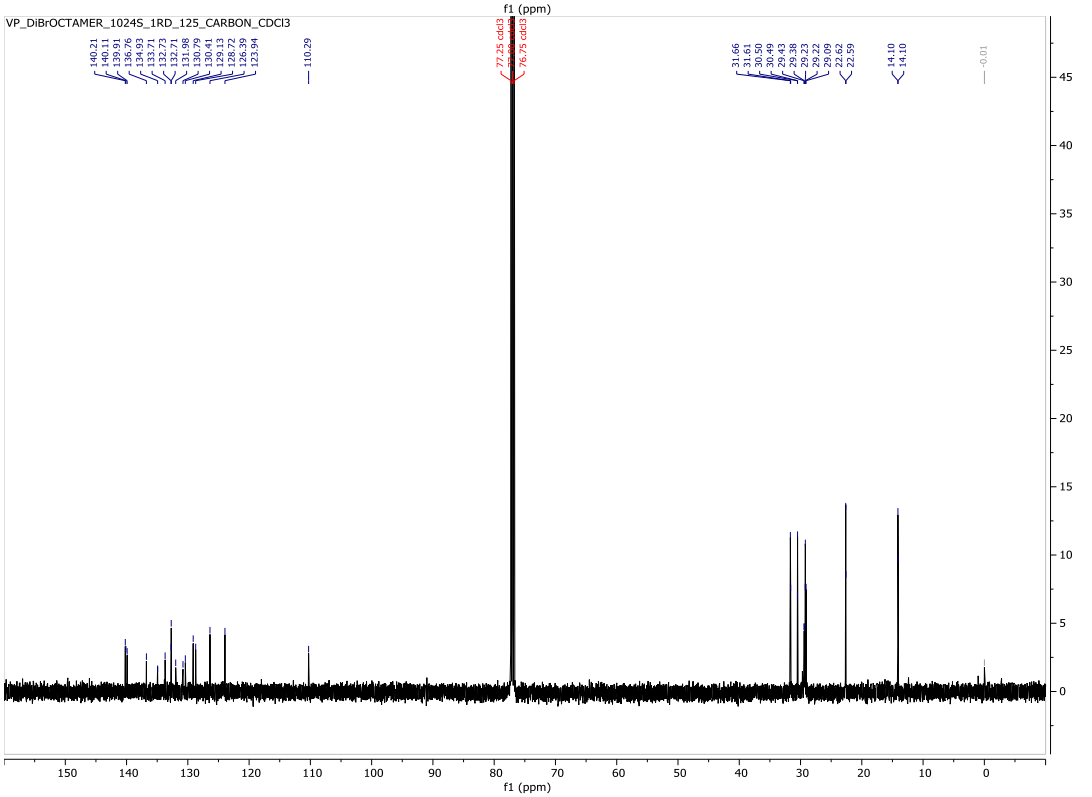




5,5''''''-dibromo-3,3'''',3''''',3''''''',4',4''-hexahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''-octithiophene **(DiBr-8T)**

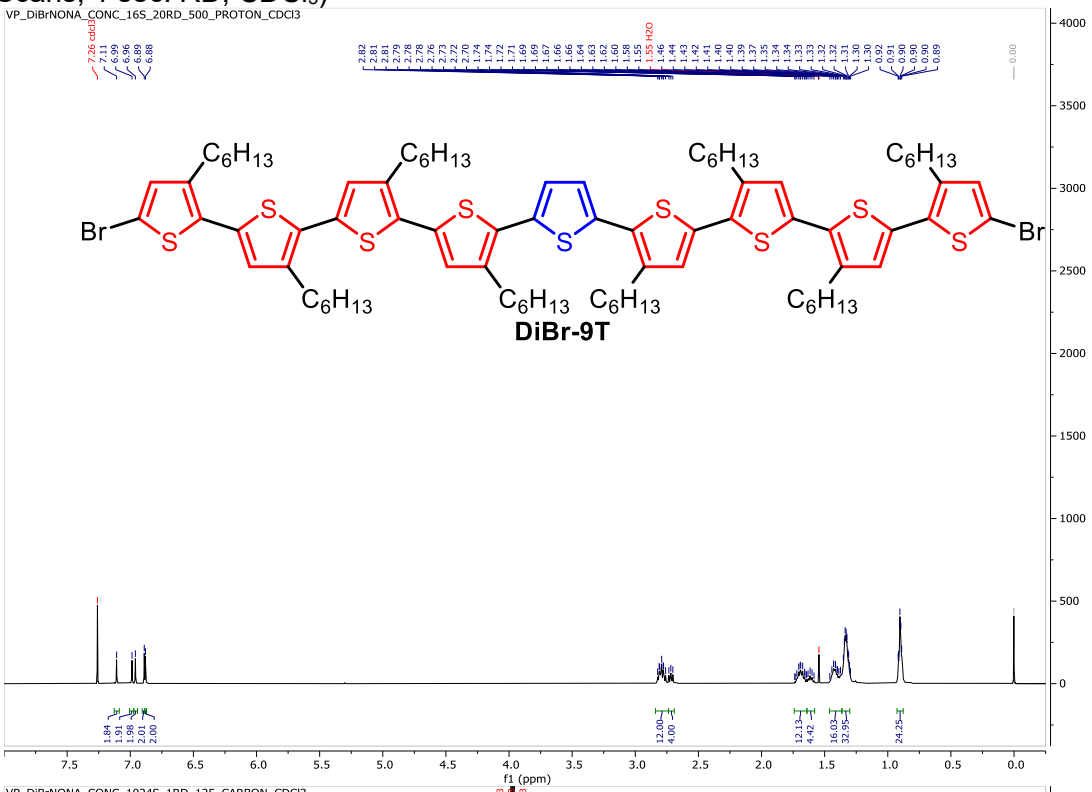
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



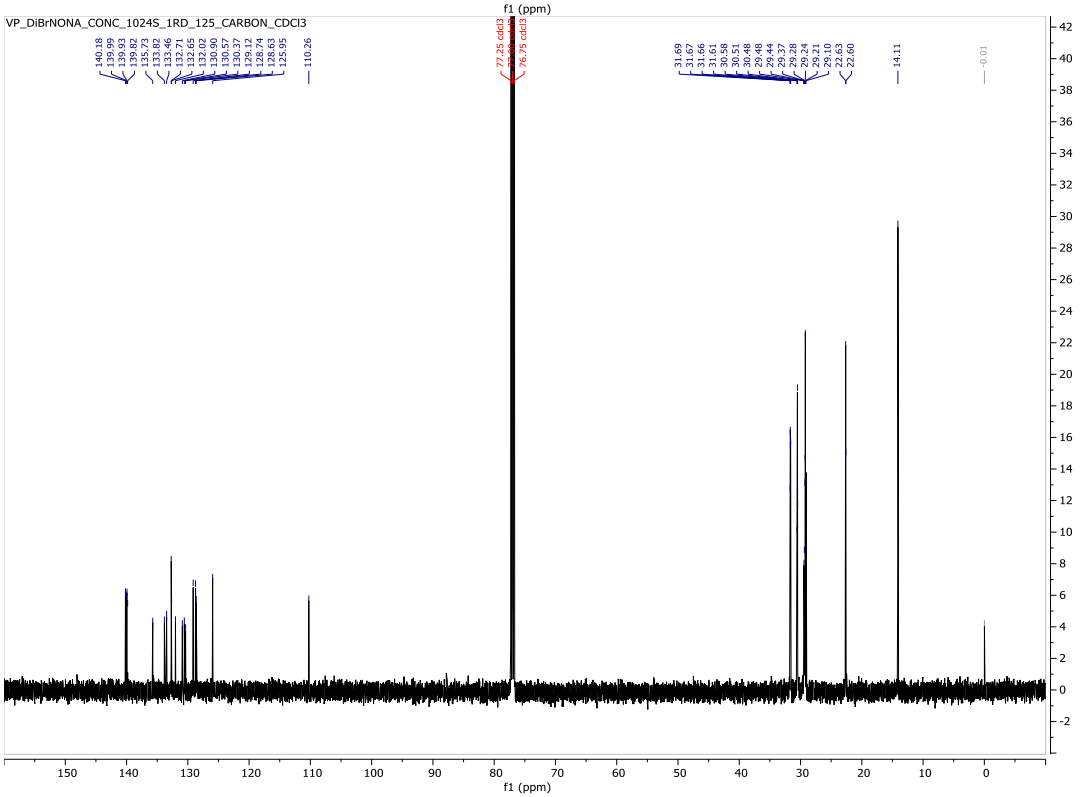


5,5''''''-dibromo-3,3'''',3''''',3''''',3''''''',4',4'',4'''-octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''':5''''',2''''''':5''''''-novithiophene **(DiBr-9T)**

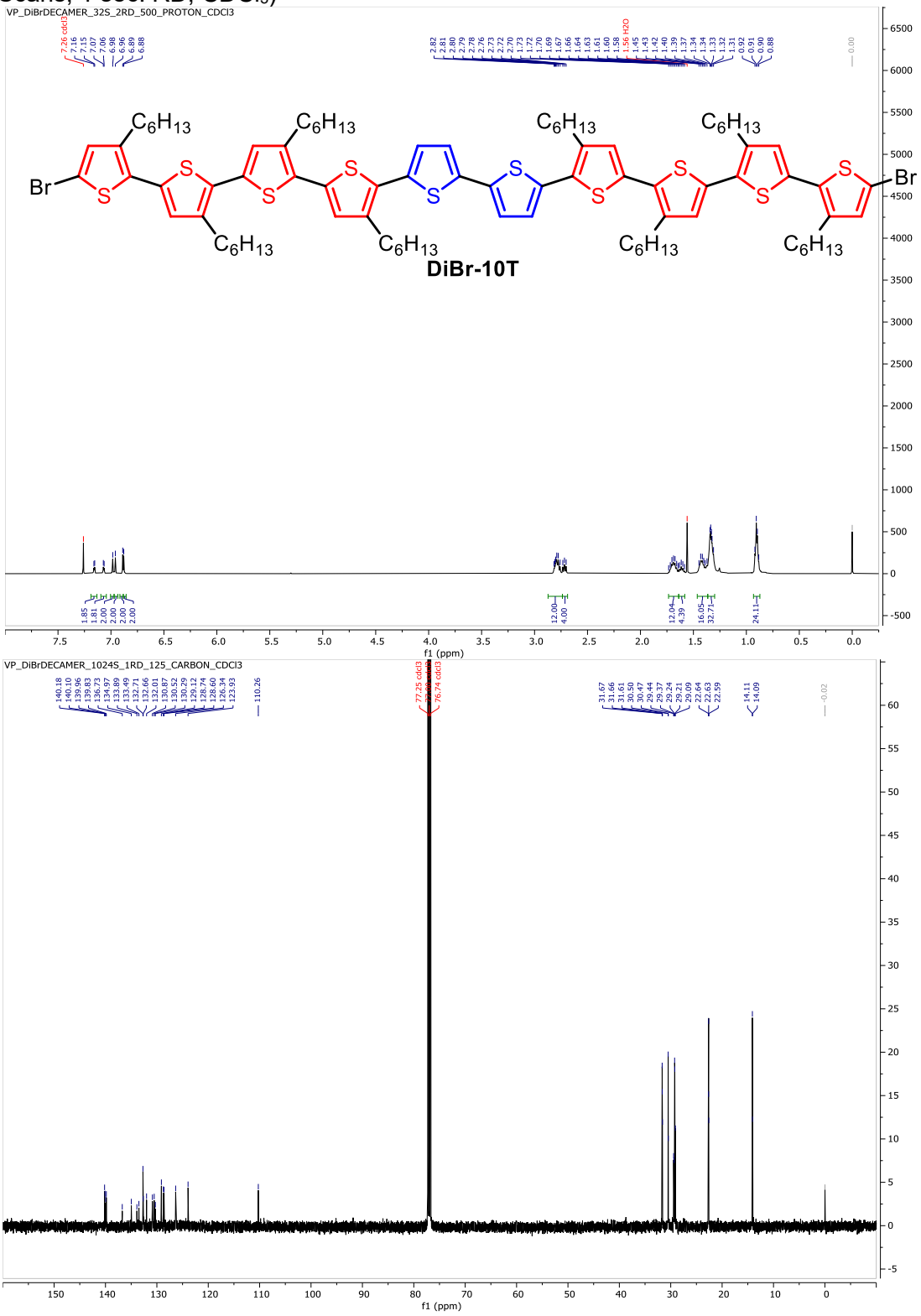
^{1}H NMR Spectrum (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



DiBr-9T

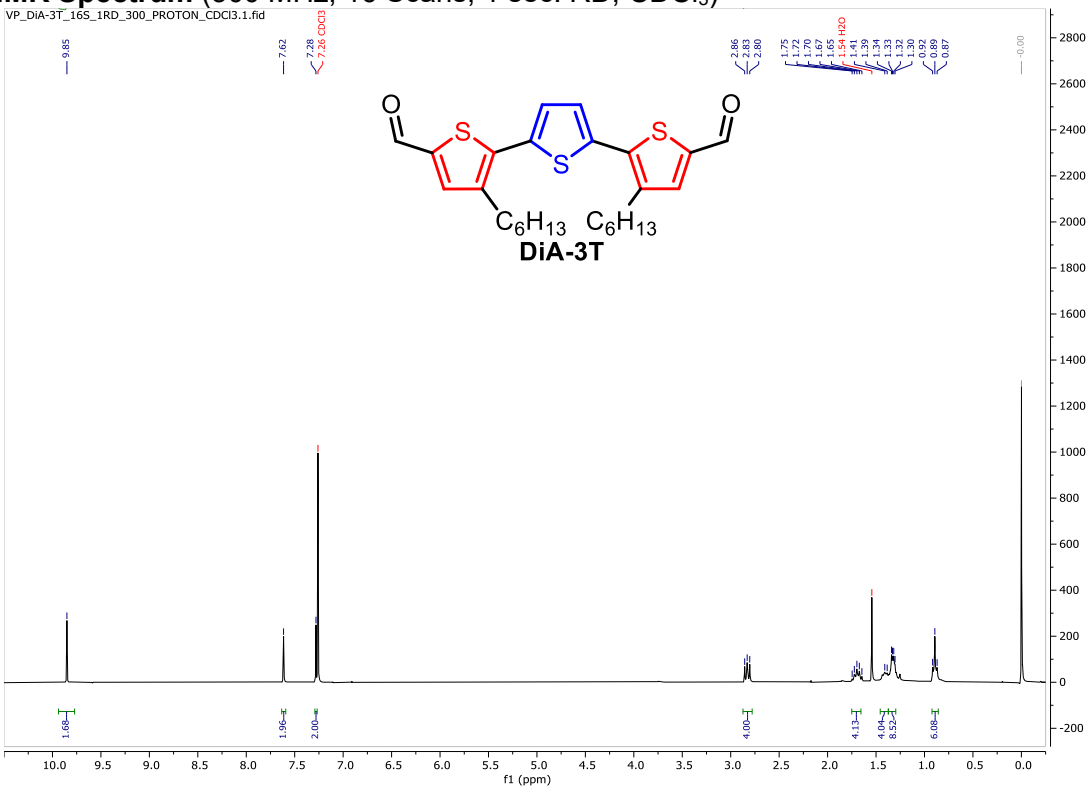


5,5'''''''-dibromo-3,3''''',3''''',3'''''',3''''''',4',4'',4'''-octahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2'''''''-decithiophene **(DiBr-10T)** **^{1}H NMR Spectrum** (500 MHz, 16 Scans, 2 sec. RD, $CDCl_3$) and **^{13}C NMR Spectrum** (125 MHz, 512 Scans, 1 sec. RD, $CDCl_3$)



3,3''-dihexyl-[2,2':5',2''-terthiophene]-5,5''-dicarbaldehyde **(DiA-3T)**

^{1}H NMR Spectrum (300 MHz, 16 Scans, 1 sec. RD, $CDCl_3$)



^{1}H NMR of this compound was only recorded at 300 MHz. The spectrum was compared to reported values to confirm its identity, as such no ^{13}C NMR or HRMS were recorded either.

Olinga, T.; Destri, S.; Porzio, W.; Selva, A. *Macromol. Chem. Phys.* **1997**, *198*, 1091–1107. DOI:10.1002/macp.1997.021980413.

Pasini, M.; Vercelli, B.; Zotti, G.; Berlin, A. *Electrochim. Acta* **2016**, *193*, 261–267. DOI:10.1016/j.electacta.2016.02.035.

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Appendix

Appendix A: GCMS of Miyaura Borylation Reactions

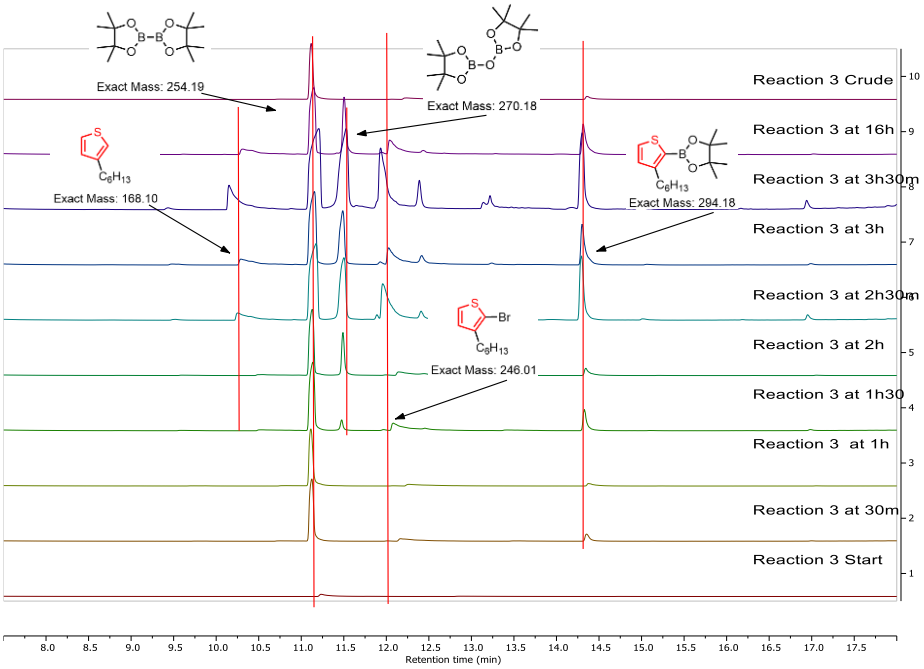

Figure A1: GCMS Aliquots of Reaction 3

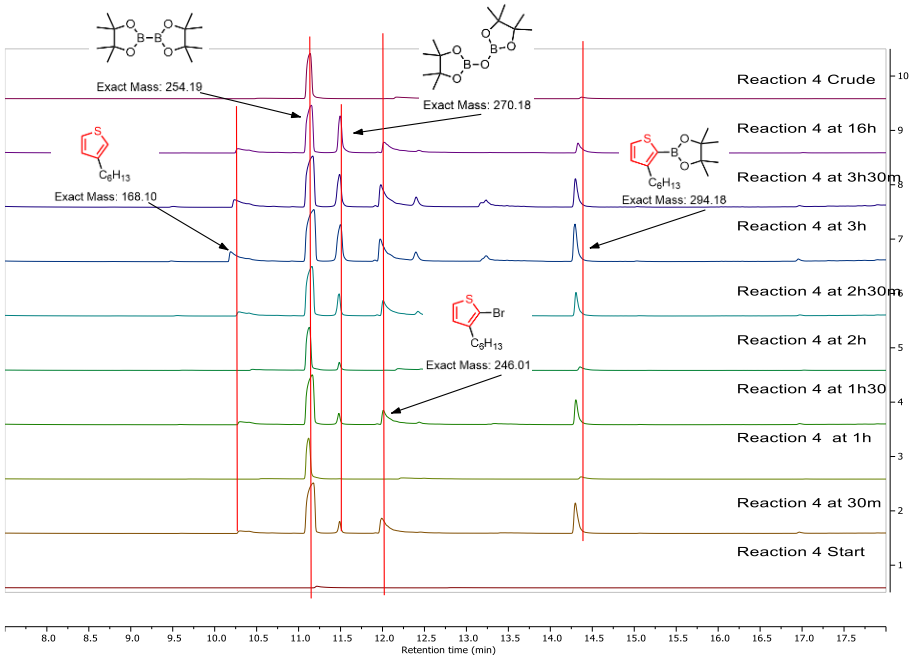

Figure A2: GCMS Aliquots of Reaction 4

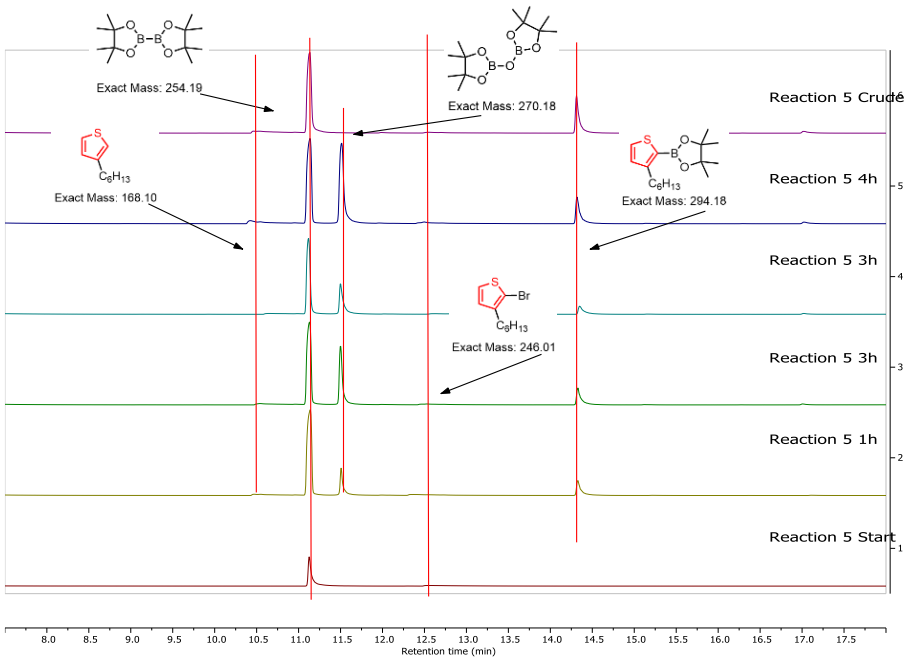

Figure A3: GCMS Aliquots of Reaction 5

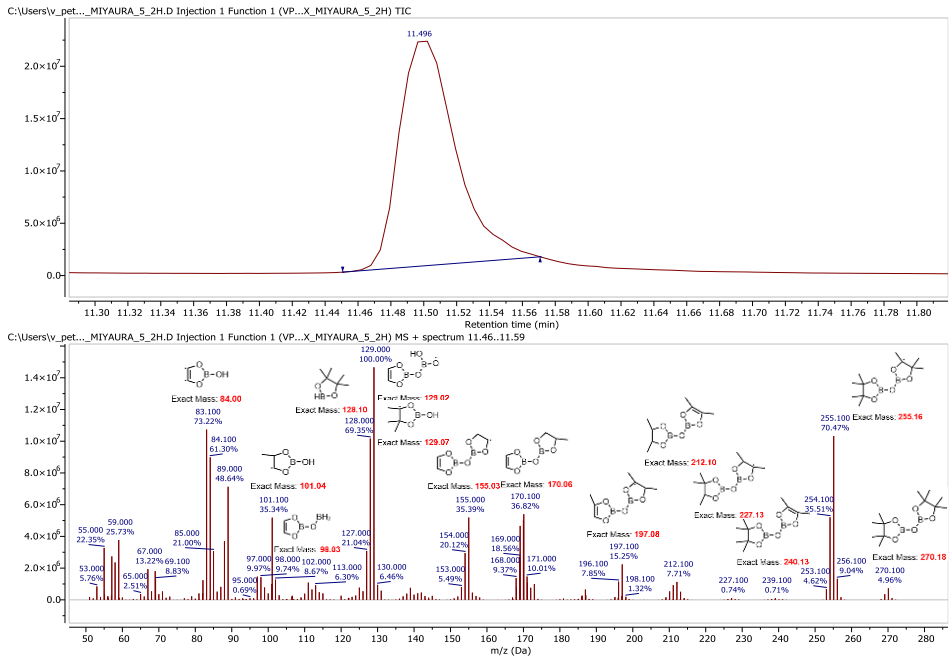

Figure A4: Analysis of GCMS Peak With 11.5 min RT

Appendix B: ^{1}H NMR and GCMS of 2-Bpin-3-Hexylthiophene (**48**) Reactions

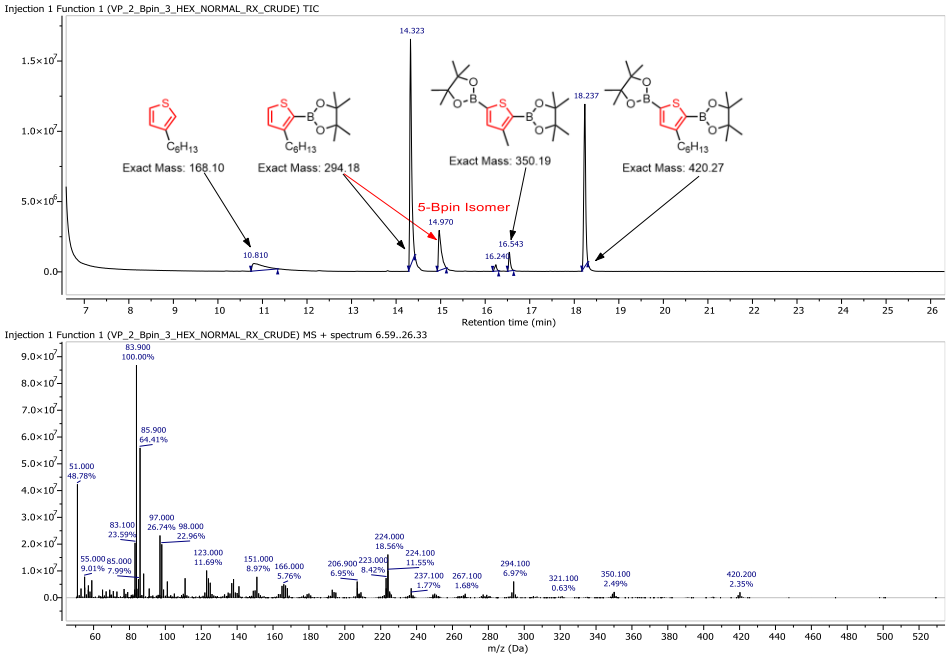

Figure B1: Literature Addition-GCMS of Crude

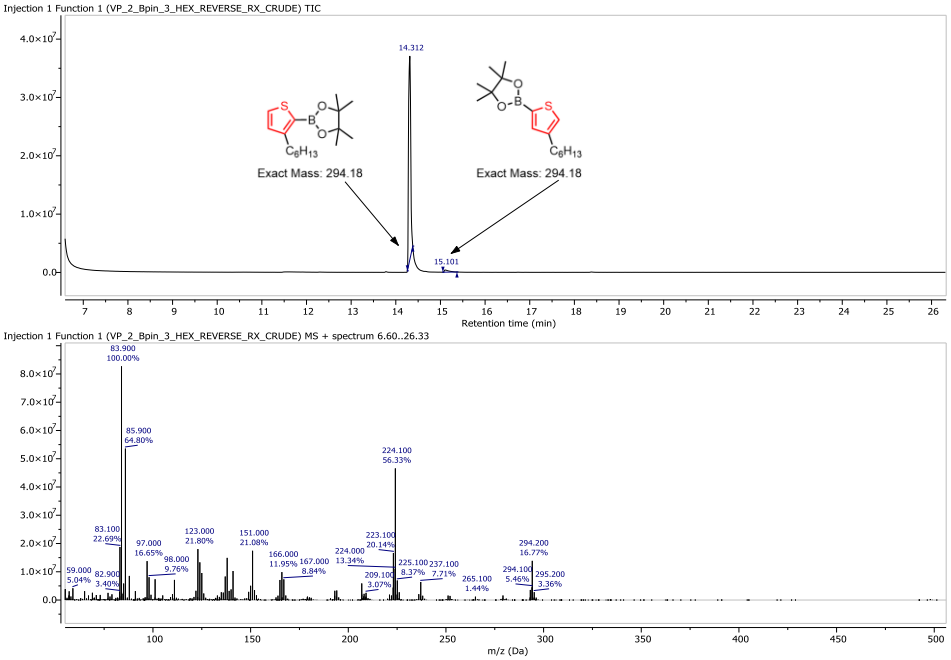

Figure B2: Reverse Addition-GCMS of Crude

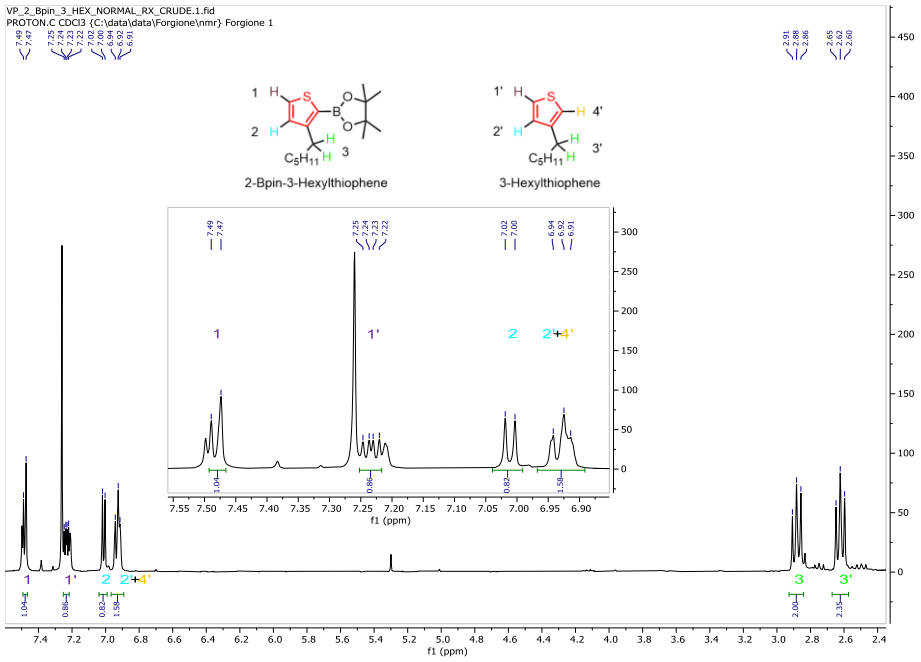

Figure B3: Literature Addition-^{1}H NMR of Crude

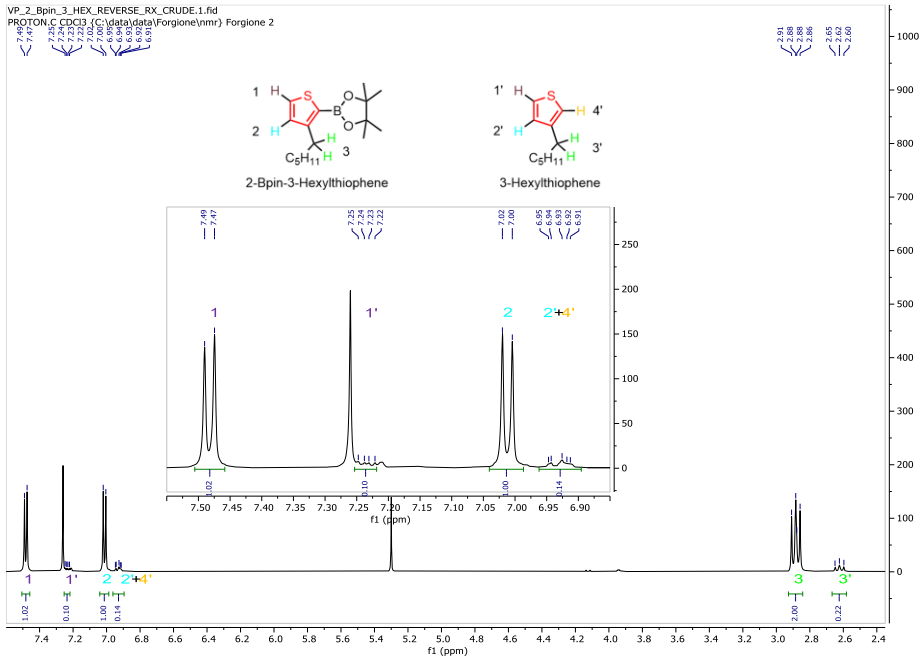

Figure B4: Reverse Addition-^{1}H NMR of Crude

Appendix C: ^{1}H NMR and GCMS of 4T Suzuki Reactions

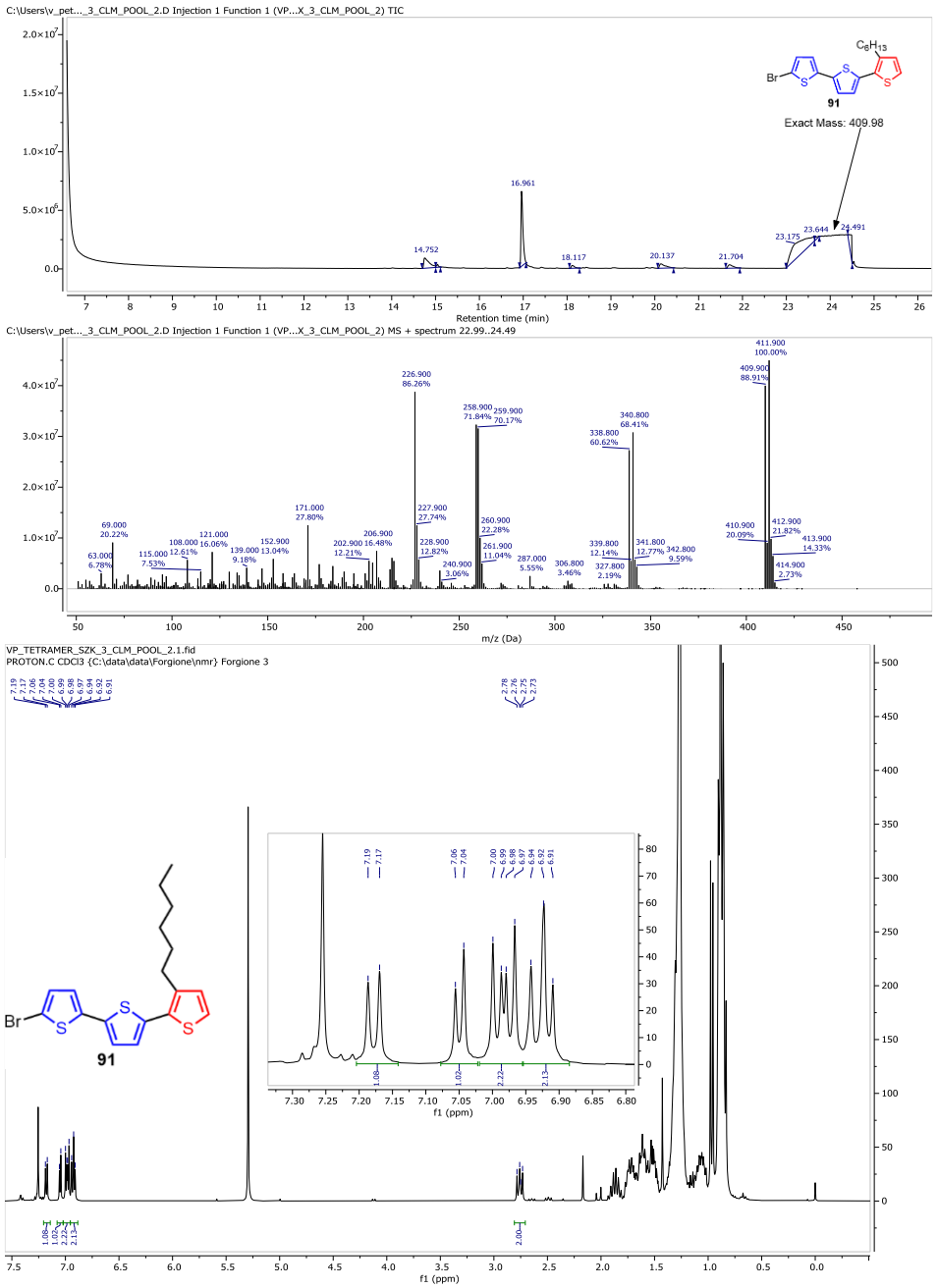

Figure C1: GCMS and ^{1}H NMR of Brominated Trimer **91** from **4T** Suzuki Reaction

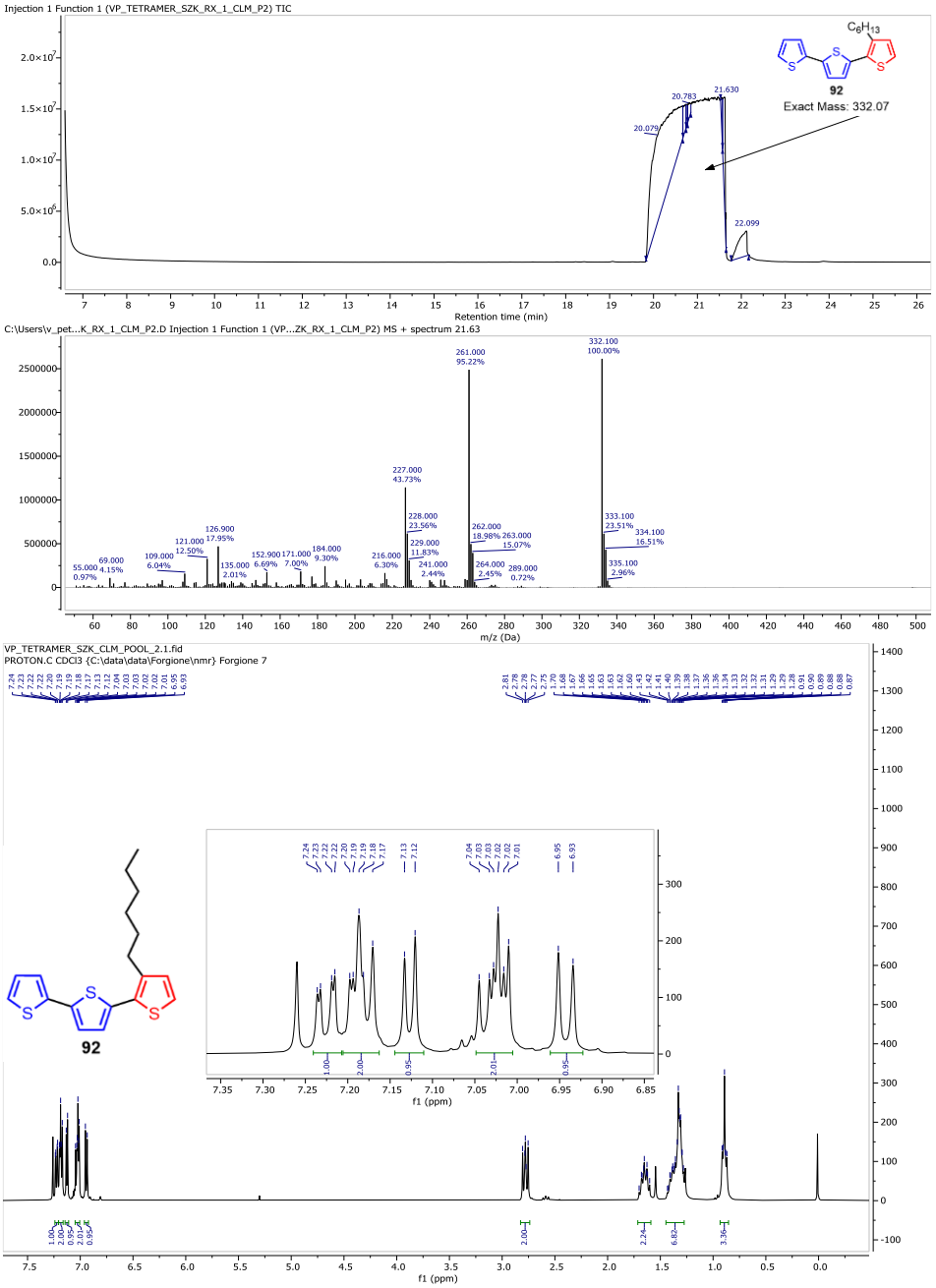

Figure C2: GCMS and ^{1}H NMR of De-Brominated Trimer **92** from **4T** Suzuki Reaction

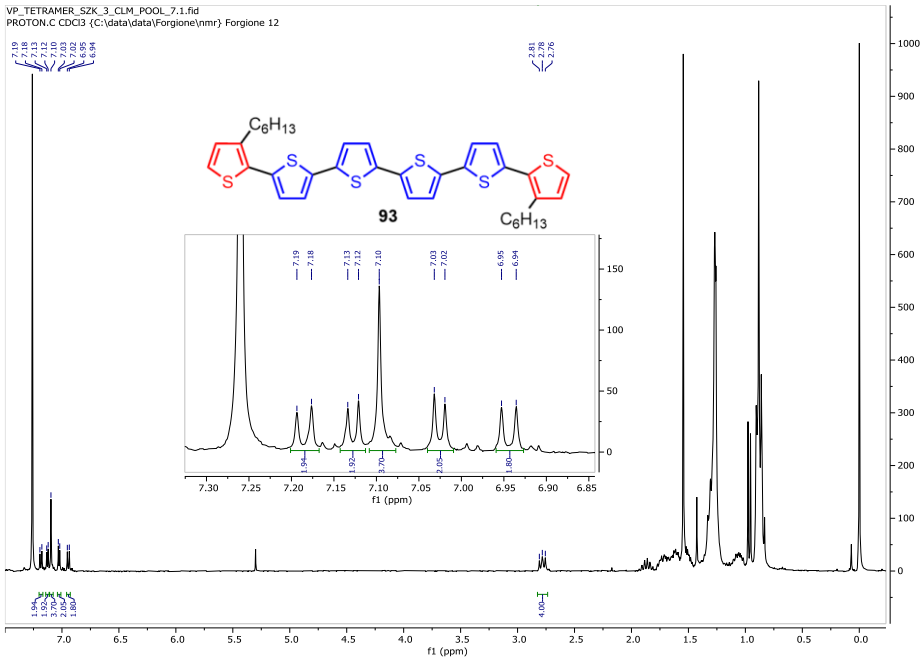

Figure C3: ^{1}H NMR of Halogen Homocoupling Product **93** from **4T** Suzuki Reaction

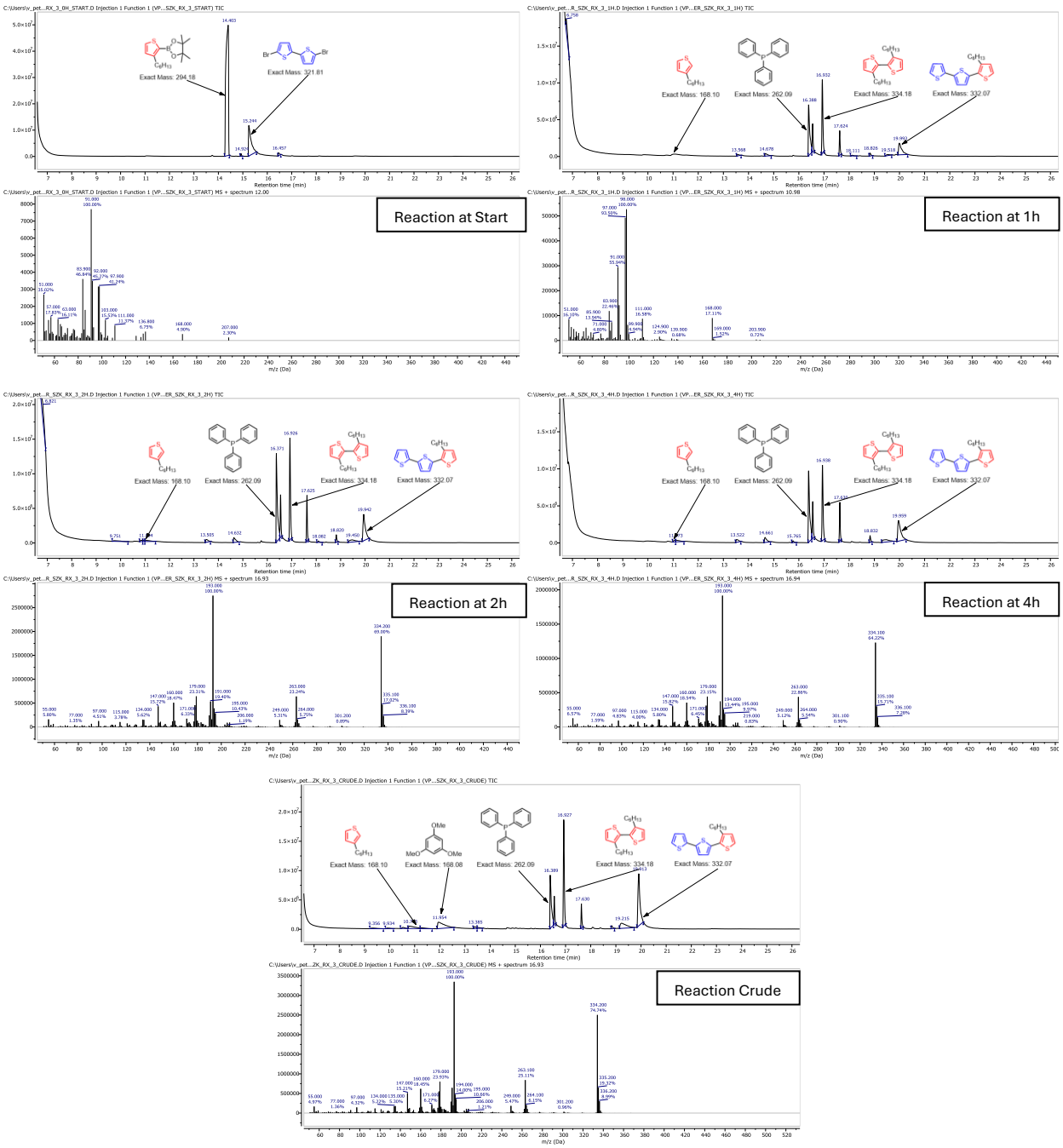

Figure C4: GCMS of **4T** Suzuki Entry 3 at Hourly Intervals and of Worked-Up Crude

Appendix D: ^{1}H NMR and GCMS of **3T** Suzuki Reactions

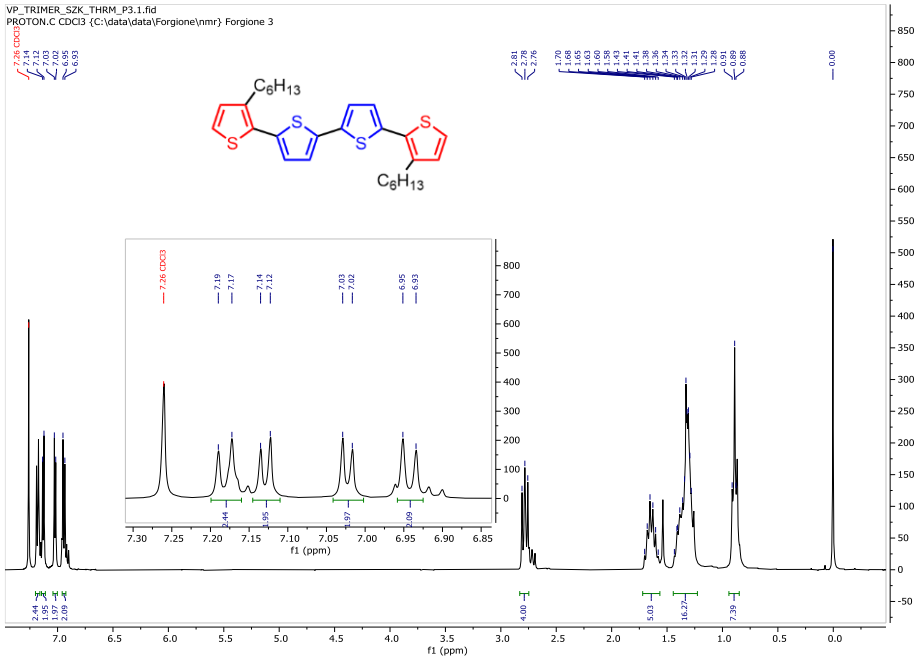

Figure D1: ^{1}H NMR of Cyan Spot Isolated from **3T** Suzuki Reaction (Determined to be **4T**)

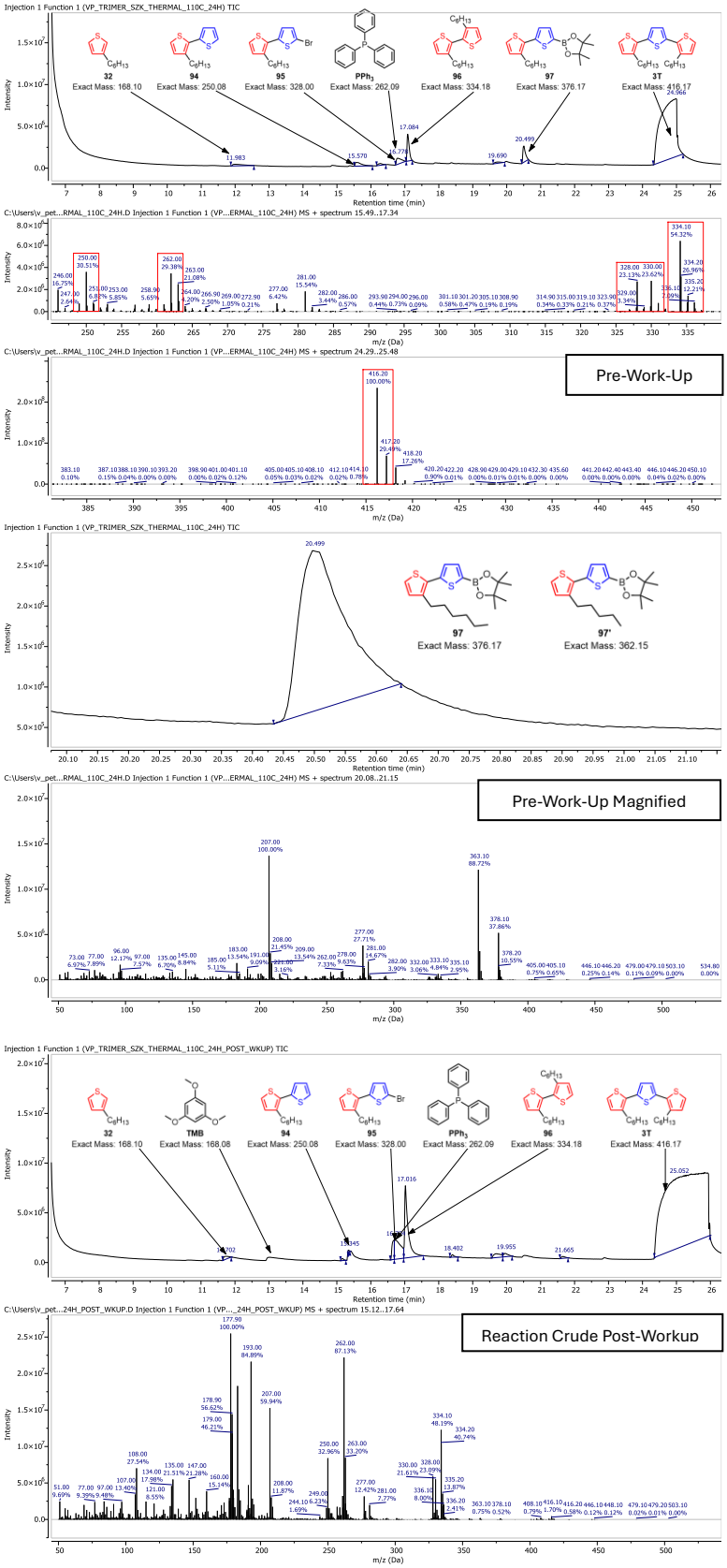

Figure D2: GCMS of **3T** Suzuki Reaction After 24 h Pre- and Post-Work-Up