EXPLORING THE DESIGN AND SYNTHESIS OF CONJUGATED MATERIALS FOR APPLICATIONS IN ORGANIC ELECTRONICS

Samuel Barrer Anderson

A dissertation submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Chemistry Department in the College of Arts and Sciences.

Chapel Hill
2016

Approved by:

Wei You

Scott Warren

Alex Miller

James Cahoon

Joanna Atkin

ABSTRACT

Samuel Barrer Anderson: Improved Design and Synthesis of Conjugated Materials for Organic Electronic Applications
(Under the direction of Wei You)

Organic electronics offer a variety of advantages over traditional electronics, but their study is hindered by their difficult syntheses. Herein, I tackle several difficult targets of interest to the molecular electronics and organic photovoltaics disciplines, and in doing so I try to illuminate what is and isn't possible with this frontier of molecular design. I explore the viability of highly sterically-hindered systems enforce intramolecular π-π stacking and tune the 3-dimensional packing of otherwise flat conjugated molecules. In general, these molecules face many of the solubility issues that face large conjugated systems, while now also facing difficult bond formation because of steric bulk. In the case of building small molecule electron acceptors for organic photovoltaics, the electron deficient nature of these compounds also appears to inhibit the formation of these constrained systems.

Then, I explore the limits of divergent synthesis by attempting to incorporate two distinct divergent steps into the synthesis of an acceptor unit for photovoltaic polymers. This proved to be a challenging goal, and many issues with orthogonality and reactivity are addressed. Ultimately, the development of this synthesis remains in progress because of

Then, I discuss the development of oligophenyl dithiols used for studying tunneling and other electron transport through self-assembled monolayers. These monolayers are a promising frontier in designing molecular electronics. First, our syntheses produce terphenyl and

quaterphenyl dithiols for a length-dependent study of electron transport. Then, we design a synthesis of similar oligophenyl dithiols that have sterically hindered rotations so that we can study the effect of inter-ring conjugation on electron transport through the monolayer.

I conclude by discussing the themes shared by each of these diverse projects in organic electronics and by touching on issues that remain in the field of organic electronics. Finally, I touch briefly on the culture of scientific publishing against which these projects have strived to be high impact and publishable.

To my therapist, Jane Vincent, who helped me grow when graduate school was uncompromising.
To my friends, family, and Seri, who supported me when I struggled to help myself.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

BDT	Benzodithiophene
CLAP	Core-Linker-Acceptor Platform
DTBT	Dithienyl benzothiadiazole, or polymers of BDT and it.
HTAZ	Benzotriazole or polymers of BDT and dithienyl benzotriazole
FF	Fill factor
FTAZ	difluoro-benzotriazole or polymers of BDT and dithienyl difluoro-benzotriazole
HOMO	Highest occupied molecular orbital
$\mathbf{J_{SC}}$	Short-Circuit Current
LUMO	Lowest unoccupied molecular orbital
NBS	*N*-Bromosuccinimide
NDI	Naphthalene diimide
nTP	nano-Transfer Printing
OLED	Organic Light Emitting Diodes
OPV	Organic photovoltaics
OTFT	Organic thin film transistors
P3HT	poly(3-hexylthiophene)
PADI	Perylene Asymmetric Diimide
PCBM	Phenyl-C61-butyric methyl ester
PCE	Power conversion efficiency
PDI	Perylene Diimide
POSS	Polyhedral oligomeric silsesquioxane
PPP	Poly(*para*-phenylene)

PPV	Poly(phenylvinylene)
PSC	Polymer Solar Cells
V_{OC}	Open circuit voltage

CHAPTER 1: Background and Themes in Organic Electronics

Organic electronics, as a discipline, have been gaining prominence since their first real successes in the mid 1980's, when Ching Tang successfully produced an organic solar cell with a power conversion efficiency of 1%[1] and, just one year later, produced the first organic LED.[2] Since then, the field has grown to encompass a wide variety of pursuits, including organic photovoltaics (solar cells), organic LEDs, organic thin-film transistors,[3] and electrochromic displays.[4] However, at the root of each of these pursuits is the use of conjugated organic materials, either polymeric or crystalline, as semiconductors that are highly tunable and may offer cost reductions from expensive inorganic semiconductors like silicon.

Now, OPVs have progressed past 11% efficiency[5] and OLEDs are commonly used in thin, bright smartphone screens. Thousands of researchers have worked over decades to realize these advancements and have uncovered design principles and limitations of these new, highly conjugated materials.

In organic photovoltaics, molecules must have favorable planarity, charge transport, absorbance or emittance, and fine-tuned HOMO and LUMO levels. These properties, in turn, often call for the synthesis of highly conjugated systems that must maintain their stability and solution processability. The modern history of synthetic chemistry is closely linked to the development of new and better materials for organic electronics.[6,7]

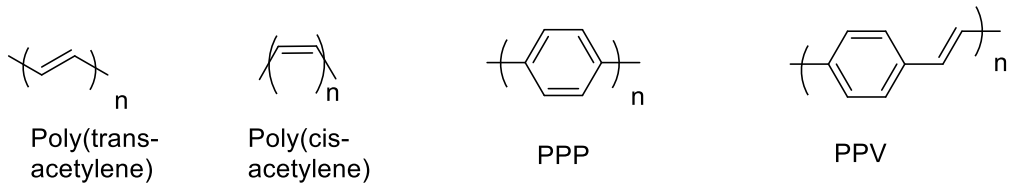


Figure 1: Older designs for conjugated polymers, which often experienced solubility and stability issues

The earliest prominent conjugated polymer was polyacetylene.[8] While the first procedure for producing polyacetylene dates back to 1958,[9] our ability to study polymeric conjugated materials was limited by polyacetylene's sensitivity to oxygen and its low solubility.[8] One method for polymerizing acetylene could produce films on a surface, but others made short-lived black flakes, and even these films were subject to high concentrations of embedded sp^3 hybridized carbons that break conductivity.

Another approach was to create a stable, soluble non-conjugated polymer *via* more traditional polymerizations and transform this precursor into polyacetylene.[8] One strategy eliminated the chlorides on PVC to form the alternating double bonds of polyacetylene.[10] However, these processes had low conjugations because an extremely high yield, without side reactions, was needed to form the backbone.[10] These approaches allowed researchers to better understand the optoelectronic properties of these new materials, but didn't grant widespread success because of their limited scope and difficulty.[11]

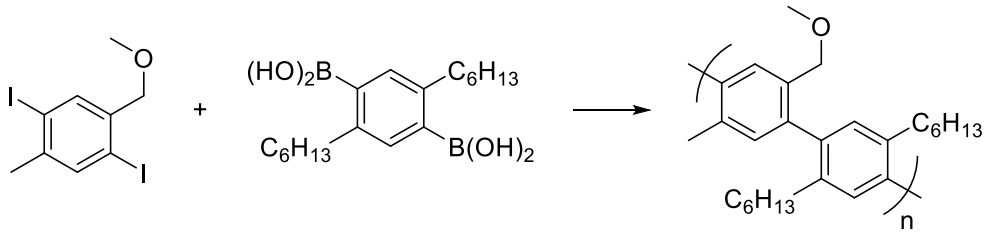
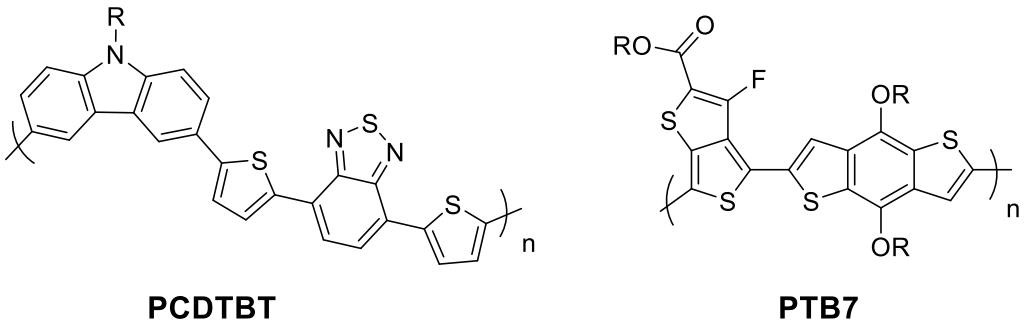


Figure 2: Suzuki Polycondensation of PPP

However, in the mid-1990's, the Suzuki coupling started to gain prominence as a means of polymerizing these conjugated systems, like the preparation of poly(*para*-phenylene) in Figure 2.[12] At first this was just one more route to PPP, but by the mid 2000's, the full promise of the Suzuki coupling (and related couplings like Stille, Heck, and Negishi) was revealing itself.

Palladium-catalyzed cross couplings opened up the door to the now dominant donor-acceptor paradigm of donor polymer design (See Section 3.1). The field has broadened from one dominated by a few, well known homopolymers (each with their own syntheses) to include a wide variety of donor polymers under more standardized connectivity. The "donor-acceptor copolymer" model, enabled by metal catalyzed cross coupling reactions, lends incredible flexibility to the field. Much of the work in OPV over the past ten years has been from the exploration of the large opportunity space offered by modular polymer precursors and OPV device layers.



PCDTBT **PTB7**

Figure 3: Complex conjugated polymers that are made possible with current syntheses

However, the field is still rooted to the synthetic schemes that are known to it. As its short history highlights, performance improvements made by new molecular designs were caused by the discovery of new synthetic transformations, particularly carbon-carbon bond forming reactions, and the application of known chemistries in new ways to produce these systems.

With this view, we have continued to work on the development of new synthetic schemes, or substantial improvements of old ones, that will yield new modular blocks systems in OPV.[13,14]

The projects in this work were made for producing targets of interest to study in polymer solar cells, but they also were intended to uncover new design paradigms in the synthesis of organic electronic materials. Thus, the projects are concerned with more than the production of enough of a single target to allow characterization. Of equal importance is creating a synthetic paradigm through which an entire class of compounds can be more easily studied.

In this way, the synthetic approaches, and even the goals, of the projects I discuss below are malleable: when one technique appears to look less promising, the method (or the endpoint) is rethought. This approach to research is ripe for storytelling, and I hope the following tales of synthetic endeavors will elucidate about the future and the struggles of organic electronics and organic photovoltaics.

CHAPTER 2: Electron Acceptors on 3D Scaffolds for Polymer Solar Cells

Introduction

Polymer solar cells (PSCs) are a promising technology on the cusp of commercial deployment because of their low materials and processing cost relative to traditional inorganic solar cells[15,16]. The most popular and successful PSCs are built on the bulk heterojunction (BHJ) design, where, typically, a polymeric electron donor is mixed with an electron acceptor to produce a complex, interweaving pattern of phases no larger than 20 nm in diameter. This arrangement, called a morphology, promotes good exciton splitting and current generation despite the low exciton diffusion length of conjugated polymer systems[17-19]. The power conversion efficiency (PCE) is the primary value by which solar cells are judged and is defined as

$$PCE = \frac{\{J_{SC} * V_{OC} * FF\}}{P_0}$$

where J_{SC} is the short circuit current, V_{OC} is the open circuit voltage, FF is the fill factor that describes the loss in V_{OC} and J_{SC} under working device load, and P_0 is the efficiency of a reference cell.[19] Each of these three variables can be tweaked with both device fabrication conditions and by tweaking the structure of the organic components.

Since its first synthesis in 1995[20], the fullerene derivative phenyl-C_{61}-butyric methyl ester (PCBM, Figure 4) has been widely

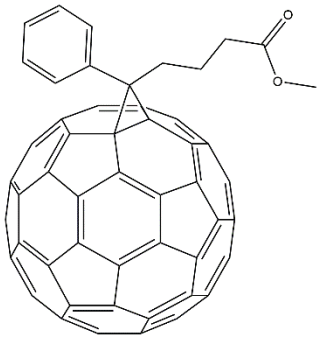


Figure 4: PCBM, the most popular electron acceptor used in PSC

employed as the electron acceptor[21,22] because it offers excellent charge separation at the interface and electron transport in bulk[19,23]. Because of PCBM's good properties and its limited possibilities for functionalization, the vast majority of research in PSC's (as of 2012) had focused on designing new donor polymers to match with PCBM. The library of donor polymer structures ballooned in the mid to late 2000's as labs created and combined structures to tease out new trends and better efficiencies. PCBM's dominance as the electron acceptor *par excellence* meant that while these polymers could be evaluated on a variety of intrinsic properties or device structures, the *de facto* means of comparison was based on their performance in PSC's with PCBM.

This unintentional standardization was useful for testing early hypotheses about the effects of device and molecular structure and performance, but it came at a cost. Even if PCBM were the perfect acceptor, which it is not, the ubiquity of PCBM has a limiting effect on the growth of the field.

Some of PCBM's properties work against the promise polymer photovoltaics hold over traditional, inorganic ones. PCBM is extraordinarily expensive, costing >$700/g (Sigma Aldrich, accessed 7/19/2016), which is problematic for devices whose stated purpose is to provide solar energy at lower costs. Tricky fullerene chemistry hampers the economies of scale that roll-to-roll solar cell production should provide.[24] Additionally, the promise of tunable organic components is compromised. PCBM is barely tunable, with perhaps a half dozen viable analog candidates. Many of these only improve one or two of PCBM's failings, like its low absorbance.

As a result, nearly all of the chemical tunability available to improve PSC performance must come from the donor. Because PCBM absorbs poorly in the visible spectrum, the donor polymers are responsible for capturing almost all of the photons used in generated electricity.[25]

And regardless of how promising a donor appears based on molar extinction coefficients or hole mobility, if it fails to match PCBM's energy levels and mix favorably with it, it can't compete. Donors that *do* fit well with PCBM often make devices where V_{OC} is limited to values below 0.8 V because donors must have a bandgap for catching visible light while being able to donate electrons to PCBM's low-lying LUMO levels.

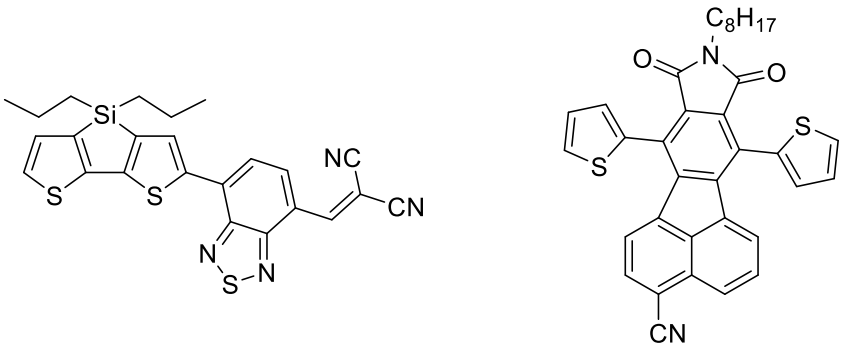
SECTION 2.1: Motivation

Thus, we became interested in applying our synthetic skills towards designing a replacement system for PCBM that would be more tunable, more absorptive, and cheaper. We began researching leaving behind fullerenes entirely, which we deemed necessary to match the chemical variability of the donor polymers.

In 2012, there had been few attempts to develop new small molecule acceptors that offer a range of energy levels at a low cost. Because poor energy-level matching with a donor is both PCBM's largest performance fault and the easiest to correct in organic systems, most novel acceptors manage to exhibit a higher V_{OC} than PCBM-based cells. However, all of these acceptors still fail to surpass PCBM in overall PCE because of generally poor J_{SC} and FF.

A typical small molecule acceptor might improve V_{OC} by 20% over PCBM-based devices but achieve only a third or half of the J_{SC}[26], as both YF25[25] and FF-1[26] do (Figure 5). Both of these studies used AFM to show that the device morphology was poor and processing problems resulted from the high crystallinity of these systems.

In 2012, PCBM-based solar cells had achieved over 10% PCE, while the highest preforming non-fullerene acceptors of the time hadn't yet broken 4%[27]. Unfortunately, there exist few good strategies to improve J_{SC} as easily as V_{OC}[17], although charge transport, exciton splitting, domain size and phase-mixing all play a role.



YF25: 1.5% PCE FF-1: 1.86% PCE

Figure 5: Two older non-fullerene acceptors, indicative of the planar, small molecule designs

Many of these compounds excel at absorbing visible light but are unable to match the electron mobilities of PCBM. For example, acceptors based on perylene diimide (PDI), have shown significant recrystallization in the solid phase,[28] leading to poor electron transport connections to the electrodes and decreasing the collected current.

However, some progress had been made towards designing away from high-crystallinity, planar non-fullerene acceptors. Narayan et al. dimerized PDI (Figure 6) and used steric interactions to ensure that the two moieties were kinked at a 90˚ angle. This acceptor achieved a respectable 2.5% PCE, a 10-fold improvement over the PDI monomer.[28] The authors hypothesize that this design blocks excessive aggregation and that electrons may be able to travel along two axes, encouraging exciton splitting and charge collection.

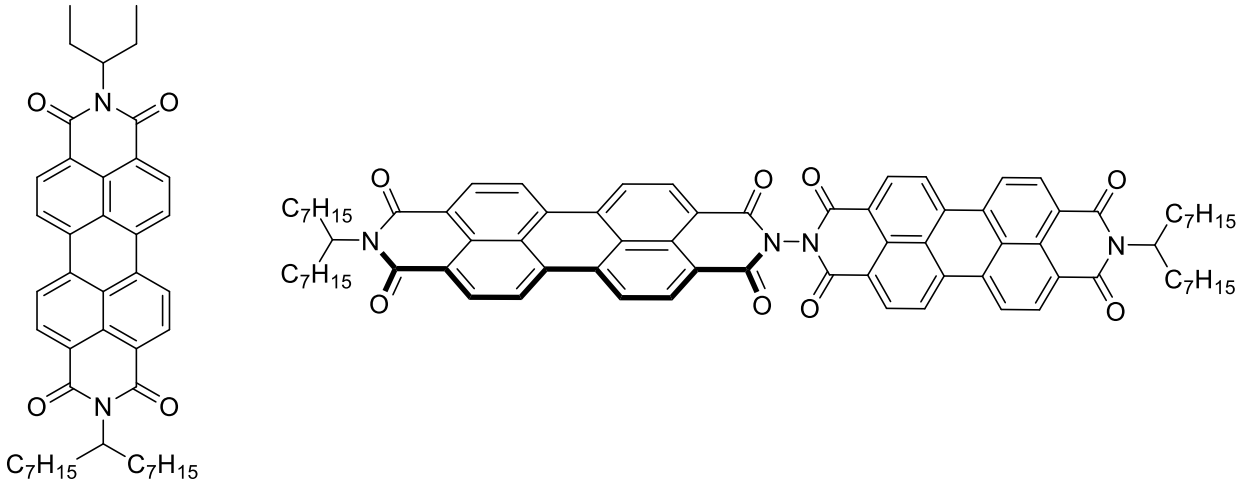


Figure 6: A perylene diimide and a twisted pereylene diimide dimer

At the same time, several theoretical investigations granted new insights into the unique properties of PCBM. Computational efforts predicted that systems with three dimensional electron diffusion (e.g., PCBM) favor exciton dissociation over 0D and 1D regimes (e.g., small molecules or polymers, respectively) because of the greater entropic term in the dissociated state[21,29,30].

PCBM is known to have two additional unfilled orbitals within 0.3 eV of the LUMO level, and one study has found that all three of these states can be acceptors in a Marcus theory-style electron transfer from a common donor, P3HT. Rather than these additional states simply tripling the rate of exciton dissociation, these extra orbitals introduce an 18-fold rate increase because of the range of rearrangement energies that allow electron transfer[23].

Last, the extreme rigidity of the bonds in PCBM means that electron transfer between the fullerenes is not governed by Marcus theory and is instead almost metallic, with a single excess electron spread out over at least 30 molecules[31]**.** None of these properties are accounted for in the above small molecule acceptor systems.

SECTION 2.2: Proposal and Design Goals

The Core-Linker Acceptor Platform (CLAP)

To address some of the deficiencies of small molecule acceptors as compared to PCBM, we proposed attaching planar electron acceptors to a small, spherical core that enforces π-π stacking interactions between the acceptor moieties (Figure 7). We hypothesized that this design should break the degeneracy in the LUMO levels of the system, allowing for a synergistic rate improvement in the Marcus theory electron transfer from an excited donor[23]. Additionally, the shape should radically change the packing of the acceptors from crystalline network to intercalation-based packing, which we expected to have several advantages. By prohibiting traditional small molecule crystallinity, we may increase the miscibility of the donor and acceptor phases, creating better interfacial contact and smaller domain sizes which are crucial to efficient exciton splitting[17,18,32]. In the bulk, the intercalation regime may build a 3D transport network out of 0D molecules, further increasing the driving force for exciton splitting. Last, as this system acts as a platform for electron acceptors, it maintains the wide tunability that chemical synthesis allows and PCBM lacks. Thus, it would be possible to build a large library of acceptors for matching a range of donor polymers and potentially giving new life to already discovered, but discarded, electron donors.

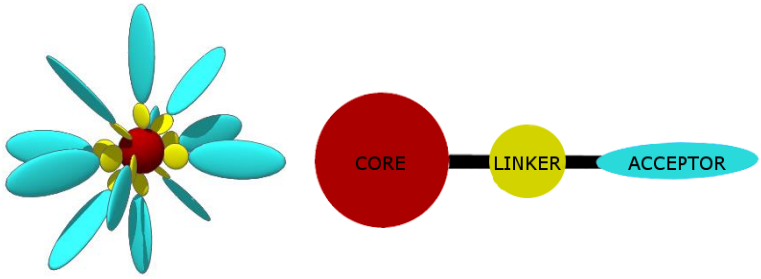


Figure 7: A generalized structure for CLAP

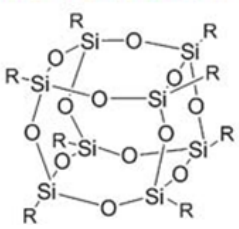
We further predicted that realizing the modularity central to this idea would require the development of a generalizable chemistry for connecting cores and acceptors. This linker could

be as small as the functional group that attaches the acceptor to the core. However, attaching a diverse array of acceptor designs may be eased by introducing a spacer, like a phenyl ring, which has separate chemistry for attaching to the core and to the acceptor.

Thus, the chemistry of connecting a range of acceptors to a pre-made platform might be standardized. If a novel core or acceptor cannot undergo the standard couplings, the linker unit might prove more adaptable to this change than the intricate design of the maintained acceptor or core, respectively. In short, the linker aids modularity.

Synthesizing these components, we arrived at a general design for new class of non-fullerene acceptors that we called the Core-Linker-Acceptor Platform (CLAP). This approach includes straightforward experimental controls. Solar cells fabricated with a CLAP compound could be directly compared to solar cells with the planar acceptor, un-functionalized core, or both. This allows us to examine our hypotheses about LUMO degeneracy and molecular packing without interference from the effect of additives.

Altering the core or even the linker moieties could tune the packing of the acceptors. The modularity of this system would enable the quantitative comparison and independent evolution of better cores, linkers, and acceptors.



$\equiv \quad (RSiO_{1.5})_8$

Figure 8: T8-POSS, the proposed Core moiety, and our synthetic shorthand

The Core: POSS

To realize this proposed platform, we began investigating polyhedral oligomeric silsesquioxane (POSS) as a core (Figure 8). The most common form, POSS-8, is comprised of 8 silicon atoms, with each attached to 3 silicon atoms via oxygen linkers to form a cube-like cage. The resulting core is rigid, cheap, and stable to

prolonged exposure to heat, water, and light. Each silicon atom can be singly functionalized with a variety of groups, allowing for linkers and acceptors to be attached to the core in a monodisperse fashion.

POSS and its production have been well studied in the literature. In polymers chemistry, incorporation of POSS units on side chains has improved the thermal stability of the polymer[33-35]. Octal-functionalized POSS has seen limited deployment in the field of organic light emitting diodes. Here, fluorescent molecules are attached to POSS, and the system is found to improve thermal stability and spincoating over the bare fluorescent molecules[34]. Some linear, rigid aryl chains have found little to no interaction between the identical groups[32,34,36], but other investigations of polycyclic aromatics on POSS found a redshift of about 20-80 nm depending on the aryl substituent[33,37]. Together, these results show that the POSS core can encourage orbital overlap and tune optoelectronic properties with proper design.

Despite its apparent complexity, the production of POSS is facile from trialkoxysilane precursors. Aryl- or alkyl-linked trialkoxysilanes are readily available both commercially and synthetically. They can be prepared by palladium-catalyzed coupling between a trialkoxysilane and an aryl-halide, but a cheaper and equally effective route utilizes a carbon nucleophile that attacks tetraethoxylsilane *via* S_N2[38]**.** Acceptable nucleophiles include aryl and alkyl Grignards as well as lithium carbanions *via* deprotonation with LDA or lithium-halide exchange.

Once a precursor has been prepared, the silyl ethers are activated with a catalytic amount of either hydroxide or activated fluoride ions, usually TBAF or a mixture of KF and 18-crown-6 ether, to allow for condensation into a siloxane bond[38,39]. The reversible process is driven forward by the removal of water *via* a Dean Stark trap, while intramolecular kinetics drive the formation of independent cages over crosslinked silicone polymer. Crucially, the closed cage

lacks free oxyanions, enabling easy purification *via* precipitation or silica plug. Thus, a wide variety of functionalized POSS molecules are accessible in high yields, with several reports of over 90% isolated yield.[39]

The Linker: Convergent and Divergent Approaches

With the synthetic ease of creating and attaching POSS to acceptors, both divergent and convergent approaches are available. In the former, a Linker functionalized with a trialkoxysilane is condensed to form the POSS Core onto which the acceptor is attached. This strategy allows for one large batch of POSS to couple with a range of prepared acceptors, clearly an advantage for assessing a large library of candidates. This is the approach most used in Aryl-POSS research[32-34,37].

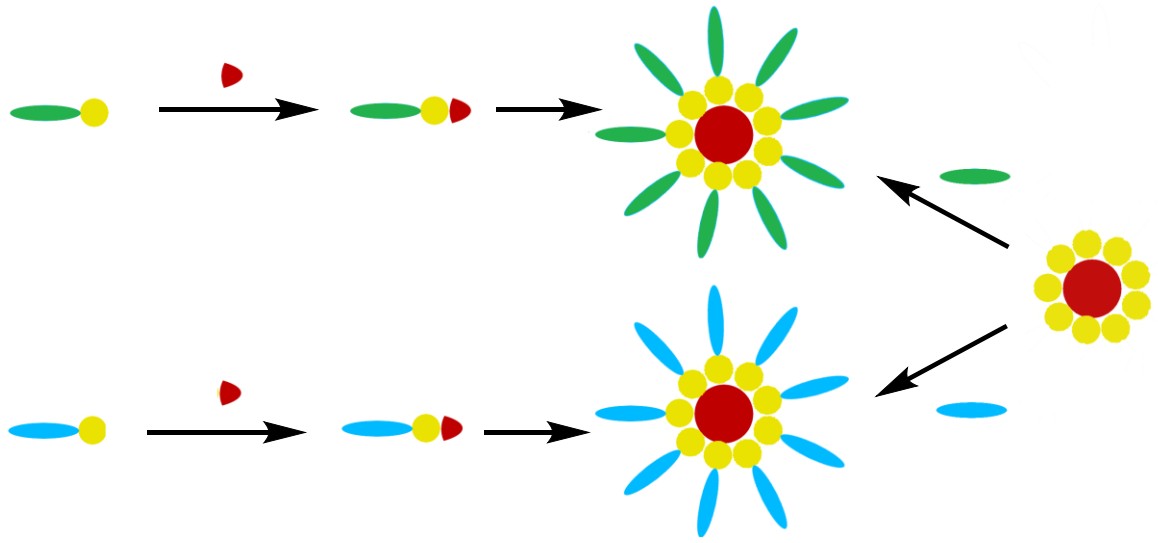


Figure 9: Two approaches to a CLAP molecule. On the left is a convergent approach, where each Acceptor arm builds the Core. On the right, a divergent approach where a completed Core is functionalized with Acceptors.

Unfortunately, coupling the Acceptor to the Linker-Core is a potentially wasteful process. Acceptor units are often expensive to generate because a series of specific heteroaromatics must be constructed and combined to create the desired orbital energy levels, solubility, and planarity.

Thus, high-conversions are desired when attaching the acceptor to the CLAP system. However, in attaching an Acceptor-Linker pair to a POSS Core, the intended product is only obtained when eight Acceptors attach to a single POSS; this is important to regularly impart the steric crowding that we believe will lead to the semi-degenerate LUMO states we wish to study.

Statistically, this is unlikely. Even assuming that coupling is not hampered by the creation of even bulkier sites (as the POSS becomes loaded with Acceptor), the yield of an octo-substituted POSS drop precipitously with reaction yield. A ^{1}H-NMR showing 90% conversion of the POSS binding sites means that each site, considered individually, has a 90% chance of conversion. Finding a POSS core with all eight sites substituted has the odds of $(0.9)^{8}$, or just 43% yield. Other calculated yields are included in Table 1.

Table 1: Isolatable POSS-R_8 yields from a given reaction conversion

Functional Group Conversion	98%	95%	90%	75%
Isolatable POSS-R_8	85%	66%	43%	10%

While Stille couplings and other metal-catalyzed condensations have successfully been applied in step-growth polymerizations, which require a high yield to produce polymers with high molecular weight, these yields are dependent on the electronics of the substrate. As discussed in the introduction to Chapter 3, the monomers being cross coupled for these copolymers are designed to encourage high-yielding Stille polycondensations, which will not necessarily be possible with the couplings needed for CLAP.

In the convergent approach, the trialkoxysilane-functionalized linker is attached to the acceptor before the formation of POSS. Because POSS is easily purified from its byproducts and forms in high yield, the losses of the divergent approach are not observed, and yields for

preparing POSS cages can be above 90%.[40] However, the Acceptor moieties must be subjected to additional synthetic alterations, not all of which will be compatible with the Acceptor, which makes preparing a wide library of compounds more difficult. As the reliability and ease of both the convergent and divergent approaches has implications for the viability of CLAP, we investigated both.

The Acceptor

Perylene diimide (PDI) and naphthalene diimide (NDI) (Figure 10) are among the more common acceptor units used to produce non-fullerene acceptors because of their strong yellow to blue absorbance, good solubility, and high electron mobility[7,27,41]. Their polycyclic aromatic design will allow the π- π stacking that we seek to exploit to break LUMO degeneracy. These traits make PDI in particular a promising target that satisfies many of our design goals for CLAP.

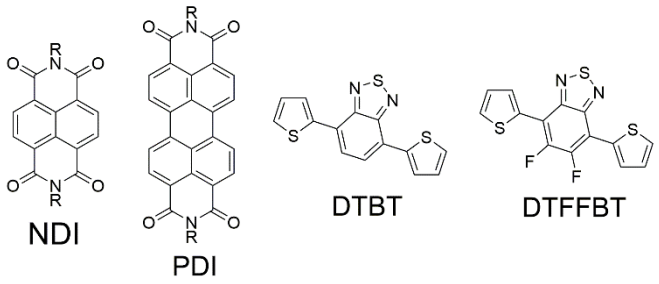


Figure 10: Proposed acceptor moieties for CLAP

An energy-minimization and molecular dynamics calculation of a Perelyne CLAP system in ChemDraw 3D predicts a slip-stacked structure that we hypothesize should break LUMO degeneracy (Figure 11). This model also shows the potential for significant intercalation of donor polymers or other CLAP chains for transport, which will be important for maintaining electron transport

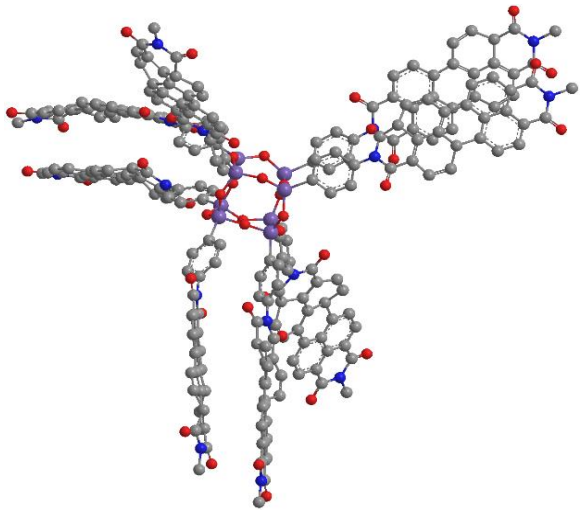


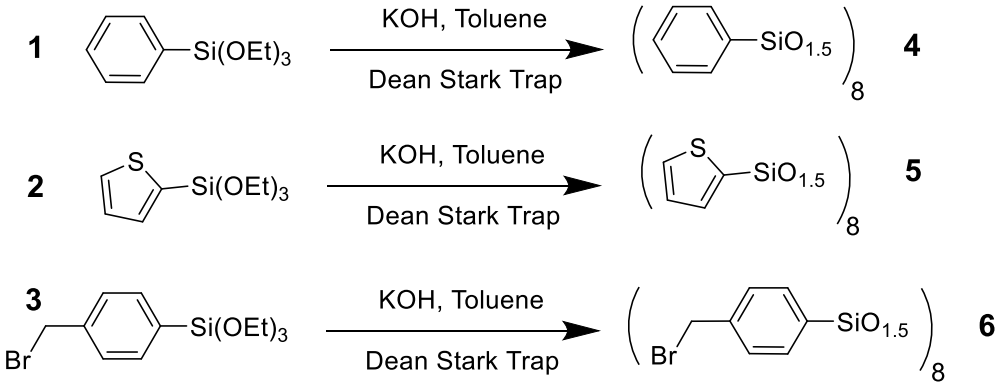
Figure 11: A molecular dynamics simulation of POSS-Ph-PDI, revealing π-π stacking motifs

while preventing aggregation.

Additionally, perylene possesses two positions that can be functionalized with a Linker: the bay position of the aromatic region and the nitrogen in the imide functional group. This allows for an investigation of acceptor shape on the π-π stacking and morphology of CLAP, which may provide crucial insights for further design.

SECTION 2.3: Preparing POSS *via* Convergent and Divergent Approaches

As discussed in Section 2.3.3, polyhedral oliomeric silsesquioxanes (POSS) were a promising Core group because they can be prepared either before or after the attachment of our Linker and Acceptor. These two approaches have their advantages and disadvantages, but the divergent approach had one clear fault: isolation of a high purity product with minimal waste. Because of the statistics presented in Table 2, we began our investigation by focusing on the convergent POSS approach.



Scheme 1: Three POSS-Aryl compounds that we used to determine how viable the convergent approach would be. Only the first reaction worked.

Following a literature procedure that utilized catalytic KOH in a Dean-Stark trap to encourage condensation,[38] we easily produced octaphenyl-POSS (**4**) in 92% yield as a white solid from the commercially available phenyltriethoxysilane (**1**). However, our attempts to expand on this success were limited.

By forming a Grignard reagent from 2-bromothiophene, we successfully prepared 2-triethoxysilanethiophene (**2**) in 76% yield.[42] Subjecting this analog to the same condensation conditions yielded a thick, black solution that no longer had the ethoxy signals on crude ^{1}H-NMR. Thus, we believe it likely that while the ethoxy groups were hydrolyzing, the result was a cross-linked siloxane polymer rather than a closed POSS cage.

We were stymied by this unforeseen difficulty until we found a report by Bassindale et al. which attempted to prepare a variety of alkyl-POSS analogs using similar precursors and under the same conditions.[43] For their condensation with fluoride, they observe 95% yields with cyclopentyl triethoxysilane, but only 26% with the similar isobutyl triethoxysilane. Phenyl triethoxysilane forms POSS cages in 49% yield, but related vinyl and allyl systems get less than 5%. Thus, the high yields we anticipated with the convergent approach may not be assured.

The success of the original octaphenyl-POSS was dependent on a solvent system that would solubilize all of the incomplete cages while forcing the completed cages to precipitate and push the reversible reaction forward. Thus, it is likely that each new Acceptor-Linker-Siloxane precursor would require a new solvent system to be optimized for it.

At the same time, results from other experiments were also casting doubt onto the viability of a convergent approach. Our attempts to produce **(3)** from its siloxane precursor produced a mixture that, on ^{1}H-NMR, appeared to have reacted at multiple sites. It is possible that the basic conditions also reacted with the alkyl bromide moiety, producing alcohols and other byproducts. This suggests that the cage-forming conditions may not be orthogonal with Acceptors containing base-sensitive functional groups like halides, amides, and imides.

While octaphenyl-POSS could be produced in high yields at the 40 mmol scale, the 3 mmol scale proved messy and inconsistent. After the filtration which usually retains the

completed POSS cage as a solid, gooey white solids, possibly incomplete cages, were captured at only 15% yield. Our attempts to force the completion of this reaction with a shorter pathlength to the Dean-Stark Trap, adding 4Å molecular sieves to the trap to further dry the system, and adjusting reaction concentration and time did not enhance yields.

The convergent route had been an appealing option because it promised to waste less of the valuable Acceptor unit than the divergent route, but the apparent need for large scales are troubling. Only 1-2 mmol of Acceptor is needed to fully characterize a compound for its optoelectronic and photovoltaic properties, and the rest would be wasted. Thus, we pivoted our time towards producing a Core-Linker compound that would readily couple to an Acceptor.

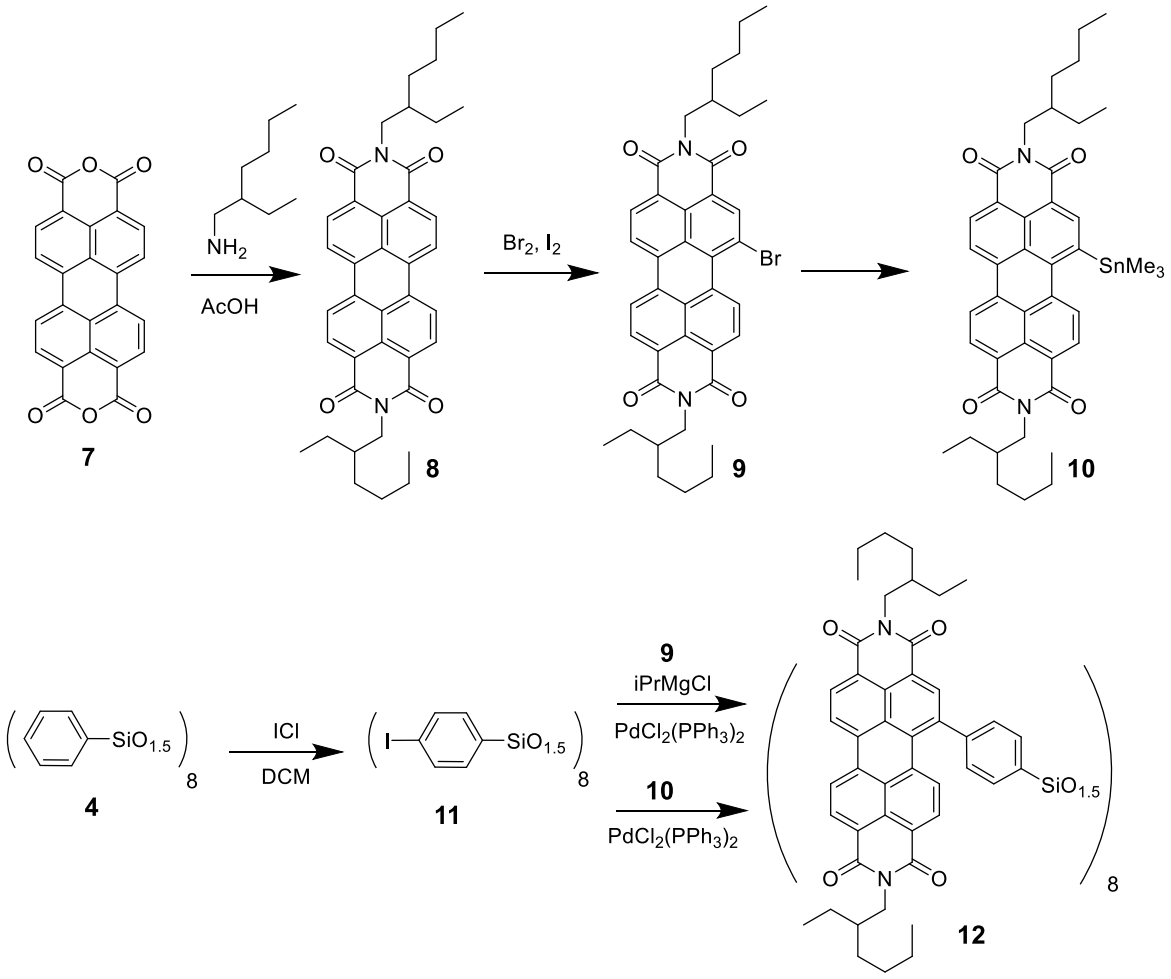
To make use of the octaphenyl-POSS (**4)** that we generated above, we attempted to brominate it so that cross coupling reactions would have a scaffold. However, refluxing **4** with molecular bromine, iron tribromide in chloroform produced no change in the aryl signals. We were able to successfully reproduce an iodination that requires a solution of iodine monochloride be kept at 40˚ C for 24 hours (Scheme 2). We isolated **(11)** in a 35% yield which contained 99% *para* selectivity, consistent with the literature, which went on to use this compound in a Stille coupling.[40]

However, this process was tedious and because only several milligrams of POSS were needed for each divergent coupling reaction, we decided to rely on commercially available POSS compounds from Gelest for the majority of this study.

SECTION 2.4: Preparing Acceptors for Cross Coupling to POSS

The perylene diimide **8** could be prepared by the heating of the dianhydride **(7)** with 2-ethylhexylamine in acetic acid at 90˚ C. Following a literature method, we could produce the dibrominated species in 90% yield by refluxing in chloroform with catalytic iodine,[44-46] but the

monobrominated species we needed was scant. Because perylene diimides (PDI) like **(8)** don't react with NBS, a softer brominating agent, molecular bromine must be used. Unfortunately, molecular bromine is dense – the neat liquid is 19 M – and it fumes, so measuring and maintaining an exact stoichiometric ratio is not feasible. However we found that we could enhance monobrominated yields to 35% by instead refluxing **(8)** in dichloromethane.



Scheme 2: A divergent approach to PDI-POSS, through either Stille or Kumada couplings

We failed to reproduce the preparation of **(10)** by palladium catalyzed coupling with hexamethylditin.[47] Instead, we recovered the bromide **(9)**. Using the non-nucleophilic Grignard reagent isopropylmagnesium chloride also failed to activate the bromide.

Against our desire to limit the number of lossy synthetic steps onto the POSS core, we subjected **(11)** to isopropylmagnesium chloride and achieved 80% activation (by ^{1}H-NMR of the quenched reaction). Unfortunately, the PDI bromide **(9)** also failed to couple under Kumada coupling conditions with this activated POSS.

Finally, we attempted to perform a Heck coupling between octavinylPOSS (OVP) and **(9)**, similar to a literature preparation of a PDI polymer, but no reaction occurred.[48] Likely this was because of the electron deficiency of the vinyl siloxane as opposed to Mikroyannidis et al.'s electron rich styrene.[48]

From these attempts, it appears that the bromide is too deactivated by the electron deficient aryl rings to react effectively. More harsh activations, such as lithium halide exchange, were not available because of the electrophilic imide moieties, so we moved towards exploring the imide positions as a means of functionalization.

SECTION 2.5: Utilizing Perylene Assymetric Diimides (PADI) as Acceptors

Generally, the imide positions on PDI are used to attach alkyl chains that maintain solubility and prevent aggregation. It may be possible to replace one of these solubilizing chains with a Linker, while the second imide continues to provide solubility.[49]

The preparation of perylene asymmetric diimides (PADI) features several challenges. Amines can easily attack the electrophilic anhydride species, and then high temperatures (above 100˚ C) are required to reclose the ring and form the imide, because the amide must perform intramolecular attack on the carboxylic acid and displace a hydroxide leaving group.

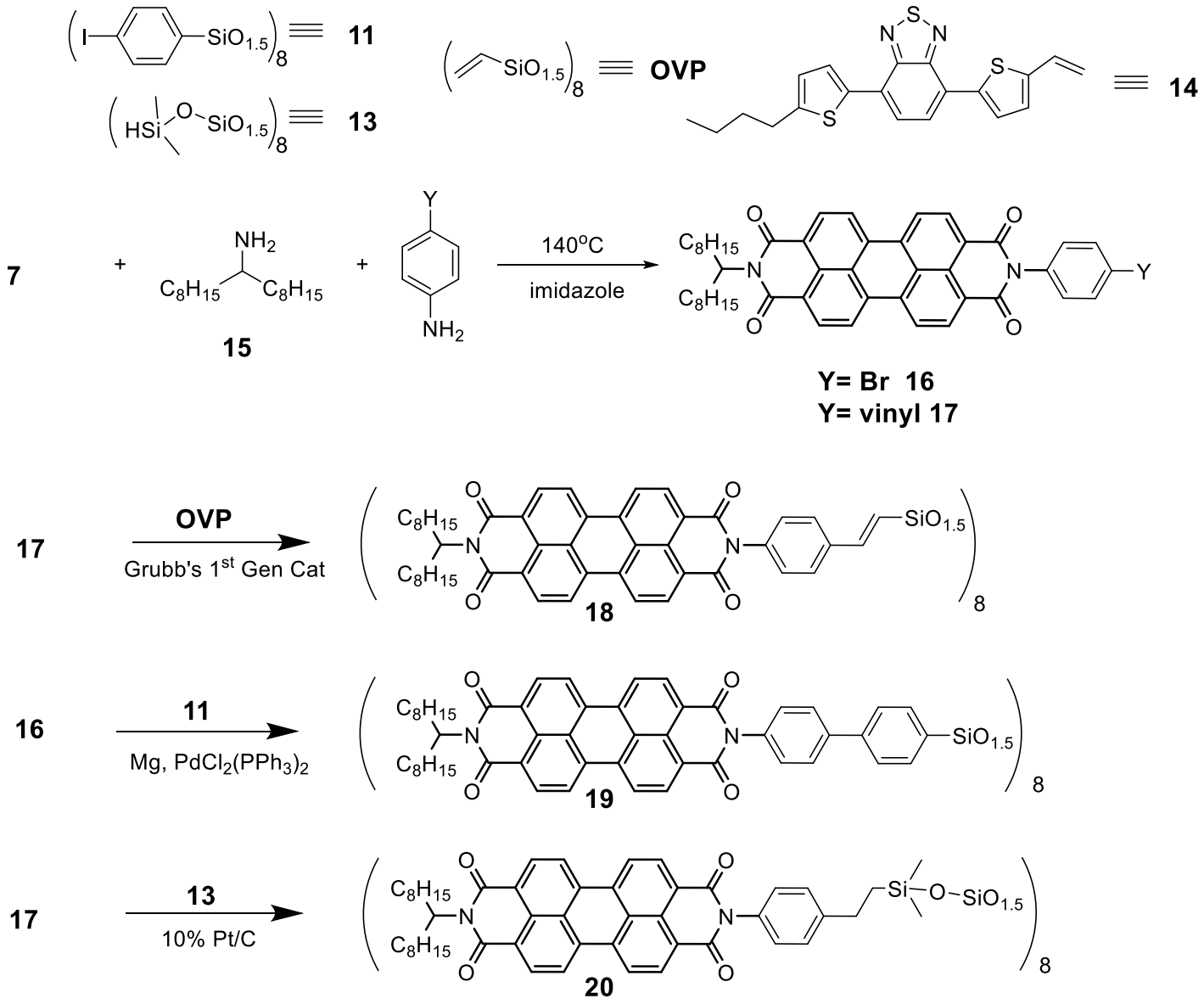
Thus, reacting only one of the two anhydrides on **(6)** is unfeasible. Not only is the first attack is quicker than the formation of imide, but the anhydride has low solubility, so when the

first amine (with its long alkyl chain) attaches, it increases the molecule's solubility and therefore its likelihood to be attacked by a second amine.

We investigated a variety of methods for hydrolyzing either the symmetric di-anhydride or the symmetric diimide to introduce asymmetry. However, we ultimately found the most reliable success with a statistical, one-pot addition of both amines simultaneously. Craig Hawker's group reported an improvement on the acetic acid method we used above, in which imidazole (a better solvent and weaker acid) is heated to 140 ˚C, just above its melting point with the amines and perylene dianhydride.[50] A bomb flask is used to prevent the lower boiling point amines from leaving the reaction.

While this method produced two symmetric diimides that were not the desirable product, our systems generally had a range of solubilities that made separation via column chromatography quite simple. Generally, the PDI with two solubilizing chains eluted quickly in chloroform, followed by the mixed PADI species. The PDI with two Linker units was generally so insoluble that it could be filtered out or remained as baseline in the column.

In these syntheses, we quickly realized that the 2-ethylhexylamine used for the brominated PDI compounds did not provide enough solubilizing power when only one of these chains was in use. Replacing 2-ethylhexylamine with *n*-hexadecylamine produced insoluble symmetric PDI compounds, underlining the importance of alkyl branching, preferably closer to the perylene moiety, in breaking up aggregation and allowing solubility.



Scheme 3: Preparation of PADI-Styrene and PADI-bromophenyl for coupling to POSS via olefin metathesis, Kumada coupling, or hydrosilation

To provide that branching as well as a long alkyl chain, we prepared **(15)** from commercially available heptadecan-8-one. Following the literature,[51] we received a 48% yield by stirring with sodium cyanoborohydride with ammonium acetate in methanol at room temperature for 2 days, but yields increased to 90% when the temperature was raised to a slow reflux. We used this alkyl chain to solubilize all PADI molecules from this point on.

We wanted the Linker to maintain the rigidity of perylene, and also found 4-bromoanisole to be commercially available. Thus, our first Acceptor-Linker target was **(16)**, which we produced in 43% yield. We planned to utilize the couplings that failed to work with the bay-substituted PDI bromide **(9)**, but similar patterns developed. Magnesium metal and isopropylmagnesium chloride failed to activate the bromide on the phenyl ring of **(16)**. Palladium-catalyzed Heck couplings with octavinylPOSS (OVP) did not appear to react.

Using 4-aminostyrene, we then prepared the alkene **(17)** in 49% yield. We anticipated its use in two potential couplings: a platinum catalyzed hydrosilation and an olefin metathesis.

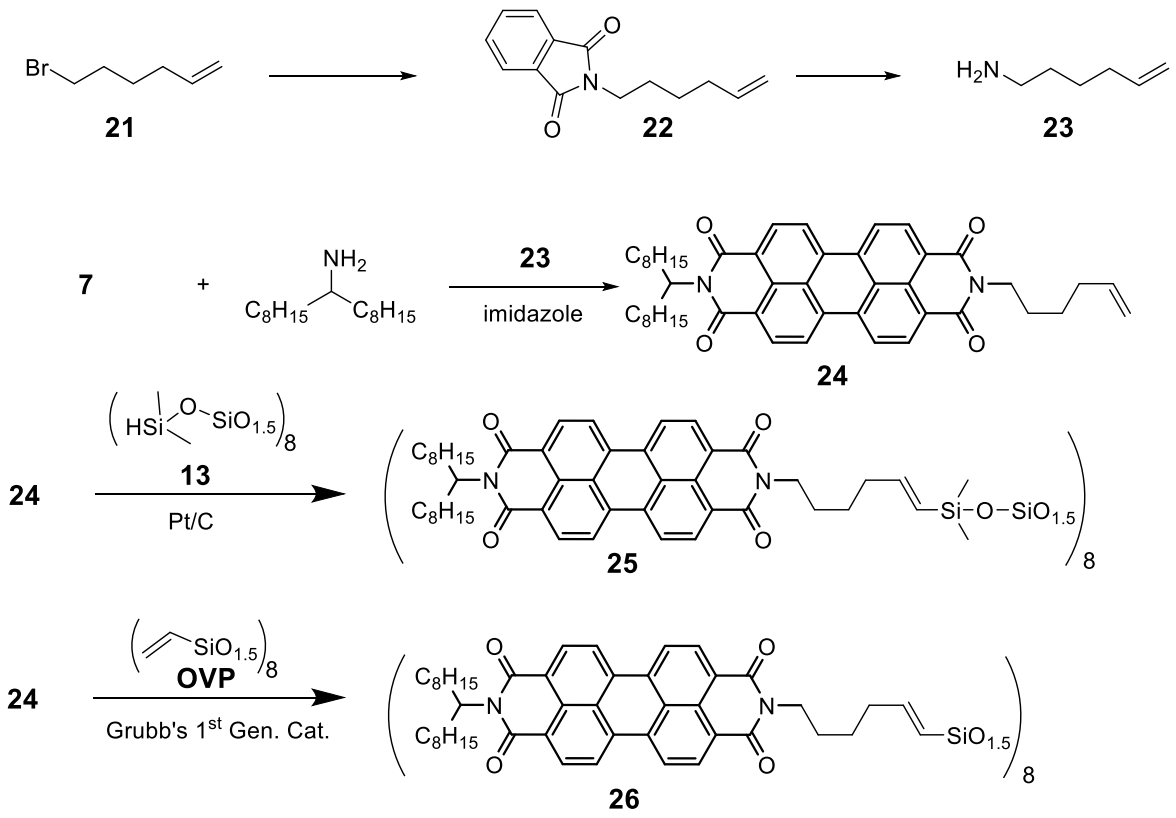
For the hydrosilation to produce **(20)**, we purchased the POSS compound **(13)**, which contains electron-rich silanes activated for coupling on each of the siloxanes that form the polyhedral siloxane core.[52] Unfortunately it only produced black solutions (likely oxidized platinum) and no apparent reaction by ^{1}H-NMR. Meanwhile, a test reaction between 1-decene and **(13)** produced 90% conversion by ^{1}H-NMR.[53] It is likely that the perylene moiety of (**17)** interfered with the hydrosilation.

For our olefin metathesis, we selected Grubb's 1st Generation catalyst because its lower reactivity prohibits vinyl siloxanes (as in octavinyl-POSS (OVP)) from forming homodimers.[53] Dimers are less reactive than terminal alkenes, and we wanted to ensure that none of the POSS arms could be trapped in a kinetically preferred state, where quick intramolecular metatheses

might reduce the number of Acceptors that a Core could hold. Furthermore, a deactivated catalyst ensures that the product peaks, once formed, will be stable and will not equilibrate back towards reactants.

While a test olefin metathesis between OVP and 3,4-dimethoxystyrene in dry dichloromethane produced octa-functionalized POSS in 95% isolated yield, applying the same conditions to **(17)** failed to produce a reaction. ^{1}H-NMR analysis of the crude mixture indicated that not even the dimers of either species formed. Replacing the 1st generation Grubb's catalyst for the more reactive Hoyveda-Grubb's catalyst did not improve yields, indicating that both reactants are significantly electronically deactivated.

Additional attempts to run both of these couplings with another Acceptor that we prepared, DTBT-Vinyl (**14**), also failed, which lead us to conclude that the electron deficiency of these acceptors removes any useful reactivity from the Linker if it is conjugated to the Acceptor system, as is the case with these phenyl-PDI and DTBT-based systems**.**



Scheme 4: The Gabriel amine synthesis of PADI-hexene for hydrosilation and olefin metathesis

We hypothesized that an olefin separated from the Acceptor by an alkyl chain would make the reactive site more electron-rich, and thus activated, while easing the issue of sterics, which may have hindered full functionalization of the POSS. We found no short-chain amino-alkenes that were commercially available, but used a Gabriel amine synthesis to produce one from, 6-bromohexene. Potassium phthalimide performs S_N2 on the bromide in DMF to form **(22)** in 85% yield. The phthalimide ring is then broken open by application of hydrazine hydrate to form the amine, **(23)**, in 92% yield.

We also applied this synthesis to 4-bromobutene, but found its derivatives to have too low of a boiling point to be easily isolated or used in the high temperature imidization process. 6-aminohexene and swallowtail amine **(15)** were combined to yield the corresponding PADI **(24)**

in 48% yield. Attempts to synthesize **(25)** failed in a similar fashion to the styrene-based hydrosilation attempt to make (**20)**.

We proceeded to submit this olefin to Grubb's 1st Generation Catalyst in OVP in dry dichloromethane. After stirring for 3 days, some homodimers of **(24)** were observed but not any cross coupling moieties indicating formation of **(26)**, and the catalyst appeared to have lost reactivity. Using freeze-pump-thawed dichloromethane improved the reaction and increased the catalyst's utility out to five days.

Over these days, the reaction of monomer **(24)** could be tracked on ^{1}H-NMR by its terminal alkene peaks, while the reaction of OVP's olefins could be tracked by the diminishment of a cluster of peaks around 6.0 ppm. In response, three new olefin peaks emerged: two for successfully cross metathesis and one for the symmetric protons in the homodimer.

Having confidently identified the major components of this mixture, we attempted to resubject the mixture to more catalyst and freeze-pump-thawed dichloromethane, which once again slowly consumed the homodimers and increased the conversion to cross coupling.

At this point, the reaction had been running for over a week and we were unable to achieve total substitution of the Core. By ^{1}H-NMR, there were approximately 6.7 PADI moieties per Core, about 84%, which we decided would be at least enough for an initial test to check the viability of this molecule design.

Removal of monomer **(24)** was easily achieved by column chromatography with a chloroform eluent. However, the homodimer and the partially coupled POSS-PADI species did not separate on a variety of columns. These two compounds differ substantially in molecular weight (1400 g/mol vs 6100 g/mol for the octa-PADI-POSS) but the moieties that interact the

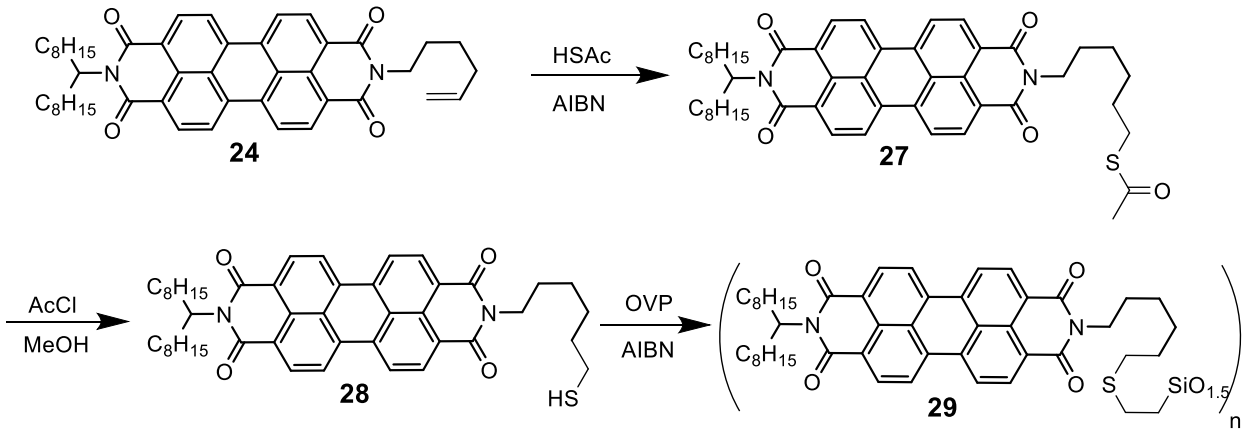
solid phase and eluent are the same. Additionally, the mediocre solubility of these systems leads to broad bands on the column, preventing fine-tuned isolation.

Recrystalization proved unsuccessful and we attempted to use the low solubilities in this mixture for a Soxhlation. This technique is used frequently to purify conjugated polymers. In a soxhlation, several hundred milliliters of solvent are refluxed, and the hot, condensed solvent is dripped onto a cellulose thimble containing the impure solids. When enough solvent has accumulated around the thimble, a siphon transfers the hot solvent along with some of the sparingly soluble impurity, to the refluxing flask below. Effectively, the system uses minimal solvent to preform repeated hot filtrations in a series of solvents that leave behind an insoluble, increasingly pure product.

As expected, all chlorinated solvents dissolved both the dimer and the POSS mixture too well to separate them. Hexanes seemed to remove some minor byproducts but neither of the main compound types. THF worked too well, but methanol developed the slight red color indicative of a dilute PDI solution. Swapping to isopropyl alcohol favored extracting the dimer, but not in a high enough ratio to isolate product.

Finally, we attempted to react the homodimer into a more soluble species, like the monomer had been. To a flask of freeze-pump-thawed dichloromethane, the product mixture, and Grubb's catalyst, we added 4-bromobutene to encourage the formation of monomers. Using a more electron-rich olefin will almost certainly irreversibly metathesize with the remaining siloxane olefins, capping our yield at 84%, but should also encourage the reaction of the homodimer towards more soluble species. Unfortunately, even when 2 equivalents of 4-bromobutene were stirred overnight, no substantial reaction was observed. Ultimately, we failed

to isolate the polyfunctionalized POSS mixture, and applying the impure mixture in a polymer solar cell was deemed not likely to produce meaningful feedback.



Scheme 5: Using Thiol-ene click chemistry to make PADI-POSS

We then explored the possible utility of the radical-initiated thiol-ene click reaction, but no suitable octathiol-POSS was commercially available. Standard preparation of a terminal thiol from a terminal alkene involves a click reaction with either thioacetic acid or thiourea, both of which can be hydrolyzed to produce the thiol under basic conditions. However, our concerns over the high base-sensitivity of POSS lead us to avoid preparing octathiol-POSS ourselves from OVP.

Instead, we sought to prepare a PADI-thiol species, **(28)**. Test reactions with propane thiol and thiophenol and OVP showed that alkyl thiols could almost quantitatively convert to the thioether, though arylthiols degraded, lending credence to the choice to use a hexanethiol linker.

When we combined recrystallized AIBN, thioacetic acid and the olefin **(24)** in chloroform, the product mixture contained several inseparable products and, on ^{1}H-NMR, broadened perylene signals indicative of an unintended reaction of the perylene moiety.

To test whether the perylene system was reactive to radicals, we performed a battery of test reactions. Decene, AIBN, and thioacetic acid were heated four separate flasks in chloroform

with 5 mg of each of the following Acceptors: diethylhexyl perylene diimide **(7)**, diethylhexyl naphthalene diimide, DTBT, and no additive. Of the additives, only PDI showed degradation, and the conversion of decene was low in that flask. It appeared that PDI is unstable to radicals.

Toluene is also sometimes applied during click reactions, so we replaced chloroform for it and received a clean, quantitative conversion to the thioester overnight. This reaction proceeds more slowly than radical-based thiol-ene click reactions often do, but it the high conversion is worth it. Deprotection was attempted by adding acetyl chloride to a solution of the thioester in methanol, but the resultant mixture was messy and difficult to purify, as might be expected for the small change in molecular weight. Still, a crude ^{1}H-NMR showed about 60% conversion to thiol **(28)**.

However, this new thiol species was no longer soluble in toluene, and any attempts to perform a thiol-ene click with octa-vinylPOSS resulted in no reaction. PDI systems are typically only soluble in chlorinated solvents (e.g., CH_2Cl_2, $CHCl_3$), aromatic solvents (e.g., benzene, toluene), and are sparingly soluble in strongly polar solvents (e.g. DMF), so there were few options for solvents that might allow this click reaction to proceed, and none did so.

SECTION 2.6: PADI Dimers To Break LUMO Degeneracy

At this point, we had been attempting to build the CLAP system for about two years without success, so we took a critical look at the project's goals. Our original hypothesis was inspired by the computational work of Troisi et al.,[23] who first proposed disrupting LUMO degeneracy by enforcing a packing regime. However, we had added project goals such as a designing a modular synthesis and replicating the spherical shape and 3-dimensional transport of PCBM.

While the CLAP approach seemed to be burdened by its own weight, we sought to simplify by focusing only on the simplest hypothesis: can we improve exciton splitting in non-fullerene acceptors by breaking LUMO degeneracy?

We deemed Troisi's design,[23] in which two Acceptors are attached to a single methylene unit to encourage π-π overlap, to be synthetically incompatible with PDI and likely many other Acceptors. However, a rigid framework, such as a ring, would still be needed to enforce the proper molecular overlap. Additionally, the hexene chain that had been used on the more successful CLAP efforts would have to be abandoned so that the two acceptors would be close to the bridge and forced into our desired geometry.

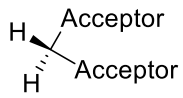


Figure 12: Liu and Troisi's proposal for a framework which may separate degenerate LUMO levels

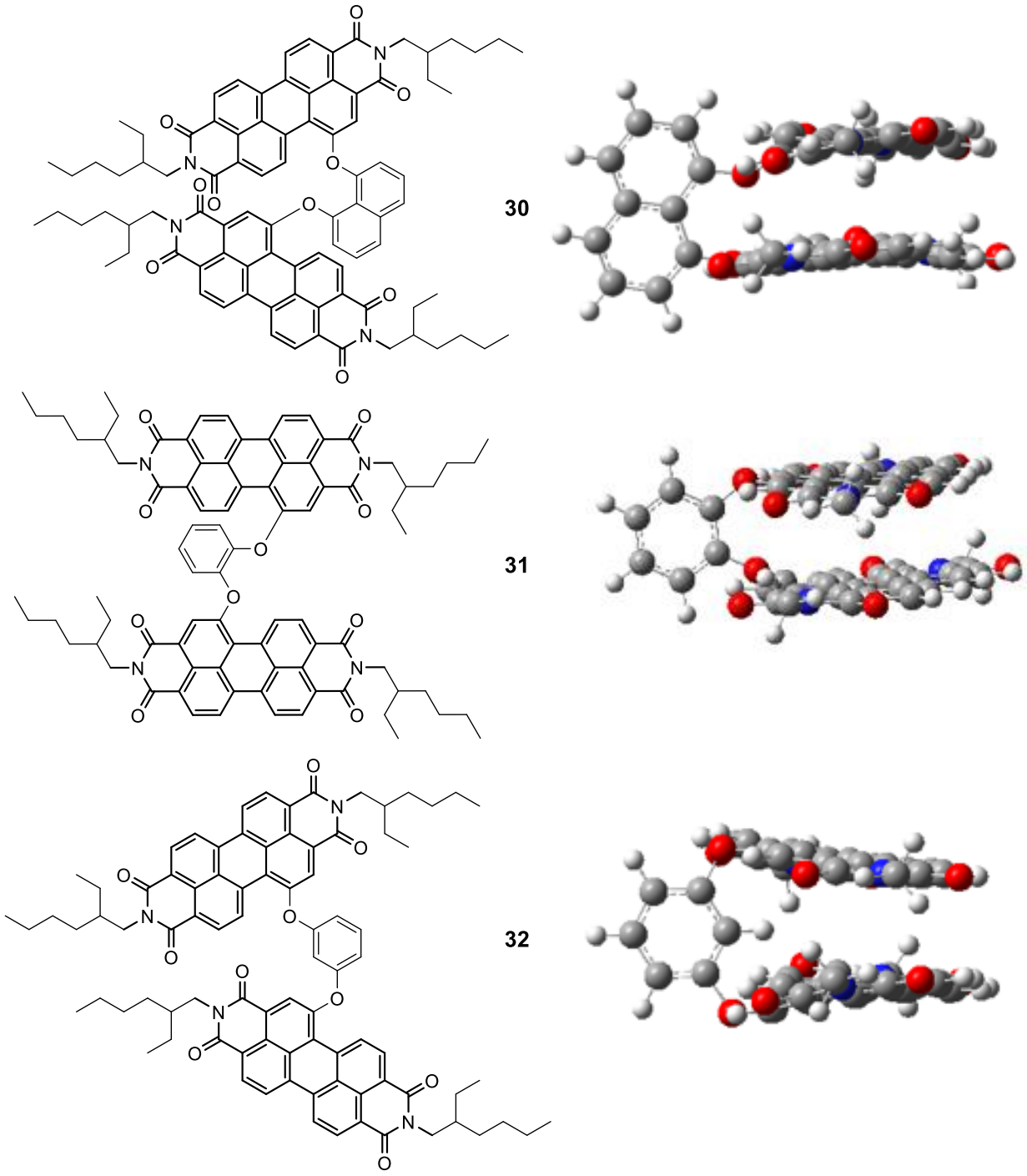
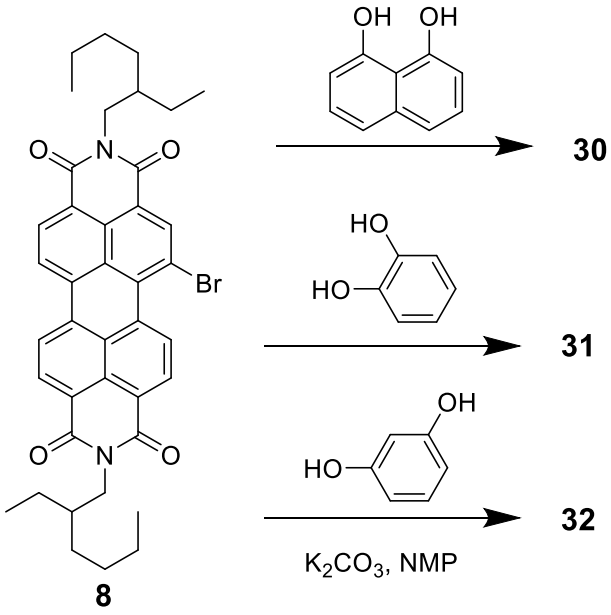


Figure 13: The structures and optimized geometries of three new acceptors which may break the LUMO degeneracy of PDI

We selected benzene and naphthalene-based bridges because they provided commercially accessible reactants, rigid structures, and multiple geometries. In particular, we were interested in the highly co-planar geometry induced by the naphthalene bridge system, as shown in Figure 13.

We created a scheme to couple the monobrominated PDI species **(8)** to 1,2-catechol, 1,3-catchol, and 1,7-Naphtalenediol via a nucleophilic aromatic substitution, which should be favored by the electron deficient PDI system. We subjected **(8)** to a solution of potassium carbonate and diol in NMP at 100 ˚C.[54] This solution rapidly turned a dark green and neither product nor perylene diimide was not recovered.



Scheme 6: Synthesis of PDI dimers

To single out the problematic interaction, we subjected these species to a battery of test reactions. A flask of PDI **(8)** in NMP was stable at 100 ˚C, as was a similar flask that also contained 4-methoxyphenol. A flask with **(8)**, potassium carbonate, and NMP at 100 ˚C quickly became the same deep green observed in the reaction mixture and no perylene diimide was observed via ^{1}H-NMR.

A polar, aprotic solvent like NMP should be necessary to allowing the deprotonation of the phenol and its subsequent attack onto the perylene. Supplementing the NMP with 5 parts toluene raised solubility but did not prevent the degredation of **(8)**. Neither DMAc nor THF, both polar aprotic solvents, dissolved the PDI, so no reaction occurred.

Eventually, a 1:4 solution of DMF:toluene achieved solubility of both the hydrophobic perylene and the ionic, depronated phenols, yielding modest couplings. Attempts to enhance the yield by using additional equivalents of the perylene **(8)** and adjusting the reaction temperature and duration achieved the mono-coupled intermediate with 1,3-catechol, but failed to achieve more. Viswanath et al. report making this same mono-coupled system on their route to an assymetric system, and perhaps it is telling that they do not mention isolating any of **(32)**.[55]

We expected the 1,3-catechol system to be the least sterically demanding of the three targets, so these results ultimately match those of the other couplings we discussed in this chapter, particularly the olefin metathesis. The system's unwillingness to produce even some product makes it likely that deactivated electronic and bulky steric factors reproducibly prohibit the formation of these induced-geometry, π-π overlapped Acceptor systems.

SECTION 2.7: Conclusions and Outlook

This work details our more fruitful attempts, out of a larger set of mostly unremarkable failures, to create a synthetic route to prepare a fullerene-mimicking electron acceptor for organic photovoltaics. While no particular outcome yields a strong conclusion, together they share clear, recurring themes.

Often, perylene diimide's limited solubility in all but aromatic and chlorinated solvents led to conflicts with more polar or ionic-based chemistry. In the thiol-click route, the addition of a single polar, acidic thiol proved to add just enough intermolecular attraction to decrease

solubility in toluene and prevent reactivity. Similarly, the purification of multiple of these compounds, including the PADI-POSS mixture, may have been possible with the ability to use hexanes and ethyl acetate as co-eluents in column chromatography.

Perylene diimide is a promising acceptor with low-lying LUMO energy levels, but this same electronic property often lies in conflict with the reactivity needed to derivatize it. For all of the Linker chemistries we report here that are conjugated with the PDI ring, neither magnesium nor palladium is shown to effectively activate Grignard reactions or metal-catalyzed cross couplings. Separation of the Linker provided additional reactivity, as in the hexene moiety, but difficulties remained.

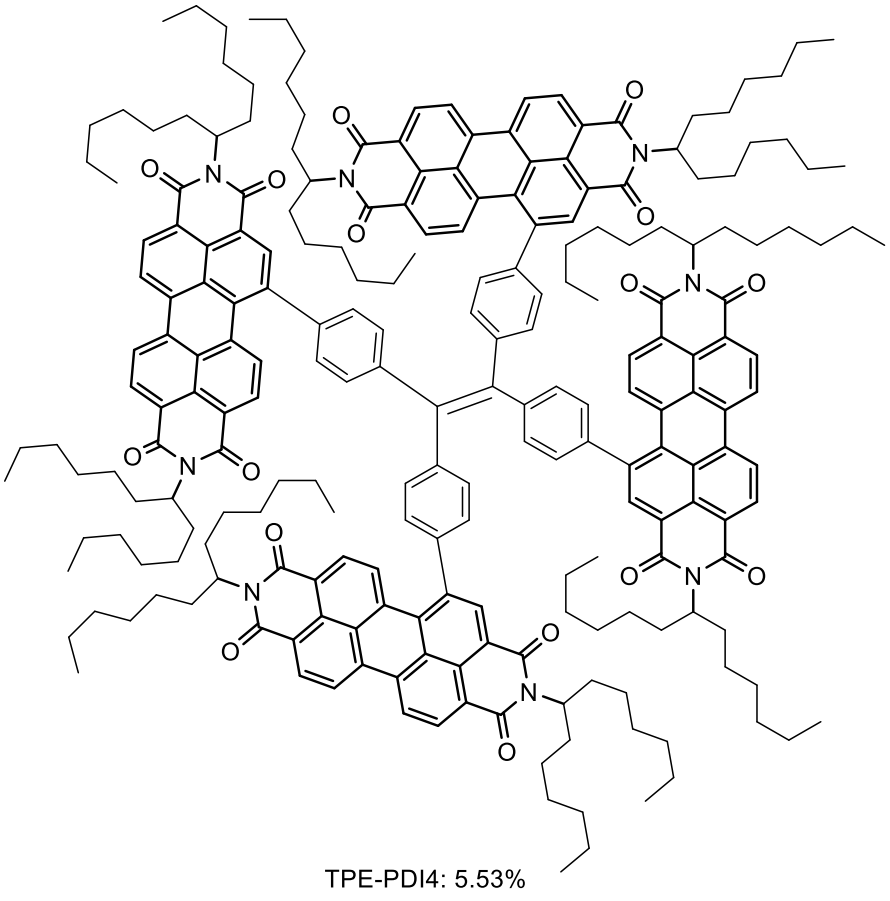


Figure 14: Tetraphenylethylene-PDI contorts into a propeller shape and achieves 3D transport.

Since we stopped work on this project, other researchers have continued to explore some of the hypotheses that drove our study. It would be fitting to finish by taking a look at what has been proved and what remains to be investigated.

One study investigates using tetraphenylethane (TPE) as a core to hold four PDI units, which are rotated 50˚ out of plane to produce a propeller-like shape.[56] They achieved a V_{OC} of 0.91 V, about what would be expected, but managed to push J_{SC} to an impressive 11.7 $cm^2V^{-1}s^{-1}$. The domain size reduces to just 20 nm, and the mobility increases by an order of magnitude over a PDI-dimer system to practically match PCBM. Both of these properties likely contribute to the high current. However, they do not see any redshifting of the absorption spectrum, indicating that the cores are not electronically interacting with each other.

Then, Ie et al did what we could not by producing two perylene-linker-core systems, including one with POSS.[57] The first molecule attaches four PDI units to a tetra-biphenyl carbon core (Figure 15) that fails to change the absorption spectrum or enhance the photovoltaic properties over the monomer (Figure 15). The POSS species, made by a convergent approach that we backed away from early on and purified with prepatory GPC, shows a significant broadening in its absorption spectrum. This and other studies indicating the formation of H-aggregates, meaning that the PDI orbitals do interact intramolecularly. However, these properties only lead to a PCE of 0.18% with the POSS system, a modest gain over the tetramer and monomer systems.

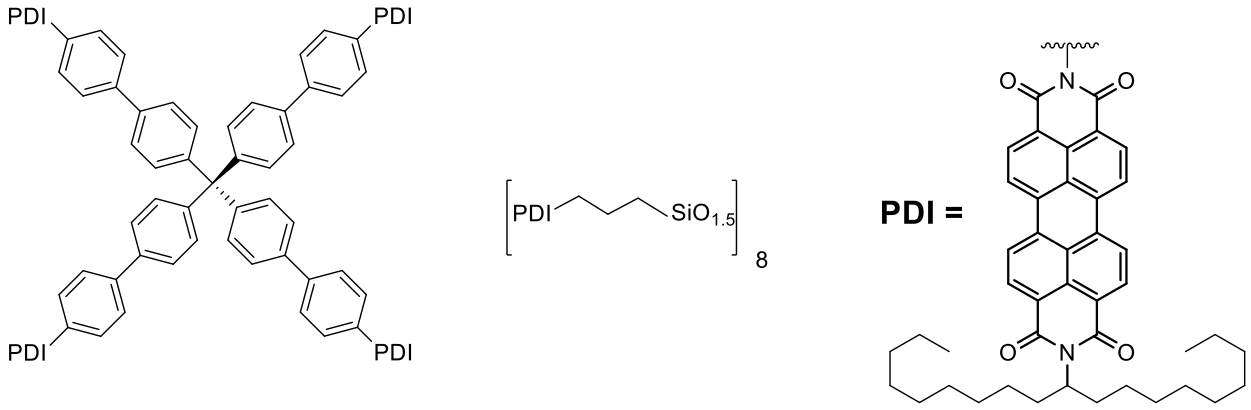


Figure 15: The 3D PDI-based acceptors made by Ie et al.

Work towards a non-fullerene electron acceptor for OPV continues. It seems more certain now that ever that the crystallinity and morphology issues that plagued earlier acceptors can be solved by the application of 3-D topologies. However, these topologies are often based on twisted or spiro acceptor systems.[58-60]

Ie et al.'s work casts doubt on the utility of Troisi and Lu's proposed acceptor design that was supposed to enhance exciton splitting by breaking the degeneracy of the LUMO levels. Furthermore, our efforts point to the extreme difficulty in achieving this molecular design.

Regardless, the field of non-fullerene acceptors is accelerating, and has even begun to surpass PCBM.[60] The further development of cheap and tunable components for organic photovoltaics drums a steady beat towards their commercial deployment.

CHAPTER 3: Exploring Routes to A Doubly Divergent Triazole Synthesis

SECTION 3.1: Background and Motivations

The active layer of polymer solar cells (PSC's) generally consists of two components: an electron-rich conjugated polymer (the donor) that gives excited state electrons to an electron poor small molecule or polymer. Generally, the all-polymer systems underperform relative to the polymer-small molecule systems, largely because of the success of fullerene-based small molecule acceptors.

Because of the difficulties in replacing fullerenes as acceptors (see Chapter 2), many researchers have devoted their attention and effort to the design and synthesis of the polymeric donors. Early polymer systems, up until the success of P3HT in 2002,[61] were simple homopolymers, like those shown in Figure 1. However, a growing trend in polymer design in the late 2000's moved towards the design of push-pull (or Donor-Acceptor) copolymers,[62] which has been the source of nearly all high performing polymer donors since.

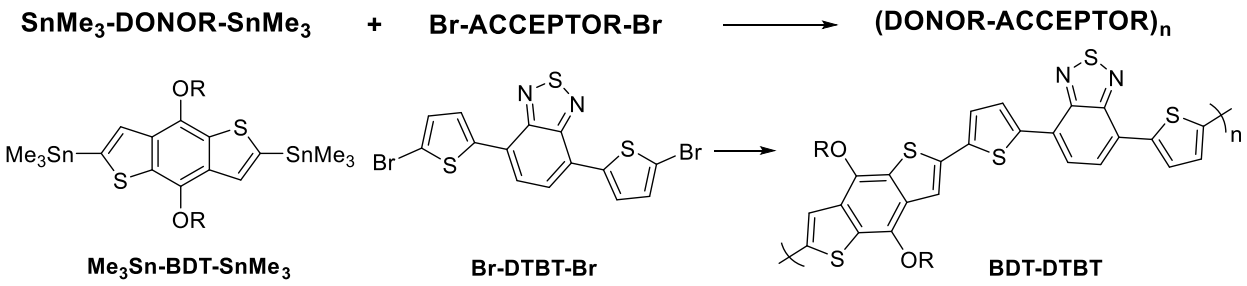


Figure 16: One example of the Donor-Acceptor approach to OPV polymer design, using Stile Coupling

In the Donor-Acceptor (DA) design, an electron rich monomer such as benzodithiophene (BDT) polymerizes with an electron poor moiety like benzothiadiazole (BT) to form an

alternating copolymer (Figure 16). This design, similar in goals but distinct from the BHJ physical mixing of a polymeric donor and fullerene acceptor, produces a polymer with several advantages over homopolymers.

The DA design gives greater control over the HOMO and LUMO energy levels, as well as the corresponding bandgap. In homopolymers, the selected moiety had to be carefully tuned to have both a low enough bandgap to absorb the visible spectrum, but also have a low-lying LUMO to effectively donate electrons to the fullerene-based electron acceptor. In the DA approach, the LUMO of the polymer is mostly centered on the electron-deficient Acceptor moiety, and the LUMO energy level is largely dependent on the Acceptor's LUMO level. The HOMO level of the polymer tends to spread out over both moieties but the energy level is generally close to the Donor. Thus, a high degree of modularity is allowed to tune the bandgap and electron donating capability of the donor polymer.

Also, many of the palladium-catalyzed cross couplings that are employed to form the carbon-carbon bonds that make up the conjugated polymer backbone work best when coupling an electron-rich and electron-poor species to each other. For example, in Stille couplings, placing the trialkyltin moiety on a more electron-rich component improves yield by encouraging transmetallation, while placing the corresponding halide on an electron poor species improves yield by encouraging oxidative addition. With DA copolymers, both monomers can be easily symmetrically functionalized (with either halides or organostannanes, respectively) and the electron poor and rich natures of these monomers can accelerate the synthesis as well as produce a polymer with highly desirable properties.

Many high performing polymers have been designed by introducing new Acceptor and Donor components and then polymerizing them with a battery of comonomers. This modular

approach also allowed the field to develop many theories about what features make for a high quality donor polymer, including proper side chain length and branching,[63] combining a weak donor with a strong acceptor, and enforcing planarity to increase conjugation length.[62]

However, as organic photovoltaics have matured as a field, it has naturally drifted towards engineering concerns, where smaller tweaks (with weaker trends) grow in importance when selecting molecular candidates. In earlier, more strongly hypothesis-driven work, one or two alternate monomers might be painstakingly prepared through different synthetic methods using separate batches of material. Often only less important tweaks, like the branching and length of the solubilizing chain,[63] were accessible in a divergent manner. To this end, we were curious in expanding what modularity was possible with common monomer units from a single synthetic path.

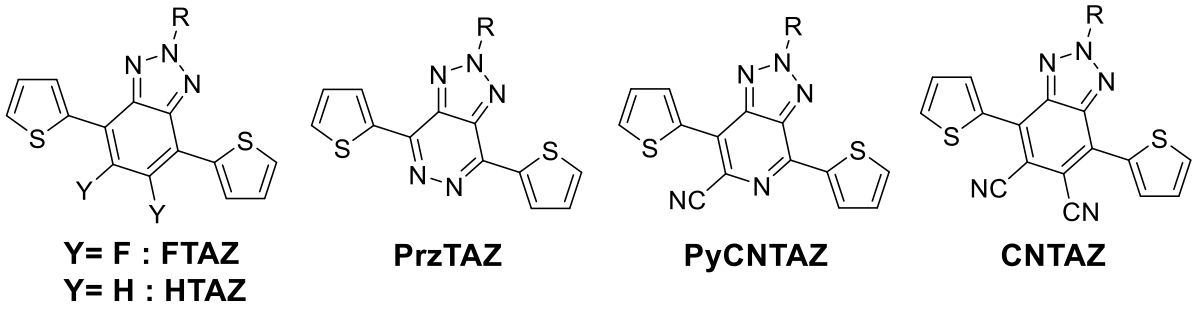
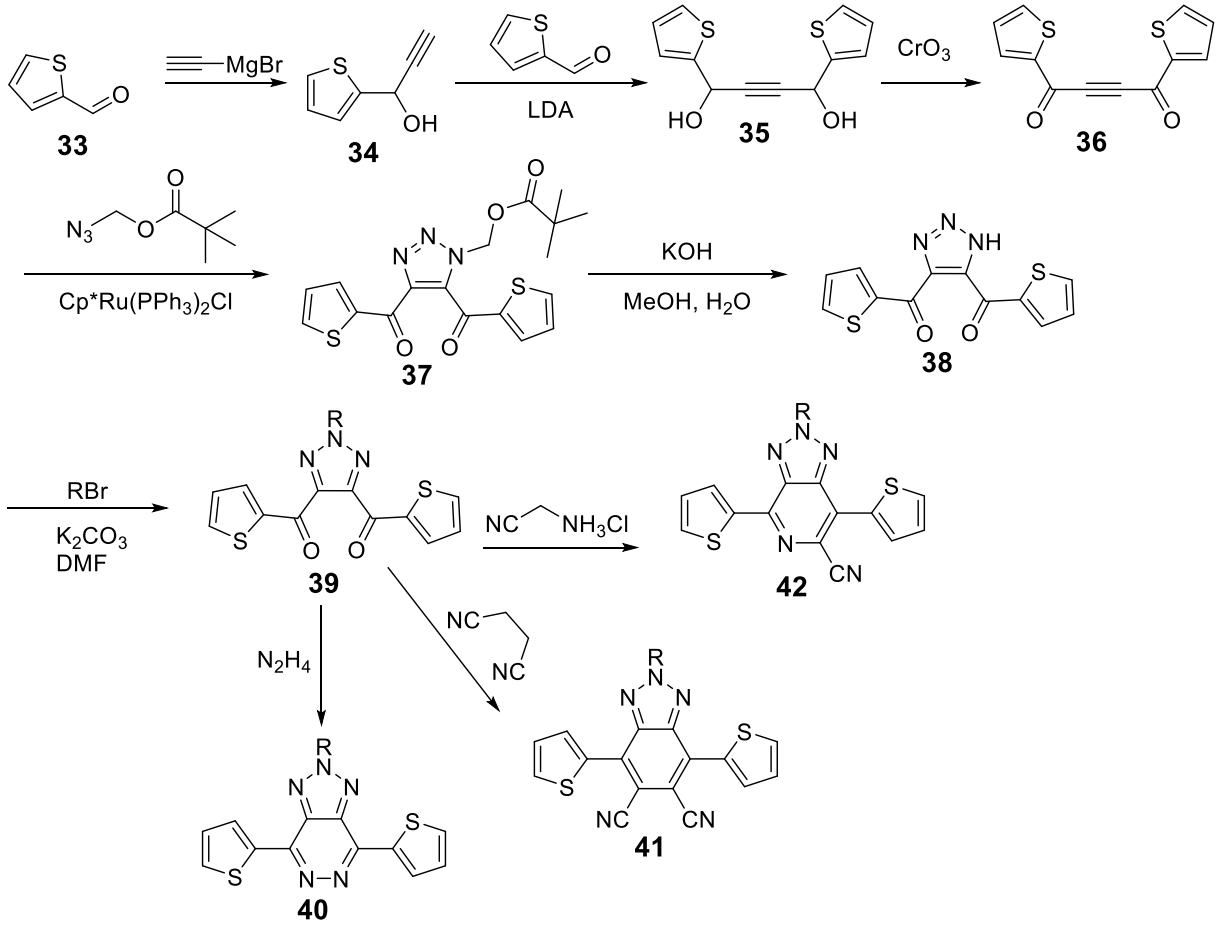


Figure 17: Analogs of dithienyl benzotriazole (HTAZ)

HTAZ and FTAZ (Figure 17) have been known as useful acceptor units in donor polymers since 2010,[64] with FTAZ showing unique thickness-dependent properties and a PCE of over 7%.[65,66] After studying the impact of fluorine content and position on BDT-TAZ based polymers,[67] Wentao Li, a former member of the You group, turned his attention to other TAZ analogs which would modify the backbone of the polymer itself.

FTAZ makes a high performing polymer with BDT, but it has a large bandgap (2.0 eV) which prevents it from making good use of the entire solar spectrum. Meanwhile, pyradine-

analogs of DTBT (related to HTAZ) have been shown to decrease the bandgap and cyano groups offer less powerful electron withdrawing effects than fluorine.



Scheme 7: Li's original divergent synthesis of three analogs to dithienyl benzotriazole

Individually creating each of these compounds would take substantial effort, so Li designed a divergent synthesis for these compounds. First, he attached thiophene units, essential flanking units around many Acceptor moieties in donor polymers, to an acetylene unit *via* Grignard reagents. A Jones oxidation of the alcohols recovers the ketones that are crucial for several of the following synthetic transformations.

In **(37),** Li then forms the triazole ring *via* a Huisgen cycloaddition of the symmetric alkyne and azido methylpivalate. Internal alkynes cannot be reacted with the inexpensive copper (I) catalyst that activates terminal alkynes, so an expensive ruthenium (I) catalyst was used, resulting in high yields.

The selection of a methylpivalate protecting group for the azide is of considerable importance to the investigation to follow, and is worth discussing in detail here. Li recognized that using sodium azide resulted in extremely poor cycloaddition yields of 4%, while organic azides proved more reliable. However, attaching the alkyl chain intended as a solubilizing chain for the polymer target also is not feasible. When organic azides cyclize to form triazoles, the organic moiety rests at the N1 position of the triazole ring, instead of the preferred N2 position. In the N1 position, the alkyl chain extends alongside the polymer chain and can kink the chain, negatively impacting effective conjugation length and thereby charge transport.

Thus, the azide must be functionalized with a protecting group which can be removed so that the intended alkyl chain can be attached at the proper position (N2). Sharpless's group studied a variety of protecting groups for this purpose, and concluded that methylpivalate provided the most facile, efficient cleavage of the groups they investigated. It deprotects under mild conditions: 30 minutes in 1 M NaOH and methanol.[68]

The subsequent alkylation of the triazole ring is nontrivial, and Li investigated the effects of triazole ring functionalization on the formation N2 and N1 alkylated products. Briefly put, more electron poor triazole rings alkylate predominantly at the N2 position. With a diketo-triazole, like **(38)**, alkylation occurs at the N2 position with 99% selectivity**.** The synthesis concludes with a Paul-Knorr-like cyclization that crucially gives pyridinyl and anilinyl analogs of benzotriazole in good yields. Not shown is the bromination of the flanking thiophene units, a

typical procedure for Acceptor monomers, and the Stille polycondensation with distannyl-BDT to product the final polymer.

These compounds were then polymerized with TAZ's common co-monomer, BDT, and their properties were tested in OPV devices. All three analogs decreased their bandgap (absorbing more of the solar spectrum) relative to FTAZ. They also produced a V_{OC} of nearly 1.0 V, which is rare for cells that use fullerene-based electron acceptor. One of FTAZ's major deficiencies is its large (2.0 eV) bandgap, and the CNTAZ polymer achieved a respectable 1.77 eV. However, PyCNTAZ produced a better morphology and beat CNTAZ in both FF and J_{SC}, ultimately producing a PCE over 1% higher than the FTAZ reference cells.[14] This is impressive, given fluorine's propensity to reduce charge recombination.[67]

These successes highlight the utility of a higher throughput method of testing monomer units in D-A copolymers and bolstered our future interest in this avenue of research.

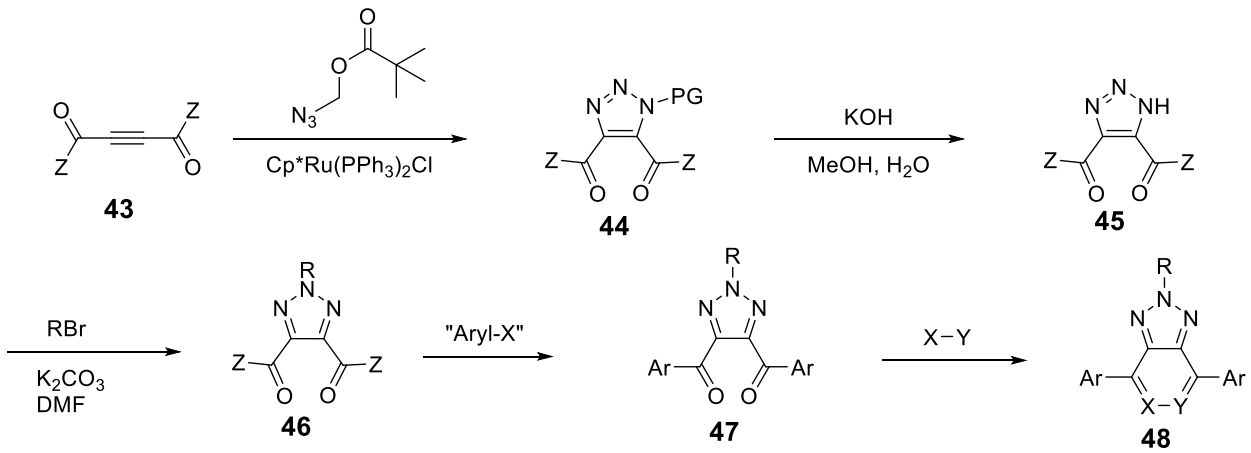
SECTION 3.2: Designing a Doubly-Divergent Synthesis

Inspired by the success of Li's investigation, we wanted to push the idea to its limits. Was it possible to incorporate even more modularity into this synthesis, so that enterprising researchers could more easily investigate benzotriazole's analogs? In other words: could we scientifically design a synthetic route which would allow less synthetically talented groups to focus on characterization and engineering concerns? We decided to become proponents of the idea that the field would now benefit from a focus on creating more divergent syntheses and decided to lead by example.

Another common point of tunability of OPV polymers is the flanking electron donating units around the acceptor unit (e.g. TAZ). Li's efforts used the common thienyl flanking units,

but there are other promising moieties that might yield polymers with even higher power conversion efficiencies,[69] if given the chance. However, his synthesis starts by attaching these flanking thiophenes to the central alkyne, so all attempts to investigate other units would have to start over from the first step, with no reusable compounds.

When I analyzed Li's scheme for this effort (Scheme 9), several key features became apparent. First, that a symmetric alkyne is built up assymetrically, possibly wasting resources and time. Second, that building it assymetrically required the use of a Jones oxidation, which unfavorably employs stoichiometric amounts of chromium (VI) and generates significant amounts of heavy metal waste. Third, that functionalizing the alkyne before the Huisgen cycloaddition would provide useful scaffolds for introducing the flanking aryl rings at a later step. Thus, some precursor to the aryl-ketone species would have to be attached to the alkyne early on in the synthesis and be orthogonal to all of the chemistry used until the aryl unit was attached. Logically, this would occur as one of the final steps in the synthetic scheme, so as to minimize performing identical synthetic steps to different batches of analogs.



Scheme 8: A generalized scheme that modifies Li's synthesis to allow two divergent steps.

However, Li's synthesis only shows that the Paul-Knorr-like cyclization was stable and reliable when the ketones are stabilized by thiophenes. Thus, the aryl-unit precursor that we

select, **Z**, should react to form the desired thiophene-replacements before the Paul-Knorr-like cyclization. This design hedges against the possibility that Li's cyclization requires an aryl ketone to efficiently generate a benzotriazole analog.

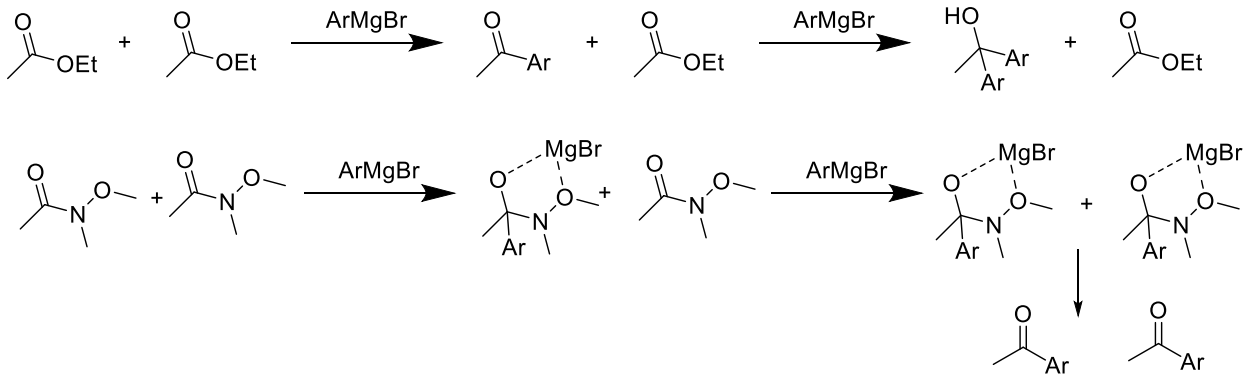
SECTION 3.3: Weinreb Amides as A Tool for Divergency

We researched several promising methods for adding the aryl groups to the triazole ring and forming a ketone. The Weinreb amide ketone synthesis was an obvious frontrunner because it allows carbon nucleophiles to form ketones from a stable, easily made precursor (like how **(47**) is formed from **(46)**).

Usually, when strong nucleophiles (like carbon nucleophiles) attack an ester or amide, the ketone is formed immediately. However, ketones are better electrophiles than esters because they lack the heteroatom's stabilizing lone pair donation into the carbonyl's π^* orbital. As a result, these reactions often lead to overfunctionalization and the formation of a sizable quantity of tertiary alcohol, rather than the desired ketone. Logically, any equivalents of nucleophile consumed during overfunctionalization cannot also react with the remaining ester. Thus, the final reaction mixture chiefly contains the initial ester and the undesired tertiary alcohol, with minimal desired ketone.

Weinreb amides solve this issue by preventing the immediate formation of the electrophilic ketone. When a strong electrophile (Such as C-Li) attacks a Weinreb amide, the *N*-methoxide lone pairs of the amide stabilizes the Li-O binding at the oxyanion intermediate, as shown in Scheme 8. Often, but not always, cold reaction temperatures (below 0 or -40 ˚C) are required to stabilize the oxyanion so that it does not immediately collapse into a ketone. The

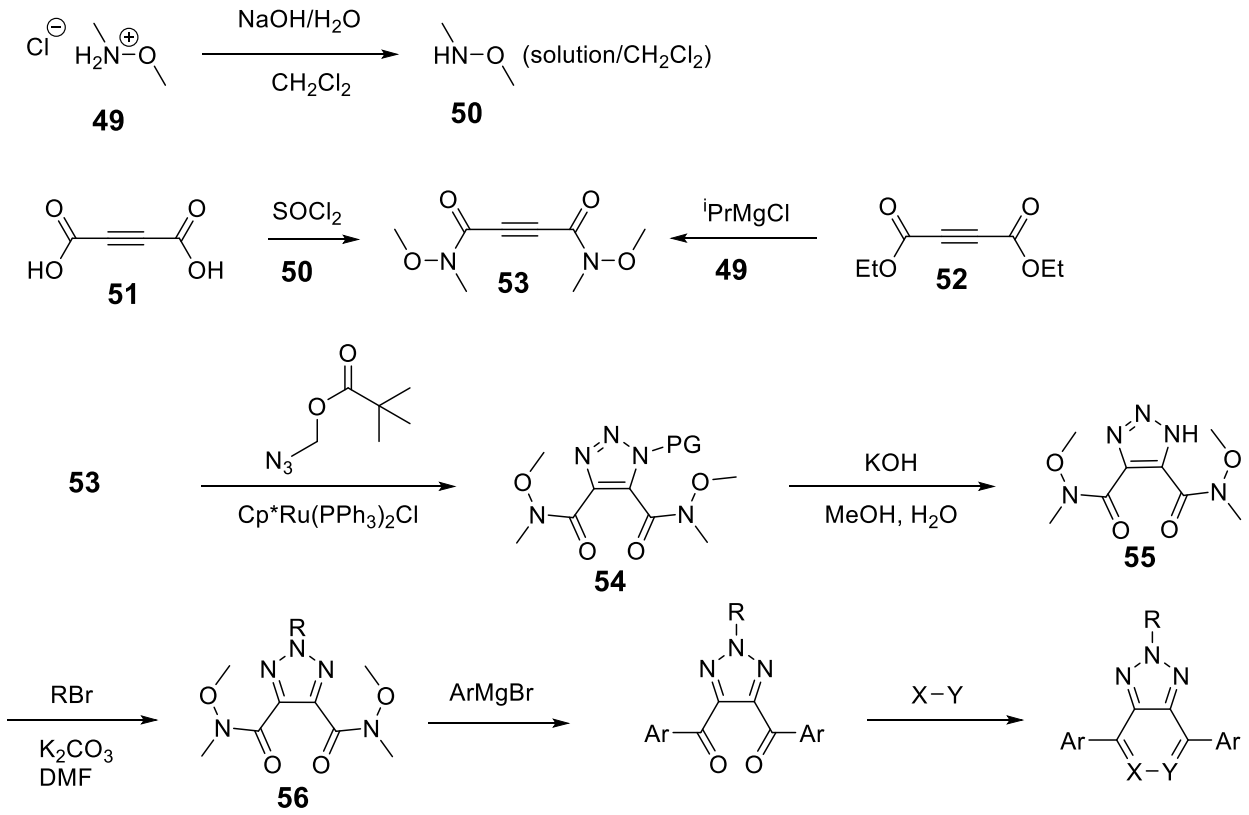
non-electrophilic quaternary intermediate form is kept until the reaction mixture is quenched, cold, along with any still-reactive nucleophile.



Scheme 9: Weinreb amides prevent overfunctionalization by forming a stabilized tetrahedral intermediate that is stable until workup.

Applying the Weinreb amide to our analysis of this system (as **Z** in Scheme 8), we now had a promising route to doubly-divergent triazole-based monomers. Weinreb amides can be prepared from both esters and carboxylic acids using inexpensive *N,O*-dimethylhydroxylamine hydrochloride (**49**), which is often deprotonated immediately prior to use or in situ. We found that both the acetylene dicarboxylic acid (**51)** and the acetylene diethyl ester (**52**) were commercially available and purchased both to investigate them as starting materials. As desired, both the acetylene dicarboxylic acid and the acetylene diethyl ester are symmetric diacyl alkynes, alleviating the inefficiency of the original route's need to make them over three steps.

However, many of the common procedures for forming Weinreb amides caused significant or total decomposition of these reactants and isolating the Weinreb amide product proved consistently difficult.



Scheme 10: Applying Weinreb amides to the divergent synthesis of benzotriazole analogs

One common method to preparing the Weinreb amine is to use two equivalents of isopropylmagnesium chloride to deprotonate the hydrochloride salt **(49)** in dry THF, which in turn performs a nucleophilic attack on the esters. The dimethylhydroxylamine moiety, newly added to the carbonyl, immediately performs its function as a stabilizer and prevents two amines from attacking a single ester.

In practice, however, this reaction often produced a brown oil in our hands. When we increased the flask temperature for the nucleophilic attack from -15 ˚C to 25 ˚C, crude ^{1}H-NMR spectra indicated low conversion. Decreasing the flask temperature to -78 ˚C did not improve yield, but did decrease byproducts. A distillation at 0.33 torr and 110 ˚C yielded a yellow oil with fewer impurities, but never gave isolatable product. Because the yields were low, it is probable that mono-Weinreb species were forming more than the intended product.

Turning our attention to the dicarboxylic acid species **(51)**, the most common methods involve passing through an acyl chloride intermediate, which is quenched in situ by the free amine **(50)**. We were unable to obtain more than trace amounts of the product from this method, but believe that the partial optimizations detailed below are worth reporting.

To our surprise, application of excess thionyl chloride in dichloromethane produced little acyl chloride unless the reaction flask was heated to a slow reflux (40 ˚C) overnight. Quenching with freshly prepared amine **(50)** created brown solutions with significant byproduct, which could be cleaned up somewhat by gentle removal of the dichloromethane and thionyl chloride via distillation. Adding in a dry mixture of fresh dichloromethane, triethylamine and the hydrochloride salt **(49)** produced our best results, albeit in low (<15%) yields.

There are only two NMR active protons on **(51)**, both on carboxylic acids, so analysis of this reaction is difficult. In persistence, we hypothesized that thionyl chloride's reactivity may have been contributing to the degradation, and that the diacyl chloride intermediate might itself be stable. Thus, we investigated the use of oxalyl chloride, which is generally considered a softer chlorinating agent than thionyl chloride.[70]

When excess oxalyl chloride was used to form the acyl chloride, the reaction still often turned brown but did appear to produce fewer byproducts. However, the characterization of product was confused by a curious signal on ^{1}H-NMR. In the expected product, the Weinreb amide provides two proton singles, each corresponding to a methyl group on either the oxygen or nitrogen atoms. These reactions, however, produced a doublet of doublets in that chemical shift region. Figure 18 shows a common ^{1}H-NMR spectra produced by using oxalyl chloride as the chlorinating agent. Over the course of several reactions, we were able to demystify this curious signal.

Increasing the amount of oxalyl chloride revealed that the apparent doublet of doublets is actually two compounds, each with a pair of equal-integration singlets. Because this major byproduct was not removed by washing with saturated sodium bicarbonate solution, we can deduce that the compound does not have any carboxylic acids, and so is not the mono-functionalized intermediate. Column chromatography in hexanes and distillation failed to separate these two compounds.

It took some lateral thinking to realize that our imposter compound was the double-edged sword of using oxalyl chloride for this reaction. When placed side-by-side (Figure 18), the two chemical reactions are obvious counterparts, and their difficult separation is immediately apparent.

By reducing the equivalents of oxalyl chloride to two (exactly what the reaction mechanism calls for) and running the activation step for longer, we were able to successfully produce **53** in 66% yield and with minimal oxalic diamide. However, this reaction continued to be difficult to reproduce, and often yields less than 10% product.

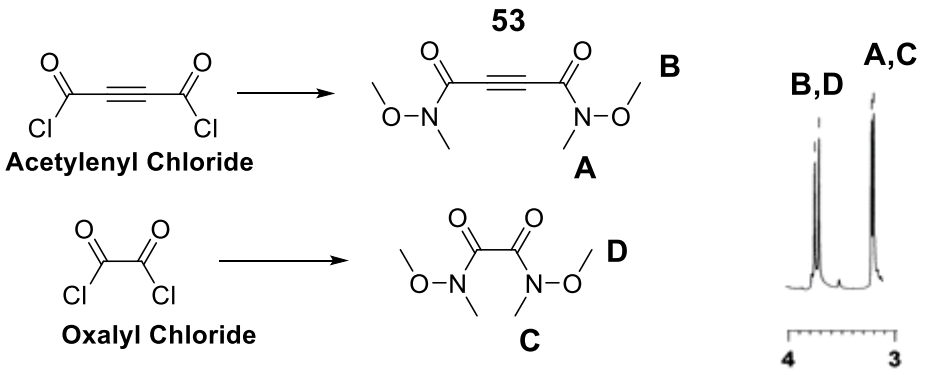
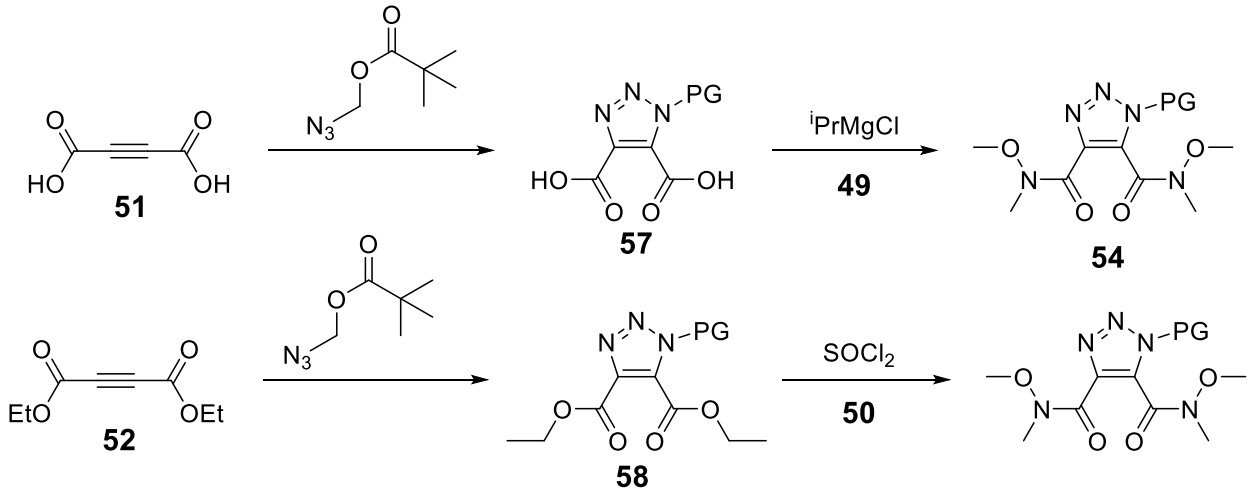


Figure 18: The "imposter" weinreib amide that is inseperable from acetylene diamide

SECTION 3.4: Optimizing the Huisgen Cycloaddition of Diacyl Acetylenes

While we were able to follow Sharpless's method for producing azidomethyl pivalate, we did encounter one quirk which is worth mentioning. The conditions call for the two reagents (sodium azide, chloromethyl pivalate) are added to room temperature water and then heated to 90 ˚C overnight, which would hint that the order of addition at room temperature would have little effect on the outcome. However, the order of addition is crucial to success. Suspending the chloromethyl pivalate in water, and subsequently adding the sodium azide, will result in ~90% yields, while forming a solution of azide in water first generally yields <10%.

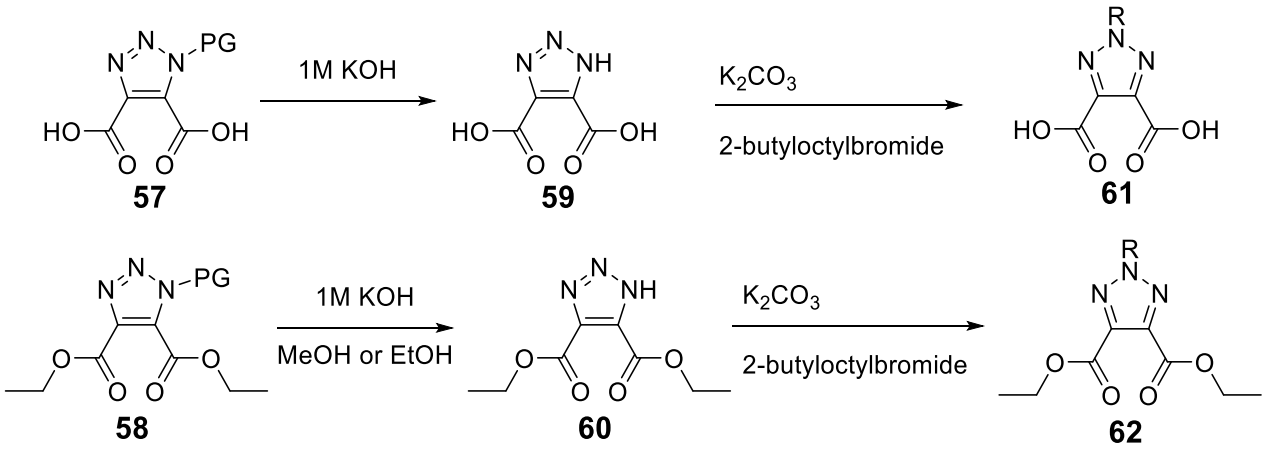
We were able to reproduce Li's ruthenium catalyzed Huisgen cycloaddition on his original diketone **(36)**, in which the two cycloaddition partners are stirred in DMF at 90 ˚C overnight. However, when we submitted acetylene diamide **(53)**, acetylene diethyl ester **(52)**, and acetylene dicarboxylic acid **(51)** to the same conditions, no reaction ensued. Adjusting the heat of the reaction and utilizing a higher catalyst loading also did not produce detectable product.



Scheme 11: "Click-first" routes to triazole-diamide **(54)**

Uncatalyzed versions of the azide-alkyne cycloaddition are known, so we began to investigate a variety of literature-reported conditions that did not include the use of the expensive ruthenium catalyst. At the very least, we reasoned, we would develop hands-on knowledge of the reaction without wasting this expensive reagent, and we might be able to remove it entirely.

Increasing the concentration of the reagents did not originally yield results, but heating to a slow reflux in ether, overnight, gave the triazole dicarboxylic acid **57** in a promising 50% yield.[71] However, because both the incompletely reacted starting material and the product contained two carboxylic acids, neither distillation nor column chromatography presented a good means of separating them. Thus, **57** proved to be difficult to isolate in high purity.



Scheme 12: Deprotecting the methylpivalate as another approach towards divergent target **(54)**

With this slightly impure sample, we proceeded to investigate whether the Weinreb amide **54** could be prepared on this, hopefully more stable, species. The methods attempted above for the preparation of Weinreb amide, including thionyl chloride, oxalyl chloride, and in-situ deprotonation with triethylamine, again tended to yield a dark brown sludge or oil with generally messy NMRs and a no clear major product. Meanwhile, the methylpivalate group seemed to cleanly deprotect from the triazole when subjected to Sharpless's deprotection

conditions, but the resultant molecule (**59**) was extremely water soluble and never appreciably isolated.

Submitting the acetylene diethyl ester to the same cycloaddition conditions gave a 42% conversion into **(58)**. However, the diethyl ester has the advantage of being a liquid, as opposed to acetylene dicarboxylic acid which melts at 180 ˚C. Inspired by Bertozzi's development of a catalyst-free azide-yne click reaction,[72] I attempted an uncatalyzed Huisgen cycloaddition under neat conditions, heated to 70 ˚C. Full conversion to **(58)** was achieved in two hours.

Unfortunately, we had run out of our supply of acetylene diamide **(43)** at this point, and a string of failed preparations dissuaded us from attempting a neat cycloaddition between it and azidomethyl pivalate to form **(54)**. We reasoned, however, that the diester **(58)** no longer had its reactive alkyne and might more cleanly transform into the Weinreb amide **(54)**.

With a reliable supply of **(58)**, we began investigating the next two synthetic transformations that were available: the deprotection of the methylpivalate to alkylate the triazole, and the preparation of the Weinreb amide from the diethyl ester.

We began by applying Sharpless's deprotection method, a 1:1 mixture of 1 M NaOH and methanol stirred for 30 minutes, to **(58)**. While we observed 70% deprotection of the methylpivalate by NMR, we also saw the formation of methyl ester groups that indicated the transesterification of methanol and the ethyl ester. Because this product mixture was more difficult to purify, isolate, and characterize, we sought to remedy this issue by switching the solvent to ethanol, so that any transesterifications would reform the ethyl ester.

An identical deprotection in ethanol reproducibly produced complex mixtures with ^{1}H-NMR indicating a mixture of products, or possible polymerization, that broadened the ethyl ester signals. Running the reaction without an alcohol cosolvent (i.e., in 1M NaOH) resulted in two

phases that did not react. Using distilled, dry ethanol and either sodium metal or lithium methoxide to generate sodium ethoxide or lithium ethoxide lead to decomposition of **(58)**.

Still, the methylpivalate species *should* be more reactive than the ester, so we ran a battery of tests to try to thread the needle on reactivity. We tested various equivalents of hydroxide, at varying concentrations, temperatures, and reaction times. Eventually, we were able to isolate **(60)**, though the synthesis is not always reproducible. Our optimized method utilizes an excess (~2.5 equivalents per ester) of 1 M hydroxide, in a 1:1 mixture with ethanol, stirred for two hours.

We then submitted the naked-triazole ethyl-ester **(60)** to the conditions for alkylating the triazole ring: potassium carbonate and bromo-2-butyloctane stirred in DMF. While the appropriate methylene signal indicated an *N2*-alkylated species on ^{1}H-NMR (**62)**, the ester peaks were consumed and the alkylated product was never isolated. It is probable that, as we were concerned it might, the nucleophilic triazole anion was a strong enough nucleophile to attack the esters in solution, resulting in an undesirable mixture of products.

Even though methylpivalate is supposed to deprotect under very mild conditions, the difficulties described above indicate that it is not wholly orthogonal from the ester. Thus, we decided to briefly investigate one-pot transformations that would leverage this shared reactivity. Removing all three ethers (including the methylpivalate) with a single nucleophile, like *N,O*-dimethylhydroxylamine **(50)**, should produce the Weinreb amide as well as the deprotected triazole, as long as the deprotection of methylpivalate performs identically with non-hydroxide nucleophiles.

Combining **(58)** with 10 equivalents of **(50)** in dichloromethane (its extraction solvent) produced no reaction after three days of stirring, but combining the salt, **(49)**, mixed with

triethylamine in methanol was more promising. The resulting solid was not soluble in chloroform, as is expected for deprotected triazoles, and an ^{1}H-NMR in MeOD revealed the formation of Weinreb amide and the removal of the t-butyl group characteristic of methylpivalate.

Closer examination of the major product, however, revealed an additional methylene unit, likely connected to the triazole**.** Dhanak et al. report that methylpivalate sometimes fails to properly deprotect, and instead forms the methanol moiety expected from the simple cleavage of the t-butyl ester. [73] They recommend a heated solution of dilute KOH for stripping off the remaining functional group to expose the bare amine, but attempts to apply this ended in either no reaction or degradation of this delicate system.

SECTION 3.5: Investigating the Use of Brominated Triazole

While the di-acyl alkyne species were proving too unwieldy to make substantial progress, we turned a critical eye to our original synthetic analysis. As per my criticism of the need to slowly construct a symmetric alkyne, we had focused on commercially available compounds which already contained a diacyl alkyne. However, speaking retrosynthetically, the ketones of the target molecules could also be formed on the other side of the carbonyl. Here, a triazole ring could be attached to the flanking aryl rings, which already are functionalized with a ketone precursor, like a Weinreb amide.

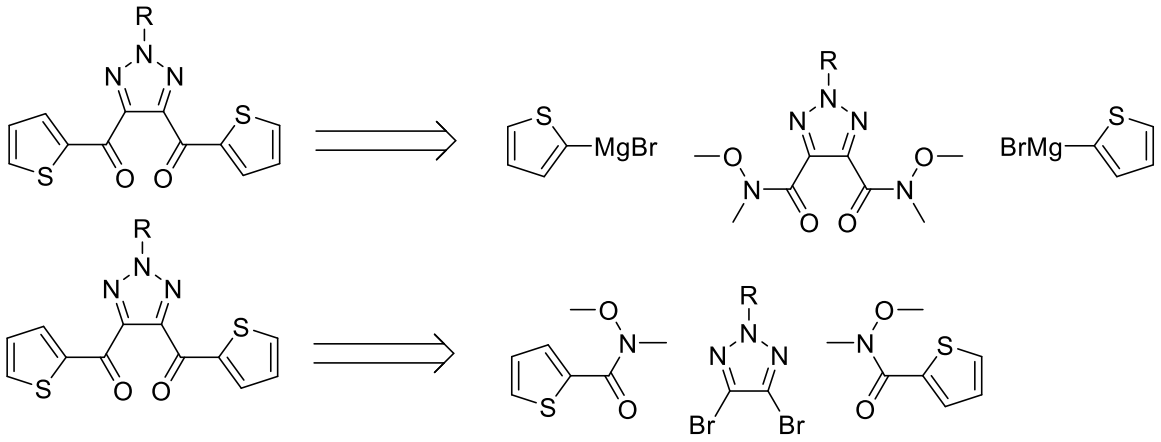
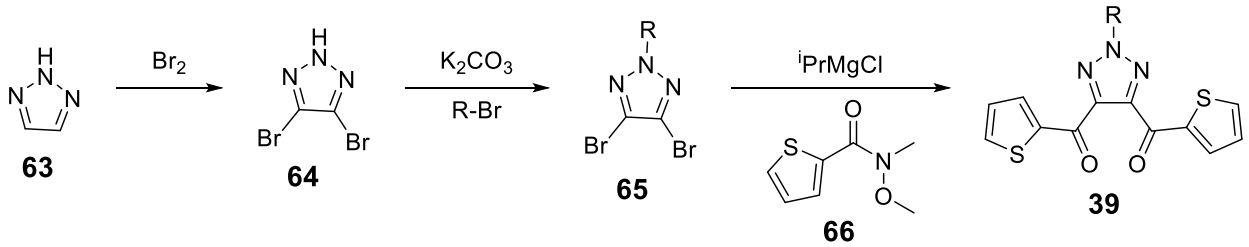


Figure 19: Two possible retrosyntheses using the Weinreb ketone synthesis

Previous reports have shown a facile bromination of commercially available 1*H*-triazole.[74] These bromines are electron withdrawing enough to ensure that nearly 99% of the subsequent alkylation occurs at the *N2* position preferred for donor polymers. Thus, the only remaining hurdle would be to leverage the brominated sites as nucleophiles to attack a Weinreb amide housed on our flanking aryl ring of choice. The authors of the original study[74] reported that they were able to use isopropylmagnesium chloride to activate alkylated dibromo-triazole to produce the bis-TMS derivative in 65% yield, and we hoped to repeat that success with our electrophiles.



Scheme 13: A new route to the diaryl benzotriazole precursor.

Our bromination[75] and alkylation reactions[14] happened in high yield and without difficulty. While the 2-butyloctylbromide could not be separated from the alkylated triazole *via*

column chromatography, it could be safely distilled off under vacuum, yielding the pure alkylated dibromotriazole **(65)**.

Contrary to the difficulty of preparing the Weinreb amide on the triazole and alkyne systems above, we prepared and easily purified 2-thienyl Weinreb amide from 2-thienyl carboxylic acid and thionyl chloride. As a test, we prepared thienyl-butyl ketone from a reaction of **(66)** with *n*-butyllithium at 0 ˚C in high conversion.

Thus, we began to investigate the reaction of **(65)** and **(66)** to recreate Li's **(39)**. Following the (unfortunately scant) procedures by Wang et al.,[74] we added isopropylmagnesium chloride solution to dibromide **(65)** for 2 hours before adding **(66)** at -78 ˚C to raise stability of the tetrahedral intermediate that prevents overreaction of the acyl moiety. Unfortunately, while the magnesium inserted in 60% of the bromines expected (30% of total bromines), all of it quenched to protons; no addition product was observed via ^{1}H-NMR. Raising the reaction temperature to 0˚ C improved the reaction of one bromine to include 40% ketone and 30% proton quench: 70% bromide replacement in total. Lengthening the reaction time by another 6 hours only marginally improved yields.

At this point, we investigated other methods of converting the bromide unit into a nucleophile. We found that magnesium metal refused to perform oxidative addition onto the bromide bond even after washing the surface with 1 M HCl, utilizing the entrainment reagent 1,2-dibromoethane, and heating to 65 ˚C for multiple days. Our attempts to utilize *n*-butyllithium for lithium-halide exchange gave yields consistent with isopropyl magnesium chloride at low temperatures (-50 ˚C and 0 ˚C), but caused degradation of the triazole ring at higher temperatures (45 ˚C), agreeing with a literature report.[75]

Since the two-step reaction, alternating additions of Grignard and Weinreb reagents, did not yield the di-ketone we sought, we attempted another route. **(65)** and **(66)** (2 equivalents) were stirred in dry THF at 0 ˚C , into which of isopropylmagnesium chloride was added (2 equivalents). 3 hours of stirring provided a familiar mixture of 20% conversion to ketone and 15% quench to proton. Leaving this reaction for 5 hours produced 23% ketone and ~12% quench, but no net gain in the formation of the Grignard triazole.

While these more recent yields seem like promising progress, they still fall short of what the synthetic design calls for. The mixture of products make it difficult to ascertain whether or not any of the triazole rings become functionalized with two ketones, but the following results indicate that they likely are singly functionalized.

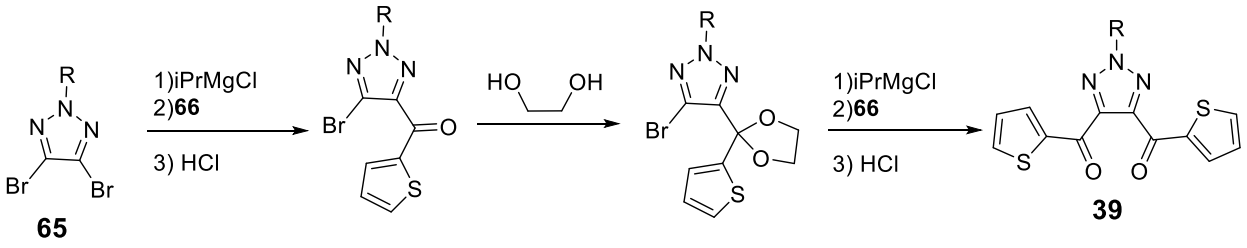
Wang et al. produce a bis-trimethylsilane substitution by adding a second portion of isopropylmagnesium chloride after the first TMS group has been attached.[74] First, the attachment of both bulky TMS groups shows that sterics are not the reason for incomplete functionalization. However, when we added the second portion of isopropylmagnesium chloride, it failed to increase yields or produce **(39).** Likely the second bromide remains unactivated, indicating an electronic cause. Our observations so far are consistent with conclusion that the electron withdrawing nature of the quatenary, Weinreb-stabilized intermediate further deactivates the triazole ring from activating at the second bromide.

At this point in our investigation, time limitations precluded further progress. However, I believe that there are several initial conclusions worth drawing from this work and a few possible solutions that would carry this work forward towards its original goals.

SECTION 3.6: Conclusions and Future Work

This effort has been dominated by the delicate balance between reactivity and orthogonality. Each of these systems has had a high density of heteroatoms and reactive functional groups which have made it difficult to achieve clean conversions in high yields. These setbacks point to the high difficulty, and maybe even futility, of realizing the highly divergent synthesis we sought. However, there may still be some methods to explore.

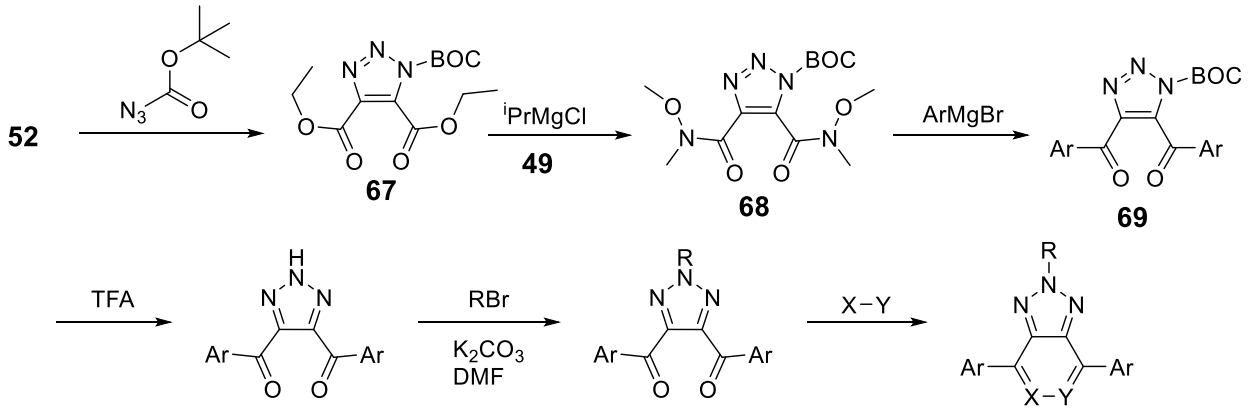
For the dibromo-triazole approach, if unfavorable electronics are preventing the full functionalization of the triazole ring, it may be possible to fix this issue. Quenching the quatenary intermediate would form the ketone which would be open to nucleophilic attack during the next round of magnesium exchange and nucleophilic attack. Treating the crude product mixture with ethylene glycol would convert the reactive, electron-withdrawing ketone to an orthogonal, electron donating ketal**.** However, without a more efficient attachment of the first thienyl species, there is little foundation to build this approach on. Also, this approach adds an additional workup, protection, and deprotection to the scheme, which adds complexity even though they are facile steps.



Scheme 14: A method of activating dibromotriazole for activating the second bromide for Grignard activation

For the alkyne-based approach, it is clear that these non-orthogonal chemistries must be addressed. To that end, using a much less labile protecting group for the azide (and triazole) may prove essential. Preferably, this new protecting group would be stable to the production of and

the nucleophilic attack onto the Weinreb amide. One possible candidate is the *t*-butoxycarbonyl (BOC) protecting group, common to peptide synthesis and other heteroatom protections, which is stable to most conditions except strong acid. We have already produced the BOC-protected azide, but have not yet attempted the neat Huisgen cycloaddition to acetylene diethyl ester.



Scheme 15: An alternate divergent synthesis with a more robust protecting group

While this substitution would allow more aggressive conditions to be applied to the diethyl ester or dicarboxylic acid triazole compounds to form the Weinreb amide, it comes at a cost. This would unfortunately require the alkylation of FTAZ to occur after the first divergent step, when the flanking aryl groups have already been attached. However, the Paul-Kropp-like cyclization would remain in its place in the scheme, so the divergent steps would occur at the last and third-to-last steps. Given the ease and reliability of the alkylation reaction, we believe this is an acceptable loss towards the realization of this versatile synthetic approach.

At this point, we have likely spent more time investigating this highly divergent scheme than it would have taken to produce many of our original target molecules under Li's original route. However, we believe that the intellectual gain from these efforts is worth the struggle. One goal of this project was to begin a conversation about moving towards more divergent syntheses. While the initial results are not promising, we believe it is important to release this data

regardless, so that other researchers may make informed decisions about their own pursuits. In the end, the fact that we found such rough terrain in trying to find this path just underlines the importance of this endeavor—if we had easily constructed a route, then perhaps anyone could do so without struggle, and a project highlighting one path to success would be unnecessary.

CHAPTER 4: Synthesizing Oligophenyl Dithiols for Self-Assembled Monolayers in Molecular Electronics

SECTION 4.1: Background and Motivation

Molecular electronics are a field of organic electronics in which traditional device structures like diodes are created with even smaller polymeric or small-molecule organic or organometallic species. Similar to OPVs, the versatile tunability of these species and their low cost relative to electronics-grade silicon are selling points against the traditional inorganic semiconductors.

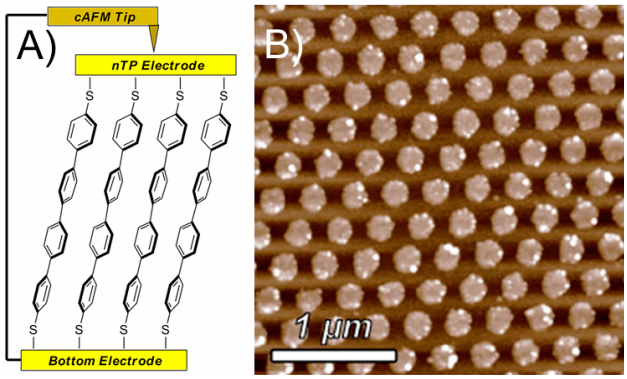


Figure 20: Diagram of nTP device which is characterized by cAFM. B) Representative 200 nm diameter gold contacts, printed via nTP onto a terphenyl dithiol monolayer. Pad height is measured to be around 13 nm.

Figure 20 shows the structure of a self-assembled monolayer, a useful device structure for testing the promising metal-molecule-metal junction on the frontier of molecular electronics,[76] which is still in its infancy. Generally, a linker such as phosphonates or free thiols are used to bind to a wide variety of inorganic surfaces, including metals like gold and aluminum and oxides like silicon dioxide.[77-79] Alkanedithiols are the standards of this device structure as they produce the tight packing the forces the molecules upright and forms a strong monolayer.[80]

These SAMs can be made using a variety of techniques including indirect metal evaporation, liquid mercury droplets, and colloidal metal aggregation.[78] This variety is important

because often the deposition of the top electrode can penetrate the monolayer or deform it, causing electrical shorting or irreproducible behavior, respectively. Our lab has shown the viability of producing SAMs from alkanedithiols using a soft deposition technique called nano-transfer printing (nTP).[76]

In that study, we showed that perfluoropolyether (PFPE) had favorable surface energy and elastomeric properties to perform nTP. Gold is thermally deposited onto a patterened PFPE stamp to create raised pads, 200 nm across. This functionalized stamp is brought into contact with the SAM. Sulfur-gold bonds form, and the stamp can be deformed away from the surface to leave behind gold contacts (Figure 20 B), each of which comprise a full device that can be tested.

It is important to investigate the properties of each of these deposition techniques, particularly soft ones like nTP, so that more complex systems can be explored within a well-understood framework. However, alkanedithiol SAMs show electron transport dominated by tunneling[81], so the field will eventually have to move towards more systems of greater complexity to meet the high goals required by applications such as organic spintronics[82] and rectifiers.[83]

Oligophenyl dithiols, like the quaterphenyl dithiol in Figure 20, are one step closer to electronic applications because their conjugation modifies the tunneling barriers between the two electrodes.[77,84] These systems have also been studied with a variety of the deposition techniques used on alkanedithiols, but had not been studied using nTP.

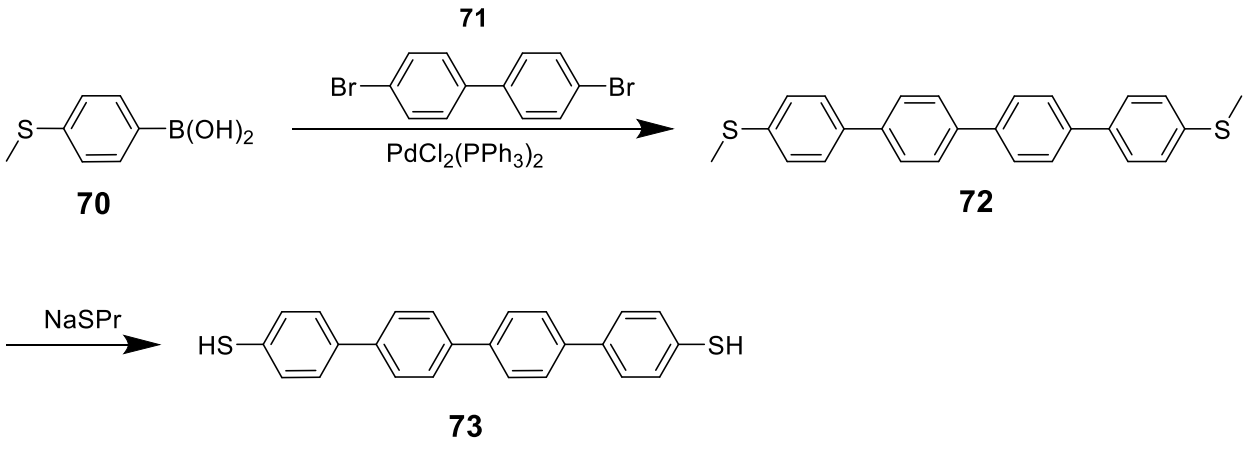
To fully characterize the tunneling and device properties of this system, we'll need to vary the length of the dithiol molecules to adjust the thickness of the SAM. Once a series of lengths have been measured, the tunneling parameter, β, can be calculated from the equation[76]:

$$R = R_0 \times e^{(L\beta)} \qquad \textbf{(4.1)}$$

where R_0 (junction resistance), R (effective contact resistance), and L (length) can be measured. Thus, we decided to prepare SAMs from four oligophenyl dithiols. Monophenyl dithiol, biphenyl dithiol, and terphenyl dithiol were commercially available, leaving quaterphenyl dithiol to be synthesized in house. I set out to produce quaterphenyl dithiol, a smaller goal than the ambitious syntheses of the previous two chapters, but this quick endeavor has since expanded into a larger synthetic effort.

SECTION 4.2: Synthesizing Terphenyl and Quaterphenyl Dithiols

Inspired by de Boer et al.'s synthesis of a wide variety of oligophenyl and oligothienyl dithiols,[85] we attempted a standard Suzuki coupling to form our intended quaterphenyl dithioether **(72)**. While it appeared to work, the subsequent deprotection with sodium hydride and diisopropylamine in HMPA to form free thiols instead gave solids that were essentially insoluble in every solvent system that we attempted. We attempted several conditions to introduce solubilizing thioacetate groups, which have been shown to be removable in situ to form SAMs**,** but none of these preparations were successful.[83,85]

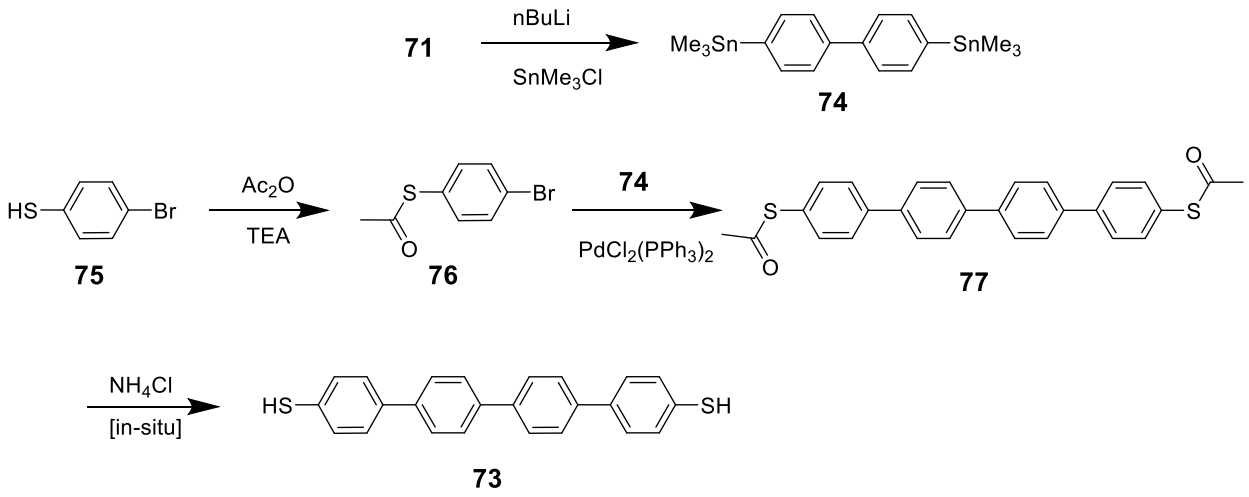


Scheme 16: A quick route to quaterphenyl dithiol

To ensure that we had successfully performed the deprotection, we used a modified deprotection with sodium propanesulfide, which also attacks the methyl protecting group *via* an

S_N2 mechanism. We received the same insoluble solids as before, but also isolated methyl propane thioether. Unfortunately, we were not able to isolate the quaterphenyl in a usable form.

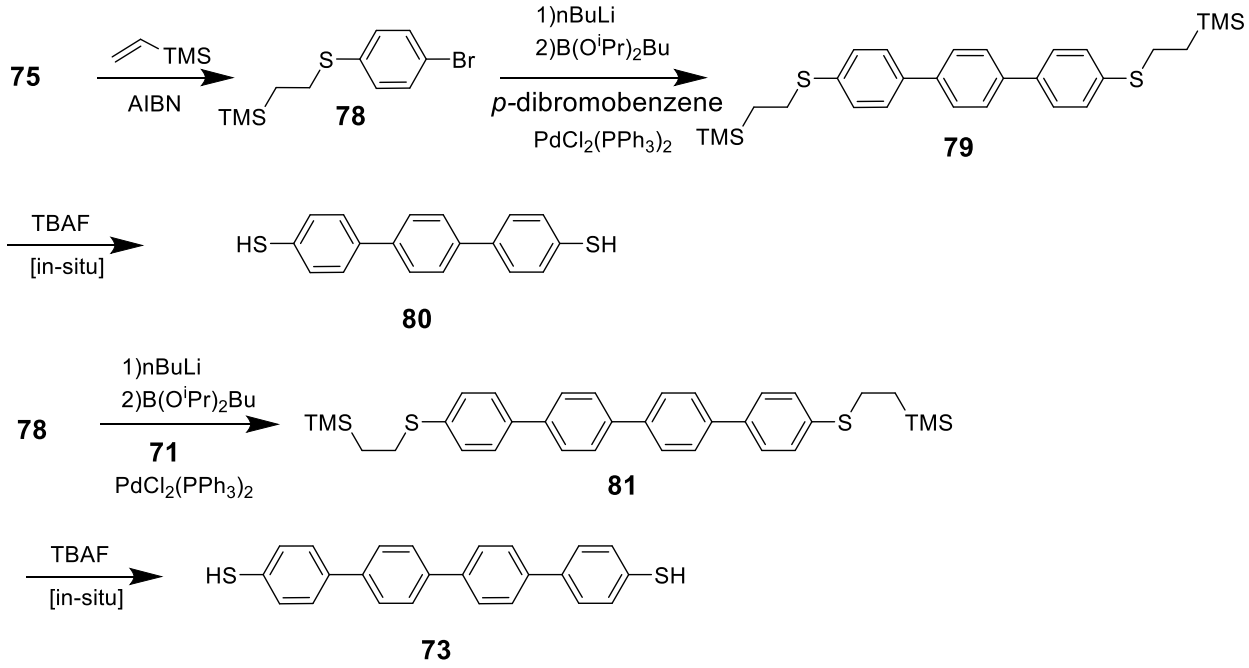
We considered starting our synthesis with thioacetate protecting groups, but concerns over the base-heavy nature of Suzuki couplings made us turn towards Stille couplings. Higher yields are achieved by utilizing Stille couplings for coupling thiophenes and Suzuki couplings for phenyl rings, but we hoped to get enough yield to prepare quaterphenyl dithioacetate for this study.



Scheme 17: A route to a protected quaterphenyl dithiol that can be deprotected *in situ* to bond to the gold surface

We produced the bromothiophenol aceteate **(76)** according to a literature source,[86] and then used lithium-halide exchange to distannylate 4,4'-dibromo-biphenyl and form **(74)** in 74% yield.[87] As is common for organotin compounds, purification via silica gel column lead to the degradation of the aryl-tin bond. This could be remedied by passivating the acidic silica with 5 weight % powdered calcium carbonate. Recrystallization in benzene also isolated the product, but at a reduced yield of 45%.

However, the ensuing Stille coupling tended to form trace amounts of the mono-coupled byproduct (i.e. an asymmetric terphenyl) and no product. Attempting to accelerate the reaction by using lithium chloride as an additive did not improve yields.[87]



Scheme 18: Our successful synthesis of protected oligophenyl dithiols

Thus, we turned our attention to a new thiol protecting group which would be stable to the basic Suzuki coupling conditions. Ethyl-trimethylsilane groups had been used by other researchers at the time to deprotect in situ and bond to gold contacts, but we had no experience with it.[83] Thus, we decided to also prepare a protected terphenyl dithiol species to compare with the commercially available terphenyl dithiol, to ensure that the deprotection conditions aren't changing the properties of quaterphenyl dithiol.

Preparation of this thioether could be achieved by a simple radical-based thiol-ene click reaction. Vinyltrimethylsilane and bromothiophenol were heated to 90 ˚C in a thick-walled bomb flask overnight with 2% AIBN as a thermal initiator. The bomb flask was necessary because

vinyltrimethylsilane boils at 55 ˚C, but higher temperatures are needed to activate the AIBN. Heating under vacuum sublimated any remaining bromothiophenol **(75)** followed by the distillation of product **(78)** in 81% yield.

Out of curiosity, we subjected this electron-rich bromide to the same Stille coupling conditions as above, but only received 6-9% yield. Thus, we turned our attention to producing a boronic acid or ester which could couple with the dibromobiphenyl. Boronic acids can be difficult to purify, so we attempted to form it in situ and quench the nucleophilic attack with the water that is required by the Suzuki coupling step. We chose to use butyldiisopropylborate because it can offer higher reactivity than boronic pinacol ester or diisopropyl ester.

After a promising test-scale reaction, we isolated the quaterphenyl **(81)** in 45% yield. The product, a white powder, had low solubility in hexanes and chlorinated solvents, so column chromatography required additional silica gel and solvent to properly isolate it from the other byproducts.

Because we were unfamiliar with the in situ deprotection of ethyl-TMS thioether, we also sought to prepare the terphenyl dithioether analog of the quaterphenyl, which could be directly compared to commercially available terphenyl dithiol. Coupling of the same protected bromothiophenol **(78)** with 1,4-dibromobenzene gave the terphenyl **(79)** is 20% yield, after column.

The in situ deprotection of the ethyl-TMS protecting group gave mixed results until a 4 times excess of TBAF was applied so that the kinetics of the deprotection favorably matched those of the SAM formation. Fewer equivalents did not fully deprotect the second thiol for attaching to the top contact, while additional equivalents were found to deprotect both thiols too quickly. This would, in turn, allow the linear molecules to connect twice to the bottom electrode,

which blocks the formation of an ordered monolayer (unpublished results). We believe that we only see the effect of this kinetic interplay with the ethyl-TMS protected oligophenyls because the deprotection produces a more reactive sulfide, instead of a protonated free thiol, which allows the sulfur to attach to surfaces with great ease.

Initial results from these SAMs show the expected length-dependence on β value, though with substantially lower tunneling barriers than in the non-conductive alkanedithiol series (unpublished results). Thus, we became interested in further understanding the interaction between tunneling barrier in these devices and conjugation of the molecules.

SECTION 4.3: Restricted Rotation Oligophenyl Dithiols

The original sequence of oligophenyls had rings which were free to rotate. This means that the favorable conjugation interaction that would encourage planarity would be countered by a (weak) steric interaction between the *ortho*-positioned hydrogens when the rings were planar. Modeling revealed that the lowest energy dihedral angle was approximately 40˚ (Figure 22), though the barrier to rotation is low.

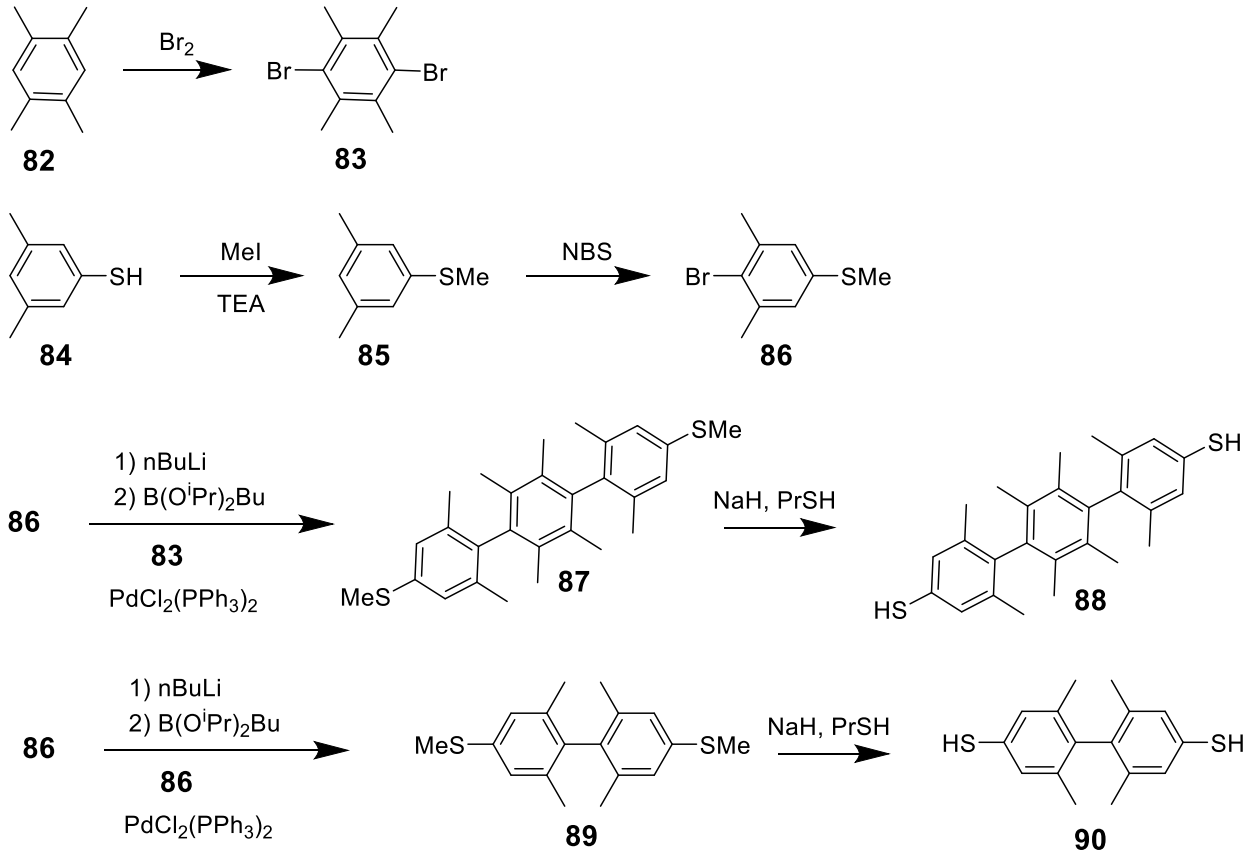
By restricting the rings to either a fully planar or fully perpendicular orientation, we could probe the effect of conjugation on the β-value for tunneling. Looking at our synthetic options, as well as the poor solubility of highly planar systems, we decided to synthesize oligophenyls with larger ortho substituents that would force the rings to lie perpendicularly. To be able to add onto our previous data, we decided we only needed two of this series, likely the biphenyl and terphenyl dithiols.

Methyls were a clear choice for the sterically-blocking *ortho* substituents. Starting materials with methylated benzenes are readily available, they are inert, and they do not interfere

with the carbon-based calculations used in the X-ray Photoelectron Spectroscopy-based elemental analysis that we regularly perform on these monolayers.

Additionally, we expected higher solubility, and generally easier to handle, compounds from this investigation. Planar, conjugated systems, especially those lacking in heteroatoms, tend to aggregate aggressively due to strong π-π stacking interactions, and thus possess low solubility. When combined with polar or even hydrogen-bonding moieties, these systems can become intractable, like the quaterphenyl dithiol **(73)** prepared above. These systems, by contrast, will not have the same enthalpic pull towards aggregation and will more readily dissolve.

This enhanced solubility gave us hope for using the inexpensive, stable, and accessible thiomethyl ether protecting group. Our original attempts with it had been foiled by quaterphenyl dithiol's extremely low solubility, necessitating the use of the ethyl-TMS protecting group that could be taken off in-situ.



Scheme 19: Our initial route to the restricted oligophenyl dithiols used cheap methyl groups that would be removed before SAM formation

As expected, the methylation of commercially available 3,5-dimethylthiophenol **(84)** proceeded easily with 61% yield. Bromination of this compound with NBS in acetonitrile is also high yielding (93%),[88] provided the order of addition is followed carefully. The functional procedure calls for *N*-bromosuccinimide (NBS) and **(85)** to be dissolved in separate batches of acetonitrile and cooled to 0 ˚C before the NBS solution is added to **(85)**. Failing to fully dissolve the NBS before addition, a process that often requires sonication, leads to the deprotection of the methyl thioether. At the extreme, if dry NBS was added to a solution of **(85)**, then 3,5-dimethylthiophenol **(84)** is returned in high yield, with no brominated product.

Preparation of the dibromide coupling partner **(83)** proceeded without note with 83% yield,[89] so we attempted the same one-pot boronation and Suzuki coupling that had yielded our

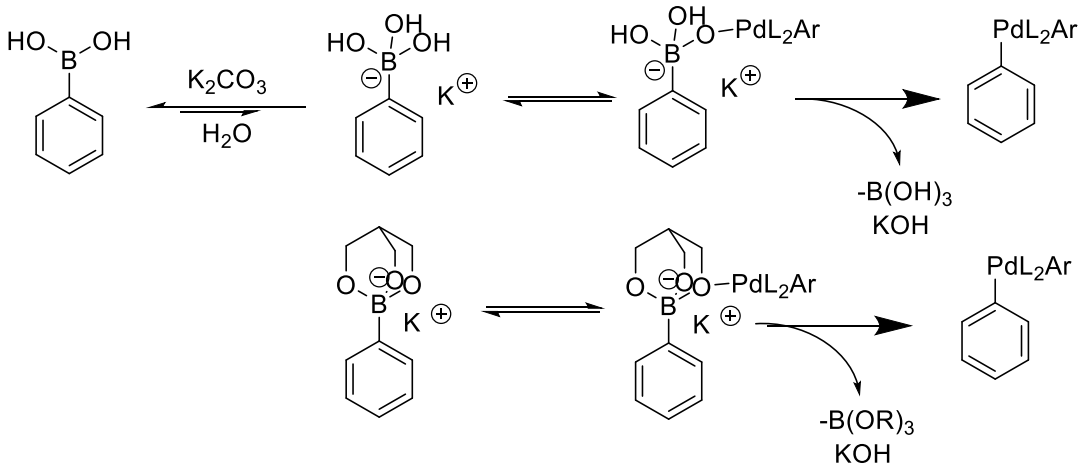
previous terphenyl and quaterphenyl targets. However, no coupling occurred, and we recovered **(86)** and **(83)**. Thus, lithium-halide exchange occurred with respectable conversion, but for some reason it quenched to hydrogen during the reaction or during the workup.

To further investigate this unforeseen issue, we attempted to isolate the boronate intermediate. By halting the one-pot reaction before adding the Suzuki reagents, we observed the formation of only 10% boronate but again a majority of the proton-quenched **(85)**. However, our experience with the boronate made with butyldiisopropylborate is that it is not very stable to being isolated, even if it is useful in situ. So, we attempted to prepare the more stable, but less reactive, boronic pinacol ester and succeeded with 86% yield. However, the Suzuki coupling of this compound returned the unreacted **(83)** and 3,5-dimethylthiophenol methyl thioester **(85)**. This led us to believe that even if the butyldiisopropyl boronate were forming in our one-pot Suzuki coupling, our boron moieties appear to degrade before they can couple. Perhaps, we reasoned, the steric interactions between four *ortho*-substituents were too strong to allow coupling.

However, when we turned to the literature, we uncovered reports about the sensitivity of aryl boronic esters and borates to decomposing under basic conditions, like those found during a Suzuki coupling, in the presence of *ortho* substituents.[90] This process, called hydrolytic deboronation, is enhanced by having substituents in both *ortho* positions, as in our system.

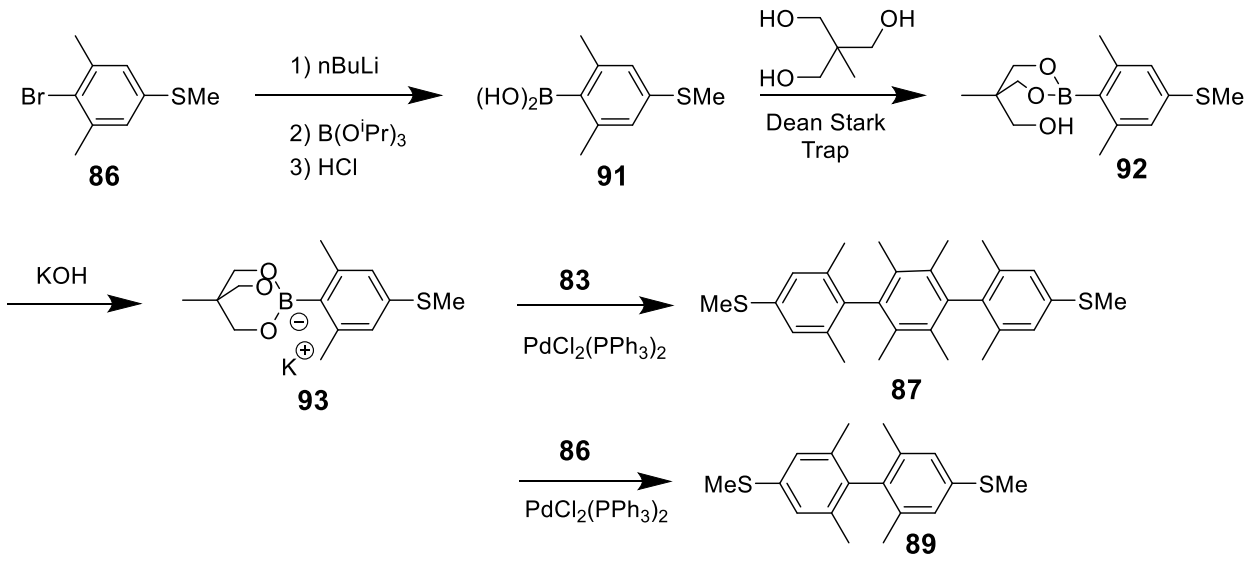
Avoiding this issue requires using either base-free conditions or exotic *N*-heterocyclic carbene-based catalysts.[91,92] We determined that using an activated borate that does not need to be activated with hydroxide anions would be more synthetically accessible. One such borate that can be easily prepared and isolated uses 1,1,1-tris(hydroxymethyl)ethane. This borate resembles MIDA-boronates, which have recently gained popularity for use in automated synthesis,[58] except

that where MIDA has a dative bond from an amine to the boron, this system has three covalent bonds (plus one to the aryl ring to be coupled). Electronically, this gives the system a negative charge which must offset by a counterion, and the molecule gains salt-like properties that ease purification.



Scheme 20: Partial mechanism of base-catalyzed Suzuki couplings and the base-free Suzuki couplings with aryltriolborates[93]

Generally, a boronic acid is condensed with 1,1,1-tris(hydroxymethyl)ethane to form a bidentate ligand with one free alcohol.[94] The borate salt does not form until treatment with an alkaline hydroxide base, which provides the counterion. However, our attempts to prepare the necessary boronic acid **(91)** from lithium halide exchange followed by quenching with triisopropyl borate and acidic hydrolysis were ill-fated. Generally, we recovered only unreacted aryl bromide **(86)** or the proton-quenched byproduct **(85)**. Drying the triisopropylborate over 4Å sieves did not improve yields, so it is likely that either sterics were preventing effective nucleophilic attack, or the boronic ester decomposed before it could be hydrolyzed.



Scheme 21: Using aryltriolborates to prepare protected oligophenyl dithiols

Having already isolated the pinacol ester, we sought to hydrolyze it and form the boronic acid. However, pinacol esters are difficult to hydrolyze into boronic acids because of the stable, bidentate-like ring. Thus, treatment with 1M HCl did not remove the pinacol moiety, and neither did another method involving the in situ production of the oxidant periodic acid.[95] Finally, we found one source[96] which agreed that periodic acid failed to remove pinacol in some systems, but their method utilizing lithium aluminum hydride also failed to yield the boronic acid in our case.

SECTION 4.4: Other Synthetic Approaches To Restricted Oligophenyl Dithiols

With these setbacks, we re-examined the necessity of having four *ortho*-substituted methyl groups at the coupling sites. The tetramethyl biphenyl connections we'd been investigating have been calculated to have a minimum energy at a dihedral angle of 80˚ – significantly more perpendicular that the bare biphenyl's 42˚. However, this is not the whole picture, as the bare biphenyl system only has a barrier to rotation (i.e. relative energy of being

planar) of 7 KJ/mol, while the tetramethylbiphenyl system's barrier is over 100 KJ/mol.[97] Thus, there is a huge barrier to allowing any significant amount of co-planarity that causes conjugation.

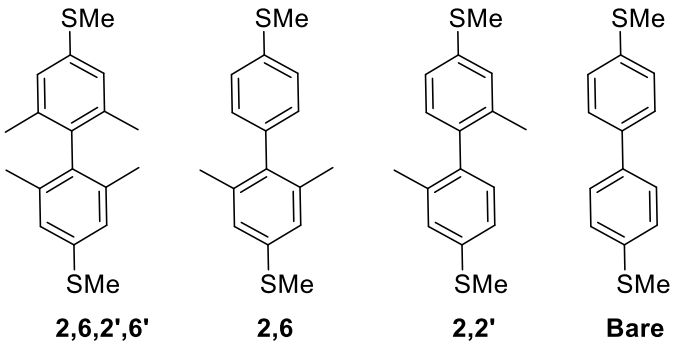
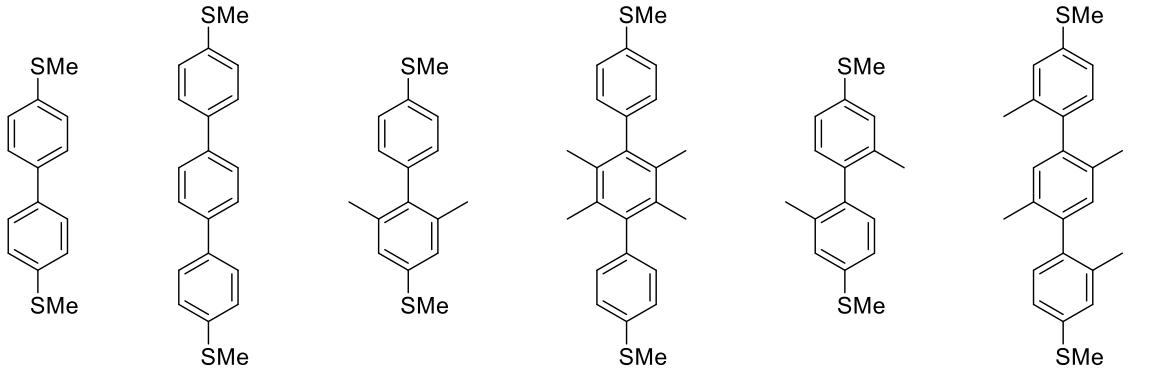


Figure 21: The different arrangements of ortho-methyl substituted biphenyls

For systems with fewer methyls, the same calculations find that the 2,6-dimethyl system (Figure 21) also has a rotational barrier over 100 KJ/mol, which should be useful for our purposes even if the lowest energy point is merely 68˚.[97] Another source estimates the rotational barrier of the 2,2' system as being perhaps around 2/3rds of the 2,6 biphenyl systems,[98] making it less preferable but perhaps still viable, as even the monomethyl biphenyl system has a barrier to rotation of 50 KJ/mol.

We confirmed these literature results by running a molecular mechanics simulation on our actual target compounds (Figure 22). In general, the results generated by this simulation were even more favorable, with more perpendicular optimal angles and higher barriers to rotation. These calculations also confirmed that the 2,6-dimethyl design was as likely to fit our needs as the 2,2'-dimethyl design.

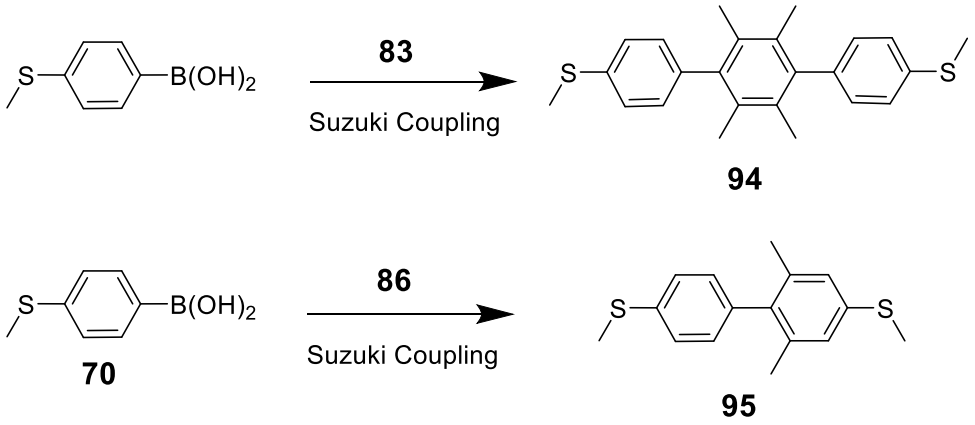


Molecule	Dihedral Angle 1	Dihedral Angle 2	Energy (a.u.)	Planar (a.u.)	Diff (kcal/mol)
A	40.5	-	-1338.467284	-1338.4639	2.15
B	39.9	39.9	-1569.570046	-1569.5637	3.96
C	90.5	-	-1417.111884	-1417.0775	21.57
D	90.2	90.2	-1726.850935	-	-
E	89.5	-	-1417.112339	-	-
F	90.6	90.6	-1726.85984	-	-

Figure 22: Molecular modeling of the optimized dihedral angles and energies of dimethyl and bare biphenyl systems relative to their planar energies

Based on available starting materials, we determined that the 2,6-dimethyl design would be more synthetically accessible than the 2,2'-dimethyl isomer. We then attempted a battery of atypical Suzuki couplings which were reported to work with 2,6-dimethyl systems.

Using the commercially available boronic acid **(70)**, we attempted coupling to our original, methylated biphenyl and terphenyl coupling partners. One air-stable method,[99] using urea as a ligand for palladium diacetate in isopropyl alcohol produced only trace amounts of the biphenyl compound, and did not improve on heating or longer reaction time.

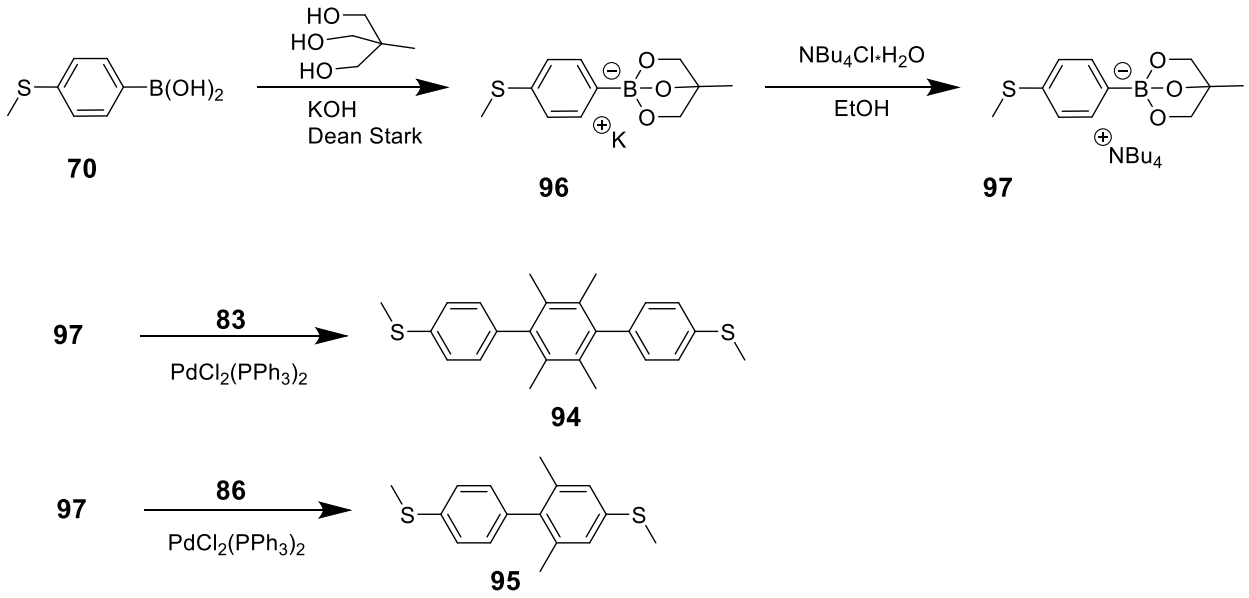


Scheme 22: We next attempted a batch of atypical Suzuki couplings from the literature

A second method suggested using potassium carbonate (safe to use because we the boronic acid is not adjacent to two methyl groups) and either palladium tetrakis triphenylphosphine or palladium diacetate in acetone.[100] This method also failed to produce the biphenyl product by crude ^{1}H-NMR.

Finally, another report suggested using 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium, or $PdCl_2$(dppf), with potassium carbonate in dimethoxyethane, but this reaction also regularly yielded only the starting materials.[101]

With these options we turned our attention again to the borate system. We no longer need its base-stability, but it is activated towards Suzuki couplings and may provide the necessary reactivity.



Scheme 23: A route to restricted oligophenyl dithiols with fewer methyls

While preparing **(96)**, we determined that the two-step process (see Scheme 22) for forming the borate could be consolidated into a single, overnight reaction. Potassium hydroxide, toluene, and the ligand 1,1,1-tris(hydroxymethyl)ethane were refluxed with the boronic acid **(70)** overnight, utilizing a Dean-Stark trap to remove water from the condensations (and the latent water in the 85% potassium hydroxide). With this method, we reproducibly isolated the borate **(96)** in 86-90% yield.[102]

It is well documented that Suzuki coupling yields with these borates are highly dependent on the counterion.[103] While potassium generally works better than stronger associating cations like sodium and lithium, the potassium salt obtained above yielded no reaction under base-free Suzuki conditions.[94] Addition of 18-crown-6 ether, to bind to the potassium ion and make the cation less strongly bound to the borate, yielded some conversion to the mono-coupled intermediate. Establishing a trend for this system, utilizing microwave irradiation (300W, 200 ˚C, 20 minutes) lead to the formation of various byproducts without additional formation of the intended product.

Thus, we investigated the preparation of tetraalkylammonium salts, which are known to work substantially better than potassium salts. Attempts to adapt the Dean Stark reaction to use tetraethylammonium hydroxide, instead of potassium hydroxide, did not result in product. Tetraalkylammonium species often decompose to trialkylamine when heated or isolated outside of solution.[104] The hot, drying conditions of the Dean-Stark trap apparatus may have triggered this decomposition.

We then investigated a means of performing an ion exchange between a tetrabutylammonium halide salt and the potassium borate prepared above. An effective ion exchange relies on an insoluble product which precipitates out of solution and pushes the equilibrium towards product, as per Le Châtelier's principle. Pinho et al. reported on the solubility of various salts in methanol and ethanol. As expected, the lowest solubility is of strongly ionic potassium chloride in ethanol: a mass fraction of 0.039 at room temperature, which gave us confidence that we could effect an ion exchange.[105]

The potassium borate **(96)** was stirred in ethanol with tetrabutylammonium chloride hydrate for twenty minutes. The product was filtered, using minimal ethanol, and yielded 70% conversion to the tetrabutylammonium salt, **(97)**. Stirring for 90 minutes lead to full conversion with just 1.02 equivalents of NBu_4Cl.

Submitting this molecule to the base-free Suzuki coupling with **(86)** yielded the desired biphenyl product **(95)** in 83% yield. Running the same Suzuki coupling with **(83)** yielded the desired terphenyl product **(94)** in 66% yield.

However, our attempts to remove the methyl protecting groups and prepare the free thiols were troubled. Deprotections that had previously worked reliably, like sodium propanesulfide and lithium diethylamine, did not react and **(94)** was recovered in full after each reaction.

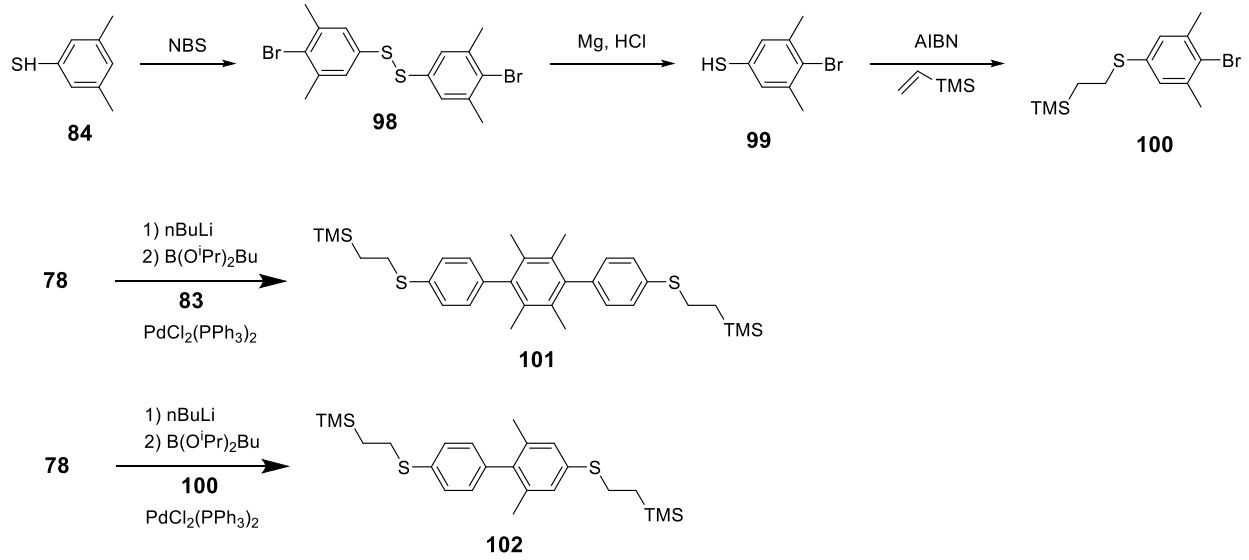
Heating the sodium propanesulfide did not seem to accelerate any reaction, until at 160 ˚C it lead to unfavorable decomposition.

Sodium naphthalenide is a strong reducing agent that has also been shown to remove methyl thioethers, but it did too did not work. Another reducing system that mixes sodium metal with butylamine and 1,2 diaminoethane produced the blue color indicated in the literature but did not affect the system.

In desperation, we tried two long shots, also without result. Boron tribromide is a strong lewis acid that is commonly used for deprotected methylethers[106] – not thioethers – and its application here also produced no reaction. Remembering our accidental discovery that NBS, improperly added, could result in deprotection, we attempted create our own method using NBS. However, these efforts generally produced to a variety of products, likely brominations of the aromatic moieties.

All of these failed deprotections point to some overlooked property or mischaracterization of this system, but we were unable to determine it. Multiple batches of the terphenyl and the biphenyl species exhibited this resilience, and we could arrive at no other interpretation of the ^{1}H-NMR and ^{13}C-NMR spectra. Defeated, we looked to using the ethyl-TMS thioether system, which was more expensive and had shown some peculiar behavior during the in situ deprotection and SAM formation.

Taking inspiration from the synthesis of the unrestricted terphenyl dithiol, we successfully applied the one-pot boronation and Suzuki coupling to the original ethyl-TMS bromide, **(78)**, and tetramethyldibromobenzne, **(83)**, to isolate the protected terphenyl **(101)** in 25% yield.



Scheme 24: A synthesis of restricted oligophenyl dithiol that works around thiophenol's reactivity with oxidizers like NBS.

The biphenyl, however, proved more difficult. This coupling can also be achieved with a one-pot boronation of the same bromide, **(78)**, and Suzuki coupling, but preparing the bromodimethylthiophenol **(99)** is more fraught. Few of the molecules used up until this point have needed to perform a bromination after the thiol was protected. With the exception of methyl thioethers, most thiol protecting groups are reactive with bromine and NBS.[107]

For example, attempting to brominate an ethyl-TMS protected thiol results in the replacement of TMS with bromide, giving a 2-bromoethane thioether that no longer cleaves cleanly; the protecting group is ruined. Attempts to circumvent this reactivity by deprotonating the ring of with n-butyllithium and quenching with NBS did not result in the desired product.

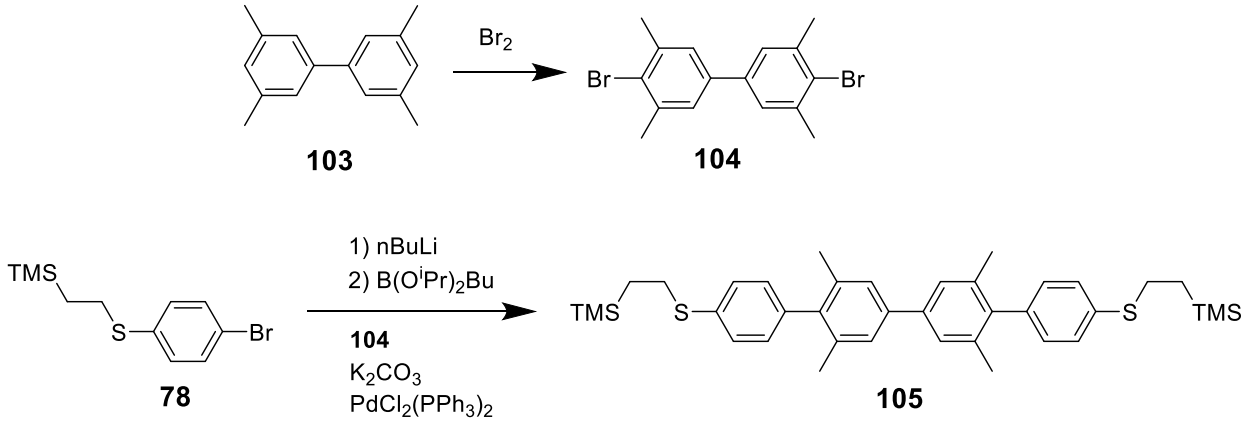
The result of attempting a bromination in the presence of an unprotected thiol is the formation of disulfide dimers. This is undesirable, but disulfides can be easily reduced back to free thiols. Thus, we attempted a bromination of **(84)** with excess NBS in acetonitrile for 3 hours. After column chromatography, we isolated the brominated disulfide **(98)** in 25% yield.

Using this compound in the one-pot Suzuki coupling did not produce recognizable products, possibly because the disulfide poisoned the palladium catalyst.

SECTION 4.5: Future Work and Conclusions

Unfortunately, time limitations have prevented us from exploring the rest of the route shown in scheme 24. The reduction of disulfide to free thiol, followed by protection with vinyl-trimethylsilane should allow us to perform a successful cross coupling and prepare the target biphenyl, **(102)**.

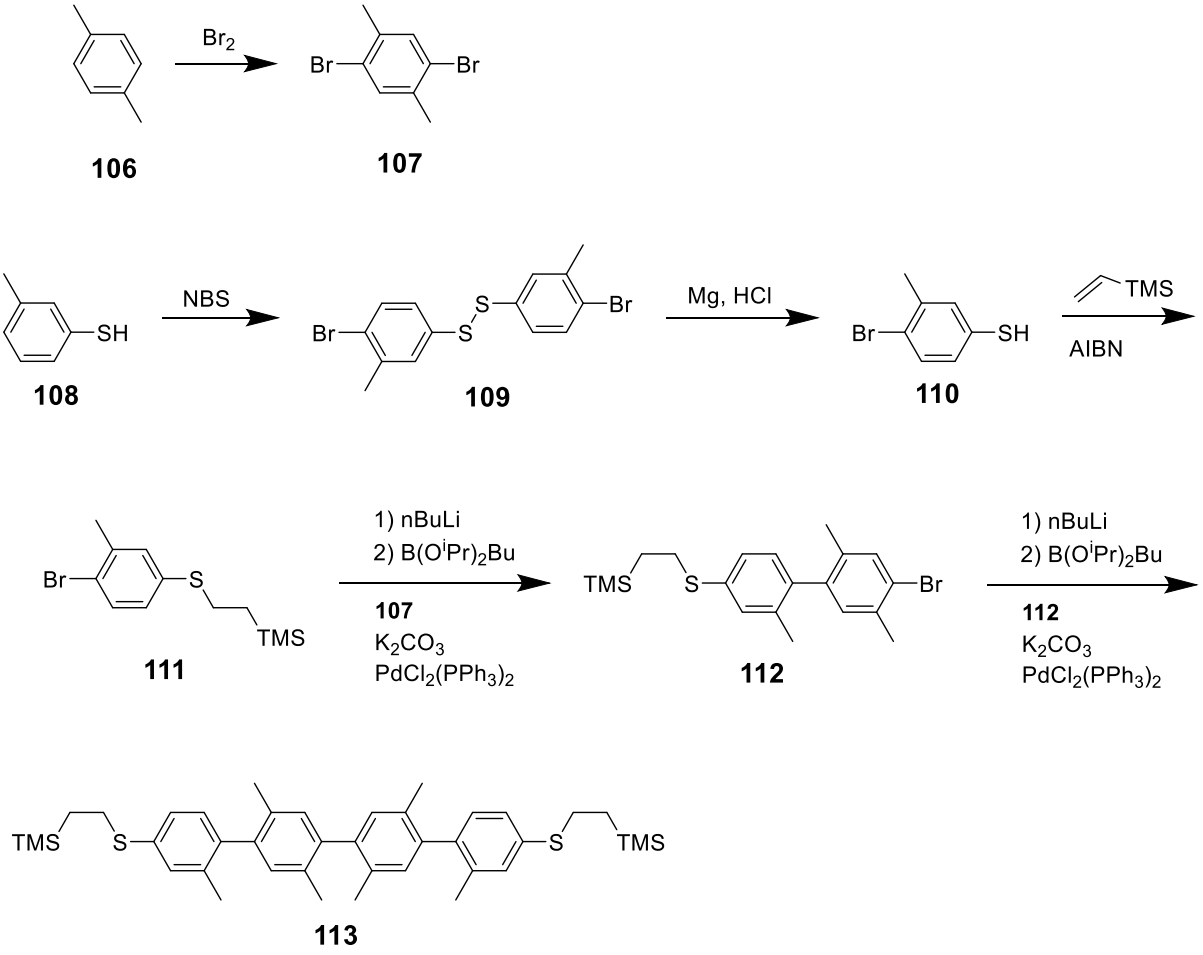
The restricted biphenyl and restricted terphenyl systems should provide initial data about the viability of our hypothesis that decreasing conjugation length of would raise the tunneling barrier of these molecular electronic devices. To solidify any promising initial results, it may be necessary to also compare the restricted quaterphenyl dithiol system. The preparation of this system is more complex than the two shorter oligophenyl dithiols. Like the restricted biphenyl, an uneven number of rotatable σ bonds must but isolated, so the molecule must be asymmetric. Any scheme we could propose up for the fully-restrained quaterphenyl system using the di-*ortho* (2,6)-dimethyl units is extremely wasteful and low yielding.



Scheme 25: A simple synthesis to restricted quaterphenyl, but only two of the three rotatable bonds are restricted.

However, the synthesis becomes much simpler if only two of the bonds are restricted, although using this design would likely hurt the rigor of this study.

Thus, we believe that the most viable synthesis for the production of a restrained quaterphenyl system is to use the 2,2'-dimethyl restriction paradigm. It is unfortunate that separate molecular designs may be employed to support our study, but the same quantity of methyl units will be used regardless of the approach. We believe that the modelling discussed above shows that the effects of this change will be negligible. The bromination of commercially available 2,4-dimethylbenzene was provided by Yang et al.[108]



Scheme 26: Proposed route to a 2,2'-dimethyl restricted quaterphenyl

With the final isolation of these molecules in near reach, we expect to soon begin preparing self-assembled monolayer devices and begin electronic characterization. Understanding the tunneling behavior through organic thin films and SAM's, in particular conjugated ones, is a crucial step towards the production technologies like organic spintronics,[82] rectifiers,[83] and other complex molecular switches.

CHAPTER 5: Conclusions and Closing Thoughts

Organic electronics is a vast field which is only partially represented in this work. Over the past five years, I have endeavored to design projects that have set short-term goals for a particular subfield (OPV acceptor design, molecular electronics, etc), but also address issues central to the field of organic electronics as a whole.

Replacing fullerene in OPV's is almost certainly a necessary step for the future of this burgeoning technology. Our analysis of the literature lead us to try building a system which addresses design constraints like stability and scalable synthesis while investigating methods of perturbing molecular packing, hole mobility, absorbance, and molecular packing in bulk and at the interface. As exemplified by the use of POSS in OLED devices to alter packing and electron transport, the delicate interplay of these properties creates problems across organic electronics.

Realizing these synthetic schemes in their entirety is a huge hurdle, and one we were not able to cross in the time I had to give to it. Still, we revealed the limitations of olefin metathesis and other cross couplings for these systems. We showed that the electronics of those arms plays a crucial role. And sterics and relative solubility also pose a significant hurdle to our ability to isolate high molecular weight acceptor complexes. These findings have implications for the design of molecules in related fields like OLEDs and organic transistors, where controlling mobility and molecular packing is crucial.

Thematically, our efforts towards synthesizing oligophenyl dithiols offer a counterpoint to the non-fullerene acceptor project. In both cases, controlling intramolecular orientation

depended on overcoming synthetically unfavorable steric interactions. While the restricted mobility oligophenyls were eventually synthesized after decreasing the number of steric interactions, our perylene systems struggled to cross that threshold. We touched on some of the literature that investigates sterically hindered Suzuki couplings, yet our efforts show the need for still more research that pushes the boundaries of catalyzed cross coupling reactions.

Our endeavors into non-fullerene acceptors and synthesizing benzotriazole analogs reveal the difficulty of applying divergent synthetic design to highly conjugated, heteroatomic systems, like those found in organic electronics. Both of these efforts shared a goal of drafting a new synthetic system for other researchers to use for their own projects. Undeniably, this focus altered the decisions that we made, encouraging us to explore riskier routes and avoid more certain, but less generalizable, chemistry. These high aspirations are partly responsible for how none of the research presented in this work met its original design goals.

Progress on each of these projects has required a substantial investment of time, funds, instrument use, and institutional oversight. Professor Wei You, the University of North Carolina Chapel Hill, the National Science Foundation, and others have all devoted precious resources to the effort. We have struggled hard to uncover knowledge through trial-and-error, synthetic troubleshooting, and studious compilation and analysis of the scientific literature. In this light, it is a shame that none of the work presented here has been published in a traditional peer-reviewed journal, and thus will be of limited availability and use to the scientific community.

For example, because we never successfully prepared a novel non-fullerene acceptor, none of the knowledge and expertise that we gained over three years of effort is widely available to other researchers attempting similar endeavors. It is tempting to question what would have made our endeavor a successful one, one worth publishing. Would more (or less) patience for a

challenging project have led to publishable results? Could we increase the number of papers we read or the time we spent testing our organic knowledge? Was there some change we could have made to our process to better ensure success?

These hypotheticals are deceptive: they are difficult to gauge and they focus on the competency of the researchers, which is a diversion from the truth that some research projects will plainly never produce the results they were intended to. I propose that the work discussed here, particularly the non-fullerene acceptor work, was never published because the original project design and the daily experimental focus did not plan for failure.

For both the divergent triazole synthesis and the non-fullerene acceptor synthesis, the original project plan involved publishing a successful synthesis, followed quickly by a second study on the properties and utility of those target molecules when applied to a polymer solar cell. Both of these projects have yet to hit the first milestone, and so have not triggered the writing of an article that would have also detailed the unsuccessful attempts, as this dissertation does. Setting more milestones with smaller goals may allow more research knowledge to reach the scientific community.

However, even with smaller milestones, some projects will not produce as intended. In the case of the non-fullerene acceptor synthesis, I believe that designing a backup plan would have encouraged behavior beneficial to the publication of our negative results and hard-won knowledge.

When a project's only goal is to produce a viable synthesis, then all non-viable synthetic steps should be abandoned without further investigation. Anomalous behavior is only of interest for as long as it might be corrected or coerced into utility. With this focus, initial, incomplete results steer the ship of research. These internally-convincing results likely do not meet the high

standards of proof that we expect for published conclusions. One of peer review's successes is that it encourages members of the community, and (proactively) members of the research group, to seriously consider the question "what would make this analysis more conclusive and convincing?"

For the synthetic challenges discussed in this work, this question was not always asked to its full extent. Even in examining my own research for this dissertation, I have found several gaps in our exploratory path, either made in error or merely from developments that were poorly documented and lost to time. A successful publication of even negative results would have encouraged this kind of intensive analysis, by myself and others, while there still remained time left to return to the lab and fill in the gaps – to say with greater certainty the conclusions I draw out above.

By not making an effort to more fully explain the anomalous behavior and nonfunctional syntheses in this synthetic endeavor, we undersold the importance and utility of our exploratory efforts. In doing so, we contributed to a literature polluted by positive results, when more negative results before us may have paved a clearer path. We silently acknowledge that another researcher, elsewhere, could try again and make many of the same mistakes, and that this is acceptable.

By refusing to add our hard-won knowledge to the scientific literature, we not only hurt our field of study, but also our junior researchers, who can toil for years under the aspiration of contributing to science. What does it tell them, when we don't find the place to teach them about writing and publication during their doctoral studies? What does it do to them, when their hard work is filed away, forever separate from the increasingly searchable databases of public human knowledge?

Of course, the intense focus on finding a sole, viable synthetic scheme was by design. It was the risk we took towards publishing a high-quality study. But this choice, when made by hundreds of researchers, is ultimately harmful to the growth of our field as a whole, and we should take care to design projects in the future that avoid it.

Individually, thoroughly investigating dead ends may appear to be a waste of precious time and resources towards a small gain, but taken as a practice these efforts can, like fallow fields, enrich the literature from which we try to grow more fruitful projects. By publishing more often and designing funding incentives to do so, I hope that we can collectively create a more sustainable Science.

APPENDIX I: METHODS

General Methods

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, Alfa Aesar, Macros) and used without further purification unless stated otherwise. Reagent grade THF was dried over sodium and benzophenone and purified by distillation. AIBN and NBS were recrystallized from methanol and water, respectively. Silica gel was obtained from Silicycle Inc. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained at 400 or 600 MHz as solutions in CDCl3, unless stated otherwise. ^{13}C NMR proton-decoupled spectra were obtained at 100 or 150 MHz as solutions in CDCl3, unless stated otherwise. Chemical shifts are reported in parts per million (ppm, δ) and referenced from tetramethyl-silane. Elemental analysis was performed by Atlantic Microlab, Inc

CHAPTER 2

General method for preparing PADI systems

Perylene tetracarboxylic dianhydride (2.0 mmol), 8-heptadecylamine (2.0 mmol) and the Linker amine (2.0 mmol) were added into a thick-walled bomb flask. Imidazole (14g, 200 mmol) was added on top of the other three reactants, the flask was sealed and heated to 140 ˚C overnight. The hot suspension was poured into a mixture of methanol (125 mL) and 2M HCl (125 mL) and the bomb flask was washed with more of this solution. The flask was cooled to 0 ˚C overnight, filtered, and the solids were washed with methanol to yield a dark red solid, which was dried in an 80 ˚C oven. The product could be isolated by silica column in dichloromethane as the middle of the three main red products.

2-(4-bromophenyl)-9-(heptadecan-9-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (16)

Used the General Method outlined above with the amine 4-bromoaniline. 43% Yield. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 8.66 (dd, J = 8.0 Hz, J = 36.4 Hz, 8H), 7.71 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.18 (m, 1H), 2.23 (m, 2H), 1.87 (m, 2H), 1.30 (m, 24H), 0.828 (t, J = 6.8 Hz, 6H).

2-(heptadecan-9-yl)-9-(4-vinylphenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (17)

Used the General Method outlined above with the amine 4-vinylaniline**.** 49% Yield. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 8.74 (m, 4H), 8.65 (m, 4H), 7.63 (d, J = 6.8 Hz, 2H), 7.35 (d, J = 6.4 Hz, 2H), 6.83 (dd, J = 8.8 Hz, J = 14 Hz, 1H), 5.86 (d, J = 14 Hz, 1H), 5.37 (d, J = 8.8 Hz, 1H), 5.21 (m, 1H), 2.26 (m, 2H), 1.90 (m, 2H), 1.27 (m, 24H), 0.89 (t, J = 6.8 Hz, 6H).

2-(heptadecan-9-yl)-9-(hex-5-en-1-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (24)

Used the General Method outlined above with the amine (**23)**. 48% Yield. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 8.63 (m, 8H), 5.85 (m, 1H), 5.20 (m, 1H), 5. 05 (17.2 Hz, 1H), 4.99 (d, J = 24 Hz, 1H), 4.23 (t, J = 7.6 Hz, 2H), 2.25 (m, 2H), 2.15 (m, 2H), 1.88 (m, 2H), 1.79 (m, 2H), 1.78 (br, 24H), 0.84 (t, J = 7.2 Hz, 6H).

2-(5-hexen-1-yl)isoindoline-1,3-dione (22)

6-bromo-1-hexene (5.00 g, 31.5 mmol), and potassium phthlimide (11.67g, 63.0 mmol) were added to DMF (120 mL) and the mixture was heated to a slow reflux for 18 hrs. The

solution was poured into 300 mL water and extracted 3 times with ethyl acetate. The organics were concentrated in vacuo and then a stream of air was blown over the oil for 24 hours to remove residual DMF. The oil was run through a silica plug with 9:1 hexanes:ethyl acetate to yield a yellow oil (6.1 g, 85%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.84 (dd, J = 2.8 Hz, J = 5.6 Hz, 2H), 7. 70 (dd, J = 3.2 Hz, J = 5.6 Hz, 2H), 5.77 (m, 1H), 4.99 (d, J = 17 Hz, 1H), 4.93 (d, J = 10.)**,** 3.68 (t, 7.2 Hz, 2H), 2.09 (q, J = 7.2 Hz, 2H), 1.68 (m, 2H), 1.45 (m, 2H).

5-hexen-1-amine (23)

Phthalimide compound **(22)** (6.1 g, 27 mmol), was added to a solution of methanol (60 mL) and hydrazine monohydrate (3.5 mL, 72 mmol) and stirred for 18 hours. 2 M HCl (36 mL) was added, and the mixture was stirred for another 24 hours. The reaction was brought to pH > 12 and extracted into chloroform. The organics were concentrated in vacuo to produce a yellow oil (2.43 g, 92%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 5.80 (m, 1H), 5.00 (d, J = 17 Hz, 1H), 4.94 (d, J = 10. Hz, 1H), 2.69 (t, J = 6.4 Hz, 2H), 2.06 (q, J = 6.8 Hz, 2H), 1.43 (m, 6).

CHAPTER 3

N1,N4-dimethoxy-N1,N4-dimethylbut-2-ynediamide (53)

Acetylenedicarboxylic acid (890 mg, 7.8 mmol) was dissolved in dichloromethane and cooled to 0 ˚C. A solution of oxalyl chloride (1.35 mL, 15.5 mmol) in dichloromethane was added and stirred overnight at 25 ˚C. The free amine **(50)** was prepared by adding N,O-dimethylhydroxylamine hydrochloride **(49)** (1.6 g, 16 mmol) to a separatory funnel with saturated aqueous sodium bicarbonate (3 mL), and dichloromethane (5 mL). The organics layer was extracted, dried over $MgSO_4$, and filtered. This solution of prepared amine was added to the

reaction vessel and stirred overnight. The reaction was poured into saturated aqueous ammonium chloride, and then the organic layer was extracted, washed with brine, and concentrated in vacuo to yield a yellow oil (920 mg, 66%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 3.74 (s, 6H), 3.24 (s, 6H).

1-((pivaloyloxy)methyl)-1H-1,2,3-triazole-4,5-dicarboxylic acid (57)

Acetylenedicarboxylic acid (410 mg, 4.3 mmol) and azidomethylpivalate (550 mg, 3.5 mmol) were stirred in diethylether (10 mL) under argon at a slow reflux for 16 hours. The reactants were removed *via* rotary evaporation (42%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 6.72 (s, 2H), 2.05 (br), 1.20 (s, 9H).

diethyl 1-((pivaloyloxy)methyl)-1H-1,2,3-triazole-4,5-dicarboxylate (58)

Diethyl acetylenedicarboxylate (360 mg, 2.11 mmol) and azidomethylpivalate (330 mg, 2.11 mmol) were stirred at 70 ˚C for 2 hours. The reactants were removed in vacuo to yield a yellow oil (643 mg, 93%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 6.45 (s, 2H), 4.46 (q, J = 7.2 Hz, 4H), 1.42 (t, J = 7.2 Hz, 6H), 1.17 (s, 9H).

CHAPTER 4

(2-((4-bromophenyl)thio)ethyl)trimethylsilane (78)[109]

4-bromothiophenol (5.00 g, 26.5 mmol), vinyltrimethylsilane (4.5 mL, 31.5 mmol), and AIBN (50 mg, 0.25 mmol) were added to a bomb flask, which was sealed and stirred at 100 °C for 20 hours. The crude product was distilled at 160 °C under 0.55 torr vacuum to produce a clear oil (6.2 g, 81%). If present, unreacted 4-bromothiophenol sublimes first as a white solid, necessitating a fractional distillation with a heat gun to progress the solid through the distillation

glassware. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.39 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 2.93(t, J = 8.4 Hz, 2H), 0.92 (t, J = 8.8 Hz, 2H), 0.04 (s, 9H).

4,4'''-bis((2-(trimethylsilyl)ethyl)thio)-1,1':4',1'':4'',1'''-quaterphenyl (81)

A solution of **(78)** (4.40 g, 15.2 mmol) in dry THF (20 ml) was added to a flame-dried flask (w/ condenser) under argon. The solution was cooled to -78 °C in a dry ice/acetone bath and sparged with Ar for 15 minutes. 2.5 M nBuLi/hexanes (9.5 mL, 24 mmol) was added and stirred for 2 hours. Butyldiisopropoxyborane (3.6 mL, 15.2 mmol) was added and stirred for 1 hour, after which the reaction was warmed to room temperature and stirred for 30 minutes. Na_2CO_3•H_2O (3.6 g, 29 mmol) was dissolved in distilled H_2O (9 mL), sparged with Ar for 30 minutes, and added to the reaction. 4,4'-dibromobiphenyl (1.87 g, 6.0 mmol) and THF (24 mL) were added, and the reaction was sparged with Ar for 15 minutes. $PdCl_2(PPh_3)_2$ (940 mg, 1.34 mmol, 9 mol %) was added in one portion and the reaction was stirred under reflux for 16 hours. The reaction mixture was poured into water and extracted into dichloromethane. The organic layer was washed twice with brine, dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by column chromatography on silica gel, using 4:1 hexanes:dichloromethane as the eluent to yield a white solid (1.96 g, 45%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.70 (q, J=8.4 Hz, 8H), 7.58 (d, J = 8.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 4H), 3.02 (m, J = 8.8 Hz, 4H), 0.98 (m, 4H), 0.07 (s, 18H). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ): 139.54, 138.03, 136.65, 129.25, 127.37, 127.33, 127.24, 29.70, 29.62, 16.98, -1.73. Anal. Calc'd for $C_{34}H_{42}S_2Si_2$: C, 71.52; H, 7.41; S, 11.23. Found: C, 71.13; H, 7.18; S 10.94.

4,4''-bis((2-(trimethylsilyl)ethyl)thio)-1,1':4',1''-terphenyl (79)

(79) was prepared using the same method used for **(81)**, substituting in dibromobenzene for dibromobiphenyl and running the same column to yield a white solid (20%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ):7.66 (s, 4H), 7.58 (d, 8.4 Hz), 7.40 (d, J = 8.0 Hz, 4H), 3.03 (t, J = 8.8 Hz, 4H), 1.00 (t, J = 8.8 Hz, 4H), 0.08 (s, 18H). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ): 139.41, 138.01, 136.65, 129.26, 127.32, 127.23, 29.62, 16.99, -1.69. Anal. Calc'd for $C_{28}H_{38}S_2Si_2$: C, 67.95; H, 7.74; S, 12.96. Found: C, 68.01; H, 7.46; S, 12.90.

3,5-dimethylthiophenol (85)

Triethylamine (6 mL, 40. mmol) was added to a stirring solution of 3,5-dimethylthiophenol (5.0 mL, 36.3 mmol) and methyliodide (2.5 mL, 40. mmol) in dichloromethane (100mL) and stirred overnight. The organics were washed twice with 1 M HCl and once with saturated aqueous sodium bicarbonate. The organics were dried down to a clear oil (6.6 g, 60%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 6.89 (s, 2H), 6.78 (s, 1H), 2.47 (s, 3H), 2.29 (s, 6H).

4-bromo-3,5-dimethylthioanisole (86)

N-bromosuccinimide (1.42g, 8.0 mmol) was fully dissolved into acetonitrile (20 mL) and added to a solution of 3,5-dimethylthioanisole **(85)** (1.2g, 8.0 mmol) in acetonitrile (20 mL) at 0˚ C. The reaction mixture was stirred overnight in the dark. The acetonitrile was removed in vacuo, and the resultant solids were purified *via* a silica plug in hexanes to yield a yellow oil (1.72 g, 93%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 6.97 (s, 2H), 2.46 (s, 3H), 2.39 (s, 6H).

2-(2,6-dimethyl-4-(methylthio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Bromide **(86)** (700 mg, 3.0 mmol) was added to a flame-dried flask and pump-purged with vacuum and argon for 3 cycles. Distilled THF (20 mL) was added, the solution was cooled to -78 ˚C. 2.5 M nBuLi/Hexanes (1.4 mL, 3.3 mmol) was added and the solution was stirred at 90 minutes at -78 ˚C. Isopropoxyboronic acid pinacol ester (0.67 mL, 3.3 mmol) was added and stirring continued at -78 ˚C for 30 minutes before being warmed to room temperature. The reaction was stirred at room temperature for 2 hours. Water (10 mL) was added to quench the reaction, and THF was removed in vacuo. The aqueous mixture was extracted into dichloromethane and the organics were dried over $MgSO_4$, filtered, and concentrated in vacuo to a white solid with a low melting point (720 mg, 86%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.33 (s, 2H), 2.92 (s, 3H), 2.87 (s, 6H), 1.85 (s, 12H).

(2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)bis(methylsulfane) (94)

Dibromide **(83)** (170 mg, 0.58 mmol), Borate **(97)** (620mg, 1.38 mmol), $Pd(OAc)_2$ (11mg, 0.049 mmol), BIPHEP (28 mg, 0.054 mmol) and CuBr (28 mg, 0.20 mmol) were added to a flame dried flask, which was pump/purged with vacuum and argon for 3 cycles. SureSeal DMF (6 mL) was added and the mixture was heated to 100 ˚C overnight under argon. The reaction was poured into 200 mL water and extracted 3x into ethyl acetate. The organic were dried over $MgSO_4$, filtered, and concentrated in vacuo to produce a solid. The solids were run through a silica plug in hexanes to yield tan solids (213 mg, 93%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.32 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 2.54 (s, 6H), 1.95 (s, 6H).

(2,6-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(methylsulfane) (95)

Bromide **(86)** (204 mg, 0.88 mmol), Borate **(97)** (587 mg, 1.31 mmol), $Pd(OAc)_2$ (10 mg, 0.044 mmol), CuBr (25 mg, 0.17 mmol), and BIPHEP (25 mg, 0.048 mmol) were added to a flame-dried flask, which was pump-purged with vacuum and argon for 3 cycles. Dry DMF (8 mL) added and heated to 100 ˚C for 16 hours under argon. The reaction was poured into 200 mL of water, extracted into ethyl acetate, dried over magnesium sulfate, and concentrated in vacuo. The solids were subjected to a silica plug in dichloromethane to yield pale yellow solids (200. mg, 83%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.31 (d, J = 3.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.02 (s, 2H), 2.54 (s, 3H), 2.51 (s, 3H), 2.02 (s, 6H).

potassium 4-methyl-1-(4-(methylthio)phenyl)-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (96)

4-(methylthio)phenylboronic acid **(91)** (340 mg, 2.0 mmol), Tris 1,1,1-hydroxymethylethane (240 mg, 2.0 mmol), and 85% KOH (130 mg, 2.0 mmol) were added to toluene (10 mL) and were refluxed overnight with a Dean Stark Trap. The suspension was filtered and washed with minimal acetone to yield white solids (520 mg, 90%). ^{1}H-NMR (d_6-DMSO, 400 MHz, δ): 7.25 (d, J= 7.6 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.55 (s, 6H), 2.37 (s, 3H), 0.46 (s, 3H).

tetrabutylammonium 4-methyl-1-(4-(methylthio)phenyl)-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (97)

Potassium salt **(95)** (580 mg, 2.0 mmol) and tetrabutylammonium chloride hydrate (880mg, 3.2 mmol) were added to ethanol (8 mL) and sonicated until no large chunks persisted. The suspension was stirred for 2 hours, filtered, and the filtrate was dried down to a white solid

(quantitative). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.45 (d, J = 7.6 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.74 (s, 6H), 2.76-2.80 (m, 8H), 2.30 (s, 3H), 1.22-1.30 (m, 16H), 0.89 (t, J = 6.8Hz, 12H), 0.51 (s, 3H).

1,2-bis(4-bromo-3,5-dimethylphenyl)disulfane (98)

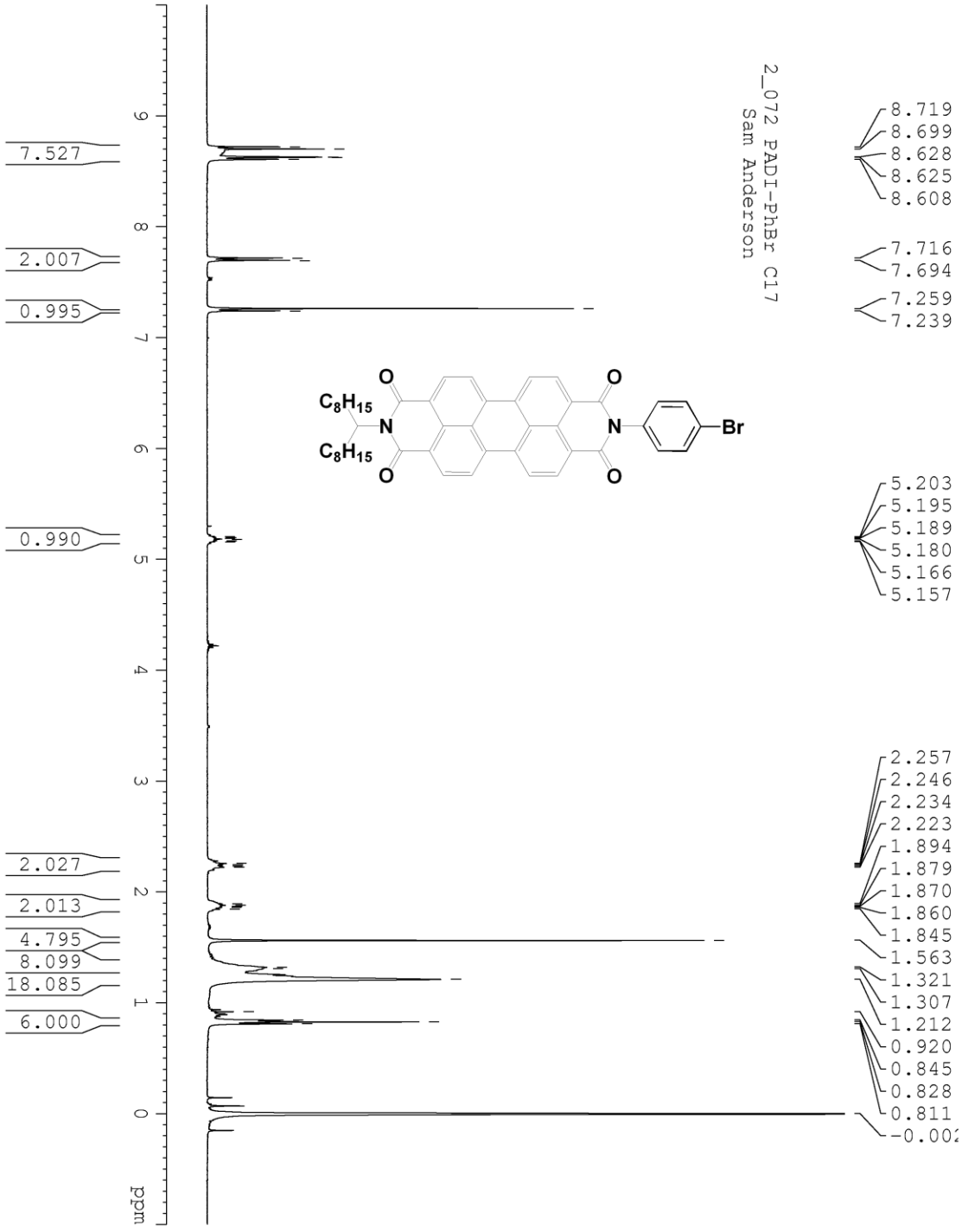
N-bromosuccinimide (720 mg, 4.0 mmol) in acetonitrile (5 mL) was added to a solution of XySH (280 mg, 2.0 mmol) in acetonitrile (5 mL) at 0C. This was stirred overnight, extracted into ethyl acetate. The solids were purified by column chromatography in hexanes to yield tan solids (110 mg, 25%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.69 (s, 4H), 2.54 (s, 12H).

(((2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)bis(sulfanediyl))bis(ethane-2,1-diyl))bis(trimethylsilane) (101)

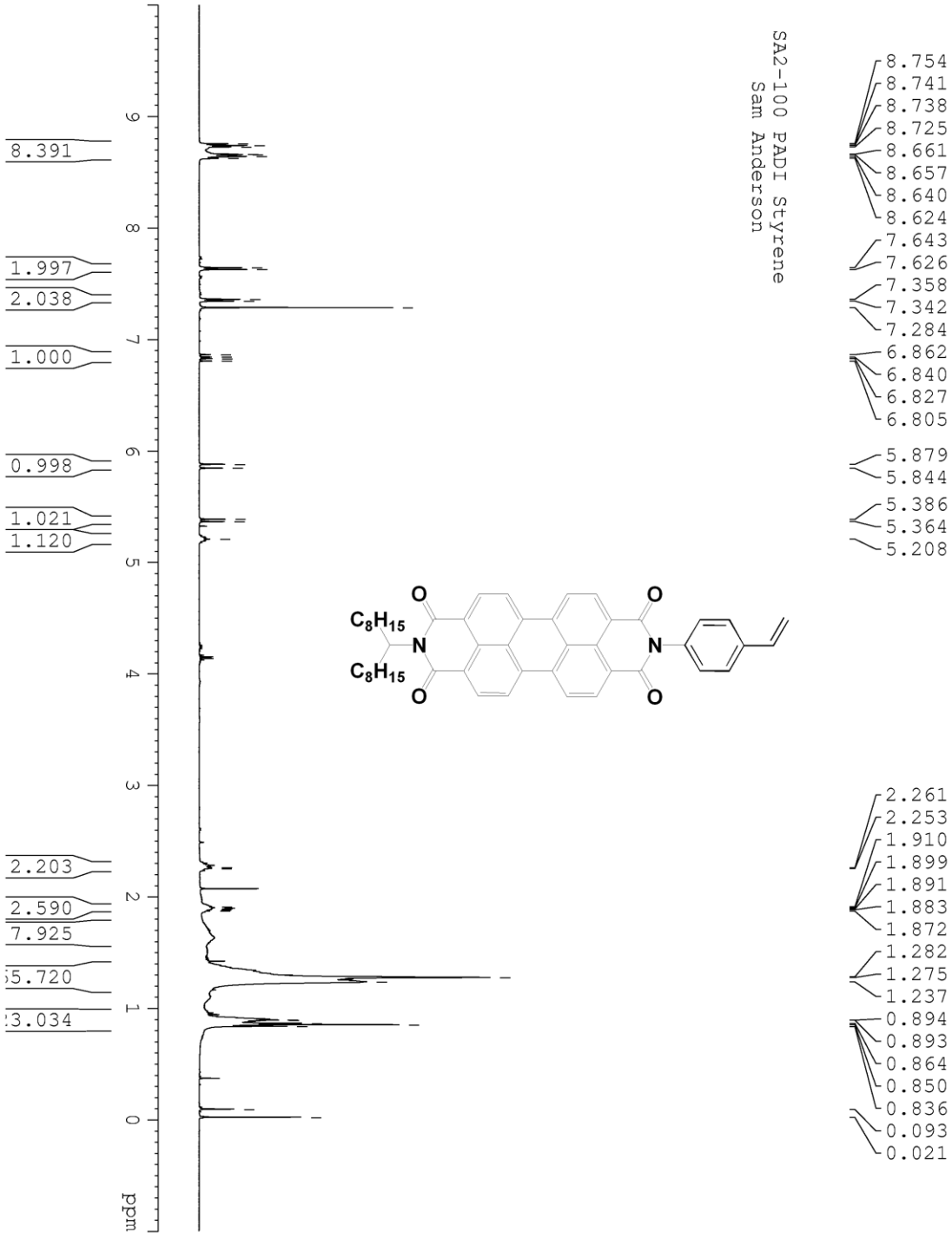
A condenser was affixed to a two neck RB flask, which was pump/purged 3x with argon. Bromide **(78)** (725 mg, 2.5 mmol) and Distilled THF (10 mL) was added under argon and cooled to -78 ˚C. 2.5 M nBuLi/Hexanes (1.2 mL, 3.0 mmol) was added via syringe and stirred at -78 ˚C for 2.5 hours, during which the solution turned orange. Butyldiisopropyl borate (588 mg, 2.5 mmol) was added and stirred at -78 ˚C for 1 hour. The solution was removed from the dry ice bath and allowed to warm to room temperature for 30 minutes, during which the color reached a pale yellow. A flask of water was purged with Ar for 15 minutes, and 1.3 mL was added to the reaction flask. Sodium carbonate monohydrate (520 mg, 4.4 mmol) was added while the system was flushed with Ar for 10 minutes. A flask of $PdCl_2(PPh_3)_3$ (315 mg, 0.45 mmol) in argon was poured into the reaction, and it was stirred at a slow reflux for 18 hours. The reaction was poured into water (60 mL) and extracted 3 times into dichloromethane. The organics were dried over $MgSO_4$, filtered, and concentrated in vacuo. A silica plug in 1:1 EA:Hexanes removed the

baseline impurities before a column was run in hexanes to yield a white solid (130 mg, 25%). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 7.37 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 8.4 Hz, 4H), 3.03 (m, 4H), 1.95 (s, 12H), 0.99 (m, 4H), 0.07 (s, 18H).

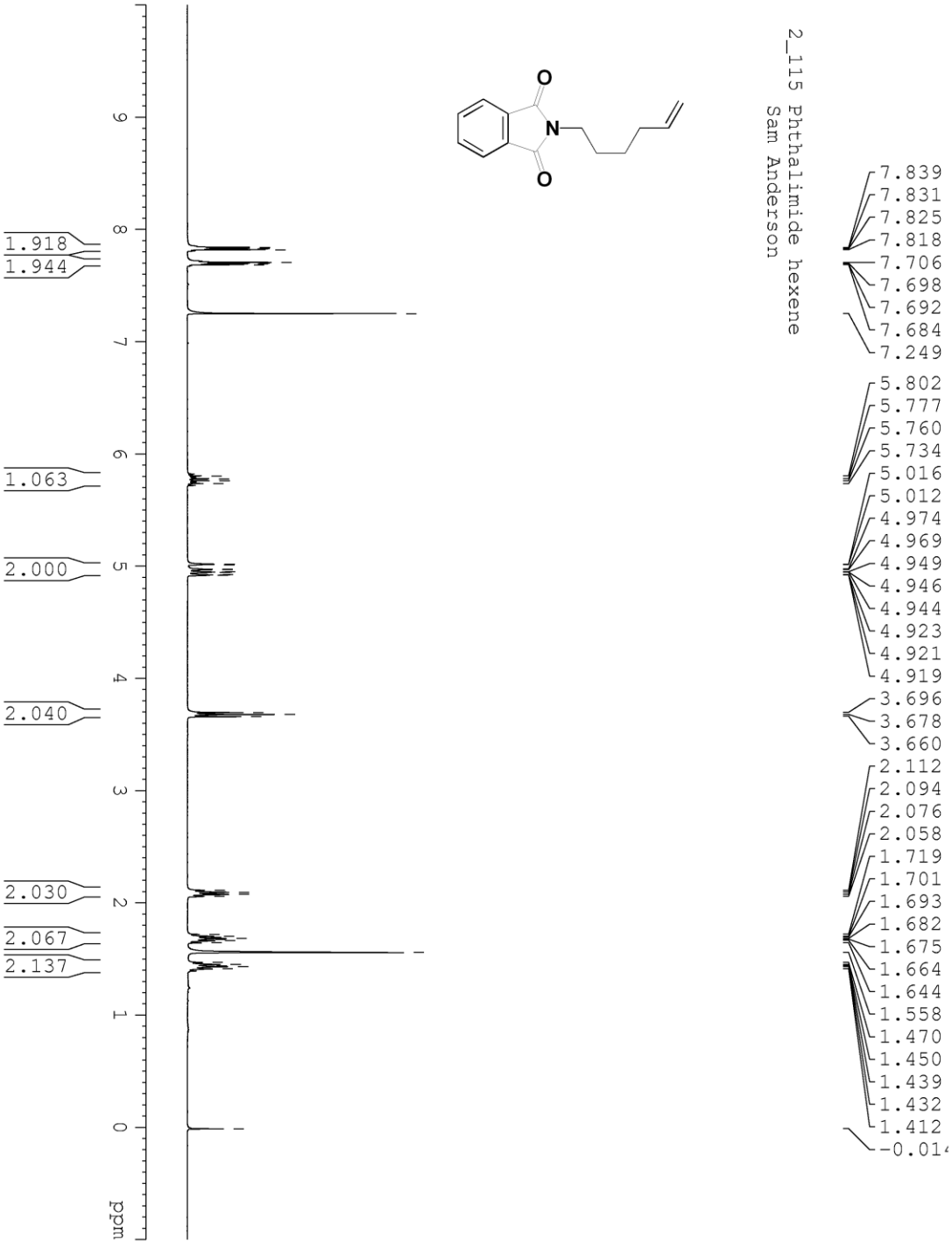
APPENDIX 2: NMR SPECTRA



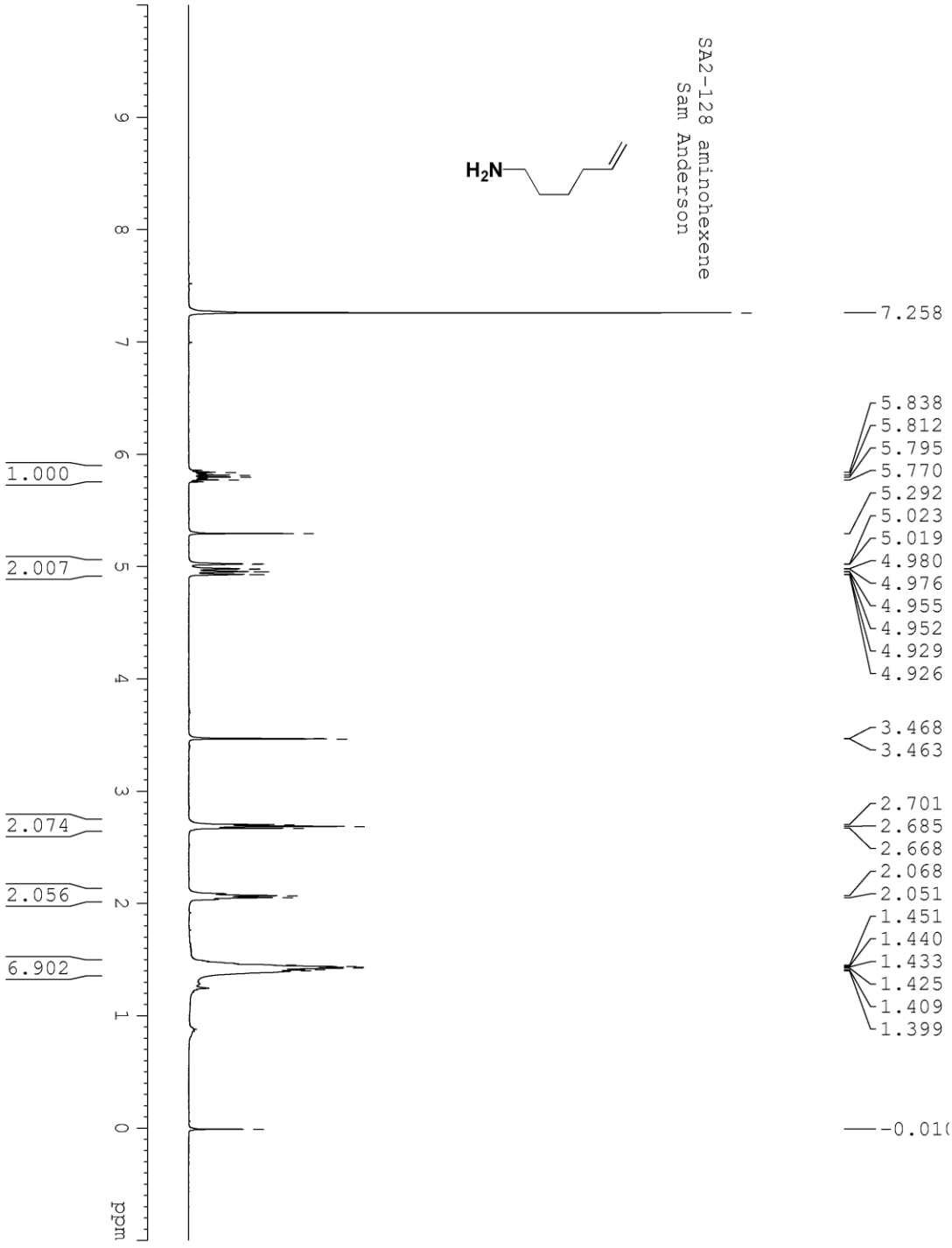
^{1}H-NMR Spectrum of Compound **(16)**



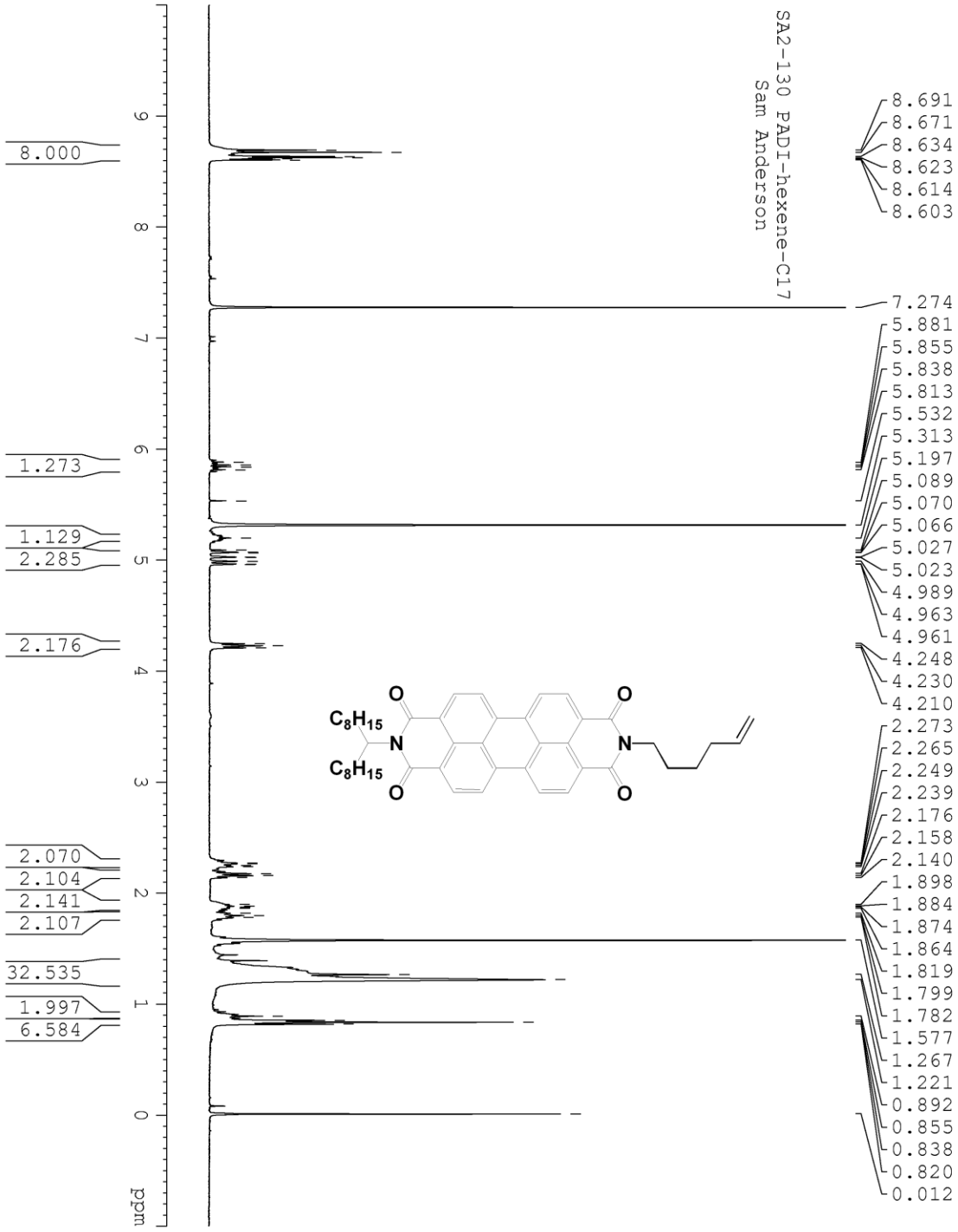
^{1}H-NMR Spectrum of Compound **(17)**



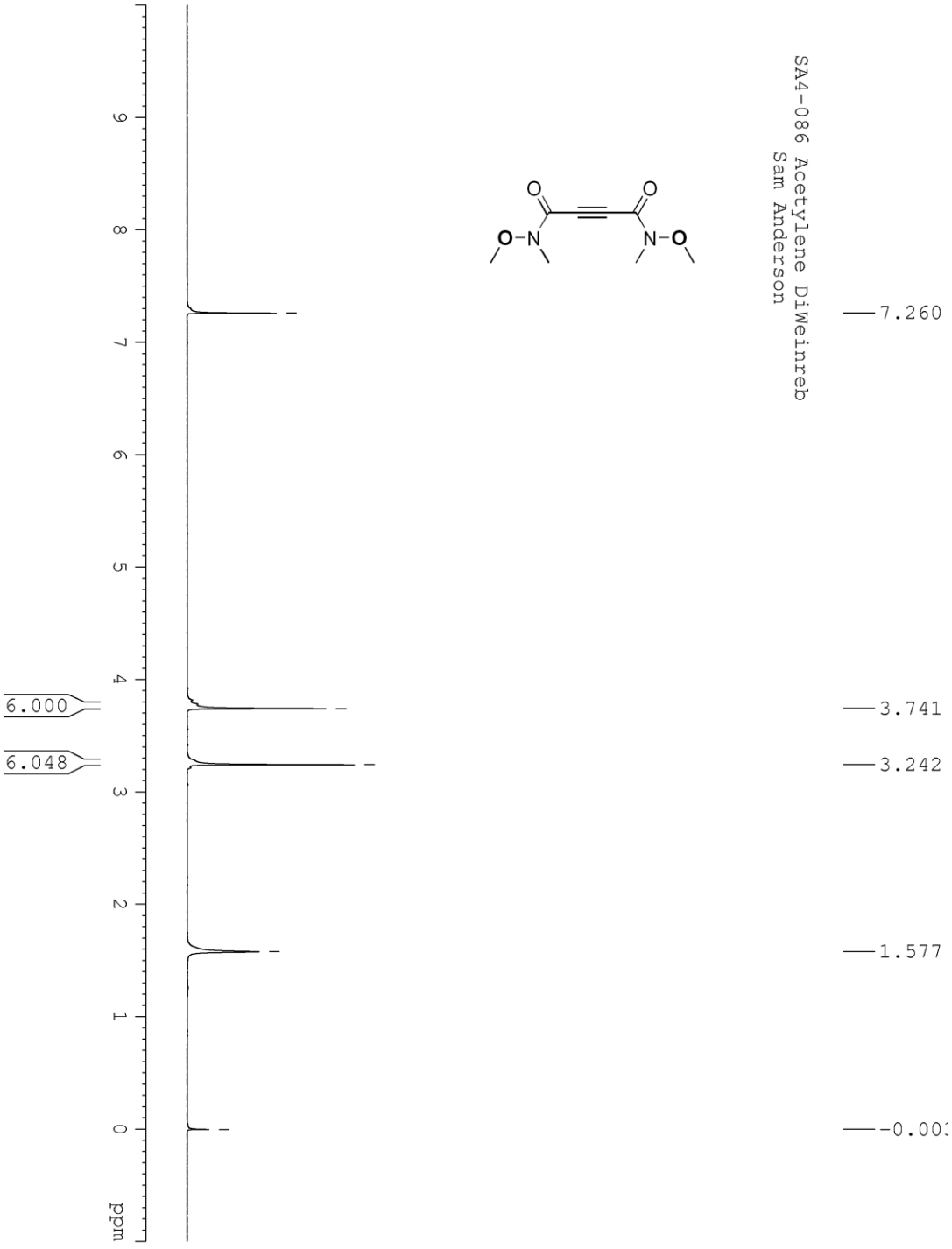
^{1}H-NMR Spectrum of Compound **(22)**



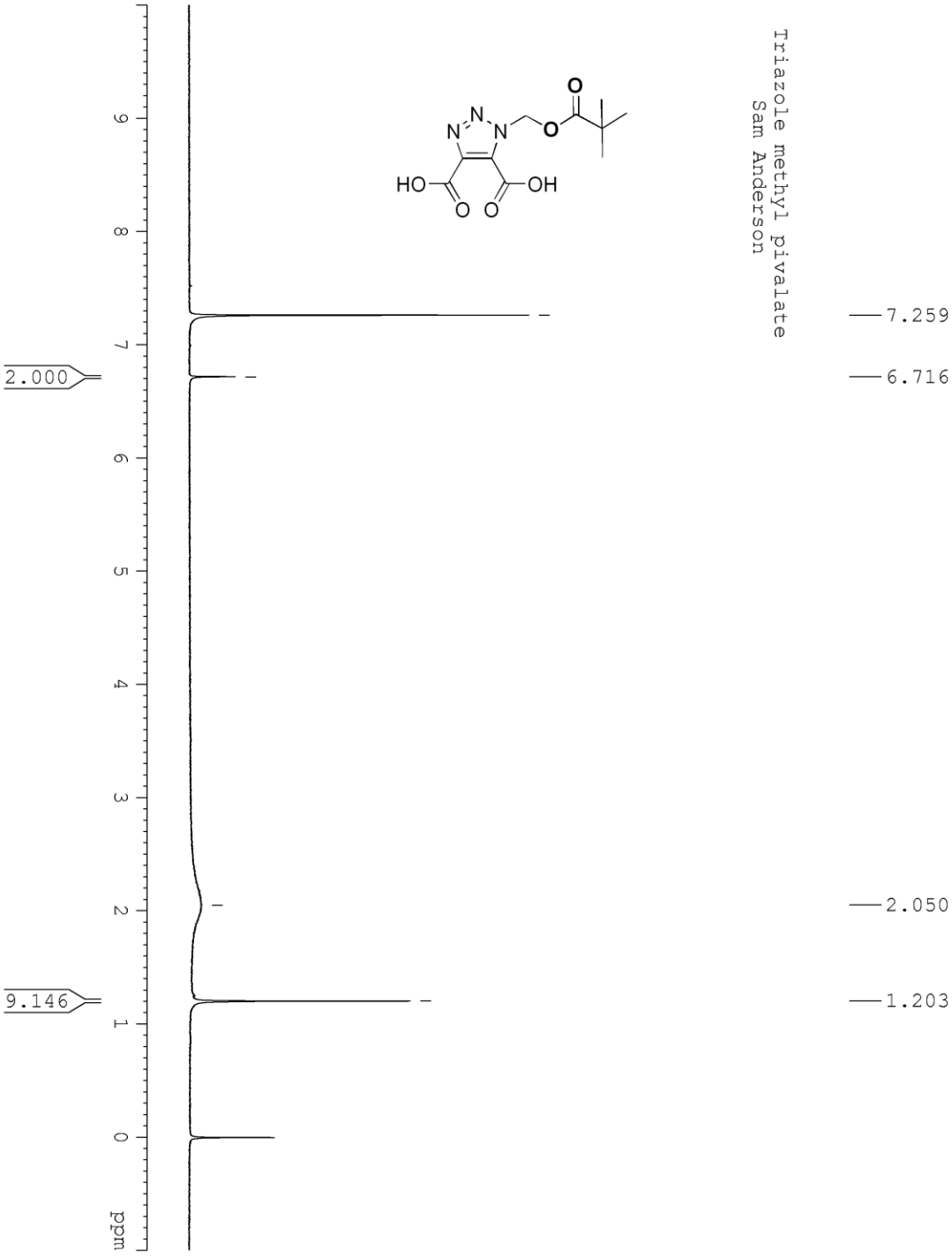
^{1}H-NMR Spectrum of Compound **(23)**



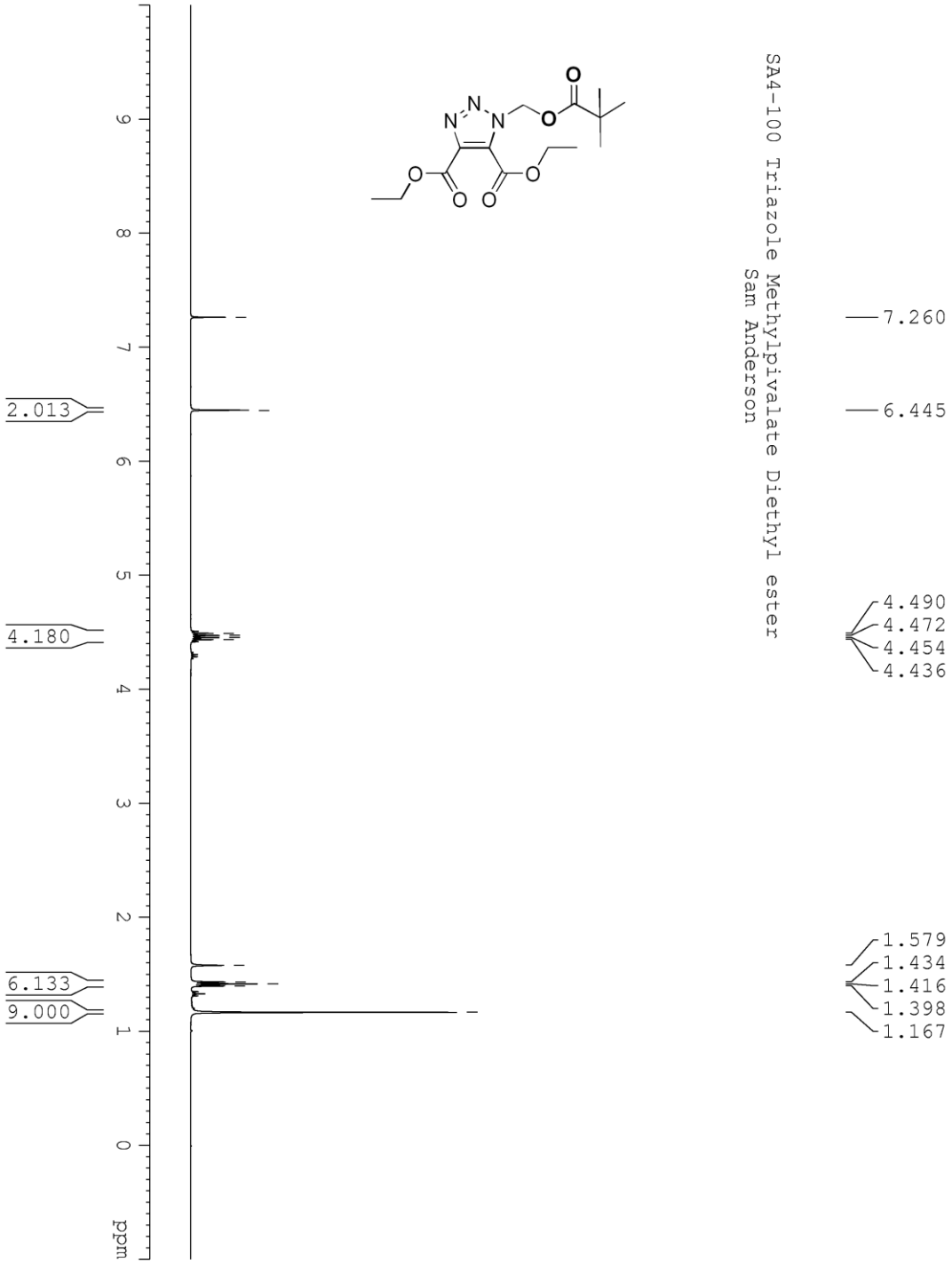
^{1}H-NMR Spectrum of Compound **(24)**



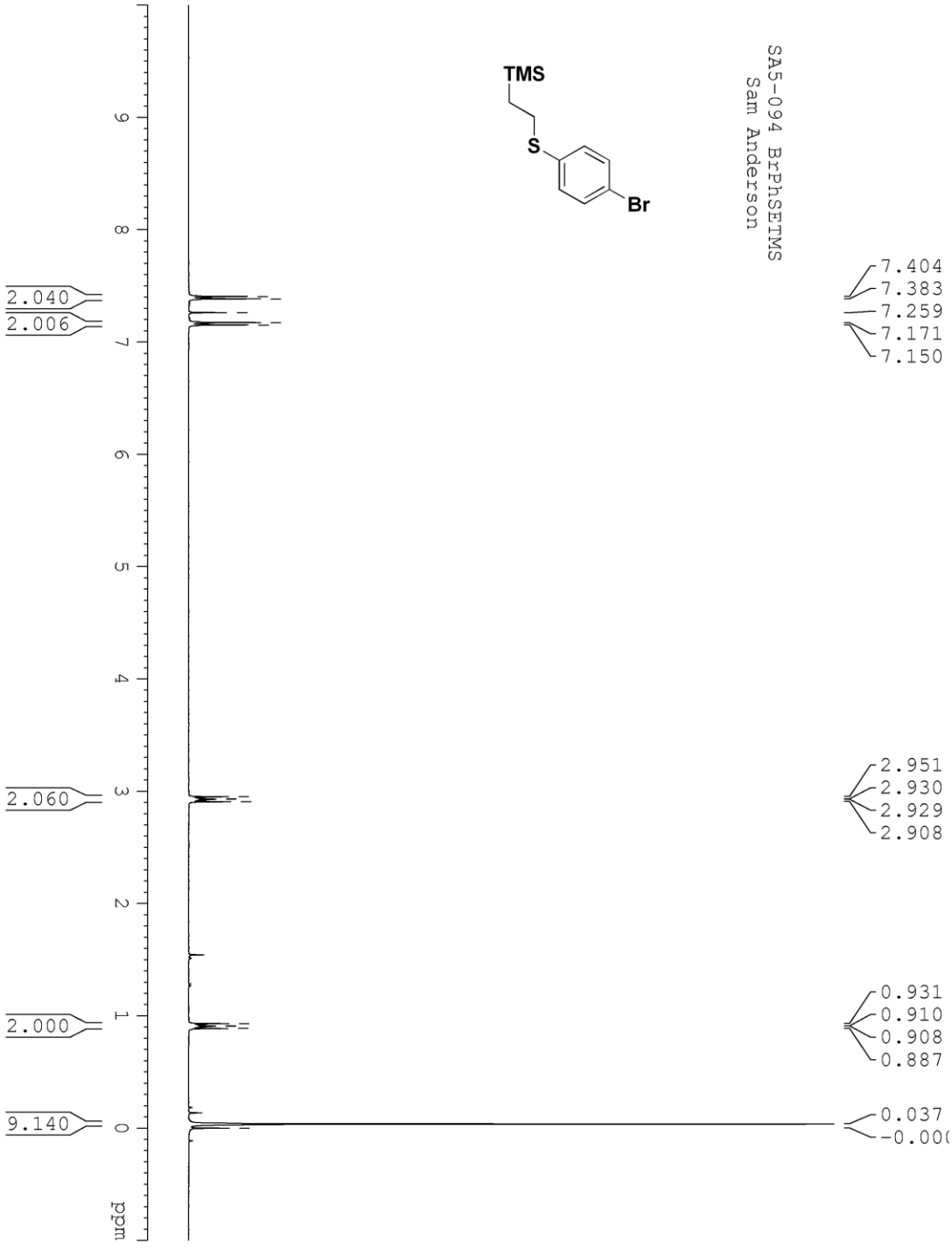
^{1}H-NMR Spectrum of Compound **(53)**



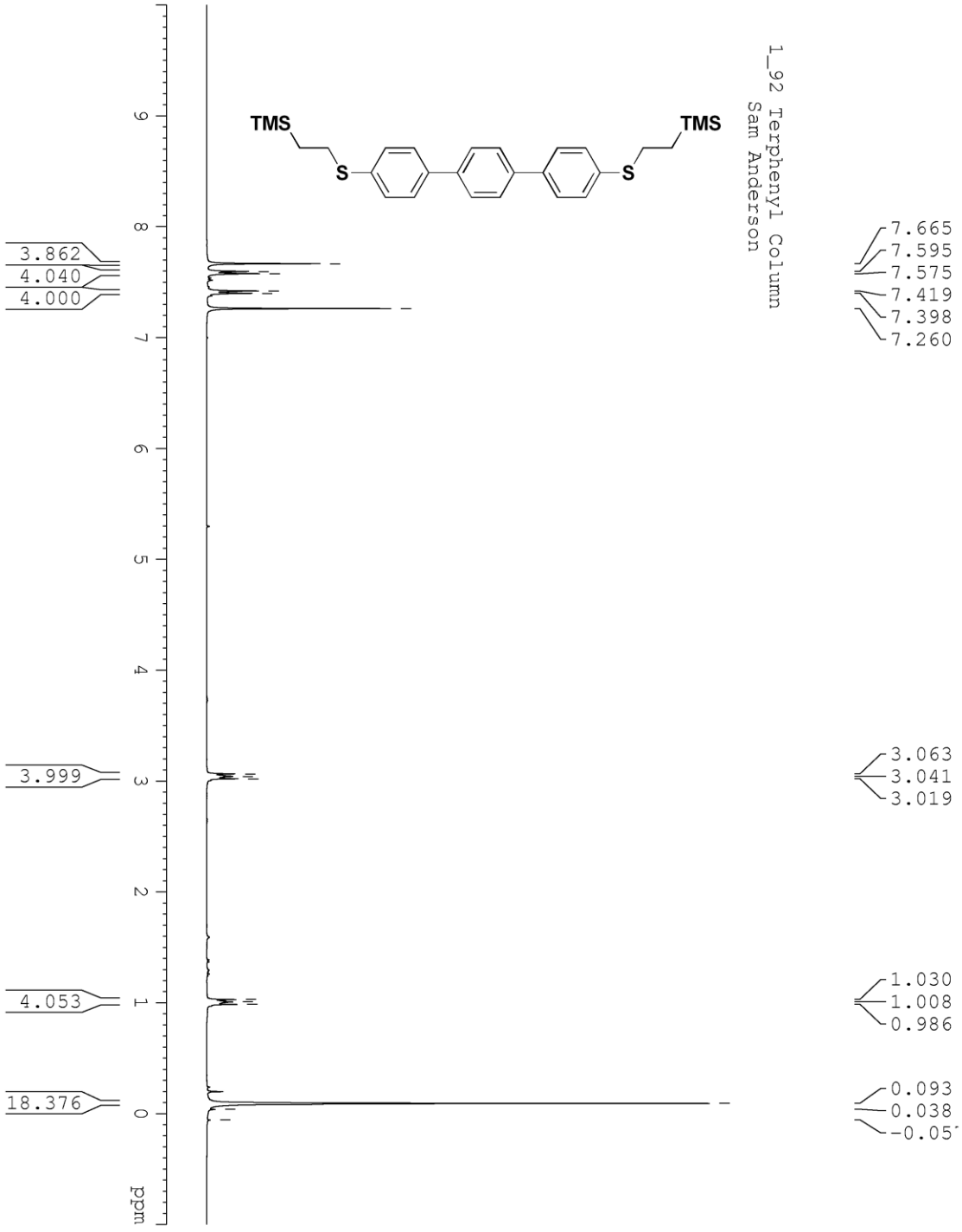
^{1}H-NMR Spectrum of Compound **(57)**



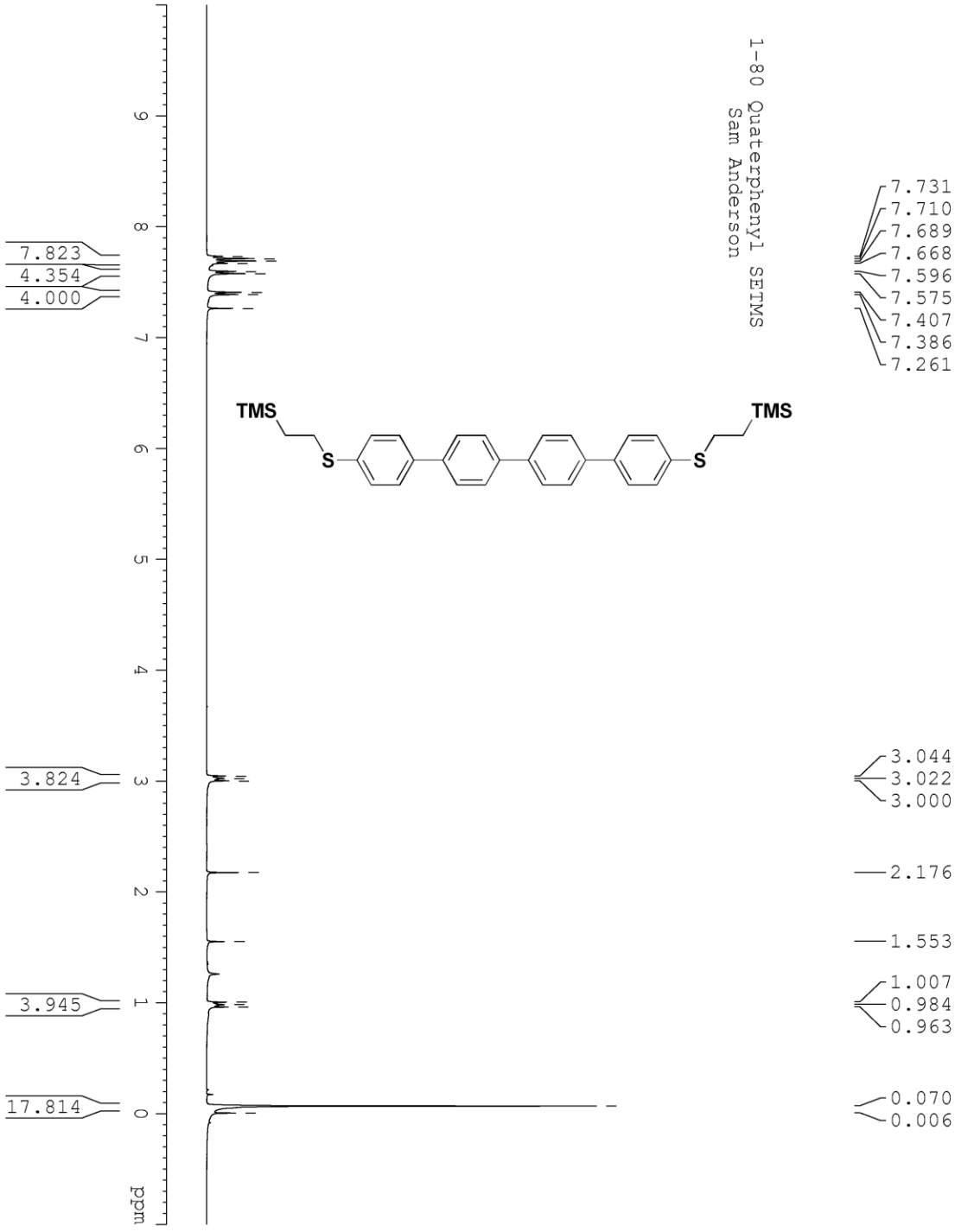
^{1}H-NMR Spectrum of Compound **(58)**



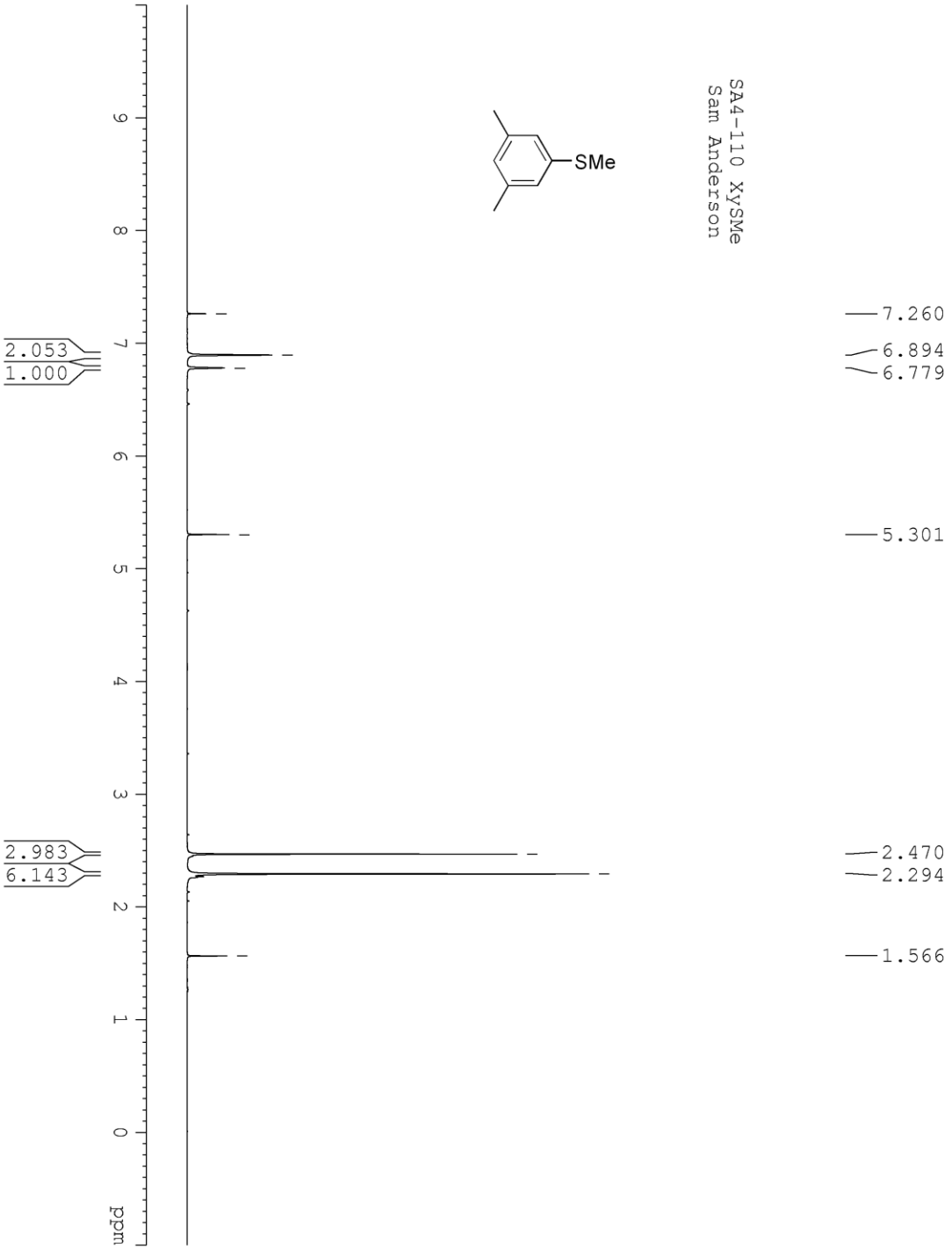
^{1}H-NMR Spectrum of Compound **(78)**



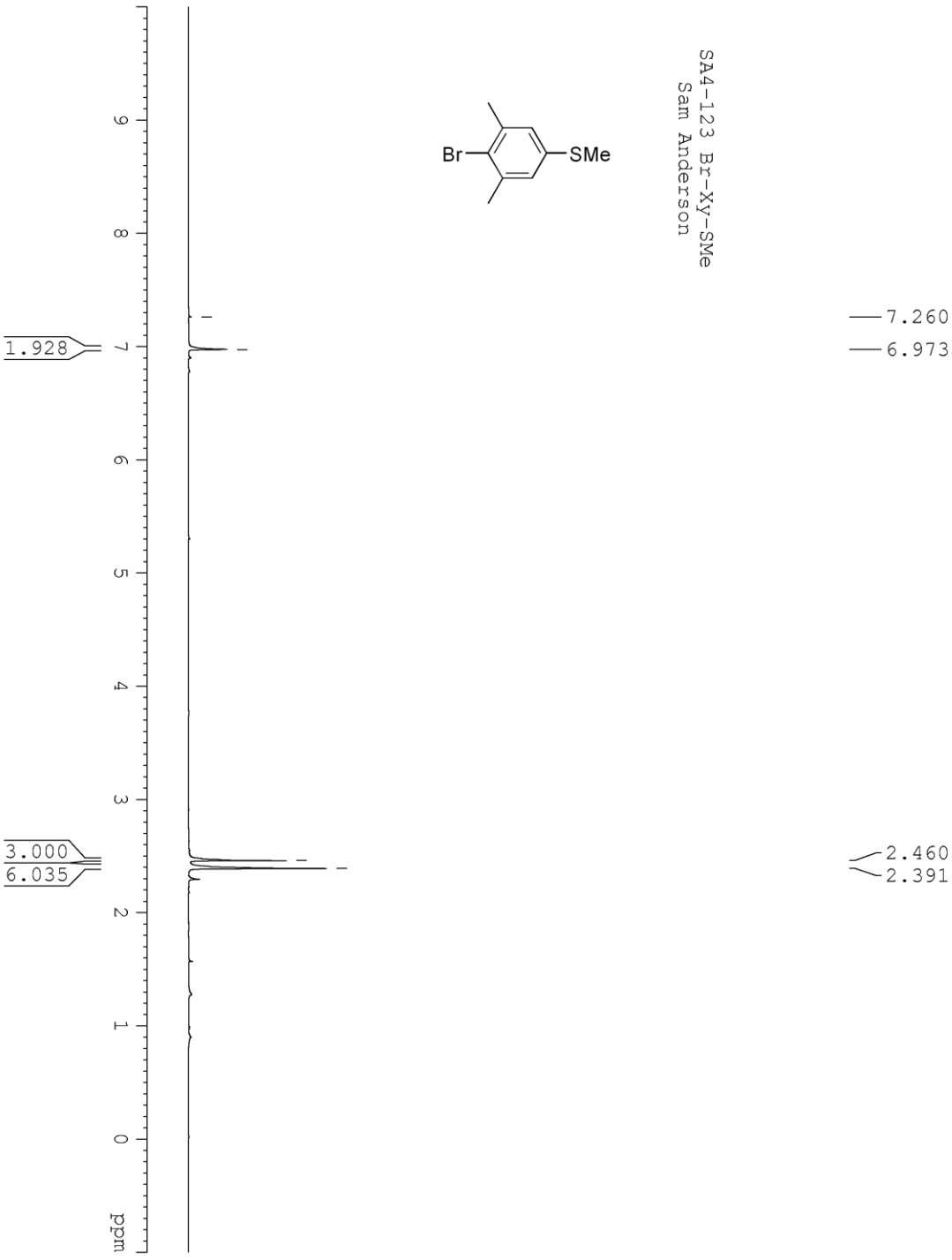
^{1}H-NMR Spectrum of Compound **(79)**



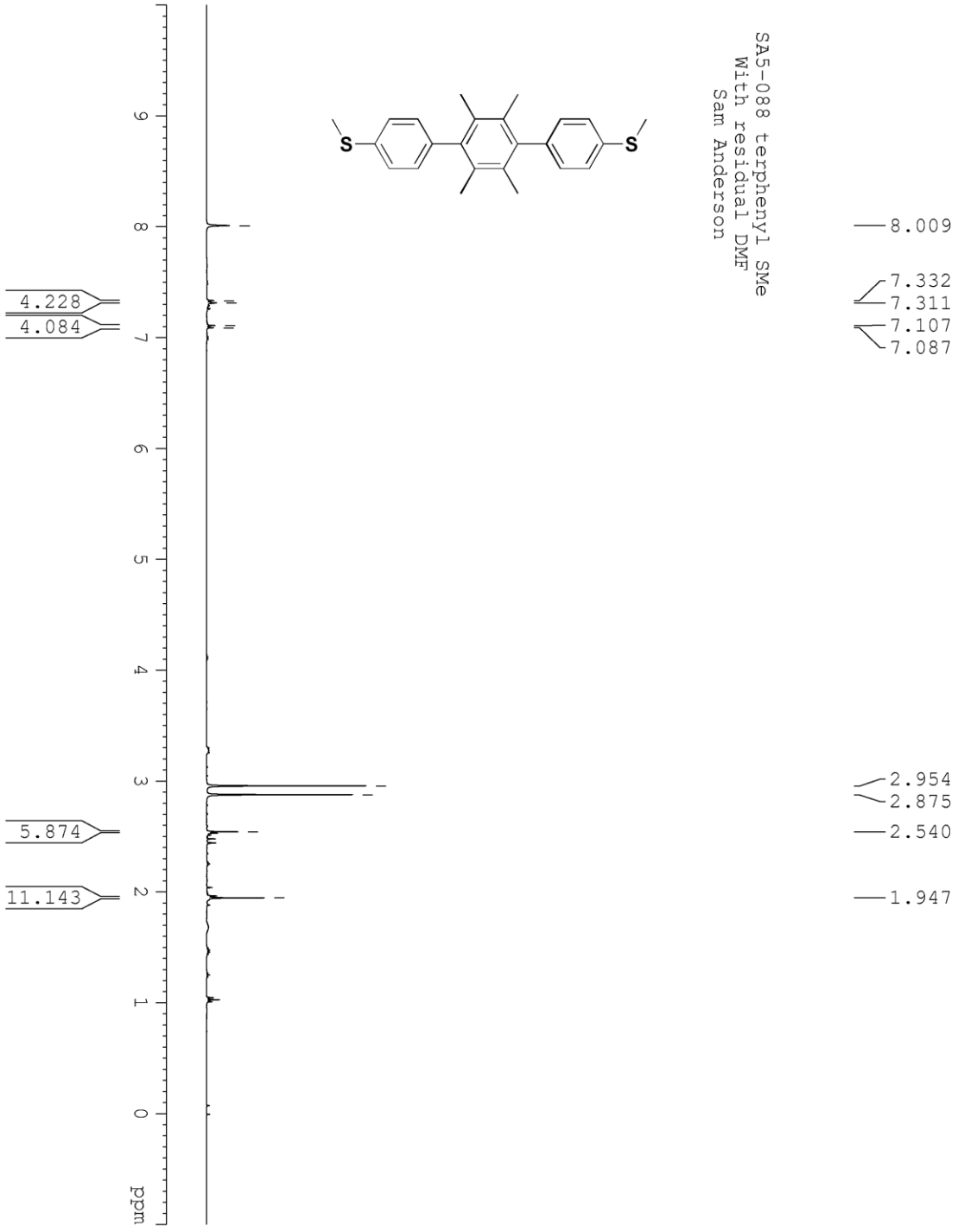
^{1}H-NMR Spectrum of Compound **(81)**



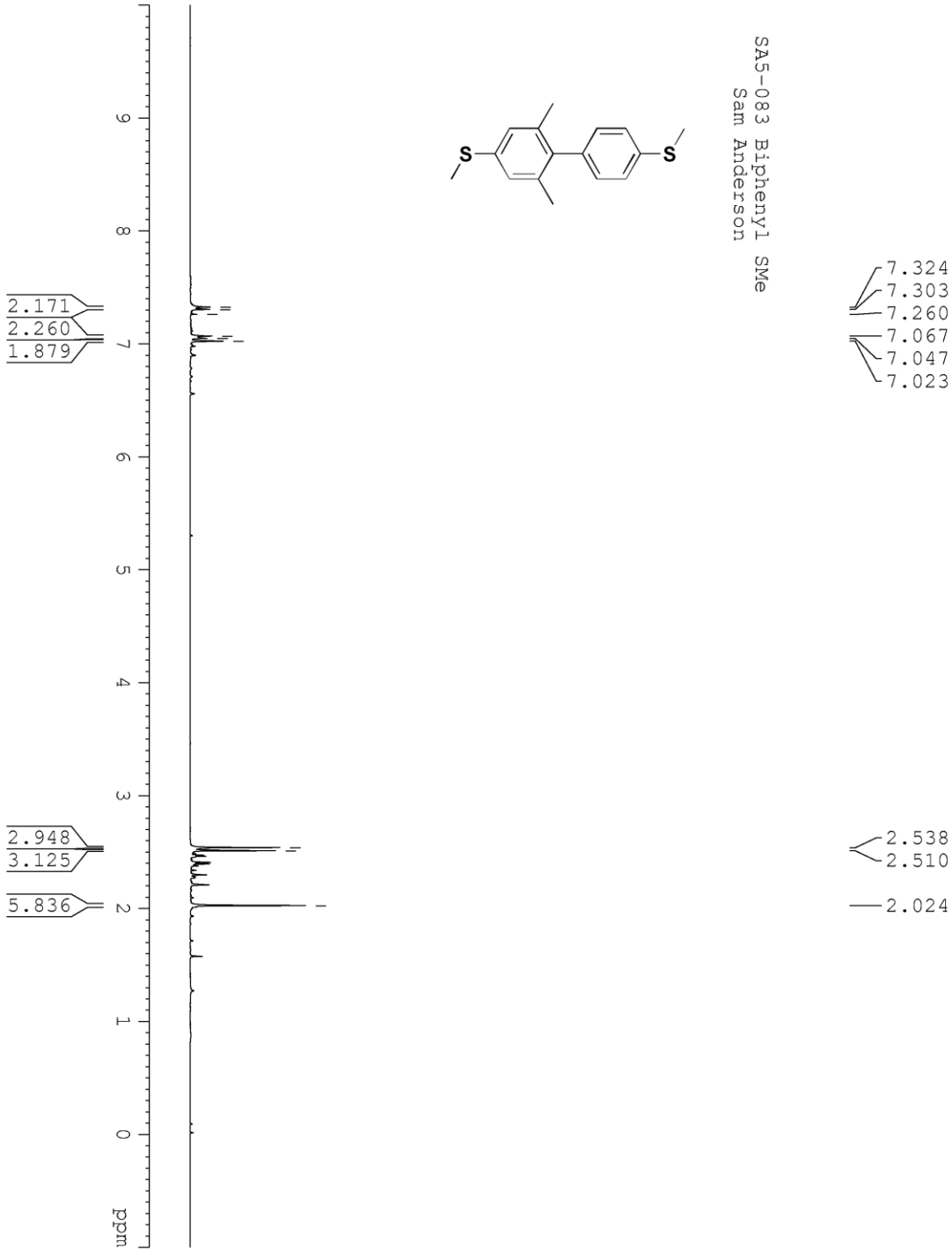
^{1}H-NMR Spectrum of Compound **(85)**



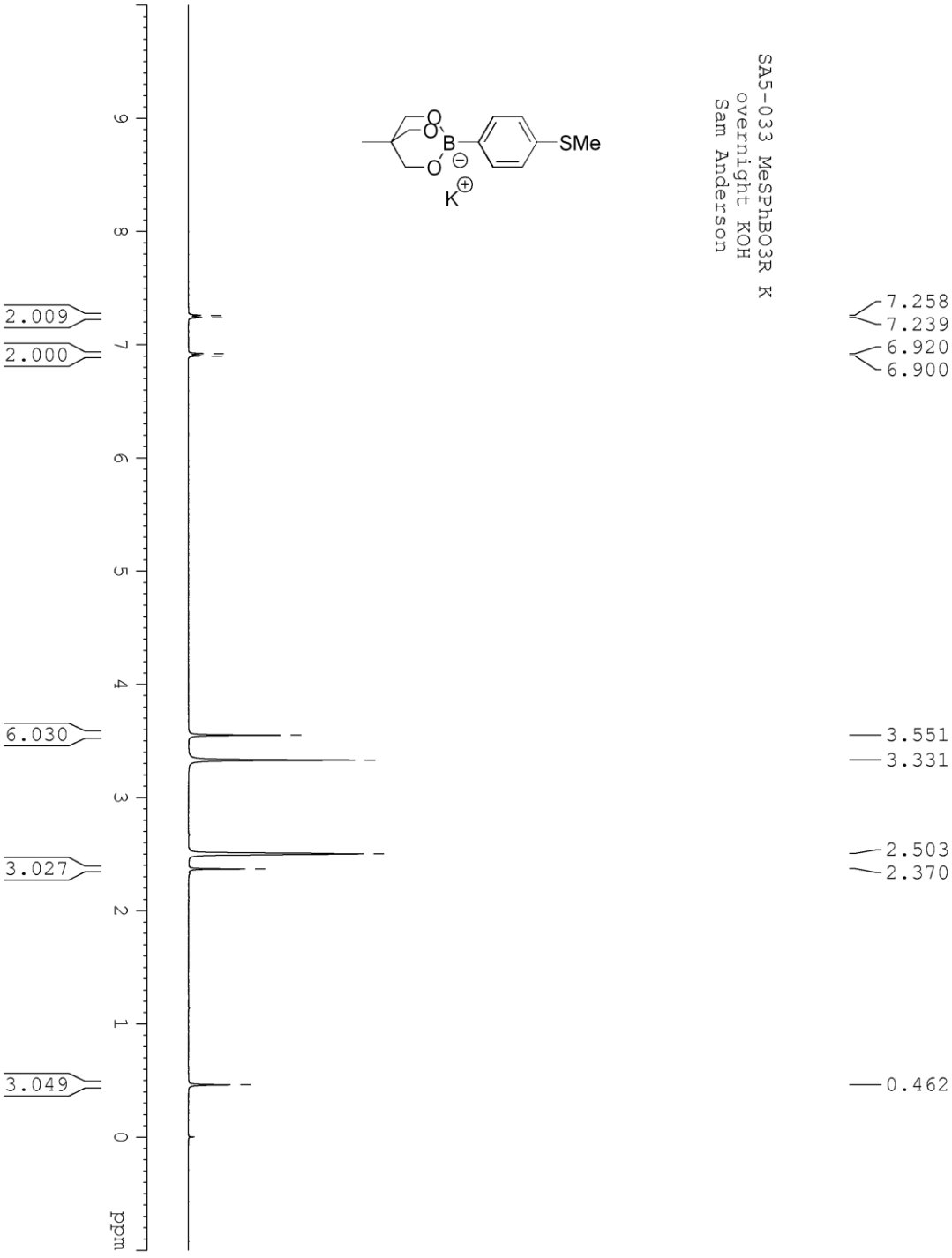
^{1}H-NMR Spectrum of Compound **(86)**



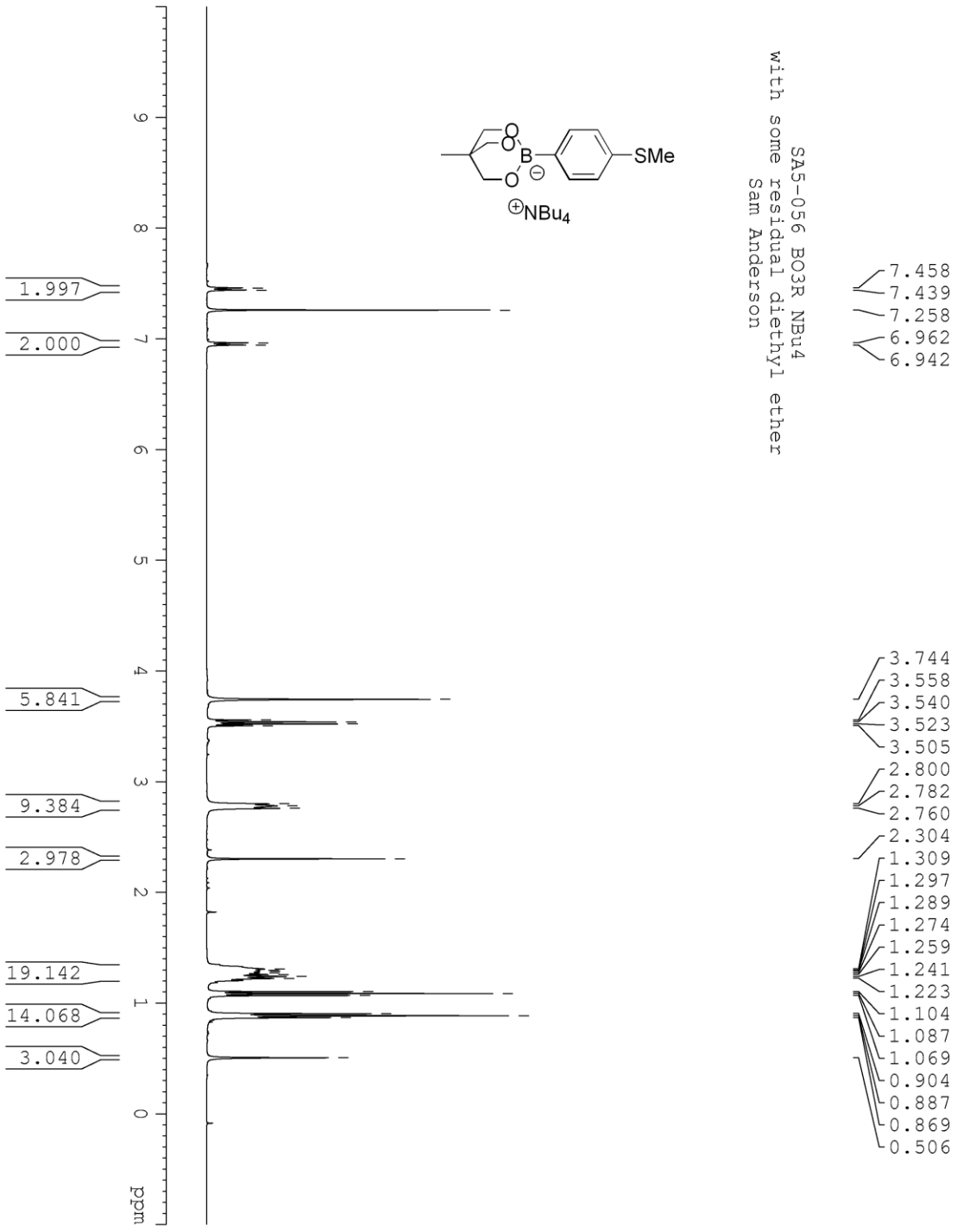
^{1}H-NMR Spectrum of Compound **(94)**



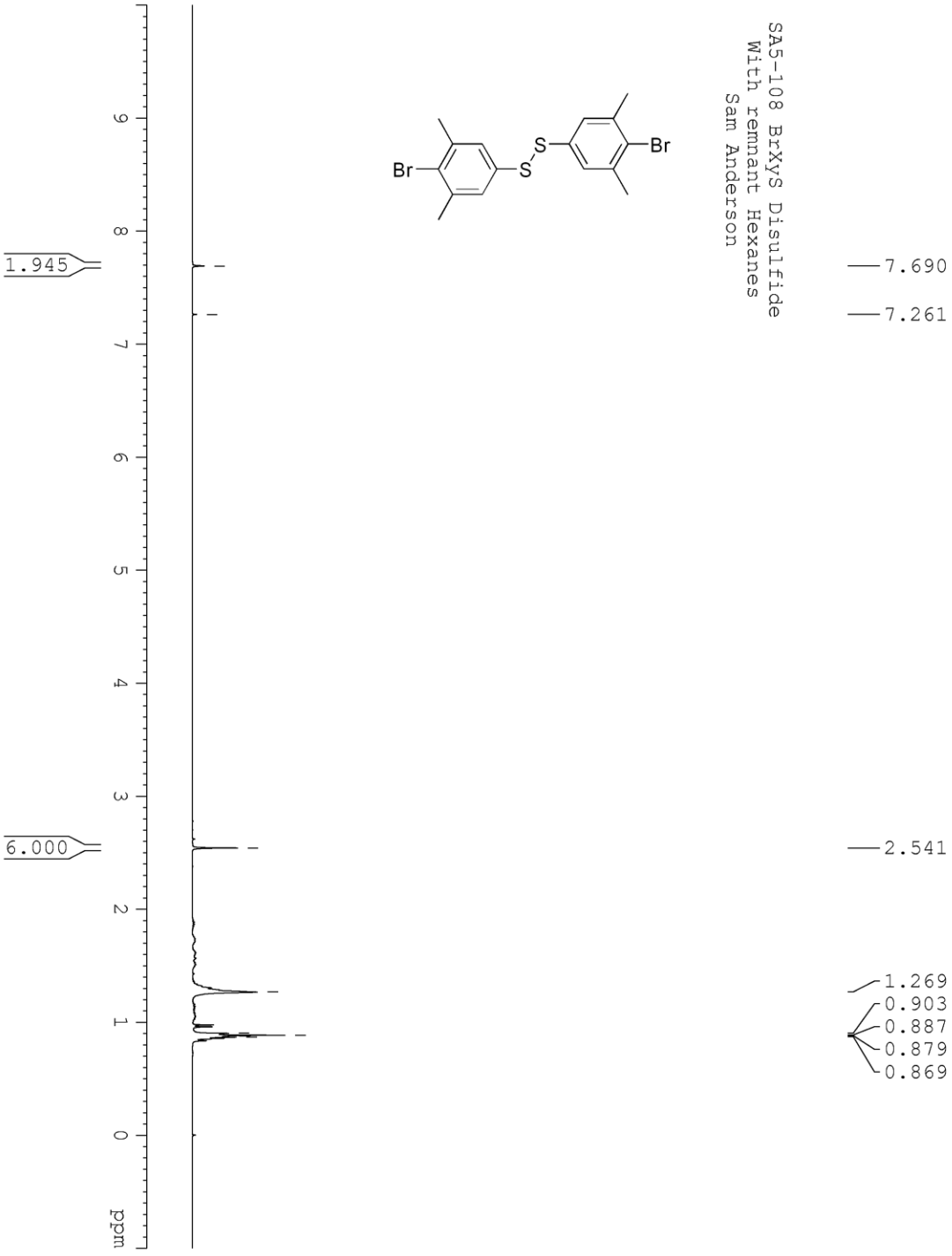
^{1}H-NMR Spectrum of Compound **(95)**



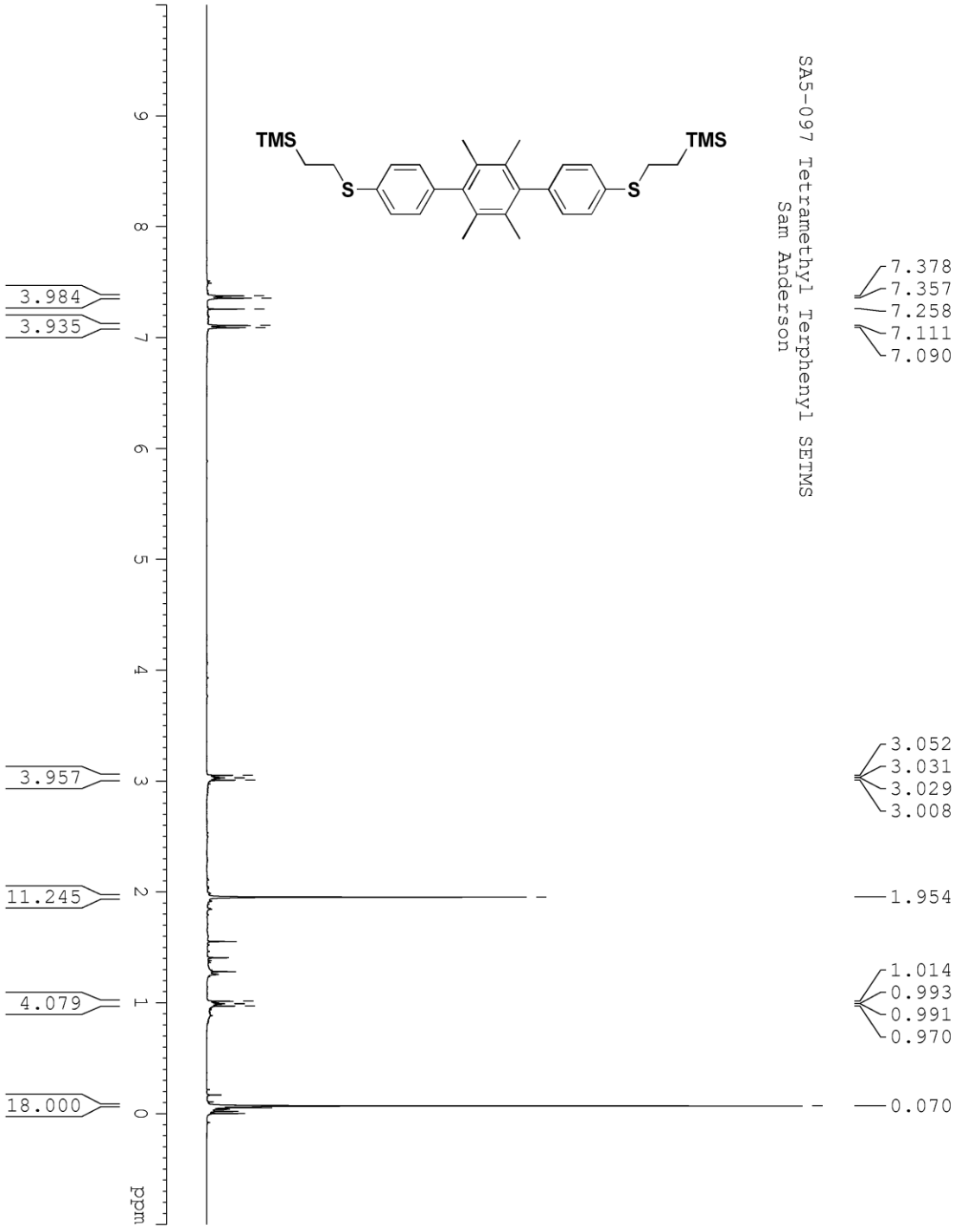
^{1}H-NMR Spectrum of Compound **(96)**



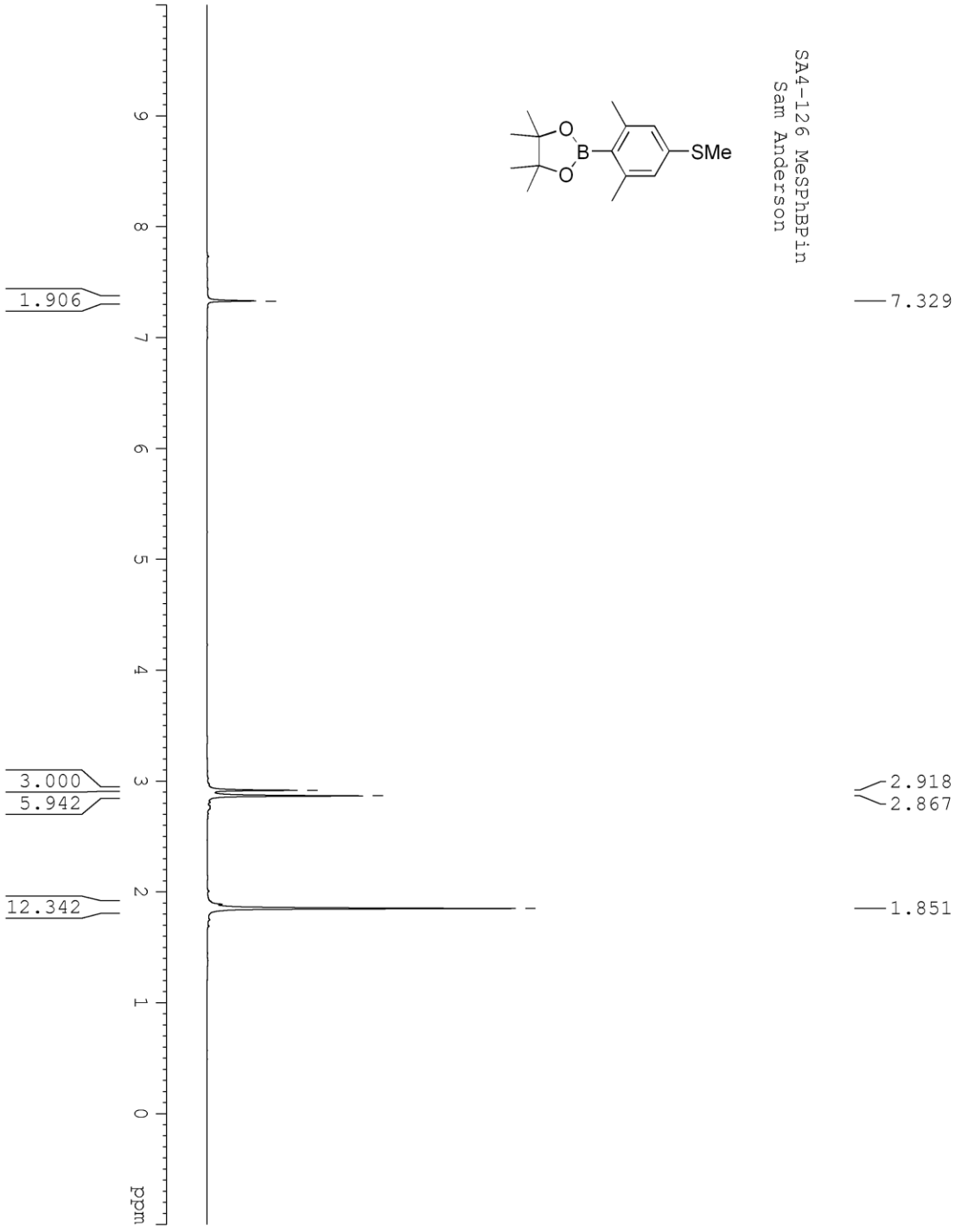
^{1}H-NMR Spectrum of Compound **(97)**



^{1}H-NMR Spectrum of Compound **(98)**



[1]H-NMR Spectrum of Compound **(101)**



[1]H-NMR Spectrum of the boronic acid pinacol ester referenced in Section 4.3

REFERENCES

(1) Tang, C. W. *Applied Physics Letters* **1986**, *48*, 183.

(2) Tang, C. W.; VanSlyke, S. A. *Applied Physics Letters* **1987**, *51*, 913.

(3) Kymissis, I.; Dimitrakopoulos, C. D.; Purushothaman, S. *IEEE Transactions on Electron Devices* **2001**, *48*, 1060.

(4) Beaujuge, P. M.; Reynolds, J. R. *Chemical reviews* **2010**, *110*, 268.

(5) Chen, C.-C.; Chang, W.-H.; Yoshimura, K.; Ohya, K.; You, J.; Gao, J.; Hong, Z.; Yang, Y. *Advanced Materials* **2014**, *26*, 5670.

(6) Uy, R. L.; Price, S. C.; You, W. *Macromolecular Rapid Communications* **2012**, *33*, 1162.

(7) Li, C.; Wonneberger, H. *Adv Mater* **2012**, *24*, 613.

(8) Bradley, D. D. C. *Journal of Physics D: Applied Physics* **1987**, *20*, 1389.

(9) Natta, G.; Mazzanti, G.; Corradini, P. *Sci. Fis., Mat. Nat., Rend* **1958**, *25*.

(10) *Organic Bulk Heterojunction Solar Cells Based on Poly (p-Phenylene-Vinylene) Derivatives*; Yumusak, C.; Egbe, D. A., Eds.; Intech: Rijeka, Croatia, 2011.

(11) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017.

(12) Schlüter, A. *Journal of Polymer Science Part A: Polymer Chemistry* **2001**, *39*, 1533.

(13) Uy, R.; Yang, L.; Zhou, H.; Price, S. C.; You, W. *Macromolecules* **2011**, *44*, 9146.

(14) Li, W.; Yan, L.; Zhou, H.; You, W. *Chemistry of Materials* **2015**, *27*, 6470.

(15) Osedach, T. P.; Andrew, T. L.; Bulovic, V. *Energy & Environmental Science* **2013**, *6*, 711.

(16) Hoth, C. N.; Choulis, S. A.; Schilinsky, P.; Brabec, C. J. *Advanced Materials* **2007**, *19*, 3973.

(17) Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganas, O.; Manca, J. V. *Nat Mater* **2009**, *8*, 904.

(18) Grzegorczyk, W. J.; Savenije, T. J.; Dykstra, T. E.; Piris, J.; Schins, J. M.; Siebbeles, L. D. A. *The Journal of Physical Chemistry C* **2010**, *114*, 5182.

(19) Mishra, A.; Bäuerle, P. *Angewandte Chemie International Edition* **2012**, *51*, 2020.

(20) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *The Journal of Organic Chemistry* **1995**, *60*, 532.

(21) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(22) Sonar, P.; Fong Lim, J. P.; Chan, K. L. *Energy & Environmental Science* **2011**, *4*, 1558.

(23) Liu, T.; Troisi, A. *Advanced Materials* **2013**, *25*, 1038.

(24) Machui, F.; Hosel, M.; Li, N.; Spyropoulos, G. D.; Ameri, T.; Sondergaard, R. R.; Jorgensen, M.; Scheel, A.; Gaiser, D.; Kreul, K.; Lenssen, D.; Legros, M.; Lemaitre, N.; Vilkman, M.; Valimaki, M.; Nordman, S.; Brabec, C. J.; Krebs, F. C. *Energy & Environmental Science* **2014**, *7*, 2792.

(25) Fang, Y.; Pandey, A. K.; Nardes, A. M.; Kopidakis, N.; Burn, P. L.; Meredith, P. *Advanced Energy Materials* **2013**, *3*, 54.

(26) Zhou, Y.; Ding, L.; Shi, K.; Dai, Y.-Z.; Ai, N.; Wang, J.; Pei, J. *Advanced Materials* **2012**, *24*, 957.

(27) Mikroyannidis, J. A.; Suresh, P.; Sharma, G. D. *Synthetic Metals* **2010**, *160*, 932.

(28) Rajaram, S.; Shivanna, R.; Kandappa, S. K.; Narayan, K. *The Journal of Physical Chemistry Letters* **2012**, *3*, 2405.

(29) Gregg, B. A. *The Journal of Physical Chemistry Letters* **2011**, *2*, 3013.

(30) Vehoff, T.; Baumeier, B.; Troisi, A.; Andrienko, D. *Journal of the American Chemical Society* **2010**, *132*, 11702.

(31) Cheung, D. L.; Troisi, A. *The Journal of Physical Chemistry C* **2010**, *114*, 20479.

(32) Wang, F.; Lu, X.; He, C. *Journal of Materials Chemistry* **2011**, *21*, 2775.

(33) Brick, C. M.; Ouchi, Y.; Chujo, Y.; Laine, R. M. *Macromolecules* **2005**, *38*, 4661.

(34) Froehlich, J. D.; Young, R.; Nakamura, T.; Ohmori, Y.; Li, S.; Mochizuki, A.; Lauters, M.; Jabbour, G. E. *Chemistry of Materials* **2007**, *19*, 4991.

(35) Huang, X.; Zhi, C.; Jiang, P.; Golberg, D.; Bando, Y.; Tanaka, T. *Advanced Functional Materials* **2012**, *23*, 1824.

(36) He; Xiao, Y.; Huang; Lin; Mya, K. Y.; Zhang *Journal of the American Chemical Society* **2004**, *126*, 7792.

(37) Cheng, G.; Hasell, T.; Trewin, A.; Adams, D. J.; Cooper, A. I. *Angewandte Chemie International Edition* **2012**, *51*, 12727.

(38) Laine, R. M.; Roll, M. F. *Macromolecules* **2011**, *44*, 1073.

(39) Kozelj, M.; Orel, B. *Dalton Transactions* **2008**, *0*, 5072.

(40) Roll, M. F.; Asuncion, M. Z.; Kampf, J.; Laine, R. M. *ACS nano* **2008**, *2*, 320.

(41) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Advanced Materials* **2011**, *23*, 268.

(42) Lee, A. S.-Y.; Chang, Y.-T.; Chu, S.-F.; Tsao, K.-W. *Tetrahedron Letters* **2006**, *47*, 7085.

(43) Bassindale, A. R.; Liu, Z.; MacKinnon, I. A.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *Dalton Transactions* **2003**, 2945.

(44) Rajasingh, P.; Cohen, R.; Shirman, E.; Shimon, L. J. W.; Rybtchinski, B. *The Journal of Organic Chemistry* **2007**, *72*, 5973.

(45) Polander, L. E.; Romanov, A. S.; Barlow, S.; Hwang, D. K.; Kippelen, B.; Timofeeva, T. V.; Marder, S. R. *Organic Letters* **2012**, *14*, 918.

(46) Harrowven, D. C.; Curran, D. P.; Kostiuk, S. L.; Wallis-Guy, I. L.; Whiting, S.; Stenning, K. J.; Tang, B.; Packard, E.; Nanson, L. *Chemical Communications* **2010**, *46*, 6335.

(47) Choi, J.; Sakong, C.; Choi, J.-H.; Yoon, C.; Kim, J. P. *Dyes and Pigments* **2011**, *90*, 82.

(48) Mikroyannidis, J. A.; Cheung, K. Y.; Fung, M. K.; Djurišić, A. B. *Reactive and Functional Polymers* **2010**, *70*, 426.

(49) Kamm, V.; Battagliarin, G.; Howard, I. A.; Pisula, W.; Mavrinskiy, A.; Li, C.; Müllen, K.; Laquai, F. *Advanced Energy Materials* **2011**, *1*, 297.

(50) Robb, M. J.; Newton, B.; Fors, B. P.; Hawker, C. J. *The Journal of Organic Chemistry* **2014**, *79*, 6360.

(51) Leclerc, M.; Najari, A.; Zou, Y. 2011; WO 2011063534 A1.

(52) Ha, J.-W.; Kim, Y.; Roh, J.; Xu, F.; Il Park, J.; Kwak, J.; Lee, C.; Hwang, D.-H. *Journal of Polymer Science Part A: Polymer Chemistry* **2014**, *52*, 3260.

(53) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *Journal of the American Chemical Society* **2003**, *125*, 11360.

(54) Koyuncu, S.; Kus, M.; Demic, S.; Kaya, İ.; Ozdemir, E.; Icli, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 1974.

(55) Viswanath, L. C. K.; Shirtcliff, L. D.; Krishnan, S.; Handa, N. V.; Berlin, K. D. *Tetrahedron Letters* **2014**, *55*, 4199.

(56) Liu, Y.; Mu, C.; Jiang, K.; Zhao, J.; Li, Y.; Zhang, L.; Li, Z.; Lai, J. Y. L.; Hu, H.; Ma, T. *Advanced Materials* **2015**, *27*, 1015.

(57) Ie, Y.; Sakurai, T.; Jinnai, S.; Karakawa, M.; Okuda, K.; Mori, S.; Aso, Y. *Chemical Communications* **2013**, *49*, 8386.

(58) Lin, Y.; Zhan, X. *Advanced Energy Materials* **2015**, *5*, 1170.

(59) Zhong, Y.; Trinh, M. T.; Chen, R.; Purdum, G. E.; Khlyabich, P. P.; Sezen, M.; Oh, S.; Zhu, H.; Fowler, B.; Zhang, B. *Nature communications* **2015**, *6*, 8242.

(60) Lin, Y.; Wang, J.; Zhang, Z. G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. *Advanced Materials* **2015**, *27*, 1170.

(61) Schilinsky, P.; Waldauf, C.; Brabec, C. J. *Applied Physics Letters* **2002**, *81*, 3885.

(62) Zhou, H.; Yang, L.; Stoneking, S.; You, W. *ACS Applied Materials & Interfaces* **2010**, *2*, 1377.

(63) Yang, L.; Tumbleston, J. R.; Zhou, H.; Ade, H.; You, W. *Energy & Environmental Science* **2013**, *6*, 316.

(64) Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. *Journal of the American Chemical Society* **2011**, *133*, 4625.

(65) Li, W.; Yang, L.; Tumbleston, J. R.; Yan, L.; Ade, H.; You, W. *Advanced Materials* **2014**, *26*, 4456.

(66) Li, W.; Albrecht, S.; Yang, L.; Roland, S.; Tumbleston, J. R.; McAfee, T.; Yan, L.; Kelly, M. A.; Ade, H.; Neher, D.; You, W. *Journal of the American Chemical Society* **2014**, *136*, 15566.

(67) Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. *Journal of the American Chemical Society* **2013**, *135*, 1806.

(68) Loren, J. C.; Krasiński, A.; Fokin, V. V.; Sharpless, K. B. *Synlett* **2005**, *2005*, 2847.

(69) Uy, R. L.; Yan, L.; Li, W.; You, W. *Macromolecules* **2014**, *47*, 2289.

(70) Buschmann, H.; Scharl, H.-D. *Synthesis* **1988**, *1988*, 827.

(71) SMITH, P. A.; CLEGG, J. M.; LAKRITZ, J. *The Journal of Organic Chemistry* **1958**, *23*, 1595.

(72) Baskin, J. M.; Prescher, J. A.; Laughlin, S. T.; Agard, N. J.; Chang, P. V.; Miller, I. A.; Lo, A.; Codelli, J. A.; Bertozzi, C. R. *Proceedings of the National Academy of Sciences* **2007**, *104*, 16793.

(73) Dhanak, D.; Reese, C. B. *Journal of the Chemical Society, Perkin Transactions 1* **1986**, 2181.

(74) Wang, X.-j.; Zhang, L.; Krishnamurthy, D.; Senanayake, C. H.; Wipf, P. *Organic Letters* **2010**, *12*, 4632.

(75) Iddon, B.; Nicholas, M. *Journal of the Chemical Society, Perkin Transactions 1* **1996**, 1341.

(76) Niskala, J. R.; You, W. *Journal of the American Chemical Society* **2009**, *131*, 13202.

(77) Martin, F.; Hendriksen, B. L.; Katan, A. J.; Qi, Y.; Mauldin, C.; Fréchet, J. M.; Salmeron, M. *Langmuir* **2013**, *29*, 1206.

(78) Haick, H.; Ambrico, M.; Ghabboun, J.; Ligonzo, T.; Cahen, D. *Physical Chemistry Chemical Physics* **2004**, *6*, 4538.

(79) Fisher, G. L.; Walker, A. V.; Hooper, A. E.; Tighe, T. B.; Bahnck, K. B.; Skriba, H. T.; Reinard, M. D.; Haynie, B. C.; Opila, R. L.; Winograd, N.; Allara, D. L. *Journal of the American Chemical Society* **2002**, *124*, 5528.

(80) Seo, S.; Min, M.; Lee, J.; Lee, T.; Choi, S.-Y.; Lee, H. *Angewandte Chemie International Edition* **2012**, *51*, 108.

(81) Holmlin, R. E.; Haag, R.; Chabinyc, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. *Journal of the American Chemical Society* **2001**, *123*, 5075.

(82) Dediu, V. A.; Hueso, L. E.; Bergenti, I.; Taliani, C. *Nat Mater* **2009**, *8*, 707.

(83) Morales, G. M.; Jiang, P.; Yuan, S.; Lee, Y.; Sanchez, A.; You, W.; Yu, L. *Journal of the American Chemical Society* **2005**, *127*, 10456.

(84) Locklin, J.; Li, D.; Mannsfeld, S. C.; Borkent, E.-J.; Meng, H.; Advincula, R.; Bao, Z. *Chemistry of Materials* **2005**, *17*, 3366.

(85) De Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. *Langmuir* **2003**, *19*, 4272.

(86) Percec, S.; Getty, R.; Marshall, W.; Skidd, G.; French, R. *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, *42*, 541.

(87) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *Journal of the American Chemical Society* **2011**, *133*, 8354.

(88) Su, T. A.; Widawsky, J. R.; Li, H.; Klausen, R. S.; Leighton, J. L.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. *Journal of the American Chemical Society* **2013**, *135*, 18331.

(89) Kaur, I.; Jazdzyk, M.; Stein, N. N.; Prusevich, P.; Miller, G. P. *Journal of the American Chemical Society* **2010**, *132*, 1261.

(90) Miyaura, N.; Suzuki, A. *Chemical reviews* **1995**, *95*, 2457.

(91) Tu, T.; Sun, Z.; Fang, W.; Xu, M.; Zhou, Y. *Organic Letters* **2012**, *14*, 4250.

(92) Zhong, R.; Pöthig, A.; Feng, Y.; Riener, K.; Herrmann, W. A.; Kühn, F. E. *Green Chemistry* **2014**, *16*, 4955.

(93) Thomas, A. A.; Denmark, S. E. *Science* **2016**, *352*, 329.

(94) Li, G.-Q.; Yamamoto, Y.; Miyaura, N. *Synlett* **2011**, *2011*, 1769.

(95) Murphy, J. M.; Tzschucke, C. C.; Hartwig, J. F. *Organic Letters* **2007**, *9*, 757.

(96) Diemer, V.; Chaumeil, H.; Defoin, A.; Carré, C. *Tetrahedron* **2010**, *66*, 918.

(97) Singh, G. *Chemistry of Terpenoids and Carotenoids Vol 3*, Discovery Publishing House, 2007.

(98) Testa, B. In *Stereochemistry*; Tamm, C., Ed.; Elsevier Biomedical Press: New York, 1982; Vol. 3.

(99) Saikia, B.; Boruah, P. R.; Ali, A. A.; Sarma, D. *Tetrahedron Letters* **2015**, *56*, 633.

(100) Wallow, T. I.; Novak, B. M. *The Journal of Organic Chemistry* **1994**, *59*, 5034.

(101) Migliorini, A.; Oliviero, C.; Gasperi, T.; Loreto, M. A. *Molecules* **2012**, *17*, 4508.

(102) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angewandte Chemie International Edition* **2008**, *47*, 928.

(103) Sakashita, S.; Takizawa, M.; Sugai, J.; Ito, H.; Yamamoto, Y. *Organic Letters* **2013**, *15*, 4308.

(104) Bos, M. E. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd: 2001.

(105) Pinho, S. P.; Macedo, E. A. *Journal of Chemical & Engineering Data* **2005**, *50*, 29.

(106) Suzuki, A.; Hara, S.; Huang, X. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd: 2001.

(107) Wuts, P. G. M.; Greene, T. W. In *Greene's Protective Groups in Organic Synthesis*; John Wiley & Sons, Inc.: 2006, p 647.

(108) Yang, X.; Liu, D.; Miao, Q. *Angewandte Chemie International Edition* **2014**, *53*, 6786.

(109) Foucoin, F., Caupène, C., Lohier, J.F., de Oliveira Santos, J.S., Perrio, S., Metzneraa, P. *Synthesis* **2007**, *9*, 1315.