Novel Synthetic Approaches Toward Polymeric Acenes and Investigations in the Diels-Alder Reaction of Halogenated Cumulenes

A Thesis Presented

by

Audra Michelle Selvaggio

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Abstract of the Thesis

Novel Synthetic Approaches Toward Polymeric Acenes and Investigations in the Diels-Alder Reaction of Halogenated Cumulenes

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Acenes, polycyclic aromatic hydrocarbons composed of benzene rings fused in a linear arrangement, are of great interest both theoretically and experimentally due to their electronic properties. However, synthesis and characterization of extended acenes are difficult due to their high reactivity. The synthesis of a polymeric acene has not been achieved, and heptacene is the longest known unsubstituted homologue. The research presented in this thesis describes two design strategies and syntheses towards a polymeric acene.

Haloenyne precursor, (*Z*)-2-bromo-1,4-diphenyl-1-buten-3-yne was synthesized for solution-phase head-to-tail coupling intended for tandem ring closures. The regioregular head-to-tail coupling of monomer was not achieved. Problems with the initial design of the polyacetylene intermediate became apparent from semi-empirical PM3 calculations of small oligomeric analogues, requiring alteration of the approach. The modification in design now relies on a heterometalated five-membered ring intermediate. Work is currently underway towards the synthesis of these precursors to carry out the new proposed route of producing polyacenes.

This thesis also describes the repeated synthesis of perhalocumulene $C_4Br_2I_{2,}$ as well as its subsequent use for studying its reactivity in the Diels-Alder reaction with furan. The central cumulenic bond of $C_4Br_2I_2$ acts as the dienophile, providing a variety of possible stereoisomers as adducts. Efforts toward characterizing the products formed are currently in progress.

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B3LYP	Becke 3-parameter Lee, Yang and Parr, functional
DCE	Dichloroethane
DCM	Dichloromethane
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
DPPE	1,2-Bis(diphenylphosphino)ethane
DPPP	1,2-Bis(diphenylphosphino)propane
EI	Electron ionization
Et	Ethyl
FAB	Fast atom bombardment
FC	Ferrocenyl
FET	Field effect transistor
GC	Gas chromatography
GC-MS	Gas chromatograpy Mass spectrometry
H-H	Head-head
HOMO	Highest occupied molecular orbital
HT	Head-tail
IR	Infrared spectroscopy
ITO	Indium-doped tin oxide
LC	Liquid chromatography
LDA	Lithium diisopropylamide
LED	Light-emitting diode

LUMO	Lowest unoccupied molecular orbital
Me	Methyl
NBS	N-bromo succinimide
NIS	N-iodo succinimide
NICS	Nucleus independent chemical shift
NMR	Nuclear magnetic resonance
OFET	Organic field effect transistor
OLED	Organic light-emitting diode
PAH	Polycyclic aromatic hydrocarbon
Ph	Phenyl
PMA	Phosphomolybdic acid
PM3	Parameterized Model number 3
$\mathbf{R_f}$	Retention factor
TBACl	Tetrabutylammonium chloride
TBAI	Tetrabutylammonium iodide
TFT	Thin film transistors
THF	Tetrahydrofuran
TLC	Thin-layer chromatography
TMEDA	Tetramethylethylenediamine
TMS	Tetramethylsilane
TT	Tail-tail
UV	Ultra violet
UV/Vis	Ultra violet/visible

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God for his divine grace and inspiration. He is the chemistry of life.

Chapter I

INTRODUCTION

I.1 Introduction: Conjugated Materials

Historically, the vanguard of modern organic chemistry is driven by the very reactive nature of pi-electrons; π-bonds have been an essential means to many monumental synthetic achievements. Organic compounds possessing a high degree of conjugation have particularly grown in importance. At the molecular level, π-conjugated compounds have been proven to exhibit properties that are characteristic of materials intended for optoelectronic applications in microelectronic systems. Organic π-conjugated compounds have many other interesting functions, including uses in organic light emitting diodes,[1] field effect transistors,[2] full color large-area displays,[3,4] and molecular switches,[5] in addition to uses as building blocks toward supramolecular systems such as nanotubes and fullerenes.[6]

Highly ordered conductive materials have the ability to become increasingly conductive when an electron is either removed from the valence band (p-doping), or added to the conduction band (n-doping). Such doping generates charge carriers that move under the influence of an electric field, producing electrical conductivity. The 1976 discovery of polyacetylene $(CH)_x$ oxidation using iodine sparked significant interest in conjugated polymers because its conductivity approaches that of metals.[7] This innovative work served as the impetus for the synthesis of many novel conjugated polymers that have been studied for their physical properties and potential semi-conducting abilities. Pyrrole[8,9], aniline[10,11], thiophene[12,13], and benzene[14] were the basic aromatic precursors employed to synthesize other oxidatively doped π-conjugated polymers; by varying substituents and substitution patterns, a vast library of conjugated polymers was created.

Organic molecular-based electronic devices have greatly increased in importance and have significantly advanced in performance over the past two decades. From a field of great promise emerged new semiconductive materials with applications that have successfully been integrated into industry and used in commercial products available to the public.[15] Although much progress has more recently been made in the development of organic electronics that utilize the broad range of electronic, optoelectronic, and photonic properties of organic conjugated polymer semiconductors, organic materials must evolve to have better processability and inexpensive production processes. Increasing the range of electronic and optical properties is also integral to the progress of this field.

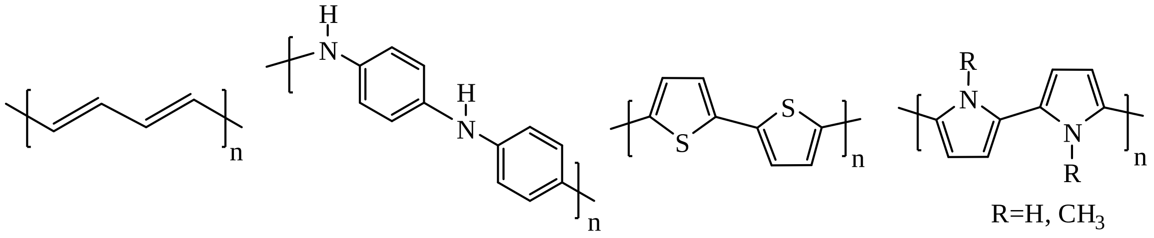


Figure I.1 Conjugated polymer segments.

The attractive optical and physical properties of conjugated molecules (Figure I.2) and conjugated polymers are strongly associated with the degree of delocalization. Extensive π-electron delocalization results in a low energy band gap.[16] The HOMO-LUMO energy gap transition between π and π^* in conjugated polymers is finite (Figure I.3).

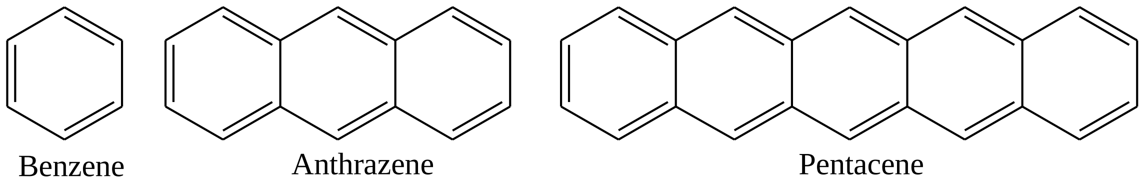


Figure I.2 Increasing delocalization in extended acenes leads to organic semiconducting properties.

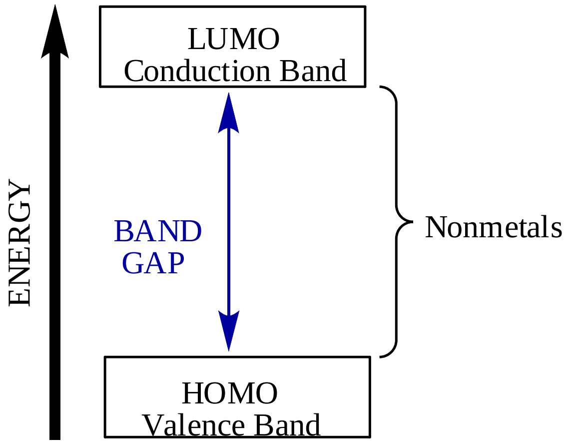


Figure I.3 Band gap transition between π and π*.

Design, synthesis, characterization, and computational studies of conjugated polymers further improve our understanding of their structural and electronic properties, which further facilitate the integration of conjugated polymers in advanced electronic and optical devices. There is a multitude of progress in the study of conjugated polymers; however, developments for solution-phase polymerization toward conjugated polymer semiconductors with high charge carrier mobilities should be extended. In the research described in this thesis, the syntheses of conjugated systems, namely polyacenes and cumulenic compounds, were pursued.

I.2 Polyacenes

I.2.1 Background

Acenes are discrete polycyclic aromatic hydrocarbons composed of benzene rings fused in a linear array. They can be considered as one-dimensional analogs of graphite, much like taking a strand from a single sheet of graphene, and can also be viewed as a combination of two parallel chains of *trans* $(CH)_x$ units connected together (Figure I.4). Due to their electronic properties, acenes are of great interest, both theoretically and experimentally.[6,17] Despite considerable interest, synthesis and characterization of extended acenes is difficult due to their high reactivity.[18,19] The synthesis of a polymeric acene has not been achieved; heptacene is the longest known unsubstituted homologue.[20,21] In this chapter we will review the syntheses and properties of known discrete acenes for preliminary insight to the unknown polymeric form.

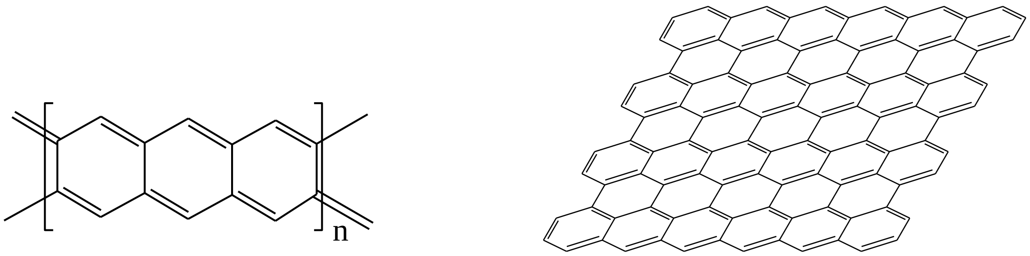
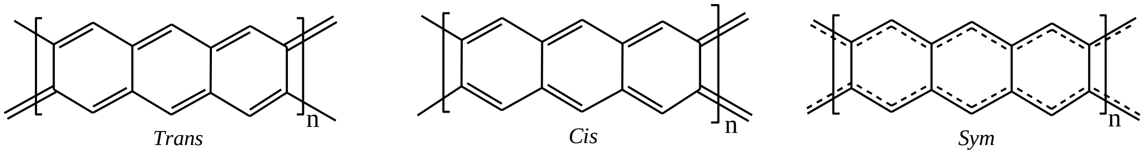


Figure I.4 A polyacene can be thought of as a single strand from graphene.

The electronic properties of polyacenes, including electronic structure, stability, and aromaticity, have been widely examined by theoretical studies.[6,17,22] Polyacenes can adopt three different types of geometries and electronic structures: *cis*, *trans*, or symmetrical (Figure I.5). Valence-bond calculations show all three structures to be close in energy, with the symmetrical structure having the lowest energy.[23]



Trans *Cis* *Sym*

Figure I.5 Electronic structures of polyacenes.

Low band gaps have been predicted for polyacenes,[24] suggesting they may be used as semiconductors, as first proposed by Kertesz and Hoffmann[25] and by Chapman and Kivelson.[26] Polyacenes potentially could serve as one-dimensional organic conductors having vanishing band gaps.[24]

A linear polyacene can also be viewed as consisting of two parallel polyacetylene chains, where both of their HOMO-LUMO gaps decrease gradually with increasing chain length (Figure I.6). The ground state of a chain containing equal bond lengths is generally unstable due to Peierls distortion.[27] Therefore, π-conjugated polyacetylenes conform to alternating bond lengths.[27] Yet, in polyacenes, the two polyacetylene ribbons are predicted to have nonalternating bonds. Ultimately, this results in different conducting properties of polyacetylenes and polyacenes, having calculated band gaps of 1.4 eV and 0 eV, respectively.[24]

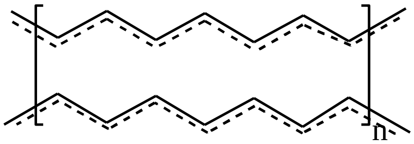


Figure I.6 Two polyacetylene chains brought together by sp^2–sp^2 single bonds resemble polyacenes.

I.2.2 Oligoacenes

Larger oligoacenes, starting with octacene, are predicted to have an open-shell singlet ground state, with a higher energy triplet state.[28] This open-shell configuration coincides with the extreme reactivity of the acene series, which increases as a function of the number of benzenoid units in the molecule. Therefore, longer acenes require the use of steric protection for bulk stability.[29]

Aromaticity is the resultant of a competition between the π-electron confinement within the rings and delocalization along the chain. Using nucleus independent chemical shift (NICS) as a measure of local aromaticity, Schleyer *et al.* found large negative values resulting in the center of the inner rings with the progression of the acene chain, and attributed these NICS values to the inner rings having more aromatic character than the outer rings.[30] However, these high NICS values are an artifact, resulting from the fact that the HOMO and LUMO orbitals have largest densities at the central rings. The inner rings of extended acenes are, in fact, highly reactive.[18,31] Aihara et al. pointed out that the successive reduction in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with increasing acene length, reflects a reduction in aromaticity.[32]

In comparison to heptacene and smaller homologues, larger acenes, namely hexacene and heptacene, show lower band gaps (ΔE) and are predicted to have superior electronic properties.[24] However, due to the instability of higher acenes, complete characterization has not been attainable. In Chapter II, exploration of methods to prepare polyacenes will be discussed.

I.2.3 Synthetic Background and Applications of Acenes

There has been a long standing interest in extended acenes mostly as materials intended for optoelectronic applications such as light emitting diodes (LEDs, Figure I.7) and field effect transistors (FETs, Figure I.8), as well as building blocks toward supramolecular systems such as nanotubes and fullerenes.[6] There are two ways of using the charge transport properties of organic semiconducting material in FETs: a bottom-contact device has the source and drain electrodes directly underneath the organic semiconductor, while a top-contact device has the source and drain electrodes on top of the molecule (Figure I.8). Although the bottom- contact arrangement is more convenient for the construction of semiconductor devices in solution, the top-contact arrangement typically generates devices with higher performance.[2]

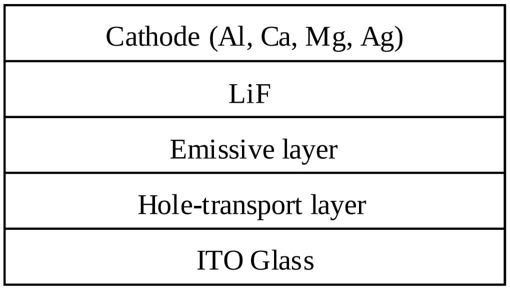


Figure I.7 Schematic of an OLED.

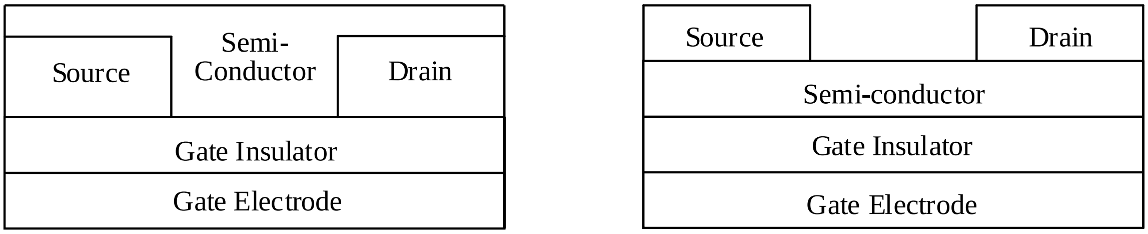
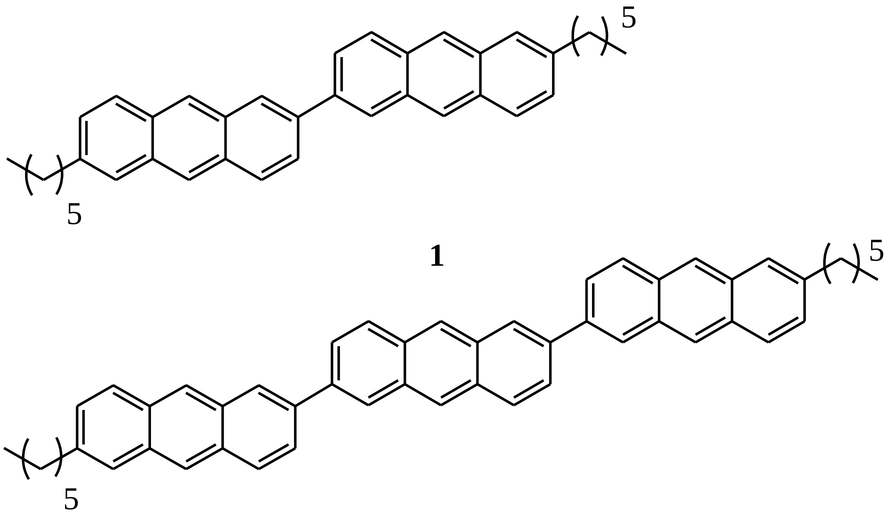


Figure I.8 OTFT Schematic: bottom-contact and top-contact devices, respectively.

In transistors, most synthetic efforts are focused on tuning the energy level of the HOMO and thus the oxidation potential for the organic material, which results in better interactions with the electrode. As for LEDs, they are most frequently made on a glass substrate which is coated with a transparent conductor (most often indium-doped tin oxide, ITO) capped by a hole transport layer that is intended to facilitate the oxidation of the electroluminescent molecule in the emissive layer (Figure I.7.). A less than 1 nm thick LiF layer serves as an electron transport layer to deliver the electrons to the cathode. Aromatic compounds, and more especially, are used as predominantly hole transport carriers.[2]

The high oxidation potential (1.9 eV)[33] and photoluminescence quantum yields of anthracene allow for its use as a semi-conducting material. With the functionalization of anthracene, its applications have surpassed use in light-emitting systems, and its derivatives are currently further incorporated in materials used for FETs. For example, a series of dimers and trimers of covalently linked anthracene units were investigated by Tokito and co-workers (Figure I.9). As the area of intermolecular overlap increases by extending the system, it was found to decrease the oxidation potential as well.[34]

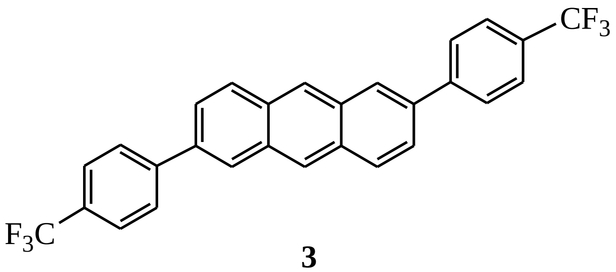


1

2

Figure I.9 Anthracene dimers and trimers.[34]

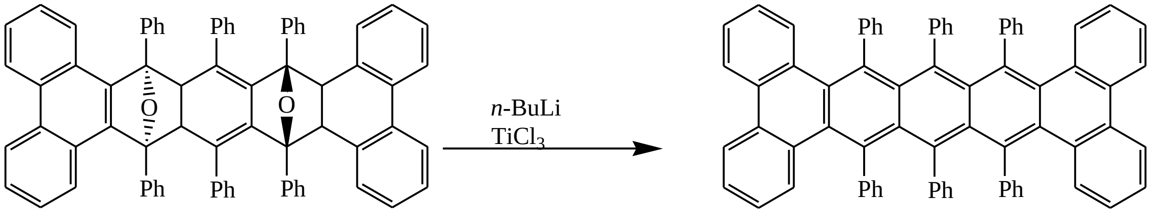
Another series of anthracene derivatives, such as compound **3**, were synthesized and studied by Yamashita and co-workers (Figure I.10).[35] When the parent material was compared with substituted anthracenes, no profound effects on the electronic properties were observed. Electron mobilities were measured at ranges of only 0.004 to 0.003 $cm^2/(V\ s)$.[36] Although transport mobilities are not high, these types of organic semiconductors are more stable than their longer counterparts (homologues), making anthracenes suitable for fabricating durable organic devices with a long life span.



3

Figure I.10 Yamashita and co-workers' reported 2,6 diarylanthracene.[35]

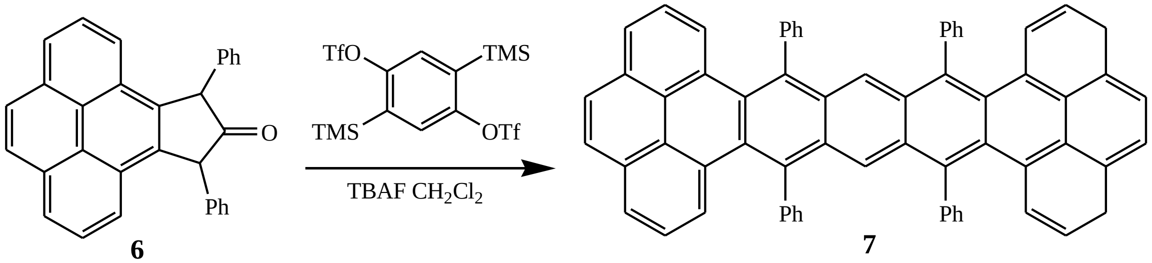
Pascal and co-workers accomplished the synthesis of a highly twisted polycyclic aromatic hydrocarbon (**5**), which shows an end-to-end twist of 144° that is evenly distributed among the central pentacene unit (Scheme I.1).[20]



4 **5**

Scheme I.1 Synthesis of a highly twisted pentacene homologue (**5**).

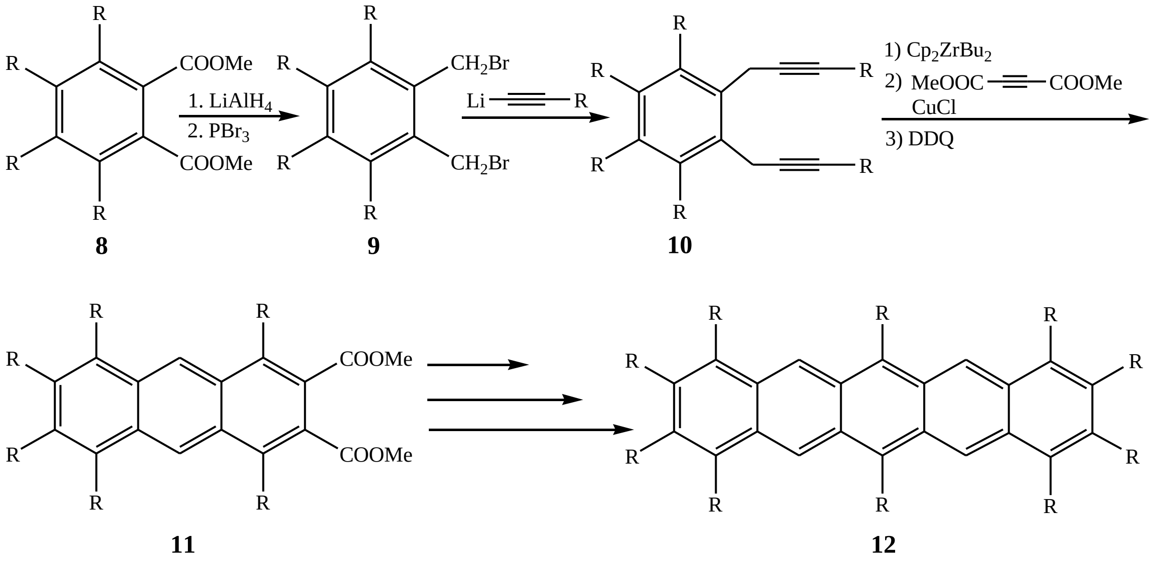
Wudl et al. achieved the synthesis of a heptacene analog (**7**) via Diels-Alder cyclization followed by evolution of one mole of CO_2 (Scheme I.2). The central anthracene unit in compounds **5** and **7** is functionalized with bulky phenyl groups, which protect the molecule from O_2 addition, while inducing a twist in the center of the molecule. The pyrene units that cap the core anthracene at each end in compound **7**, produce better fluorescence quantum yields in this material. Since the π-system remains conjugated, and electronic properties differ only slightly from its planar analogue,[21] this 'twistacene" possesses potential applications in OLEDs.



Scheme I.2 Synthesis of heptacene homologue **7** by Wudl et al.[21]

The physical and electronic properties that tetracene exhibits illustrate the tradeoff between device performance and material stability. When compared to anthracene, an additional fused ring heightens the instability of the organic semiconductor. Tetracene decomposes when exposed to light and air; however, the decomposition rate is significantly slower than that of pentacene. With electron mobilities reaching as high as 1.3 $cm^2/(V\ s)$ for single-crystal devices,[37] tetracene has been used in the fabrication of high performance FETs. Solar cells with a power conversion efficiency rate of 2.3% were generated using tetracene along with a C_{60} moiety.[38]

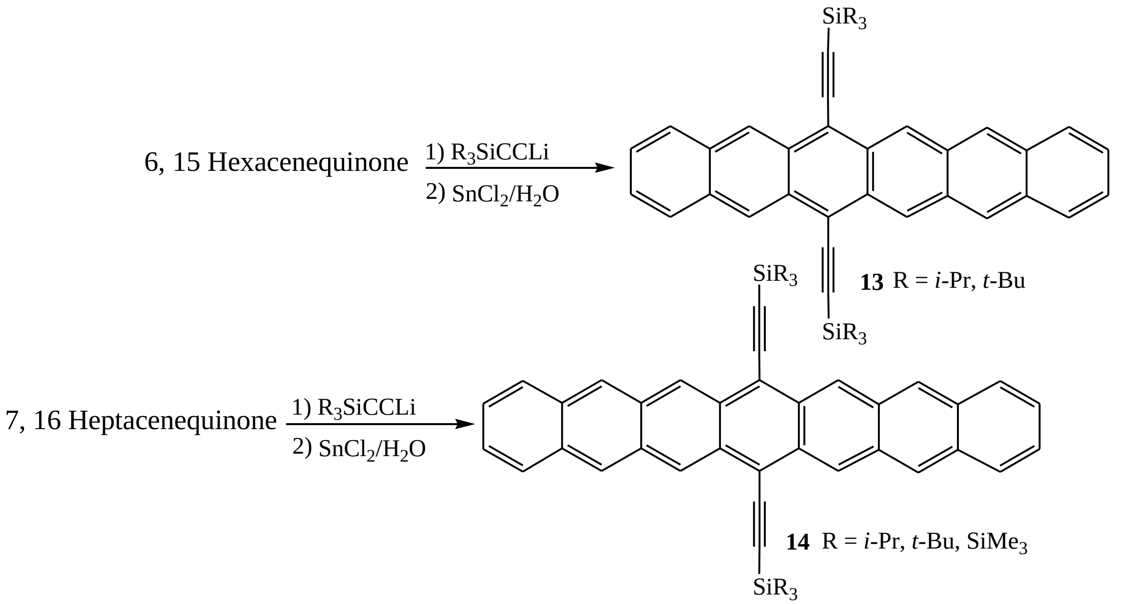
The synthesis of pentacene and its derivatives has been achieved through several different synthetic methods. The synthesis shown in scheme I.3 involves a series of steps that extends the linearly fused benzene chain by a single benzene unit with each repetition of the successive steps.[39]



Scheme I.3 One example of a pentacene synthesis.[39]

Pentacene's high charge-carrier mobility has led to its use as an active semi-conducting material in TFTs. It has also been incorporated into several types of organic electronic devices, for example, the use of organic photodiodes in solar cells.[40] FETs derived from pentacene semiconductors allow mobilities greater than 1.5 $cm^2/(V\ s)$[41] and as high as 5 $cm^2/(V\ s)$.[42] In addition to having high charge carrier mobilities, pentacenes, like tetracenes, have high photoluminescence quantum yields, which allows their versatile application in OLEDs and OFETs.

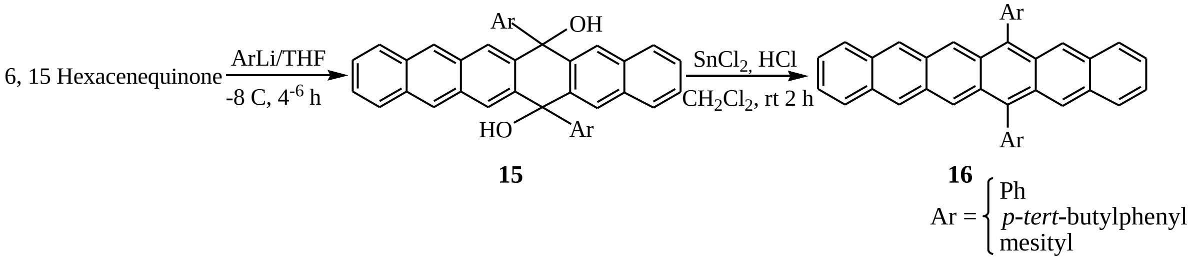
The work of Anthony et. al. has yielded functionalized higher acenes including hexacene (**13**) and heptacene (**14**) (Scheme I.4). Anthony's silylethynylation methods resulted in improved solubility and stability, and enhanced the crystalline ordering in the solid state.[31] Other hexacene derivatives with aryl substituents have been synthesized by similar methods,[43] as shown in Scheme I.5.



13 R = *i*-Pr, *t*-Bu

14 R = *i*-Pr, *t*-Bu, SiMe$_3$

Scheme I.4 Silyl protected hexacene and heptacene.[31]



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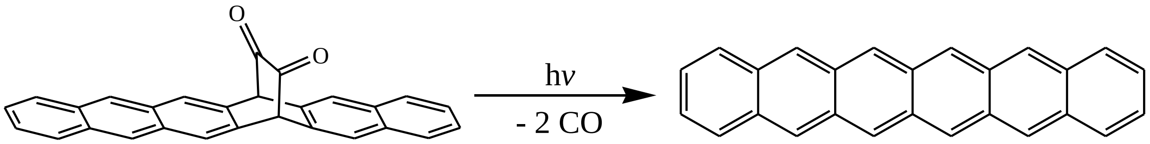
Scheme I.5 Synthesis of hexacene derivatives.[43]

Other syntheses of unsubstituted higher acenes, both hexacene and heptacene, have recently been reported by Neckers et al.[43,44] using Strating-Zwanenberg photodecarbonylation.[45] Preparing acenes through this photochemical route yields unsubstituted homologues, which were not isolated due to their high reactivity. After formation of unsubstituted hexacene via its α-diketone precursor (Scheme I.6), within minutes the monomer dimerizes or reacts with oxygen. Neckers and co-workers did successfully characterize hexacene by UV/Vis spectroscopy and mass spectrometry.



17 **18**

Scheme I.6 Strating-Zwanenberg photodecarbonylation, the final step toward hexacene.

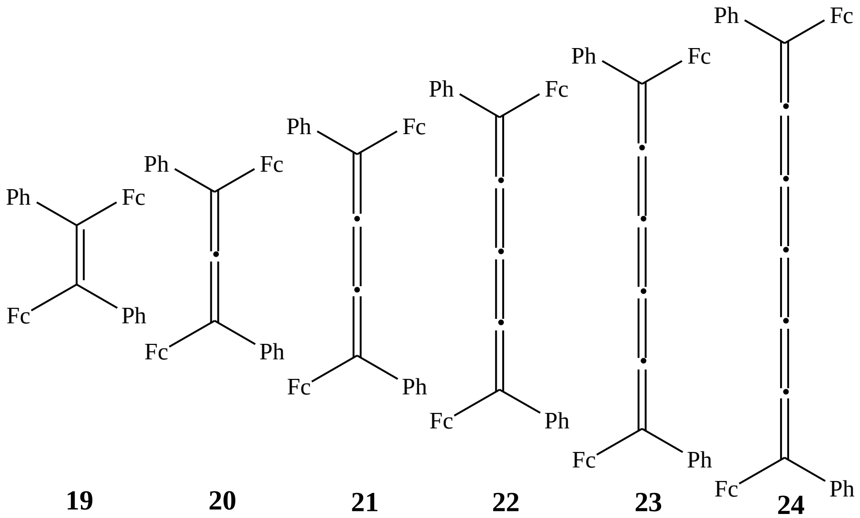
Although the potential practical applications of polyacenes are vast, including organic electronics, optical limiters[46] and electrodes for lithium ion batteries,[47] polymeric acenes have not yet been achieved. The many synthetic routes that have been used to achieve oligoacenes are efficient. However, it would be impractical to use the methods intended for synthesizing discrete acenes to synthesize polyacene.

I.3 Cumulenes

Cumulenes ($H_2C{=}(C{=}C)_n{=}CH_2$) are unsaturated linear hydrocarbons containing multiple adjacent carbon-carbon double bonds. The rigidity of cumulenes arises from the consecutive sp-hybridized carbon atoms, with two systems of perpendicularly conjugated π-obitals. Cumulene conformations alternate with the successive addition of a carbon-carbon double bond. Cumulenes with an even number of consecutive sp hybridized carbons have coplanar terminal substituents, while cumulenes of an odd number have terminal substituents that attach from two perpendicular planes, creating a chiral axis when each terminus has two different substituents.

Interestingly cumulenes, much like acenes, experience a considerable increase in reactivity with elongation of chain length, requiring steric protection for overall stability.[48] The contiguous polyene system found in cumulenic compounds allows for a highly rigid one-dimensional backbone of polarizable π-electrons. The unique chemical behavior of cumulene-cored molecules allows them to react as electrophiles, nucleophiles, and occasionally as dienophiles.[49,50] Bildstein and co-workers have proposed uses of cumulenes as active second- and third-order nonlinear optical materials for organic optical electronic devices.[51]

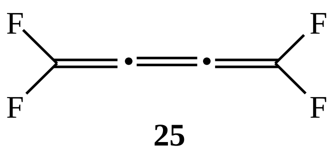
The physical properties of cumulenes are directed by the number of sp-hybridized carbon atoms in the cumulated polyene system and the functional groups attached at the ends of the molecule. An interesting example is the cumulenic series of compounds with electroactive ferrocenyl substituents at the ends (Figure I.11). These cumulenic-cored compounds are known to exhibit electronic communication through the central sp-hybridized carbon wire.[52] Bildstein and co-workers have determined that the even cumulenes (C_2, C_4, and C_6) in this series are conjugated "molecular wires" that have induced electronic communication between the terminal ferrocenyl groups, while the odd cumulenes (C_3, C_5, and C_7) are nonconjugated and electronically decoupled due to their orthogonal terminal π-systems.



19 **20** **21** **22** **23** **24**

Figure I.11 Cumulenes with terminal ferrocenyl (Fc) and phenyl substituents.

Cumulenes 1,1,4,4-tetraflurobutatriene (**25**) and 1,1,4,4-tetrachlorobutatriene (**26**) were first reported in 1959,[53] and 1968,[54] respectively. Recently, the closely related iodocumulene was reported by J. A. Webb and co-workers.[49] While investigating the crystallization of diiodobutadiyne, Webb found that compound **27** decomposes over time to form periodocumulene **28** (Scheme I.7).



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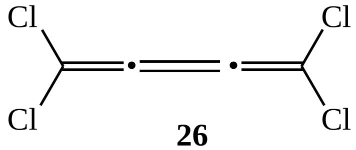

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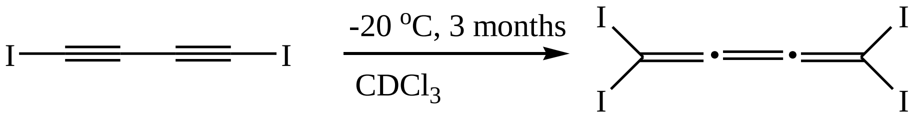
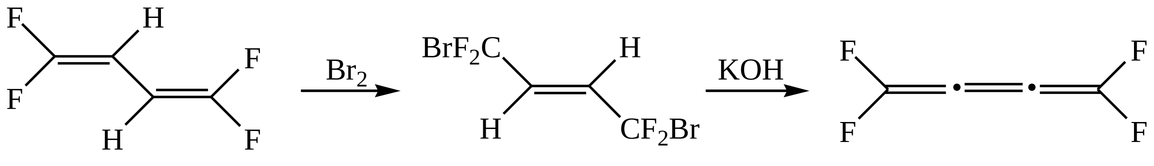
Figure I.12 Cumulenes 1,1,4,4-tetraflurobutatriene and 1,1,4,4-tetrachlorobutatriene.



27 **28**

Scheme I.7 Spontaneous reaction from diiodobutadiyne to iodocumulene.

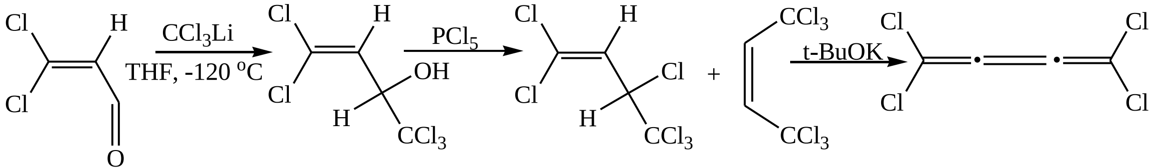
Martin and Sharkey achieved the synthesis of 1,1,4,4-tetraflurobutatriene (**25**) via bromination of tetraflurobutadiene (**29**), followed by dehydrobromination of the 1,4-addition product (**30**) (Scheme I.8).[53] At ambient temperature, 1,1,4,4-tetraflurobutatriene exists in the gaseous state. When condensed to a liquid, its boiling point is approximately -5° C. Triene **25** reacts readily with oxygen, in a highly exothermic process. Due to the explosive nature of cumulene **25**, the observed boiling point is only an estimate.



29 **30** **25**

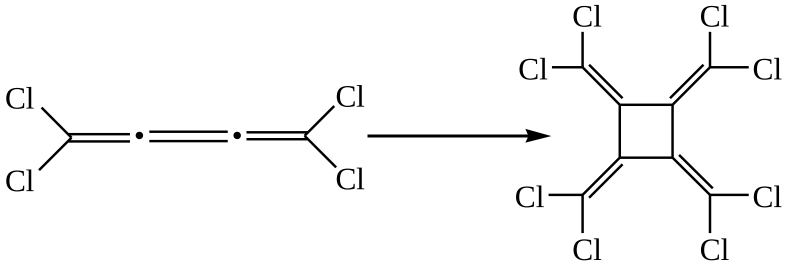
Scheme I.8 Synthesis of perfluorobutatriene.

1,1,4,4-tetrachlorobutatriene (**26**) was synthesized by reducing β,β-dichloroacrolein (**31**) with trichloromethyllithium, to afford compound **32**; the subsequent alcohol (**33**) was then treated with PCl_5, followed by dehydrochlorination of hexachlorobutene (**34**) with potassium *t*-butoxide. (Scheme I.9). At room temperature, perchlorocumulene **26** is a clear, colorless solid, with a melting point of 59-60 °C. When heated for several hours at 100 °C in aprotic solvents, tetrachlorobutatriene (**26**) dimerizes to form radialene C_8Cl_8 (**35**), (Scheme I.10).[54] In addition to the formation of compound **35**, a small amount of an explosive polymeric side product is formed.



31 **32** **33** **34** **26**

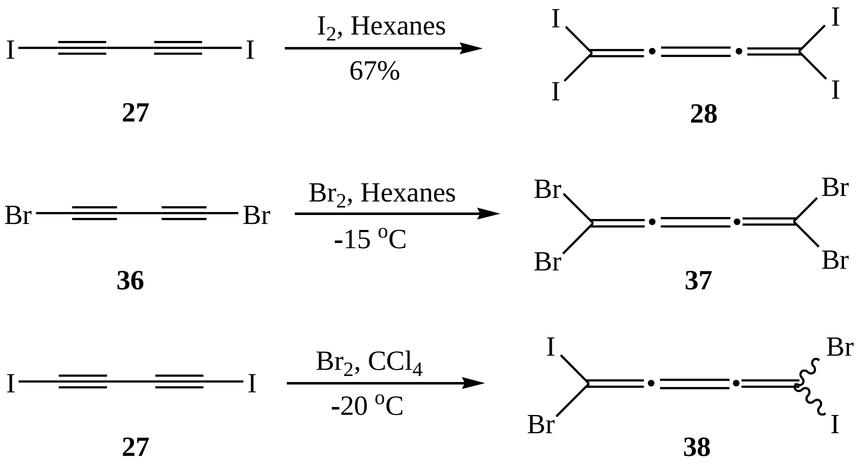
Scheme I.9 Synthesis of perchlorobutatriene.



26 **35**

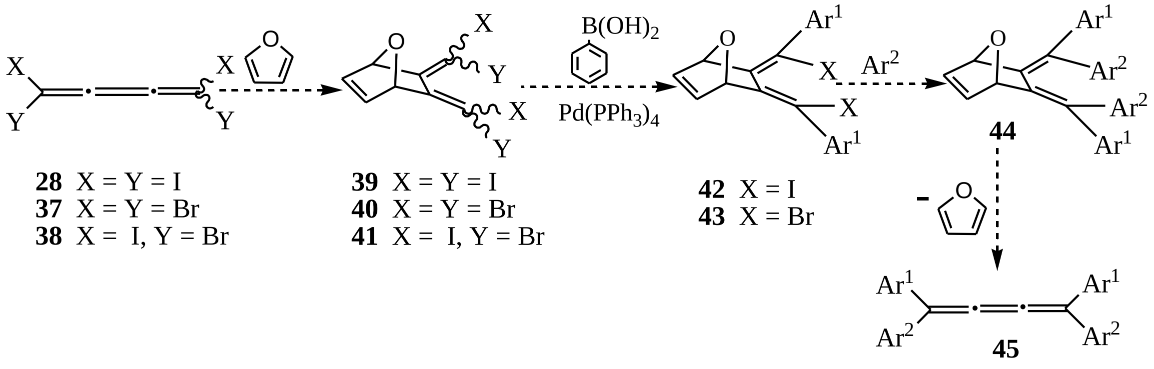
Scheme I.10 Dimerization of perchlorobutatriene to form C_8Cl_8.

P.-H. Liu developed conditions for the preparation of perhalocumulene **28**. A concentrated solution of diiodobutadiyne reacts with one equivalent of iodinated at room temperature, forming tetraiodobutatriene (**28**) as a precipitate recrystallized in 67% yield. The methodology used for this electrophilic addition reaction was employed to form tetrabromobutatriene (**37**)[49] and 1,4-dibromo-1,4-diiodobutatriene (**38**), in yields of 36% and 14%, respectively (Scheme I.11).[55]



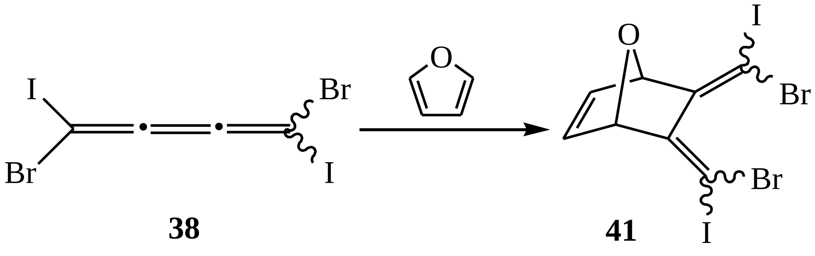
Scheme I.11 Synthesis of tetraiodobutatriene (C_4I_4), tetrabromobutatriene (C_4Br_4) and dibromodiiodobutatriene ($C_4Br_2I_2$).[55]

Perhalocumulenes C_4I_4 (**28**), C_4Br_4 (**37**) and $C_4Br_2I_2$ (**38**) have better stability, are easier to handle, and have better leaving groups (Br and I) when compared to perfluorobutatriene (**25**) and perchlorobutatriene (**26**). For that reason cumulenes **28**, **37**, and **38** were investigated for their use as general precursors for the preparation of substituted cumulenes via transition metal catalyzed coupling reactions. Methods to prepare extended cross-conjugated cumulenes from these precursors were investigated by Lei Li. Under very mild conditions, compounds **28**, **37** and **38** can undergo a Diels-Alder reaction (Scheme I.12). This step is used to protect the cumulenic core prior to coupling reactions. When adduct **40** was treated with phenyl boronic acid under Suzuki conditions, the reaction took place with the norbornenyl double bond opposite the dibromoolefin bonds. Due to the poor stability and poor solubility of C_4I_4 and $C_4Br_2I_2$, cross-conjugated coupling products were not attained.



Scheme I.12 Diels-Alder reaction of perhalocumulenes **28**, **37**, and **38**.

The X-ray crystallography and IR spectroscopy of $C_4Br_2I_2$ (**38**) suggest that cumulene **38** forms as a mixture of *cis*- and *trans*- isomers.[56] When $C_4Br_2I_2$ was treated with furan, a mixture of Diels-Alder adducts were obtained, in addition to starting material (Scheme I.13). Further investigation of this reaction is necessary to fully understand the mixture of products that are obtained. In Chapter III, preparation of $C_4Br_2I_2$ and its reaction as a Diels-Alder dienophile will be discussed.



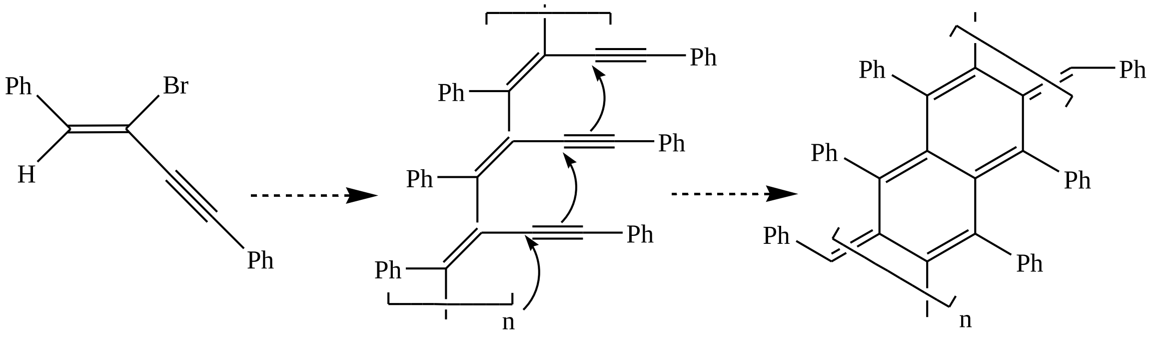
Scheme I.13 Diels-Alder reaction of $C_4Br_2I_2$ with furan.

Chapter II

SYNTHETIC EFFORTS TOWARD PHENYL-SUBSTITUTED POLYMERIC ACENES

II.1 Synthetic Design Toward Polyacenes

We have targeted the synthesis of phenyl substituted polyacene **48**, via head-to-tail polymerization of haloenyne **46**, followed by cascading ring-closing steps (Scheme II.1).



46 **47** **48**

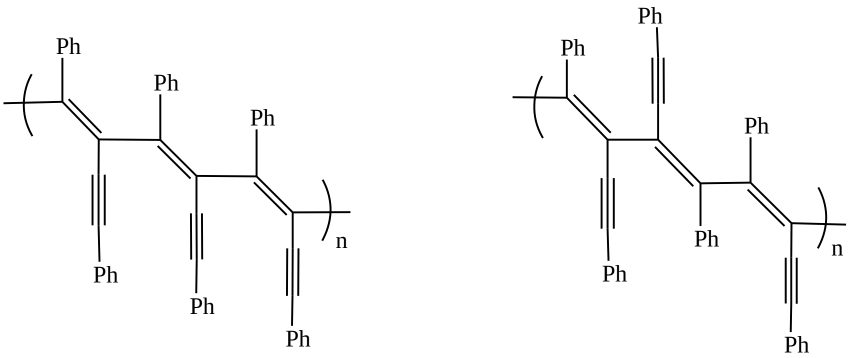
Scheme II.1 Proposed synthetic route toward polyacene.

Since the inner rings are highly reactive,[18,31] the use of phenyl substituents will reduce the chemical instability of the polymer. Steric protection has been successfully employed to overcome chemical instability.[29] Steric bulkiness of the diphenyl moiety will reinforce the twist conformation, as observed in twistacene,[20] while also preventing cross linking between polymer strands. The phenyl substituents also make the product more stable to oxidation by air.

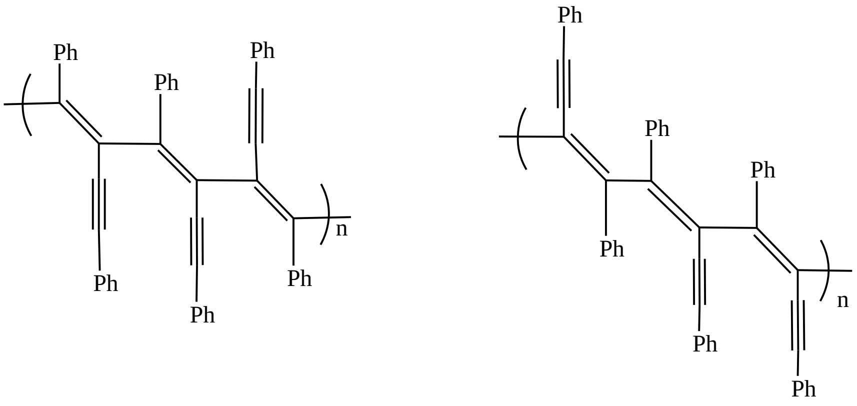
Since monomer **46** is asymmetric, polymerization may occur in a non-regiospecific fashion. Three types of dyad structures (head-head, head-tail, tail-tail) and four types of triads are therefore possible, as shown in Figure II.1. However, as demonstrated by the regioregular thiophene coupling chemistry developed by McCullough and coworkers, regiochemical control can be achieved to synthesize a structurally homogeneous head-to-tail arrangement. McCullough was able to prepare regioregular poly(3-alkylthiophenes) from the asymmetric precursor, 2-bromo-3-

allkylthiophene.[57] Ab initio calculations were completed on model dimers, trimers, and tetramers; McCullough found head-to-head couplings unfavorable since the lowest energy conformations possessed a large twisting of the rings out of coplanarity at the head-to-head junction.[57]

Once regioregular polymerization of monomer **46** is achieved, the solution-phased polyene will be treated with a Ni (II) transition metal catalyst that will induce tandem polycyclizations. Trost and co-workers have demonstrated the construction of polycycles from enepolyynes via tandem transition-metal catalyzed tandem cyclizations.[58] The acyclic polyunsaturated compounds Trost has used include aryl, alkyl or ester substituents on the alkynyl branches. The synthetic efficiency of polycycle formation using alkynylphenyl moieties in Trost's work inspired the final synthetic step in our proposed route toward polyacenes.



Head-toTail-Head-to-Tail Head-to-Head-Tail-to-Tail



Head-to-Tail-Head-to-Head Tail-to-Tail-Head-to-Tail

Figure II.1. Possible trimeric sequences.

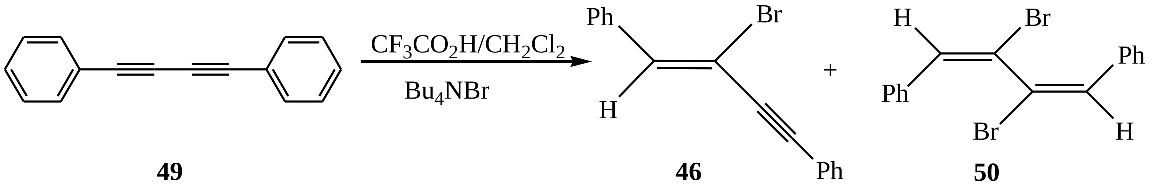
The goal of this research is to synthesize polyacenes via regioregular polymerization methods. This chapter will describe our efforts to repeat the synthesis of (*Z*)-2-bromo-1,4-diphenyl-1-buten-3-yne **46**,[59] and attempts to polymerize monomer **46** to afford the regioregular head-to-tail polyacetylene intended for tandem cyclization.

II.2 Target Monomer

Two approaches to making the monomer **46** were implemented. A direct electrophilic addition of HX or X_2 (X = Br, I) to diphenylbutadiyne was studied by undergraduate En-chi Lin in order to find a way to make haloenyne monomer **46** more efficiently and cost effectively. Negishi and co-workers have reported the *trans*-selective monoalkynylation of 1,1-dibromo-2-phenyl-ethene to give haloenyne **46** in high yield with stereoisomeric purity. This known, but relatively expensive reaction for the synthesis of haloenyne **46** will allow us to focus on an effective method to polymerize the monomer regioselectively.

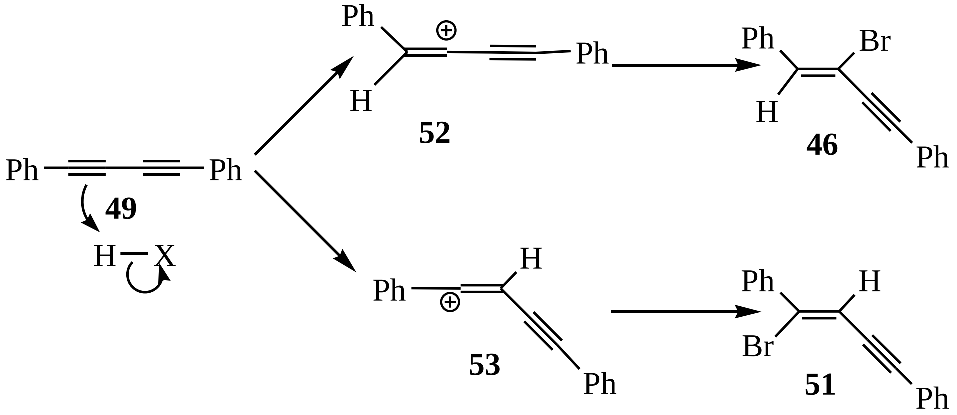
II.2.1 Hydrohalogenation Methods Toward Monomer

Undergraduate student En-chi Lin attempted the synthesis of haloenyne **46** was attempted via hydrohalogenation of diphenylbutadiyne (**49**) (Scheme II.2). However, because target **46** reacts under the same conditions as the starting material (**49**), this reaction results in a mixture of haloenyne **46** and the double-addition product, diene **50**, which are the major and minor products respectively. Since it is not feasible to stop the reaction prior to formation of the diene without compromising the yield of monomer **46** the reaction must be carried out to completion. The separation and isolation of **46** via column chromatography is difficult due to its identical chromatographic retention factors as that of compound **50**. With a significant amount of diphenylbutadiyne present in the mixture, isolation efforts by crystallization were also unsuccessful. Under varied conditions, the *cis* addition occurred instead of trans.



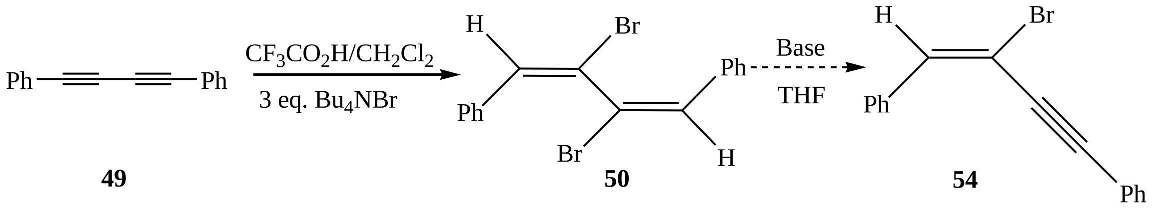
Scheme II.2 Hydrohalogenation of diphenylbutadiyne.

The electrophilic addition of HBr to 1,4-diphenyl-1,3-butadiyne could go through two possible intermediates as shown is Scheme II.3. Formation of enyne **46** is expected over (*Z*)-1-bromo-1,4-diphenyl-1-buten-3-yne (**51**) since the carbocation intermediate **52** has a larger delocalized area (has more allyl character) than that of intermediate **53**. Since the concentration of both the acid and the Bu_4NBr salt affect the regio-selectivity of the reaction,[60,61] several experiments to determine optimal conditions that favor the formation of (*Z*)-2-bromo-1,4-diphenyl-1-buten-3-yne (**46**), have been tried, however, the appropriate reaction conditions that will also limit formation of diene **50** in the process have not been achieved.



Scheme II.3 The carbocation intermediates of HBr addition of diphenylbutadiyne (**49**).

Given that synthesizing haloenyne **46** via electrophilic addition was not practicable, elimination was tried next. The revised approach toward making monomer **46** entails selectively eliminating one equivalent of HBr from the corresponding diene, however, since diene **50** is readily accessible; efforts to synthesize the double addition product (**50**) for its use towards model elimination reaction studies became a focus (Scheme II.4). Although this model reaction would result in forming the *E* isomer of the desired monomer (**54**), if the proper conditions that favor single elimination are elucidated, it will provide insight toward controlling elimination for the appropriate staring diene.



Scheme II.4 Model elimination reaction study.

Using an excess of Bu_4NBr in 50% CF_3OOH, En-Chi Lin obtained diene **50** as the major product. Via column chromatography, diene **50** was isolated from (*E*)-2-bromo-1,4-diphenyl-1-buten-3-yne (**54**) and butadiyne **49**. X-ray crystallographic studies determined the structure to be 2,3-dibromo-1,4-diphenyl-1,3-butadiene (Figure II.2).

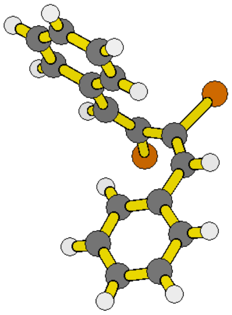


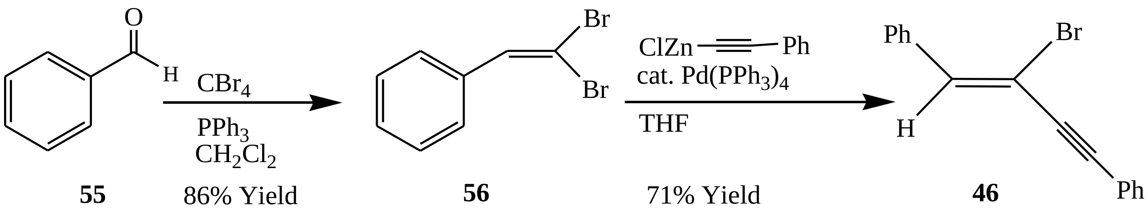
Figure II.2 Crystal structure of diene **50**.[62]

We attempted to eliminate one equivalent of HBr from compound **50** were carried out in a solution of THF using one equivalent of LDA at -78 °C. The duration of reaction time and temperature were varied for each reaction. The initial reaction was not quenched with D_2O, as were subsequent trials. According to ^{13}C- NMR, diene **50** was still present; however, there was no evidence of the formation of diyne **49**, or either of the *E/Z* isomers of 2-bromo-1,4-diphenyl-1-buten-3-yne. Other selective eliminations were attempted on other dienes, and will be discussed in section II.5.2.

II.3 Results and Discussion

II.3.1 Trans-selective Monoalkynylation Methods Toward Monomer

The synthesis of monomer **46** reported by Negishi and co-workers[59] described herein starts with the synthesis of 1,1-dibromo-1-alkene **56** via a Corey Fuchs Wittig[67] reaction, as shown in Scheme II.5. Following the preparation of **56**, Negishi coupling with the alkynyl zinc chloride gives the desired monomer **46**.[59]



55 **56** **46**

Scheme II.5 Alternative synthetic route toward monomer **46**.

In our repetition of Negishi's synthesis, the Corey-Fuchs Wittig reaction was used to obtain compound **56** in 86% yield. Benzaldehyde (**55**) was treated with carbon tetrabromide and two equivalents of triphenylphosphine in methylene chloride.[67] NMR results from the first attempt to synthesize compound **56** demonstrated that distillation of benzaldehyde (**55**) was required first to remove the benzoic acid impurity present in the starting material. When this reaction is completed on a larger scale, as indicated by TLC and ^{13}C-NMR, further purification by column chromatography is required. Investigation by ^{31}P-NMR elucidated the nature of the impurity; the single resonance peak at $\delta = -4.165$ ppm was indicative of PPh_3.[64]

Trans-selective monoalkynylation of 1,1-dibromo-2-phenyl-ethene (**56**) with phenylethynyl zinc chloride under Negishi coupling conditions[59] affords the *Z*- isomer. The alkynylzinc was generated *in situ* by treating phenylacetylene with *n*-BuLi and anhydrous $ZnCl_2$. Compound **46** was obtained after chromatographic separation and recrystallization. The various attempts at the *trans*-selective coupling of **56** with phenyl ethynyl zinc chloride are condensed in Table II.1.

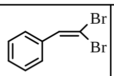
Trial	Solvent	$\mathrm{Ph}{\equiv}\mathrm{H}$ mmol	*n*-BuLi mmol	$ZnCl_2$ mmol	Catalyst 5 mol%	 mmol	Time h	%Yield (**46**)
1	THF	1.2	1.25	1.2 New ampule	$(PPh_3)_4Pd(0)$	1.0	18	11%
2	THF	1.2	1.25	1.2 Open ampule	$(PPh_3)_4Pd(0)$	1.0	26	5%
3	THF	1.2	1.25	1.2 Commercially anhydrous/THF	$(PPh_3)_4Pd(0)$	1.0	18	4%
4	THF	1.2	1.25	1.2 Commercially anhydrous/THF	$(PPh_3)_4Pd(0)$	1.0	24	6%
5	THF	1.2	1.25	1.2 Commercially anhydrous/THF	$(PPh_3)_2Pd(II)Cl_2$	1.0	20	3%
6	THF	1.2	1.25	1.3 Commercially anhydrous/THF	$(PPh_3)_2Pd(II)Cl_2$	1.0	43	4%
7	THF	1.2	1.25	1.2 Commercially anhydrous/THF	Rinsed $(PPh_3)_4Pd(0)$	1.0	40	6%
8	THF	1.2	1.25	1.3 Commercially anhydrous/THF	Rinsed $(PPh_3)_4Pd(0)$	1.0	40	3%
9	THF	1.2	1.25	1.5 – 1.8 Flame Dried	New $(PPh_3)_4Pd(0)$	1.0	24	7%
10	THF	1.2	1.25	1.7 New ampule	New $(PPh_3)_4Pd(0)$	1.0	24	71%

Table II.1 Trials of *trans*-selective alkynylation of **56** with phenyl ethynyl zinc chloride.

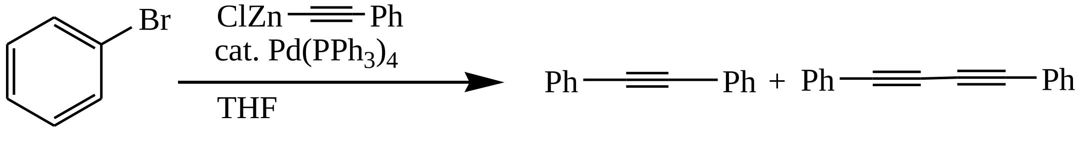
Initial attempts to prepare monomer **46** resulted in yields of ≤11% after column chromatography. The presence of starting materials **56** and phenylacetylene was confirmed by TLC in trials of failed attempts. This difficulty was initially attributed to the presence of water in the zinc chloride. The presence of water could hinder the formation of the alkynyl zinc reagent, causing the phenylethynyl lithium to react with water to form phenylacetylene.

Many extra precautions were taken to ensure the reactants were in a completely anhydrous system in the subsequent attempts, yet the yields remained under 11%. Changing the catalyst was implemented next. Using bis(triphenylphosphine)-Pd(II)chloride was tried. However, varying the catalyst did not result in increased yields; most of the starting materials (**56** and phenylacetylene) were recovered. After little success using bis(triphenylphosphine)Pd(II)chloride, various procedures for drying the $(PPh_3)_4)Pd(0)$ catalyst were implemented, yet the attempts were still unsuccessful. Washing the catalyst with absolute ethanol followed by freshly distilled anhydrous ether was employed in the next approach.[65] Although this purification procedure provided $(PPh_3)_4)Pd(0)$ as a light yellow-orange powder, rather than the dark brown-orange material used in earlier reactions, the yields remained low, with mostly starting material recovered. However, yields increased to 71% when new $(PPh_3)_4Pd(0)$ catalyst was used, in addition to flame drying new, anhydrous $ZnCl_2$ while taking the proper measures to ensure a completely anhydrous environment. Meeting both of these conditions is equally important, since meeting only one of the two conditions results in low yields.

Subsequent reactions to synthesize monomer **46** were repeated following these optimized conditions. Dialkynylation is observed by TLC when the reaction is run over 24h. The crude product is subject to column chromatography followed by crystallization. In reactions where yields are low dialkynylation is not observed. Prior to colleting data for optimal reaction conditions, a simpler Negishi coupling model was used.

II.3.2 Negishi Coupling Model Reaction

Various unsuccessful attempts at making haloenyne **46** led us to try a simpler model reaction (Scheme II.6). Using the same Negishi coupling methods, bromobenzene (**57**) was coupled with phenyl ethynyl zinc chloride to produce diphenylacetylene (**58**).



57 **58** **49**

Scheme II.6 Model reaction using Negishi coupling techniques.

The alkynylation of **57** with phenyl ethynyl zinc chloride via Negishi coupling conditions was attempted. The trials and results are condensed in Table A.1 (see appendix). The reaction was first attempted using the reported procedure for synthesizing monomer **46**.[59] A mixture of diphenylacetylene (**58**) and diphenyldiacetylene (**49**) was detected by ^{1}H- and ^{13}C-NMR in 5% and 13% yield, respectively (based on starting phenylacetylene). Using Negishi coupling conditions reported as a one pot synthesis,[66] complete recovery of compound **57** resulted. Since some reaction was previously observed using the original protocol, these conditions were used again;[66] however, a 2 mol% copper(I)iodide co-catalyst was introduced. By TLC and ^{13}C-NMR the crude product did not contain diphenylacetylene or diphenyldiacetylene, which has been previously observed; instead, a large mixture of inseparable products was formed. With the use of new, purely anhydrous zinc chloride, the final attempt to resulted in formation of diphenylacetylene and diphenyldiacetylene, in yields of 19% and 32%, respectively.

II.3.3 Summary of Negishi Coupling Toward Monomer 46

The results from the model system suggested that a completely anhydrous system must be obtained for optimal Negishi coupling to occur. *Trans*-selective monoalkynylation of 1,1-dibromo-2-phenyl-alkene (**56**) with phenylethynyl zinc chloride did provide compound **46**[59] under the most stringent anhydrous conditions. Flame drying fresh zinc chloride under reduced pressure is necessary to achieve the desired reaction. X-ray diffraction studies were inconclusive due to poor crystal quality. ^{1}H- and ^{13}C-NMR spectra matched the literature data.[59] Although the synthesis of haloenyne **46** was reported in the literature, the melting point and the physical state of this compound were not reported. We determined it to be a white solid with a melting point of 77-78 ^{o}C. With the haloenyne **46** prepared, the focus turned toward the regioregular polymerization of the monomer.

II.3.4 Computational Analyses of the Z & E Isomers of the Diphenylhaloenyne

To predict the differences in spectral data for the isomers of 2-bromo-1,4-diphenyl-1-buten-3-yne (**46** and **54**), density functional theory calculations at the B3LYP/LanL2DZ level of theory were conducted. The *Z* and *E* isomers were constructed as planar structures and then minimized, resulting in an energy difference of 2.2 kcal/mol between the two isomers, with the *E* isomer (**54)** lower in energy. A second set of geometry optimizations, carried out for the nonplanar *Z* and *E* isomers, were conducted to assure a global minimum was reached. The resultant energies of the nonplanar structures were lower in energy when compared to the planar structures. With an energy difference of 1.9 kcal/mol between the two nonplanar isomers, the *E* isomer **54** again is calculated to be more stable than the *Z*, isomer (**46**) (Figure II.3 and Figure II.4, respectively). The final structures of both isomers have phenyl substituents that deviate slightly from planarity. The small difference in energy indicates that neither isomer is strongly favored over the other thermodynamically. Experimentally, we observe only the *Z* isomer via ^{13}C-NMR, suggesting that the results are controlled by the energy difference in the Pd-complexed intermediates or transition states instead of the energy difference in the final products.

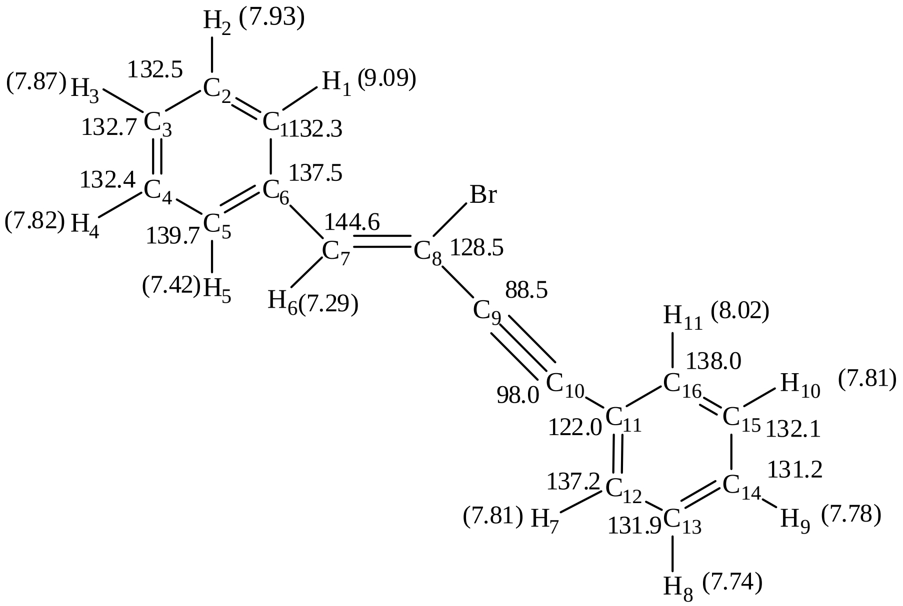


Figure II.3 Calculated NMR values (B3LYP/LanL2DZ) of the *Z* isomer **46**.

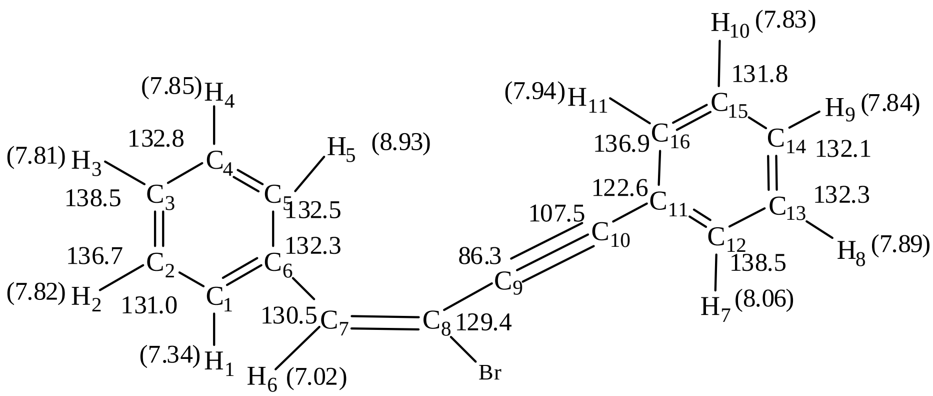
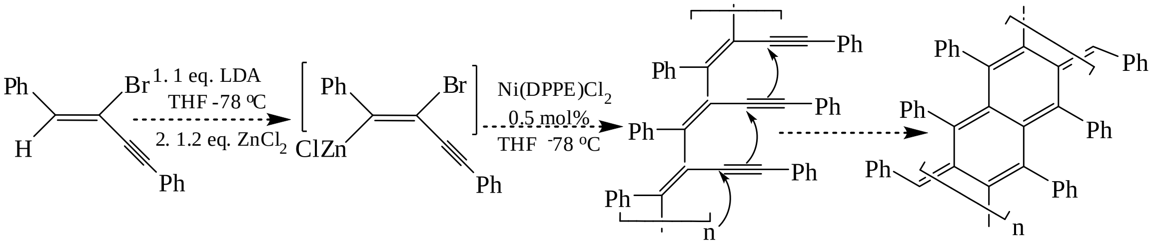


Figure II.4 Calculated NMR values (B3LYP/LanL2DZ) of the *E* isomer **54**.

Note that the calculated ^{1}H-NMR values for the equivalent protons on the benzene ring are not equivalent in these static structures. However, in reality, rotation of the benzene ring around the C_6-C_7 or C_{10}-C_{11} bond will lead to averaging of these ^{1}H signals on the NMR time scale.

II.3.5 Polymerization Trials of the Diphenylhaloenyne

Regioregular coupling of monomer **46** was modeled on McCullough's[67] and Reike's[68] head-to-tail polymerization techniques. In McCullough and Reiki's methods, LDA or *n*-BuLi was used followed by the addition of $ZnCl_2$ or $MgBr_2$ for transmetallation, and subsequent treatment with a Ni(II) catalyst. In thiophene polymerizations, the use of Ni(II) with sterically demanding ligands has been shown to have a high degree of regioselectivity toward head-to-tail couplings.[57,68] We planned to use Ni(DPPE)Cl_2 or Ni(DPPP)Cl_2 to induce regioregular coupling (Scheme II.7).

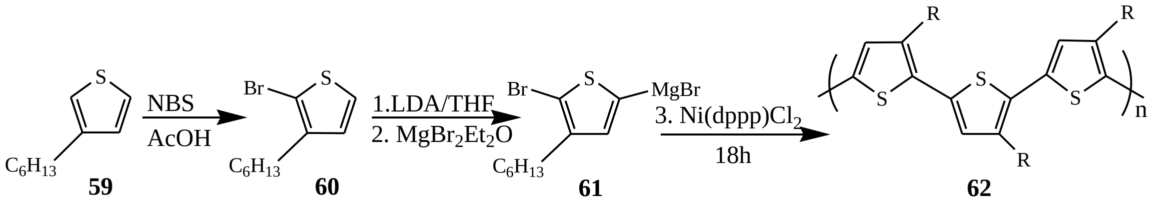


Scheme II.7 Proposed synthetic route toward regio-regular head-to-tail polymeric acene.

II.3.6 Regioregular Polymerization Model Reaction

Before testing our route to polymer **48**, we wanted to establish familiarity with the conditions developed by McCullough[67] to achieve regiochemical control of intermolecular coupling reactions. Therefore, a model reaction to form a known, structurally homogenous regioregular head-to-tail polymer was conducted. (Scheme II.8).

The synthesis of regioregular head-to-tail polythiophenes in the presence of $Ni(dppp)Cl_2$ catalyst was therefore repeated.



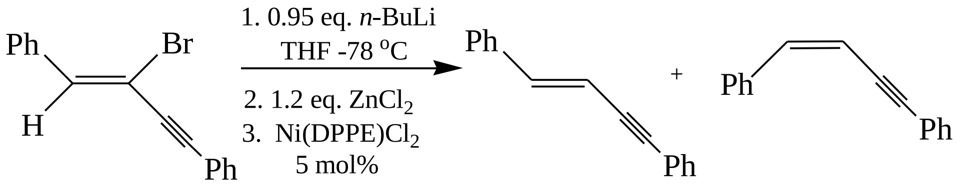
Scheme II.8 Route to regioregular head-to-tail coupled poly–(3-hexylthiophenes).

2-bromo-3-hexylthiophene was synthesized (73%) by treating 3-hexylthiophene with NBS in glacial acetic acid.[69,70] Regioregular head-to-tail polymerization proceeds in a one-pot synthesis. After lithiation of 2-bromo-3-hexylthiophene **60** at the 5-position, the intermediate was treated with anhydrous $MgBr_2$ instead of the literature reported etherate ($MgBr_2 \cdot Et_2O$). Subsequent treatment of the single metalated regioisomer, in situ with a catalytic amount of $Ni(dppp)Cl_2$[71,72] afforded the regioregular head-to-tail polymerization product. After soxhlet extractions, the purple solid was crystallized from acetone, forming long, dark purple, needle-shaped crystals. This polymer was characterized via ^1H and ^{13}C NMR.

II.3.7 Polymerization Trials of Monomer 46

Several efforts to polymerize haloenyne **46** under McCullough[72] head-to-tail coupling conditions were attempted. When monomer **46** was treated with LDA, followed by treatment with $MgBr_2$ or $ZnCl_2$ and a Ni(II) catalyst (with either $(DPPP)Cl_2$ or $(DPPE)Cl_2$ ligands), no reaction with the substrate was observed. Either the initial deprotonation did not occur, or the lithiated alkene of **46** forms, but does not react further before being reprotonated during work-up. A quenching study was carried out to determine if reaction between the monomer and LDA occurred. Haloenyne **46** was treated with LDA and quenched with D_2O. The organic layer was extracted with hexanes and dried with $MgSO_4$. Via ^{13}C-NMR, the spectra matched the reported values for compound **46**. Since a triplet was not observed in the spectra, this indicated that the hydrogen atom at the C_1 position of haloenyne **46** was never deprotonated and deuterated.

Given that LDA was ineffective, *n*-BuLi was attempted next. Once *n*-BuLi was added to the reaction flask, an immediate color change was apparent. The reaction mixture was given 5 minutes to react; $ZnCl_2$ or $MgBr_2$ was added immediately after to limit possible elimination. At -5 °C Ni(DPPE)Cl_2 was introduced to the mixture. The crude products were subject to column chromatography. According to ^{1}H-NMR, these reactions resulted in a mixture of *E* and *Z* 1,4-diphenyl-1-butene-3-yne, in the form of a pale yellow solid (Scheme II.9) .



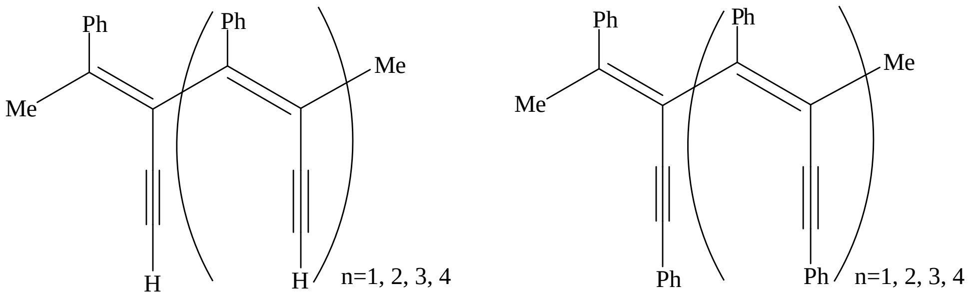
46 **63** **64**

Scheme II.9 Halogen exchange resulted in *E* and *Z* 1,4-diphenyl-1-butene-3-yne.

Since we do dot get the desired deprotonation with use of LDA on the substrate, and only halogen exchange with Br when *n*-BuLi was used, the hydrogen atom in the C-1 position of haloenyne **46** is not an acidic proton.

II.3.8 Semi-empirical (PM3) calculations

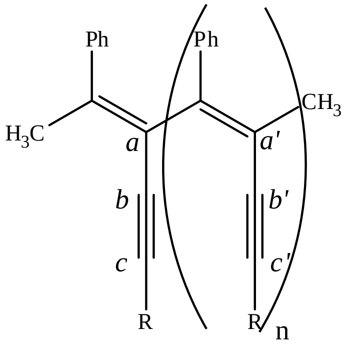
Semi-empirical (PM3) calculations were conducted on a series of model compounds (**65a-d** and **66a-d**, Figure II.6) to determine the most probable conformation of the polyacetylene intermediate (**47**), and observe the relative orientations of the alkynyl branches. With the ends capped with methyl groups, two parent sets of oligomers (n = 1-4) were computationally studied containing terminal and phenyl-substituted alkynyl side chains (**65a-d** and **66a-d**, respectively, Figure II.5).



65(a-d) **66(a-d)**

Figure II.5 Calculated PM3 model compounds **65** and **66**.

The geometries of the alkynyl branches were analyzed to assess the likelihood of conducting tandem ring closures toward polymeric acene if regioregular polymerization was achieved. The results (Figure II.6 and Table II.2) show that two reactive carbons of adjacent alkynyl branches (*b-c'*, Figure II.6), depicted in Scheme II.1, are not within Van der Waals forces and the alkynyl side chains are not coplanar. The steric hindrance amongst the phenyl substituents along the polyacetylene backbone cause the alkyne branches to splay significantly away from one another. (Figure II.7). In the longer structures (where n = 4), the alkynyl branches are slightly closer to each other. When the alkynes are capped with a phenyl group, the dihedral angles of the inner alkynes improve from 81° to approximately 60°. Nevertheless, these large dihedral angles suggest that the resulting polymerization of these intermediates would be difficult to initiate because of the major deviation. The use of a transition metal catalyst could possibly overcome this barrier.



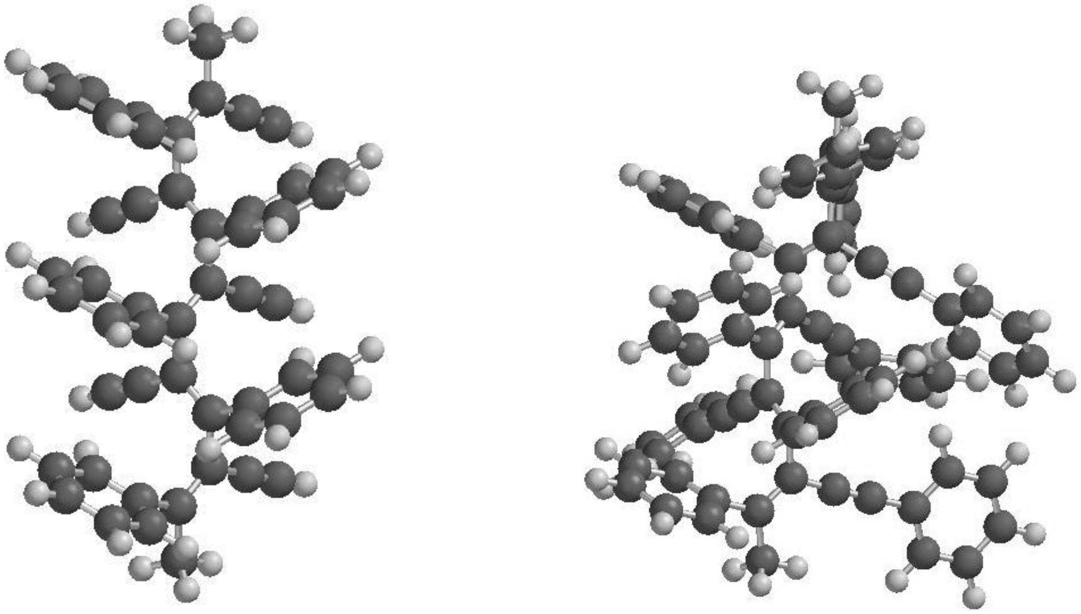
R = H, Ph

Figure II.6 Carbon labels for the measurements shown in Table II.2.

Compound	**R**	**n**	***b-c'* C-C distance**[a]	***b-a-a'-b'* Dihedral Angle**
65a	H	1	4.15	81.8°
65b	H	2	4.13[b]	81.4° [d]
65c	H	3	4.11 [b]	81.5 ° [d]
65d	H	4	4.10[c]	81.0° [d]
66a	Ph	1	4.19	83.7 °
66b	Ph	2	4.24[b]	81.7° [d]
66c	Ph	3	3.59[b]	61.2° [e]
66d	Ph	4	3.54[c]	59.8° [e]

[a]The *b-c'* C-C distances (measured in Å) are shorter than their respective *c-b'* C-C distances. [b]Average values of all the *b-c'* C-C distances. [c]Average values of the inner *b-c'* C-C distances. [d]Average values of all the *b-a-a'-b'* dihedral angles. [e]Dihedral angle of the inner alkynes.

Table II.2 Carbon-carbon distances of adjacent alkynyl side chains and dihedral angles of the semi-empirical (PM3) calculated compounds **65** and **66**.



65d **66d**

Figure II.7 Representative images of the PM3-calculated compounds **65d** and **66d**.

II.4 Summary

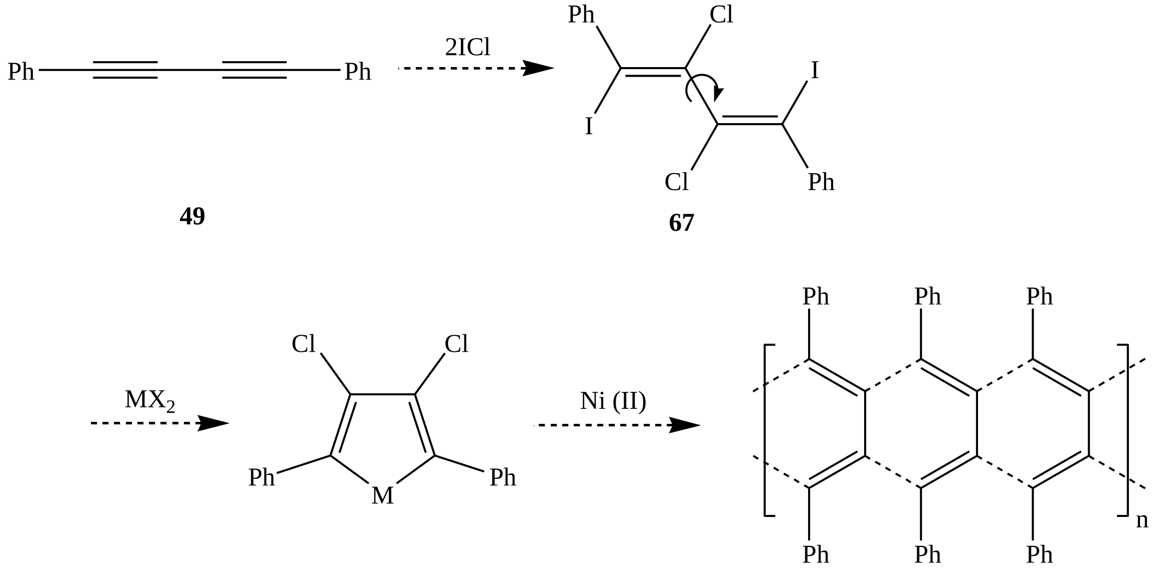
Since haloenyne **46** does not bear an acidic proton at the C-1 carbon, deprotonation was not achieved, thus, hindering our ability to use this monomer for the regioregular head-to-tail couplings intended to form our polyacetylene intermediate (**47**). The semi-empirical calculations of the small oligomeric analogues show that the alkynyl side branches are not co-planar. However, inducing a cascading ring closure to form polymeric acene might be possible with the use of a transition metal catalyst, although selectivity is still unclear.

The computational modeling studies, coupled with the observed experimental results, allowed us to begin addressing issues that were not anticipated. Currently, a new approach toward polymeric acenes is being developed.

II.5 Investigation of Alternate Proposed Synthetic Route Toward Polymeric Acenes

II.5. Synthetic Design

Preliminary exploration of an alternate synthetic route toward polymeric acenes was investigated. We explored a regioselective reaction at C-1 and C-4 in symmetrical diene **67** (Scheme II.10). Since we are able to differentiate between the inner and outer carbons of phenyl-substituted dienes (as demonstrated by En-Chi Lin's research), halogenation of **49** with ICl may be selective for 1,4 diiodo regioisomer **67**. A rotation about the center bond in isomer **67**, followed by oxidative addition, may produce a novel metalated five-membered ring intermediate (**68**). Once this intermediate is synthesized, a Ni (II) catalyst will be used to initiate regioregular coupling.



49

67

68

48

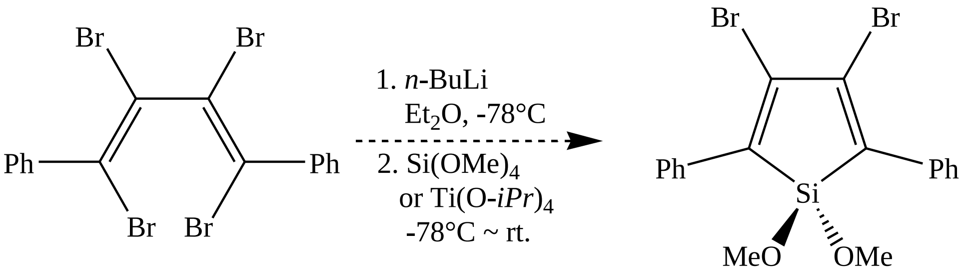
Scheme II.10 New route toward polymeric acenes.

Since we are able to differentiate between the inner and outer carbons of phenyl substituted dienes (as demonstrated by En-Chi Lin's research), the iodine atoms may assume the C_1 position to form diene **67**. With rotation about the center bond in isomer

67, the compound can undergo oxidative addition when treated with a metal having reducing capabilities, thus forming a metalated five-membered ring intermediate. A Ni(II) catalyst will be used to initiate head-to-tail regioregular coupling.

A closely related compound to our targeted intermediate **68** was reported by Tamao et al.[73] However, their silacyclopentadiene and titaniumcyclopentadiene compounds contain alkyl and/or aryl substituents instead of halogens in the C_3 and C_4 positions. Since our starting material is halogenated at four consecutive carbons, we recognize the difficulty we may encounter trying to selectively eliminate only C_1 and C_2.

Tamao and coworkers[73] used an anhydrous solution of diethylether, and reacted dihalodienes with *n*-BuLi followed by addition of $Si(OMe)_4$ at -78 °C. Our efforts to react tetrabromodiene **69** using the same set of conditions was implemented (Scheme II.11) in addition to the exploration of the selective elimination of diene **69** to find appropriate reaction conditions for the synthesis of our targeted intermediate. In this section, halogenation reactions toward precursor **67** will also be described.

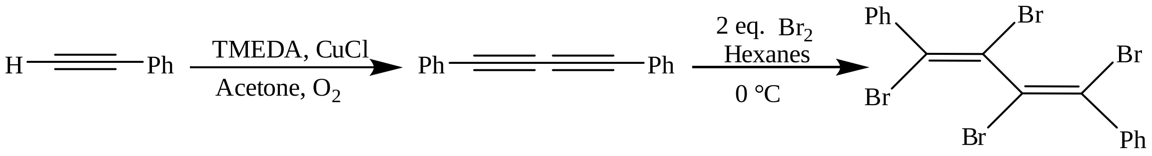


69 **70**

Scheme II.11 Proposed route to synthesize derivative of intermediate **68**.

II.5.2 Results and Discussion

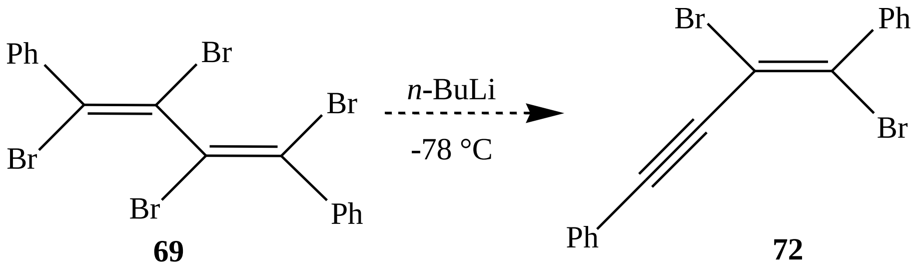
Diphenylbutadiyne was synthesized in 96% yield. Halogenation reactions of compound **49** proceeded in a solution of hexanes at 0 °C. Diene **69** (Scheme II.12) precipitated out of solution and was collected as a white/pale-yellow solid. Further purification by recrystallization (methanol/hexanes) resulted in fine white powder-like crystals. ^{13}C-NMR spectral analysis was completed. The structure was solved for the *trans* isomer by crystallographic studies conducted by Chris Wilhelm.



71 **49** **69**

Scheme II.12 Synthesis of diene **69**.

A model reaction using perhalodiene **69** was implemented for the synthesis of the silacyclopentadiene **70**. Allowing compound **69** to react with 1.95 equivalents of *n*-BuLi (1.6 M) under the conditions reported by Tamao[73] resulted in formation of the double-elimination product. This reaction was attempted using 0.95 equivalents of *n*-BuLi (0.6 M) under the same conditions. Via TLC, (hexanes/ethylacetate, 50:1), starting diene **69** was observed in addition to an unidentified product (Rf.: 0.1 and 0.24, respectively). The ^{13}C-NMR spectrum indicates the presence of starting diene **69**. However, there was is evidence of the double elimination product. The GC-MS spectrum does not match the formation of compound **70**. This reaction will be further investigated. The selective elimination of perhalodiene (Scheme II.13) was also explored to determine whether conditions can be found to prevent double elimination. Results are shown in Table A.3 (See Appendix).

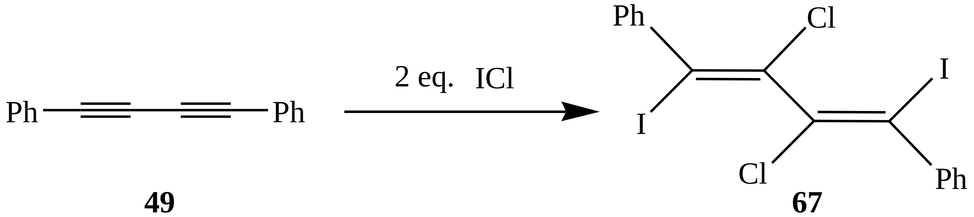


69 **72**

Scheme II.13 Selective elimination of tetrabromodiene **69**.

The formation of *(E)*-1,2-dibromo-1,4-diphenyl-1-en-3-yne or 1,4-dibromo-1,4-diphenyl-butatriene were not observed. Rather, evidence of diyne formation was apparent by NMR. Selective single elimination did not occur under these conditions.

Efforts to regiospecifically iodochlorinate diphenylbutadiyne to prepare diene **67** were also attempted (Scheme II.14). Compound **49** was treated with two equivalents of ICl in hexanes; temperature and duration of reaction times varied (0 °C for 2 hours, 25°C for 20 hours, 25°C for 2 days). At temperatures lower than 25°C, compound **49** did not react with ICl. A mixture was observed via TLC and NMR when the reaction was carried out at room temperature. However, only starting material was recovered by column chromatography.



49 **67**

Scheme II.14 Halogenation reaction of diphenylbutadiyne to form diene **67**.

In separate trials, CS_2, THF and MeOH were used in place of hexanes, following the same procedure. The reactions were stirred under anhydrous conditions at room temperature for two days. Via TLC, CS_2 gave the same R_f values as completing the reaction in hexanes. However, again, only starting material was recovered by column chromatography. NMR and GC-MS data from the reactions carried out in polar solvents were not promising. Starting material and a complex mixture of products were observed via GC-MS.

After allowing diphenylbutadiyne to react with iodine monochloride in solutions of DCM and also DCE (at both ambient and refluxing temperatures for each solvents), for 10 days, starting material was still present. GC-MS indicated that the relative abundance of iodochlorinated diene isomers formed was very low.

Using these same solvents, (DCM and DCE) the experiment was carried out with TBACl in addition to ICl. The reaction was slowed, and possibly the extra source of Cl from the TBACl could have formed $^{-}ICl_2$, preventing the possibility of an electrophilic attack.

Generally, iodination reactions alone are often more difficult when compared to bromination or chlorination reactions because iodination proceeds at very slow rates, and under standard conditions, is often reversible.[74] Since a permanent dipole exists in the reagent iodine monochloride, this should further facilitate electrophilic attack, usually forming regio- and stereoisomers. However, even with reaction times spanning over a week, we have not successfully iodochlorinated diyne **49**.

Single-isomer iodochlorinated alkenes were reported by Ogilvie and co-workers[75] by exposing various alkynes to a solution of refluxing TBAI in DCE in which ICl was generated *in situ* in addition to excess ethene. We therefore focused our attention on generating ICl *in situ* using these methods. Diphenylbutadiyne was treated with TBAI in a solution of DCE. The reaction was monitored for 7 days, but reaction toward the substrate was still not observed.

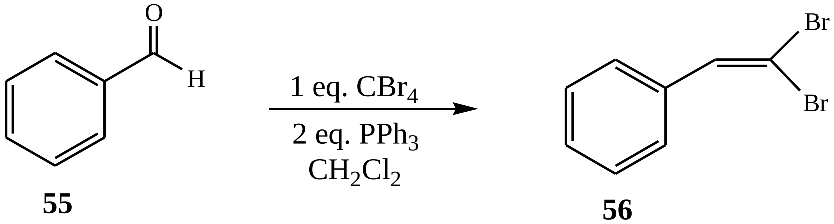
II.5.3 Summary

Efforts to synthesize compound **67** will continue. Reactions between iodine monochloride and phenyl-substituted alkynes in a solution of CCl_4 and CH_2Cl_2 have been reported by Viel and co-workers.[76] The halogenation reaction of diphenylbutadiyne will be attempted next using these conditions.

II.6 Experimental

General: Reagents were purchased reagent grade from Aldrich, Fisher Scientific/Acros Organics, Strem, and GFS Chemicals, and used without further purification. Hexanes and acetone solvents were purchased from VWR. Tetrahydrofuran and diethylether were each distilled under argon from sodium/benzophenone. $MgSO_4$ or Na_2SO_4 was used as the drying agent after aqueous work-up. All reactions were performed under an inert atmosphere of Ar. Evaporation and concentration of unstable compounds *in vacuo* was carried out at 0 ^{o}C. Thin-layer Chromatography (TLC) was performed on plastic-backed silica gel plates, developed with PMA and visualized by UV light. Melting points were measured on a Thomas Hoover Capillary melting point apparatus, uncorrected. IR spectra (cm^{-1}) were completed using a *Nicolet Magna-IR 750.* ^{1}H- and ^{13}C-NMR spectra were taken using a 300, 400, and 500 MHz Varian NMR instruments, using tetramethylsilane as the internal standard at rt in $CDCl_3$ (solvent peak references: 7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR).

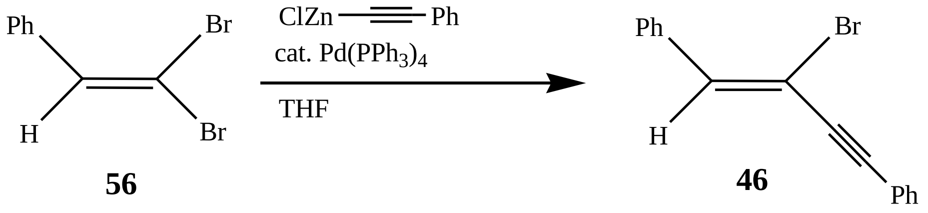
1,1-dibromo-2-phenyl-ethene (**56**)[63]



55 **56**

Under an argon atmosphere, benzaldehyde (**55**, 0.71 mL, 7.0 mmol) was added to 30 mL CCl_4 at 0 ^{o}C. Upon thorough mixing, CBr_4 (2.3201 g, 7.0 mmol) was added to the mixture followed by addition of PPh_3 (3.6646 g, 14 mmol) in 4 portions at 3 min intervals. The mixture was stirred at room temperature for 2 h. Hexanes (40 mL) was added to the reaction mixture with stirring. Twice, the resulting slurry was filtered through a silica gel plug and rinsed with hexanes. The solvent was then removed *in vacuo* to afford **56** as a yellow liquid. The crude product was subjected to column chromatography (silica gel, Hexanes) resulting in compound **56** as a yellow liquid (1.5769 g, 86% yield). ^{1}H-NMR (400 mHz) ($CDCl_3$) δ: 7.43-7.48 (m, 3H), 7.58 (s, 1H), 7.63, 7.64 (m, 2H). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 89.5, 128.2, 128.4, 135.1, 136.7.[63]

(*Z*)-2-bromo-1,4-diphenyl-1-buten-3-yne (**46**)[59]



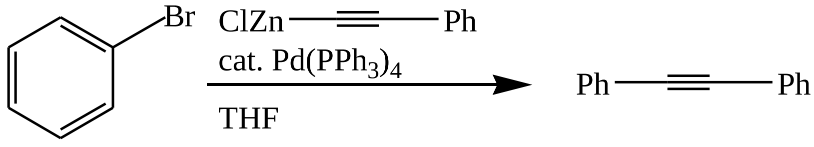
56

46

Under an atmosphere of argon, phenylacetylene (**71**, 0.14 mL, 1.2 mmol) was added to 5 mL freshly distilled THF at -78 °C. After a 30 min duration in which *n*-BuLi (0.78 mL, 1.25 mmol) was added dropwise to the reaction mixture, flame dried $ZnCl_2$ (0.1754 g, 1.2 mmol) in 5 mL THF was added via cannula at -78 °C. The resultant mixture was allowed to stir 15 min and warmed to room temperature over 45 min. The prepared zinc reagent was added to a solution of Pd(PPh_3)$_4$ (0.0586 g, 0.05 mmol), and 1,1-dibromo-2-phenyl-ethene (**56**, 0.15 mL, 1 mmol) in 5 mL THF dropwise at 0 °C. The reaction mixture was quenched with a saturated aqueous solution NH_4Cl (150 mL) and then extracted with ether (100 mL) and washed with NaCl. The organic phase was then dried with magnesium sulfate and the solvent removed *in vacuo*. The crude product, in the form of a white solid, was subjected to column chromatography (silica gel, hexanes) twice. The solvent was then removed *in vacuo* yielding (*Z*)-2-bromo-1,4-diphenyl-1-

buten-3-yne (**46**) as a white solid (0.2010 g, 71 % yield, m.p. 77-78 °C). ^{1}H-NMR (400 mHz) ($CDCl_3$) δ: 7.33-7.40 (m, 11H) 7.50-7.52 (m, 3H) 7.71-7.74 (m, 2H). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 89.4, 91.3, 100.3, 122.3, 128.5, 128.6, 129.1, 129.2, 129.5, 132.0, 135.2, 136.8.[59]

Diphenylacetylene (**58**)[59]

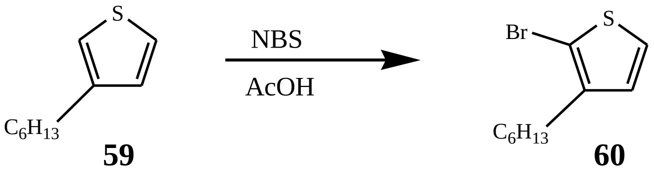


57 **58**

Under an atmosphere of argon, phenylacetylene (**71**, 0.33 mL, 3.0 mmol) was added to 5 mL freshly distilled THF at -78 °C. Via syringe, *n*-BuLi (1.88. mL, 3.0 mmol) was added dropwise to the reaction mixture (40 min). Anhydrous $ZnCl_2$ (0.431 g, 3 mmol) was flame dried under vacuum for 15 min and allowed to remain under vacuum for 1 h. Via syringe, 5 mL THF was added to the $ZnCl_2$ and transferred via cannula. The resultant mixture was allowed to stir for 15 min at -78 °C and then warmed to room temperature over 45 min. The prepared zinc reagent was added via cannula to a solution of $Pd(PPh_3)_4$ (0.149 g, 0.05 mmol), and bromobenzene (**57**, 0.27 mL, 2.5 mmol) in 5 mL THF at 0 °C. The reaction mixture was quenched with NH_4Cl (sat. aq., 150 mL) and then extracted with ether (100 mL) and washed with NaCl (sat. aq.). The organic phase was then dried with magnesium sulfate and the solvent removed *in vacuo*. The pale yellow solid was subjected to column chromatography (silica gel, hexanes). The solvent was then removed *in vacuo*, yielding diphenylacetylene (**58**) as a white solid (0.102 g, 23 % yield). ^{1}H-NMR

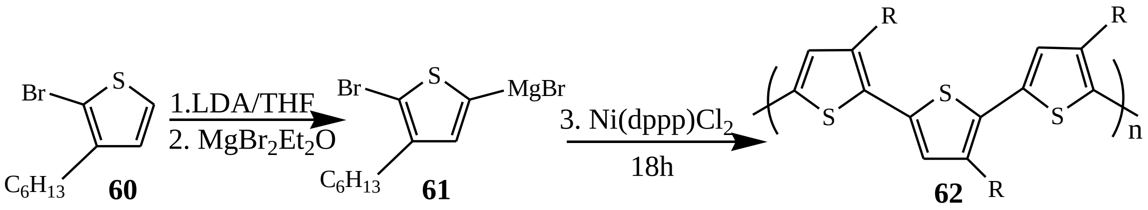
(400 mHz) ($CDCl_3$) δ: 7.35-7.41 (m, 8H) 7.53-7.67 (m, 2H). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 89.4, 121.8, 128.2, 128.3.[77]

2-bromo-3-hexylthiophene (**60**)[69,78]



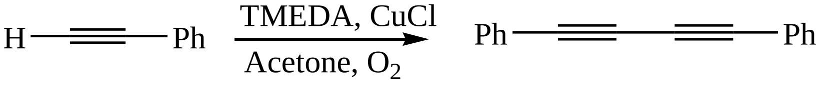
Under an atmosphere of argon, N-bromosuccinimide (0.987g, 6 mmol) was added to a solution of 3-hexylthiophene (**59**, 1.1 mL, 6 mmol) in 5 mL glacial acetic acid at 25 °C. The reaction mixture was stirred for 30 min and quenched with water (8 mL). The product was extracted with diethyl ether (30 mL) and washed with aqueous NaOH. The combined organic phase was then dried with magnesium sulfate and the solvent was removed *in vacuo*. The crude product, in the form of a yellow liquid, was purified by distillation under reduced pressure 117 °C (3 mm Hg). 2-bromo-3-hexylthiophene (**60**) was obtained as a pale yellow liquid (1.083 g, 73% yield). ^{1}H-NMR (400 mHz) ($CDCl_3$) δ: 7.19-7.21 (d, 1H, J = 5.6 Hz), 6.84-6.86 (d, 1H, J = 5.6 Hz), 2.63-2.77 (t, 2H, J = 7.6 Hz), 1.63-1.71 (m, 2H), 1.36-1.52 (m, 6H), 0.91 (t, 3H, J = 5.2 Hz). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 14.1, 22.6, 28.9, 29.4, 29.7, 31.6, 108.8, 125.0, 128.1, 141.4.[78]

Poly(3-alkylthiophene) (PAT) (**62**)[72]



Under an atmosphere of argon, diisopropylamine (0.42 mL, 3.0 mmol) was added to 20 mL of anhydrous THF at -20 ^{o}C. 1.6 M *n*-BuLi (1.88 mL, 3.0 mmol) was added dropwise to the reaction mixture and allowed to stir for 1 h at -40 ^{o}C. The reaction mixture was then cooled to -78 ^{o}C. 2-bromo-3-hexylthiophene (**60**, 0.74 g, 3.0 mmol) was dissolved in 3 ml THF and added to the reaction mixture via syringe at -78 ^{o}C. The resultant mixture was allowed to stir for 40 min at -40 ^{o}C, and then cooled to -60 ^{o}C where upon $MgBr_2$ (0.5532 g, 3.0 mmol) was added and the reaction was stirred for 20 min. The reaction was allowed to slowly warm to -5 ^{o}C, whereupon 7.8 mg (0.48 mol%) of $Ni(dppp)Cl_2$ in 3 mL THF was added via syringe. The reaction mixture was allowed to warm to room temperature overnight. After 18 h, the polymer was precipitated with 60 ml methanol, filtered and washed with MeOH, H_2O, and MeOH again. The crude product, in the form of a dark purple solid, was subjected to a soxhlet extraction using 400 mL methanol, 400 mL hexanes, and then dissolved in $CHCl_3$ using a soxhlet extractor. The solvent was then removed *in vacuo* to obtain polymer (**62**) as a dark purple solid (142 mg, 35 % yield). ^{1}H-NMR (400 mHz) ($CDCl_3$) δ: 6.98 (s, 1H), 2.78 (t, 2H), 1.62 (q, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.90 (t, 3H). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 140.0, 134.0, 130.5, 128.5, 31.8, 30.5, 29.5, 29.3, 22.8, 14.0.[72]

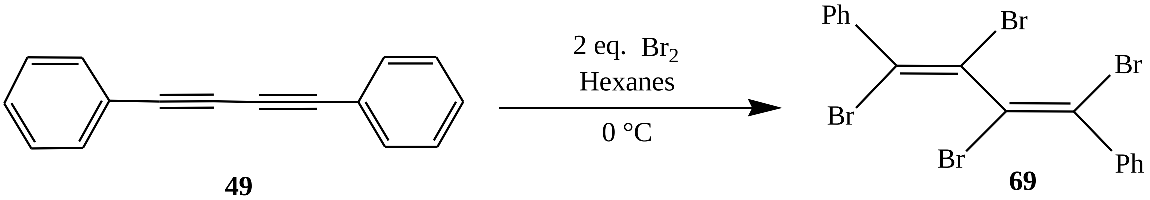
Diphenylbutadiyne (**49**)[79]



71 **49**

CuCl (6.018 g, 0.061 mol) and TMEDA (6.9 mL, 0.046 mol) were added to 150 mL acetone and allowed to stir under O_2 for 24 h. The solution resulted in a dark blue green color and was filtered into a 250 mL 3-neck round bottomed flask. Under an atmosphere of O_2, phenylacetylene (**71**, 6 mL, 0.055 mol) was added via syringe. The reaction mixture was stirred under reflux at 40 - 45 °C for 24 h. The resultant brown/black solution was subjected to vacuum filtration through a plug (silica gel, hexanes). The solvent was then removed *in vacuo* to obtain diyne **49** as a white/pale yellow solid. (5.339 g, 96% yield). ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 73.9, 81.5, 121.8, 128.4, 129.2, 132.5.[77]

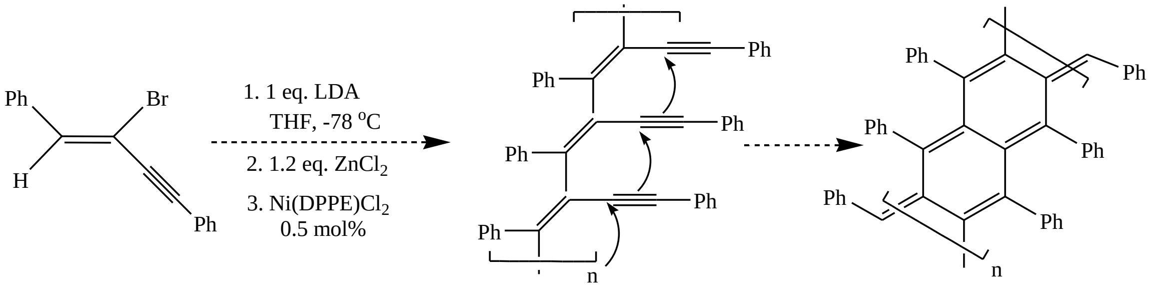
((1E,3E)-perbromobuta-1,3-diene-1,4-diyl)dibenzene (**69**)[56]



49 **69**

Under an atmosphere of argon, 11 mL of hexanes was added to diphenylbutadiyne (**49**, 0.2102 g, 0.1039 mmol). Via syringe, Br_2 (0.11 mL, 2.078 mmol) was added dropwise to the reaction mixture at 25 °C and stirred for 5 min. The reaction flask was submersed in an ice water bath and continued to stir at 0 °C for 1 h. The reaction mixture was filtered with cold hexanes and the solvent removed *in vacuo*. The light yellow solid was recrystallized in hexanes and chloroform, yielding compound **69** as a light yellow solid (41.2 mg, 76 % yield, m.p. 176-176 ^{o}C). R_f (hexanes: ethyl acetate, 50:1): 0.17. ^{13}C-NMR (400 mHz) ($CDCl_3$) δ: 116.3, 122.7, 128.3, 112.9, 113.0, 138.6.[56]

Polymeric Acenes (**48**)



46 **47** **48**

Under an atmosphere of argon, 3 mL of freshly distilled THF was added to haloenyne **46** (50.0 mg, 0.177 mmol). Dropwise, *n*-BuLi (0.11 mL, 0.177 mmol) was added at -78 ^{o}C and allowed to stir for a 5 min duration. Via syringe, the addition of flame dried $ZnCl_2$ (0.97 mg, 0.530 mmol) dissolved in THF proceeded. The reaction mixture warmed to room temperature (2-3 h), where $Ni(DPPE)Cl_2$ (5.0 mg, 0.5 mol%) in THF was added via syringe at 0^{o}C. The resultant mixture was given 14 h to stir. The reaction mixture was quenched with 1 mL MeOH and extracted with hexanes (40 mL) and washed with NaCl. The combined organic phase was then dried with magnesium sulfate and the solvent was removed *in vacuo*. After column chromatography (silica gel, hexanes), ^{13}C and ^{1}H NMR indicated only starting material **46**.

Chapter III

PERHALOCUMULENES

III.1 Synthetic Background: Planar Cross-Conjugated Molecules

When the sequential combination of sp and/or sp^2 hybridized carbons creates a cross-conjugated π-system, of the three unsaturated groups, "two centers separately conjugated to the third are themselves separated by two single bonds."[80] Examples of cross-conjugated compounds are shown in Figure III.1. Simple cross-conjugated π-systems such as butadiene and its derivatives have been studied both theoretically and experimentally.[81]

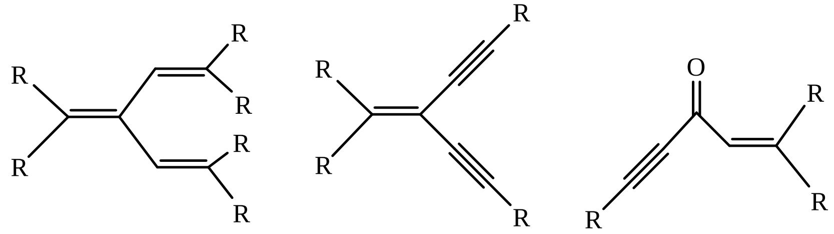
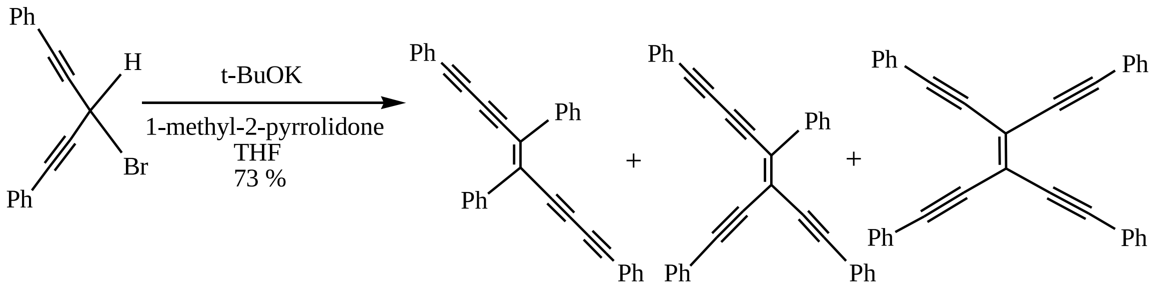


Figure III.1 Simple cross-conjugated systems.

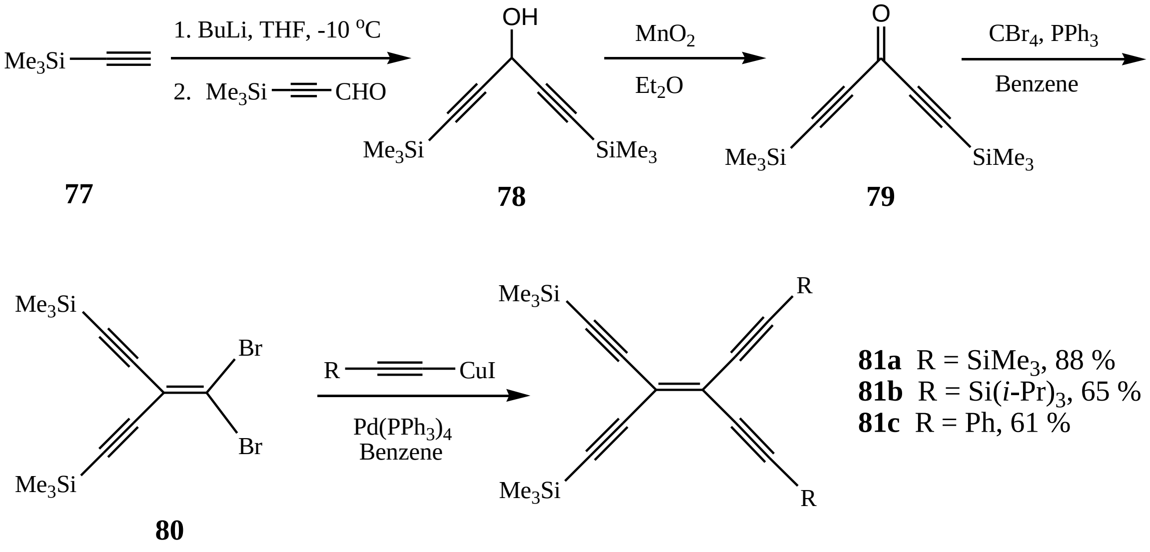
Simple cross-conjugated molecules were synthesized by Hori et al. by dimerization of 1,4-pentadiyne (Scheme III.1). 1,5-diphenyl-3-bromo-1,4-pentadiyne (**73**) was treated with a strong bulky base, yielding compounds **74, 75, 76**. However, the desired compound **76** was present in only small yields.



73 **74** **75** **76**

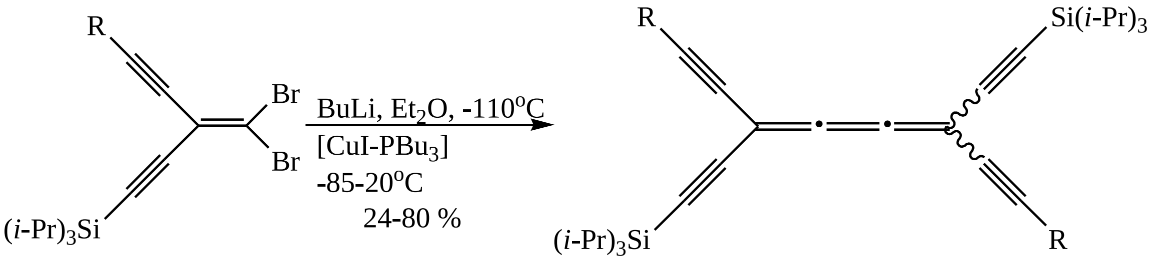
Scheme III.1. Dimerization of 1,5-diphenyl-3-bromo-1,4-pentadiyne **73**.

Diederich and co-workers have synthesized tetraethynylethene cumulenic derivatives using Sonogashira techniques.[82,83] Dibromoolefin **80** was coupled with terminal alkynes under Sonogashira conditions to yield the desired compounds **81a-c** (Scheme III.2). By using this synthetic route, many different substitution and protection patterns can be obtained.



Scheme III.2. Diederich’s tetraethynylethene cumulenic derivatives via Sonogashira coupling.

Another synthesis of cumulenic cored conjugated molecules via dimerization of dibromoolefins is shown in Scheme III.3.

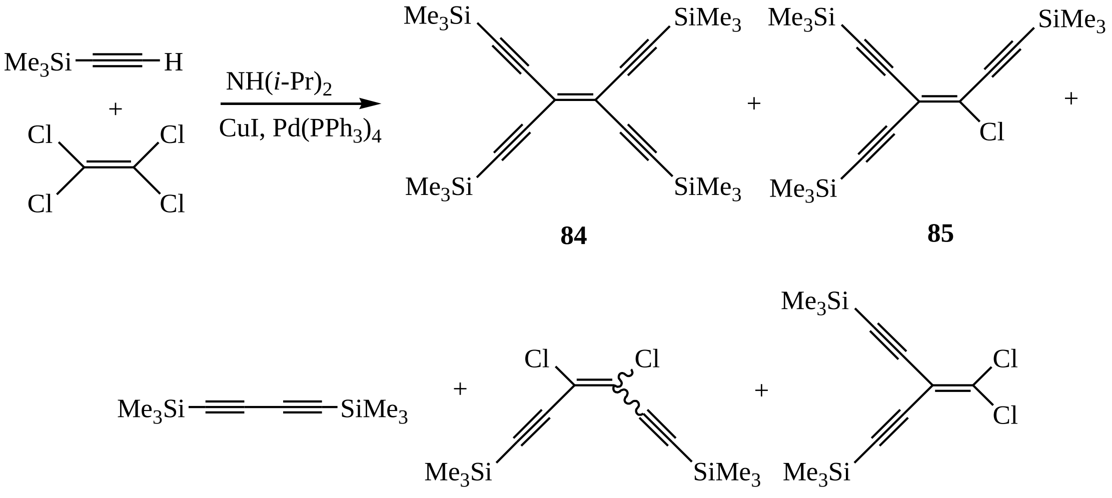


82 **83**

R = Ph, 4-NMe$_2$-C$_6$H$_4$, 3,5-(t-Bu)$_2$C$_6$H$_3$, Fc, t-Bu, 4-NO$_2$-C$_6$H$_4$, 4-MeO-C$_6$H$_4$

Scheme III.3 Diederich's route toward cumulenic cross-conjugated molecules.

An elegant, alternative synthetic route toward tetraethynylethenes was developed by Low *et al.*[84] utilizing Sonogashira conditions to directly couple trimethylsilylacetylene and tetrachloroethene (Scheme III.4).

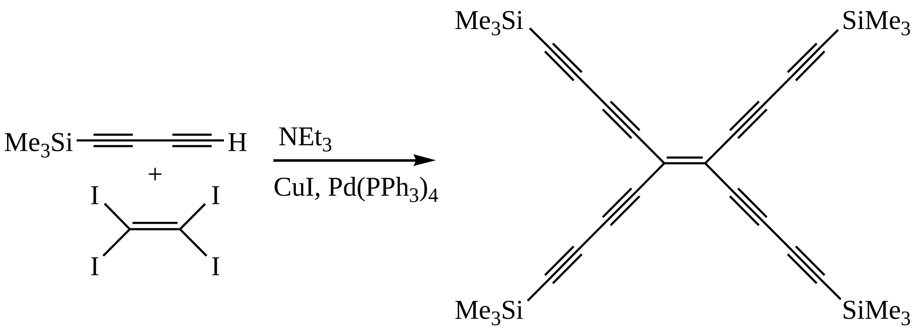


84 **85**

86 **87** **88**

Scheme III.4 Low's synthetic route towards tetraethynylethenes.

Tetrakis(trimethylsilylbutadiynyl)ethene was synthesized by Akita *et al.* utilizing the facile coupling of trimethylsilylbutadiyne and tetraiodoethene under Sonogashira conditions (Scheme III.5).[85] The product was isolated in a 50 % yield.



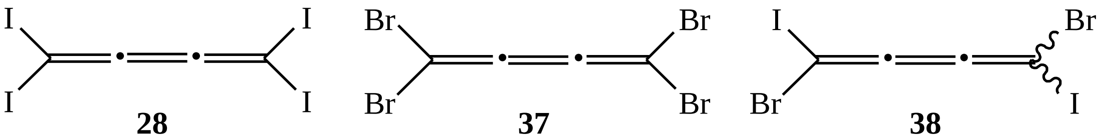
89

Scheme III.5 Akita's synthesis of tetrakis(trimethylsilylbutadiynyl)ethane (**89**).

III.2 Previous Work to Prepare Cross-Conjugated Cumulenes

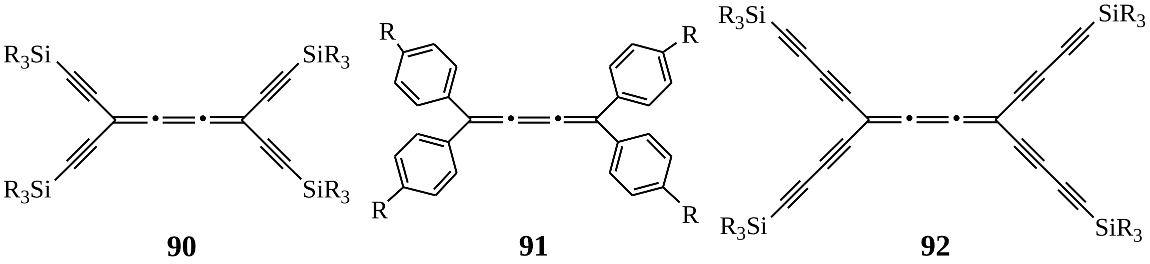
In an effort to broaden the core scaffold upon which cross-conjugated molecules are built, Goroff and co-workers attempted to use cumulenic tetrahalogenated compounds (such as C_4I_4, C_4Br_4, and $C_4Br_2I_2$, shown in Figure III.2) as precursors toward the known, previously reported cross-conjugated compounds in Figure III.3.[86] Unlike tetraiodoethene, compounds **28**, **37**, and **38** have an extended sp-hybridized core, creating a carbon rich center with the appropriate backbone for the target molecules as shown in Figure III.3. This synthetic design was intended to create an easier, more controllable route to these cumulenic cross-conjugated compounds.

The photonic and electronic properties of cross-conjugated molecules with cumulenic backbones have more recently acquired great interest. Since the full extent of their properties are unknown, due to inherent challenges of current synthetic procedures, Lei Li investigated alternate routes towards these targeted compounds using perhalocumulenes C_4I_4 (**28**), C_4Br_4 (**37**) , and $C_4Br_2I_2$ (**38**).[55]



28 **37** **38**

Figure III.2 Perhalocumulenes **28**, **37**, and **38**.

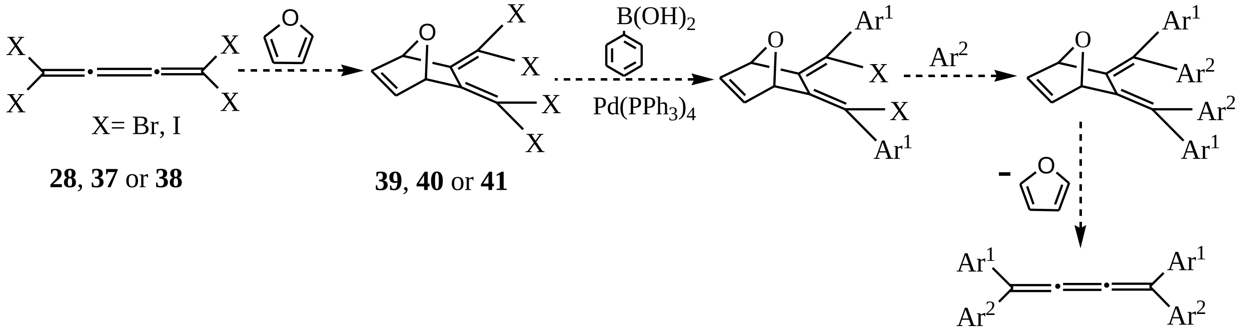


90 **91** **92**

Figure III.3 Targeted cross-conjugated compounds.

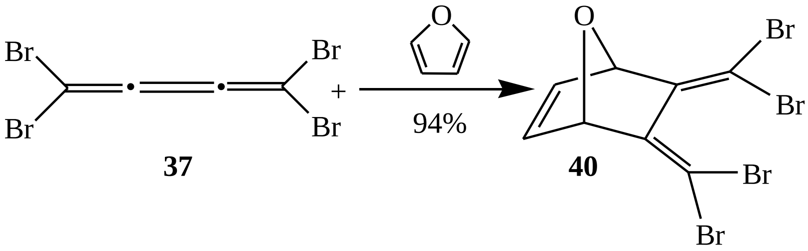
After developing synthetic procedures to synthesize perhalocumulenes C_4I_4 (**28**), C_4Br_4 (**37**), and $C_4Br_2I_2$ (**38**), Goroff and coworkers investigated their stability and solubility using TLC, NMR and GC-MS.[55,49] $C_4Br_2I_2$ is the least stable in solution, decomposing readily in most solvents, it is slightly tolerant of cyclohexanone and acetone. C_4I_4 (**28**) was found to be stable as a solid at room temperature, without decomposition. However, compound **28** has limited solubility and disproportionates in many organic solvents to form hexaiodobutadiene and other unidentified polymeric byproduct(s). C_4Br_4 is more stable and has better solubility when compared to **38** and **28**. However, all three perhalocumulenes decompose faster when exposed to light.

Although investigations show that perhalocumulenes C_4I_4 and $C_4Br_2I_2$ are not suitable starting materials for coupling to make cross-conjugated compounds, (mainly due to their poor solubility and poor stability in most organic solvents), the perhalocumulenes **28**, **37**, and **38** were found to undergo Diels-Alder reactions (Scheme III.6). These Deils-Alder adducts were subject to coupling conditions for further functionalization, and once isolated would undergo a retro Diels-Alder reaction to reform the cumulenic backbone.

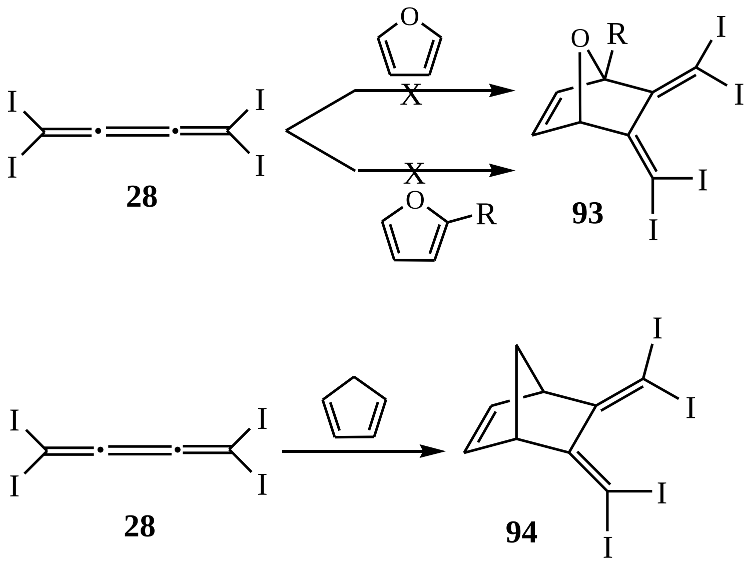


Scheme III.6 Proposed strategy toward cross-conjugated cumulenes.

When compound **37** was stirred in furan at ambient temperature for 48 hours, the Diels-Alder adduct **40** was produced in 94% yield (Scheme III.7). However, when perhalocumulene C_4I_4 was placed in furan or furfuryl alcohol, no reaction occurred due to poor solubility (Scheme III.8).[56] Cyclopentadiene was tried next. The FAB-Mass, spectrum of the products indicated a molecular weight consistent with Diels-Alder adduct **94** (Scheme III.8). Yet due to the formation of large amounts of dicyclopentadiene, adduct **94** could not be isolated or clearly observed in the NMR spectrum.[56]



SchemeIII.7 Diels-Alder reaction of perhalocumulene **37**.

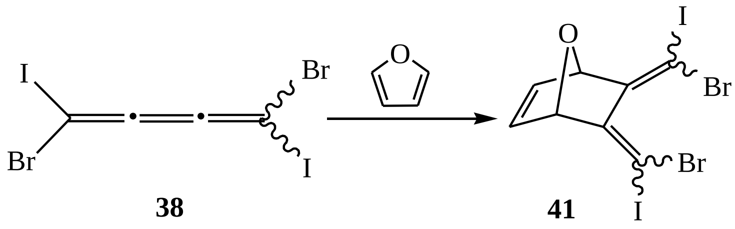


Scheme III.8 Diels-Alder reactions of perhalocumulene **28**.

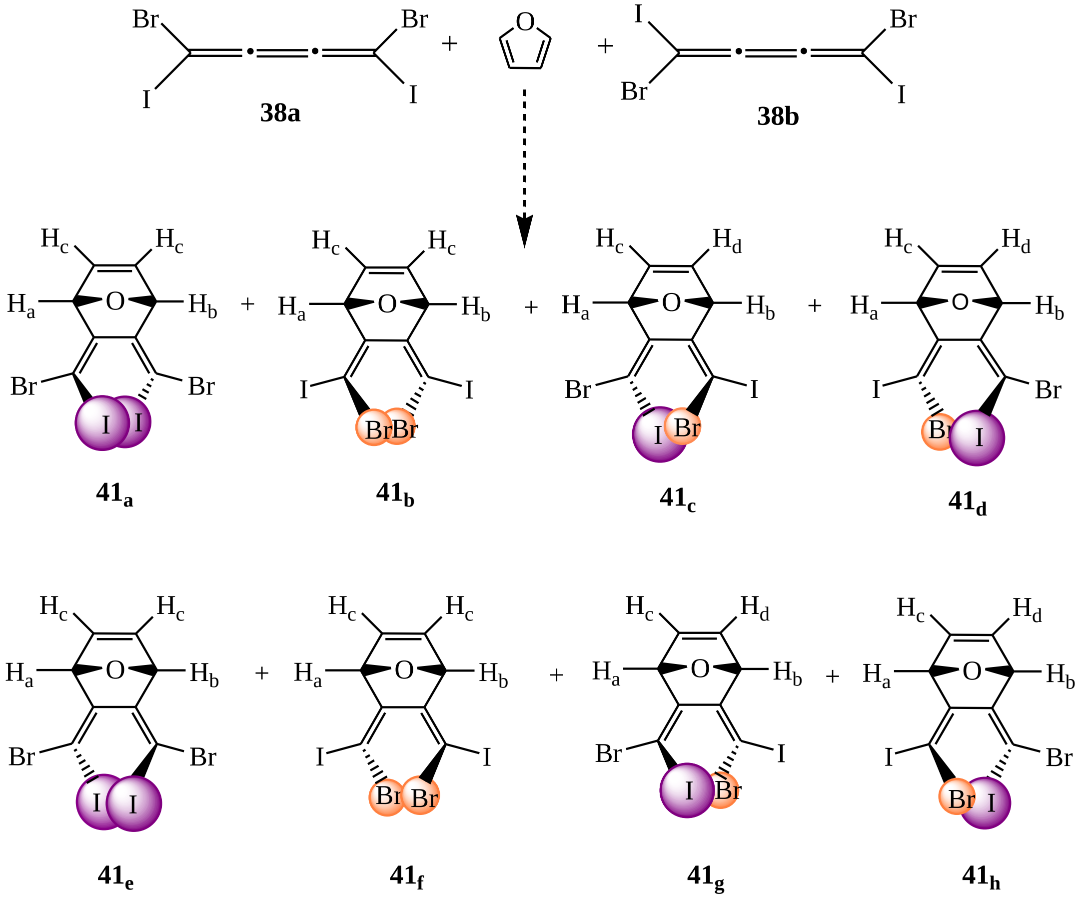
$C_4Br_2I_2$ reacted with furan for 48 hours, monitored by TLC (Scheme III.9). However, although ^{1}H NMR data show that reaction clearly occurred, isolation of adduct(s) **41** was not successful. The TLC and ^{13}C NMR indicate the presence of significant amounts of starting material, which may be attributed to several factors: the instability of adduct **41** on SiO_2, the potential for adduct **41** to undergo a retro-Diels-Alder reaction when neat, or the possibility of perhalocumulene **38** partially decomposing during the initial stages of the reaction (undergoing dehalogenation and readdition, to give other cumulenes).

The ^{1}H-NMR spectrum indicated a mixture of Diels-Alder products. Two different groups of proton signals appear in the spectrum, (δ ~5.5 - 5.9 ppm, and ~6.8 - 6.9 ppm, shown in Figure III.4) corresponding to the bridge-head and alkene protons of the adduct. The components of the mixture could not be confirmed. Due to the many possible stereoisomeric structures of the adduct **41** (as shown in Scheme III.10), identifying the major products was difficult.

However, in light of recent *ab initio* calculations conducted by Nancy Goroff, the interconversion between diastereomeric adducts is ≤ 1 kcal/mol (Figure III.5). Therefore, four possible adducts likely to be detected by NMR. Further investigation of this reaction is necessary to understand which major isomers are formed.



Scheme III.9 Diels-Alder reaction of perhalocumulene **38** and furan.



Scheme III.10 The Diels-Alder adducts of cumulene **38**.

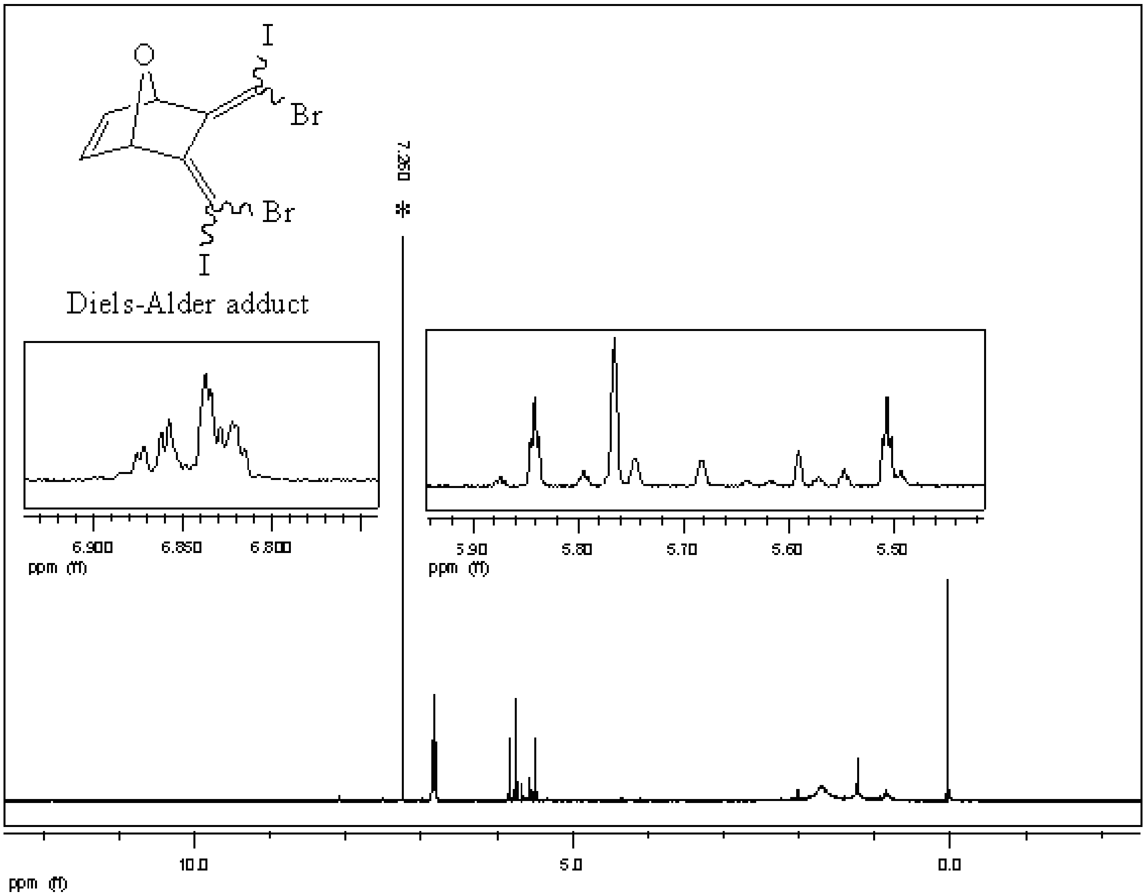


Figure III.4 ^{1}H-NMR spectrum of the Diels-Alder adducts **41**.[56]

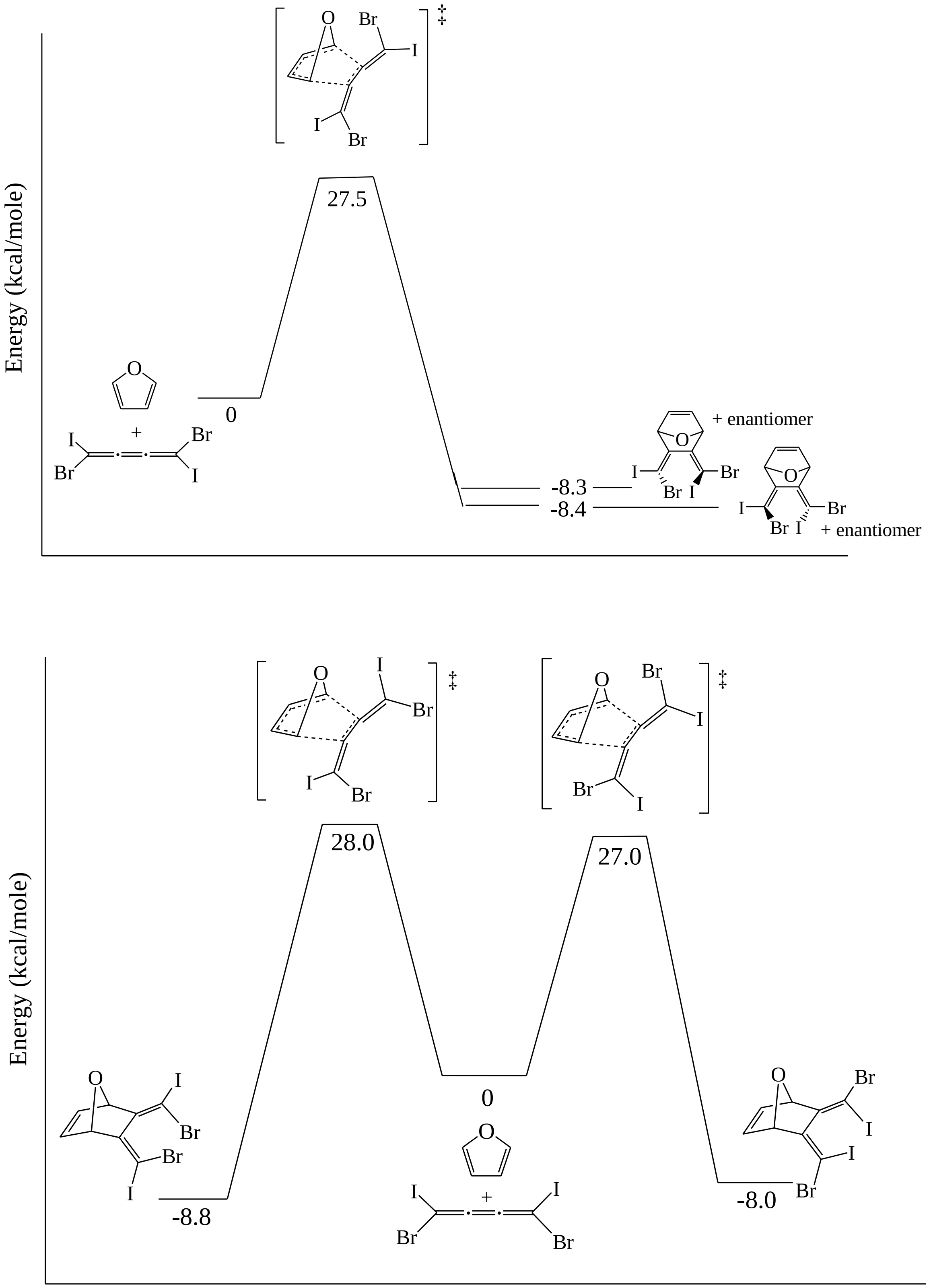
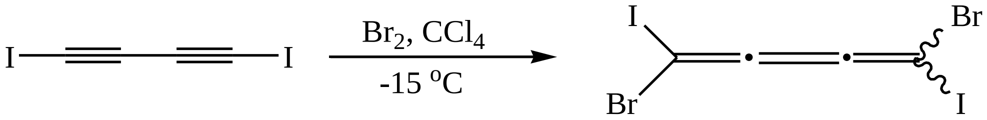


Figure III.5 Calculated stereoisomeric transition states and products for the Diels-Alder reaction of cumulene **38** and furan.

III.3 Results and Discussion

III.3.1 Preparation of Perhalocumulene 38

Several attempts were made to prepare cumulene **38** for the Diels-Alder reaction with furan (Scheme III.11). Reactions were analyzed by TLC, GC-MS, IR, and melting point, prior to and after crystallization, as summarized in Table A.5 (see appendix). Melting points described here are those taken after crystallization. All purifications and crystallizations were carried out in limited light and/or in darkness.



27 **38**

Scheme III.11 Synthesis of $C_4Br_2I_{2.}$

Following a procedure established by Yi Zhang, one equivalent of C_4I_2 was dissolved in 4 mL of CCl_4 at -20 °C, followed by addition of one equivalent of $Br_{2.}$ After one hour, 15 mL of cold pentane was added to facilitate the precipitation of product **38**. Since compound **38** decomposes with exposure to light, the reaction was carried out in the dark. Initially, a combination of over-addition and halogen exchange products were mainly observed in the GC-MS of the crude product, with a low relative abundance of cumulene **38**. These over-addition products included compounds $C_4Br_{4,}$ $C_4Br_{6,}$ C_4Br_5I, and $C_4Br_3I_3$. Detection of unreacted diiodobutadiyne in the filtrate was consistent with the addition of only a single equivalent of Br_2.

To prevent over-addition of $Br_{2,}$ diluting the reagent with *n*-pentanes was attempted using a 1.55M solution. Reaction times were limited to one hour instead of two. We also tried a single solvent system to avoid the product's prolonged exposure to

CCl_4 since **38** decomposes readily in this solvent undergoing dehalogenation followed by readdition. *n*-Pentanes was employed since diiodobutadiyne **27** is soluble in non-polar solvents and perhalocumulene **38** precipitates out of these solvents. However, the GC-MS spectrum only showed evidence of over-addition products. The use of light was also varied. When completely void of light or having limited exposure, the formation of compound **38** is hindered resulting in mostly starting material.

The conditions set forth by Yi Zhang were revisited. However, instead of using equivalent stoichiometric amounts of C_4I_2 and Br_2, compound **27** was used in 10% mmol excess. After the initial temperature of -15 ºC was reached, the reagents were added in the presence of light. The temperature was allowed to fluctuate between -15 and 0 ºC. The GC-MS spectrum of the crude material showed a very high relative abundance of cumulene **38**. A three solvent crystallization system was implemented (cyclohexanone, acetone, and *n*-pentanes) instead of the original cyclohexanone and acetone. Crude perhalocumulene **38** was dissolved in cyclohexanone while cold acetone and *n*-pentanes was added dropwise. $C_4Br_2I_2$ was isolated in the form of fine, yellow, needle crystals with a melting point of 113 ºC. Characterization of cumulene **38** was accomplished by mass spectrometry and IR spectroscopy (1617, 736, 691, 462 cm^{-1}). ^{13}C NMR data is not available due to the nature of $C_4Br_2I_2$; decomposition occurred in all of the solvents that were tried at room temperature (DMSO, cyclohexanone, pyridine, acetone, etc.).

III.3.2 Diels-Alder Reaction

Compound **38** was treated with freshly distilled furan to undergo a Diels-Alder reaction. After 48 hours the reaction was investigated by ^1H-NMR, which showed no evidence of reaction. The melting point of the recovered material was 116 ºC. This material was subjected to IR, which confirmed the presence of starting cumulene **38**. Current efforts are focused on understanding these results. Future studies will concentrate on this reaction.

III.4 Summary

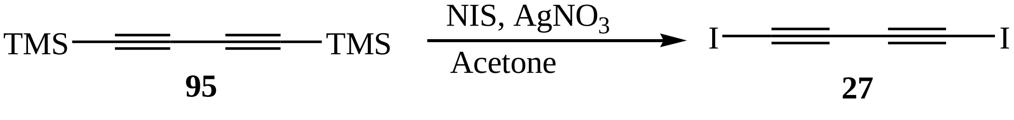
Although diiodobutadiyne decomposes when exposed to light, limited initial exposure is necessary to initiate the reaction for the formation of compound **38.** Using a slight excess of starting material also guarantees consumption of $Br_{2,}$ limiting the formation of over-addition products. Crystallization from a three-solvent system of cyclohexanone, acetone, and *n*-pentanes was most effective to achieve pure material.

Compound **38** was treated with furan to prepare the Diels-Alder adduct, but IR and NMR data do not provide evidence of reaction. This result is in conflict with the previous product that was obtained by Lei Li. This reaction will be further explored.

III.5 Experimental

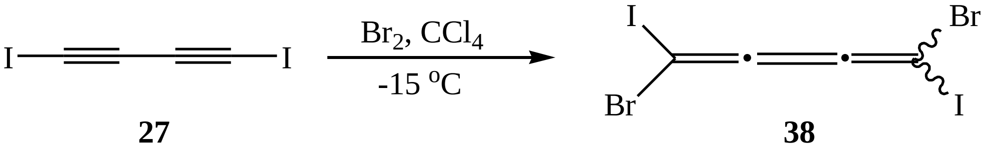
General: Reagents were purchased reagent grade from Aldrich, Fisher Scientific/Acros Organics, Strem, and GFS Chemicals, and used without further purification. Hexanes and acetone solvents were purchased from VWR. Tetrahydrofuran and diethylether were each distilled under argon from sodium/benzophenone. $MgSO_4$ or Na_2SO_4 was used as the drying agent after aqueous work-up. All reactions were performed under an inert atmosphere of Ar. Evaporation and concentration of unstable compounds *in vacuo* was carried out at 0 ^{o}C. Thin-layer Chromatography (TLC) was performed on plastic-backed silica gel plates, developed with PMA and visualized by UV light. Melting points were measured on a Thomas Hoover Capillary melting point apparatus, uncorrected. IR spectra (cm^{-1}) were completed using a *Nicolet Magna-IR 750.* ^{1}H- and ^{13}C-NMR spectra were taken using a 300, 400, and 500 MHz Varian NMR instruments, using tetramethylsilane as the internal standard at rt in $CDCl_3$ (solvent peak references: 7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR).

1,4-Diiodo-1,3-butadiyne (**27**)[87,88]



1,4-Bis(trimethylsilyl)-1, 3-butadiyne (**95**, 3.1 g, 16 mmol) was dissolved in acetone (500 mL). $AgNO_3$ (4 g, 0.02 mol) and N-iodosuccinimide (8.6 g, 38 mmol) were added to this solution. The reaction proceeded in the dark (reaction vessel wrapped in aluminum foil) and stirred at room temperature for 4 h. Ice water and cold hexanes was added to the mixture and the organic phase was extracted with hexanes (3×50 mL) and run through a plug (SiO_2 and cold hexanes). The combined organic layers were then dried with $MgSO_4$ and concentrated in *vacuo*. 1,4-Diiodo-1,3-butadiyne (**27**) was obtained as a light yellow solid (4.1 g, 87 % yield). R_f (Hexanes, SiO_2): 0.38. ^{13}C-NMR (400 MHz, $CDCl_3$): δ -3.1, 79.7.[88]

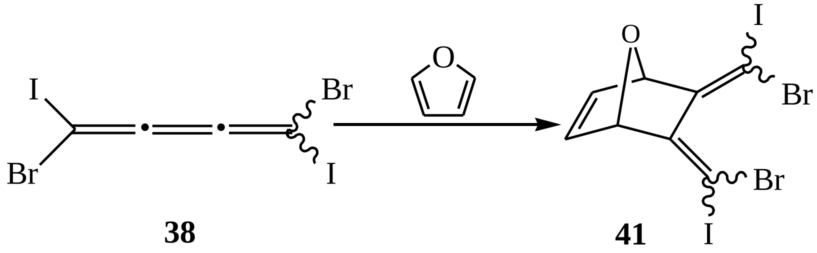
1, 4-Dibromo-1, 4-diiodo-butatriyne ($C_4Br_2I_2$) (**38**)[55]



27 **38**

A 25-mL three-necked round-bottomed flask, equipped with a magnetic stirrer bar, was charged with diiodobutadiyne (**27**, 0.98 g, 3.2 mmol), and CCl_4 (4 mL) in the absence of light. The mixture was cooled to approximately -15 ^{o}C in an ethylene glycol/CO_2 bath. Temperatures were monitored external to the reaction vessel. In the presence of light, 0.16 mL of Br_2 (490 mg, 3.1 mmol) was added via syringe. After stirring for 1 h at -15 ^{o}C, 15 mL cold *n*-pentane was added and the mixture was stirred for an additional hour. The temperature was allowed to fluctuate between -15 ^{o}C and 0 ^{o}C. The resulting precipitate was filtered and washed with cold *n*-pentane (in the dark), and crystallized from cyclohexanone, acetone and pentane to give compound **38** as yellow needle crystals (100 mg, 7 % yield, m.p. 113-113 ^{o}C). MS (EI) m/z 462 (M^+), 335 ($M\text{-}I^+$), 254 (I_2^+), 208 ($M\text{-}2(I)^+$), 127 (I^+), 91, 48 ($M\text{-}2(I)\text{-}2(Br)^+$); IR (neat) 1619, 739, 695, 464 cm^{-1}.[56]

*Perhalocumulene **41**/Diels-Adler adduct*



38 **41**

A 10-mL round-bottom flask was charged with a stir bar, and perhalocumulene **38** (30.0 mg, 0.065 mmol). Via syringe, 7 mL of freshly distilled furan was added. The solution was stirred at rt for 48 h, in the absence of light. The furan solvent was removed in *vacuo*, resulting in a white-yellow powder (24 mg). ^{1}H-NMR showed only peaks at δ 1.25, 1.54 and 7.26, corresponding to solvent. IR (neat) 1617, 736, 691, 462cm^{-1}.

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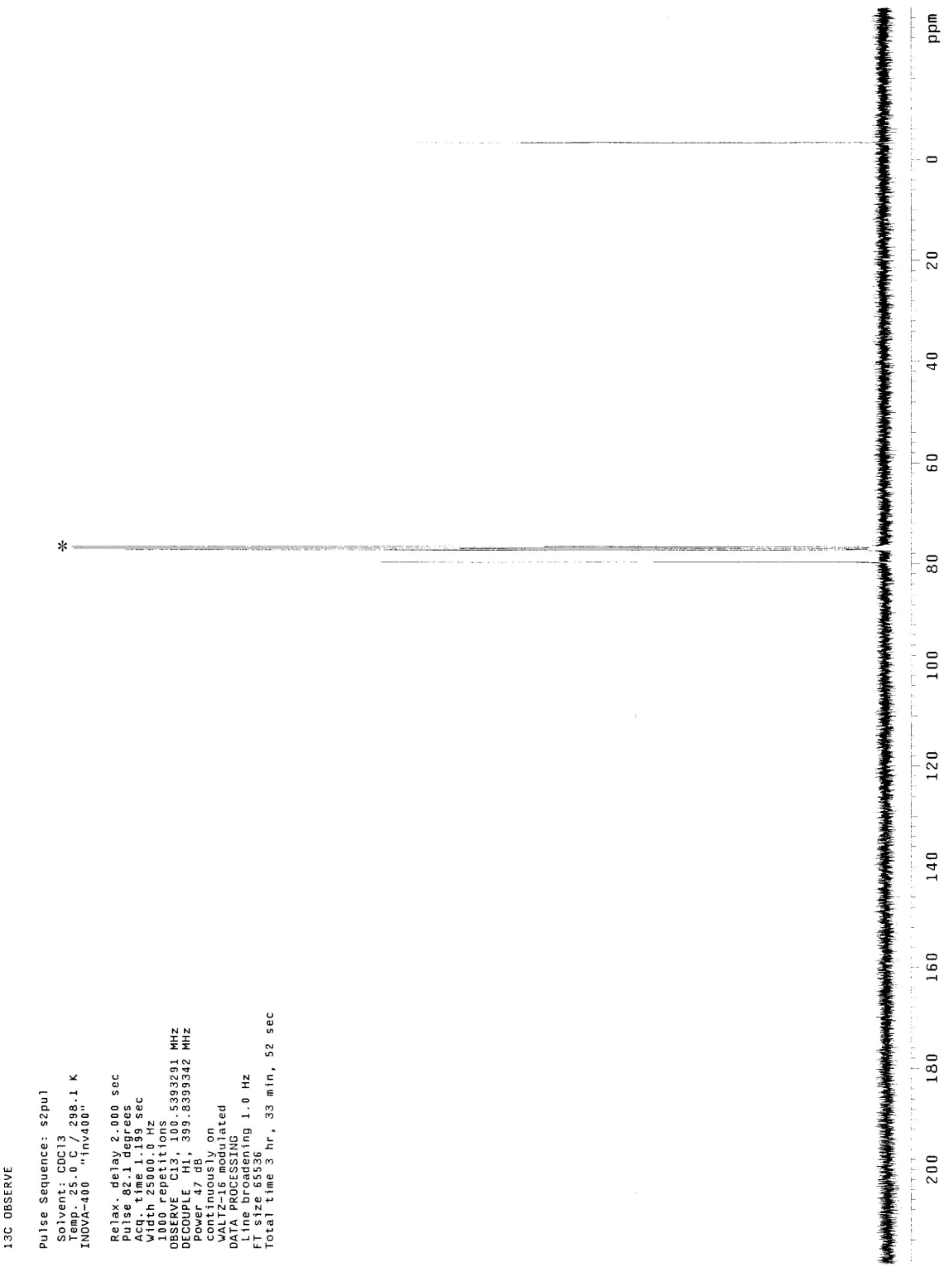
Appendix



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13C OBSERVE

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 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

Relax. delay 2.000 sec
Pulse 82.1 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1000 repetitions
OBSERVE  C13, 100.5393291 MHz
DECOUPLE  H1, 399.8399342 MHz
Power 47 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 33 min, 52 sec
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Figure A.1 ^{13}C-NMR spectrum of compound **27** in *CDCl$_3$ (400 MHz).

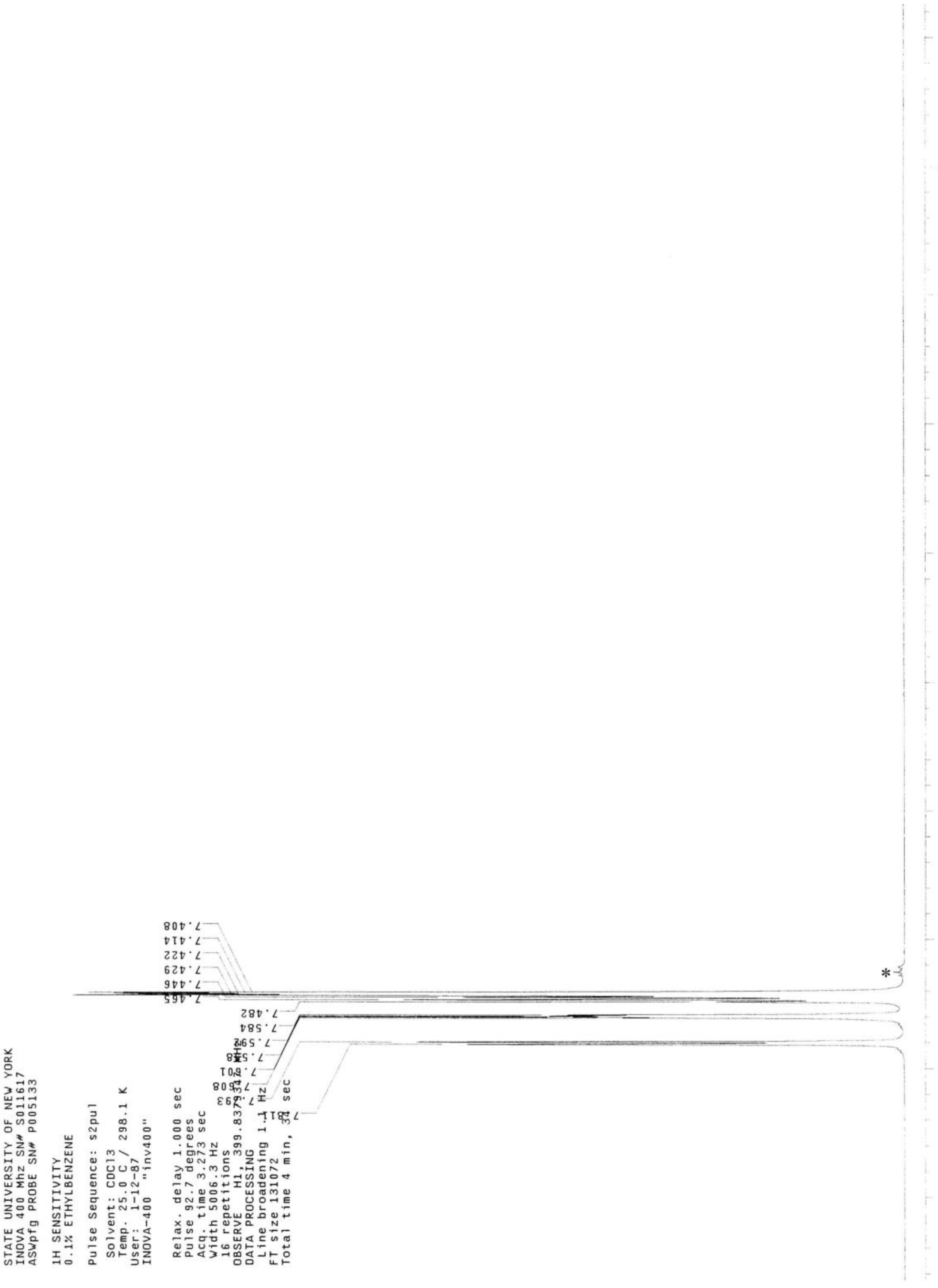


Figure A.2 ^{1}H-NMR spectrum of compound **46** in *CDCl$_3$ (400 MHz).

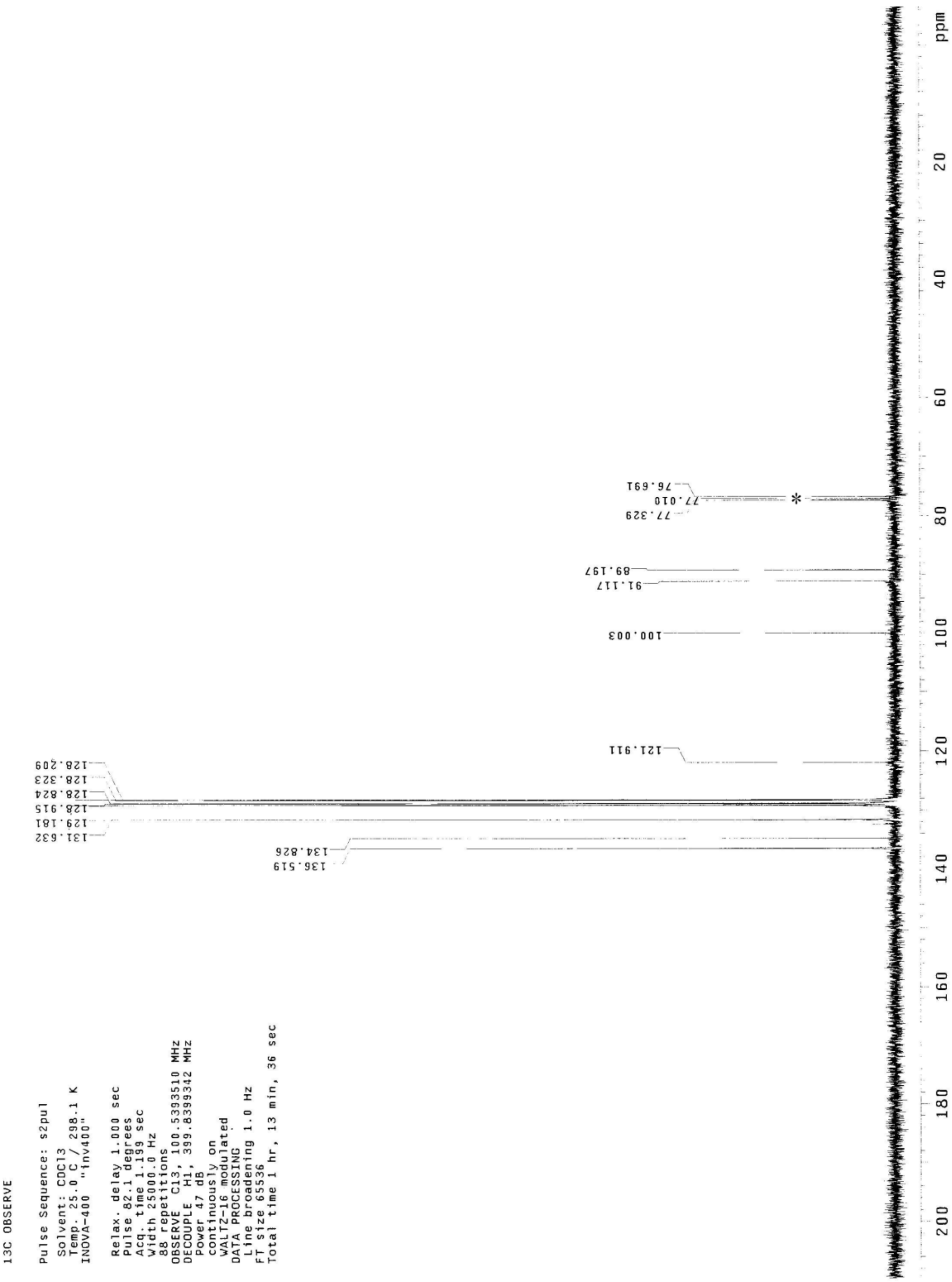
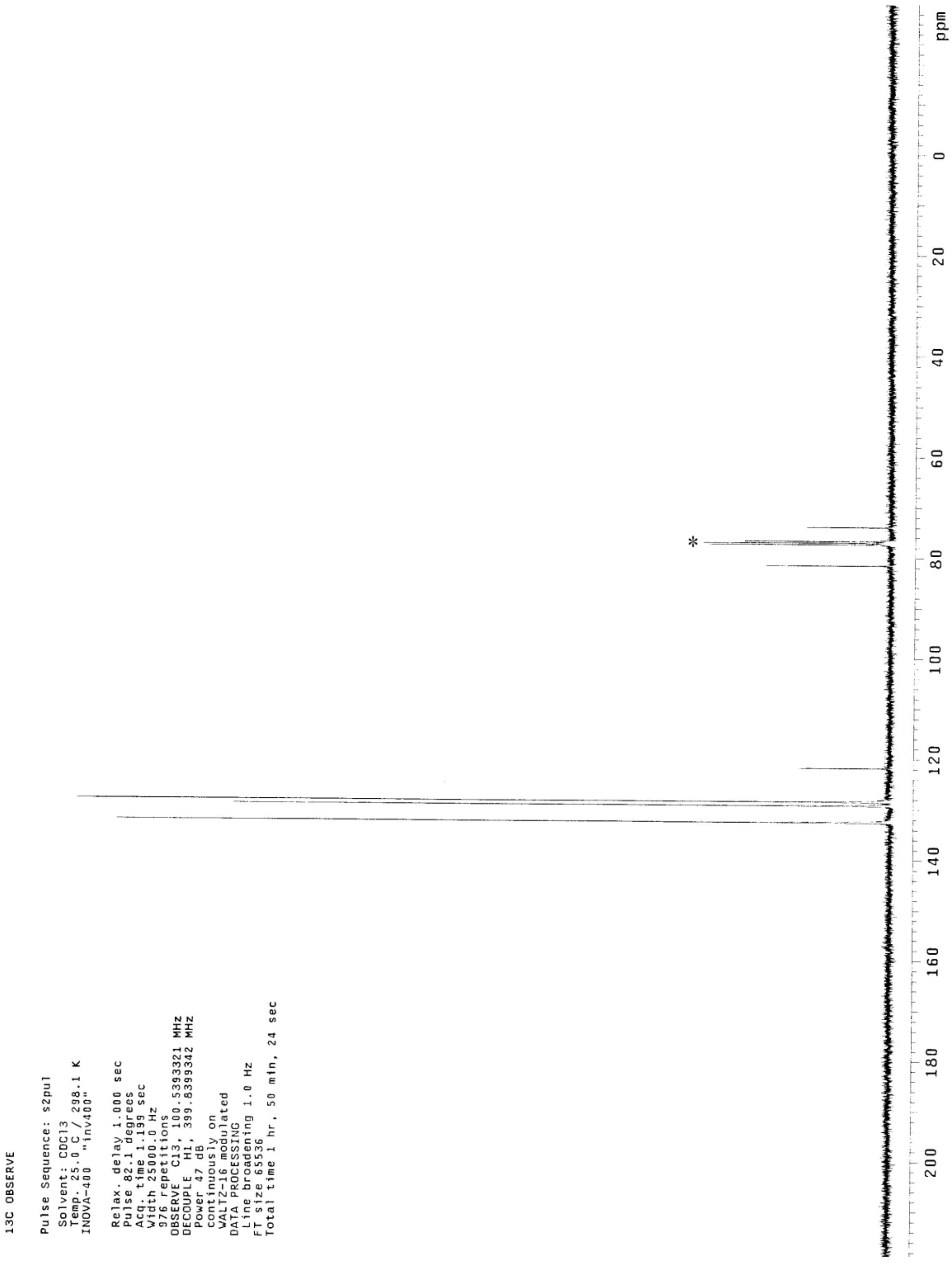


Figure A.3 ^{13}C-NMR spectrum of compound **46** in *CDCl$_3$ (400 MHz).



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 Solvent: CDCl3
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INOVA-400  "inv400"

  Relax. delay 1.000 sec
  Pulse 82.1 degrees
  Acq. time 1.199 sec
  Width 25000.0 Hz
   976 repetitions
OBSERVE  C13, 100.5393321 MHz
DECOUPLE  H1, 399.8399342 MHz
  Power 47 dB
  continuously on
  WALTZ-16 modulated
DATA PROCESSING
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FT size 65536
Total time 1 hr, 50 min, 24 sec
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Figure A.4 ^{13}C-NMR spectrum of compound **49** in *CDCl$_3$ (400 MHz).

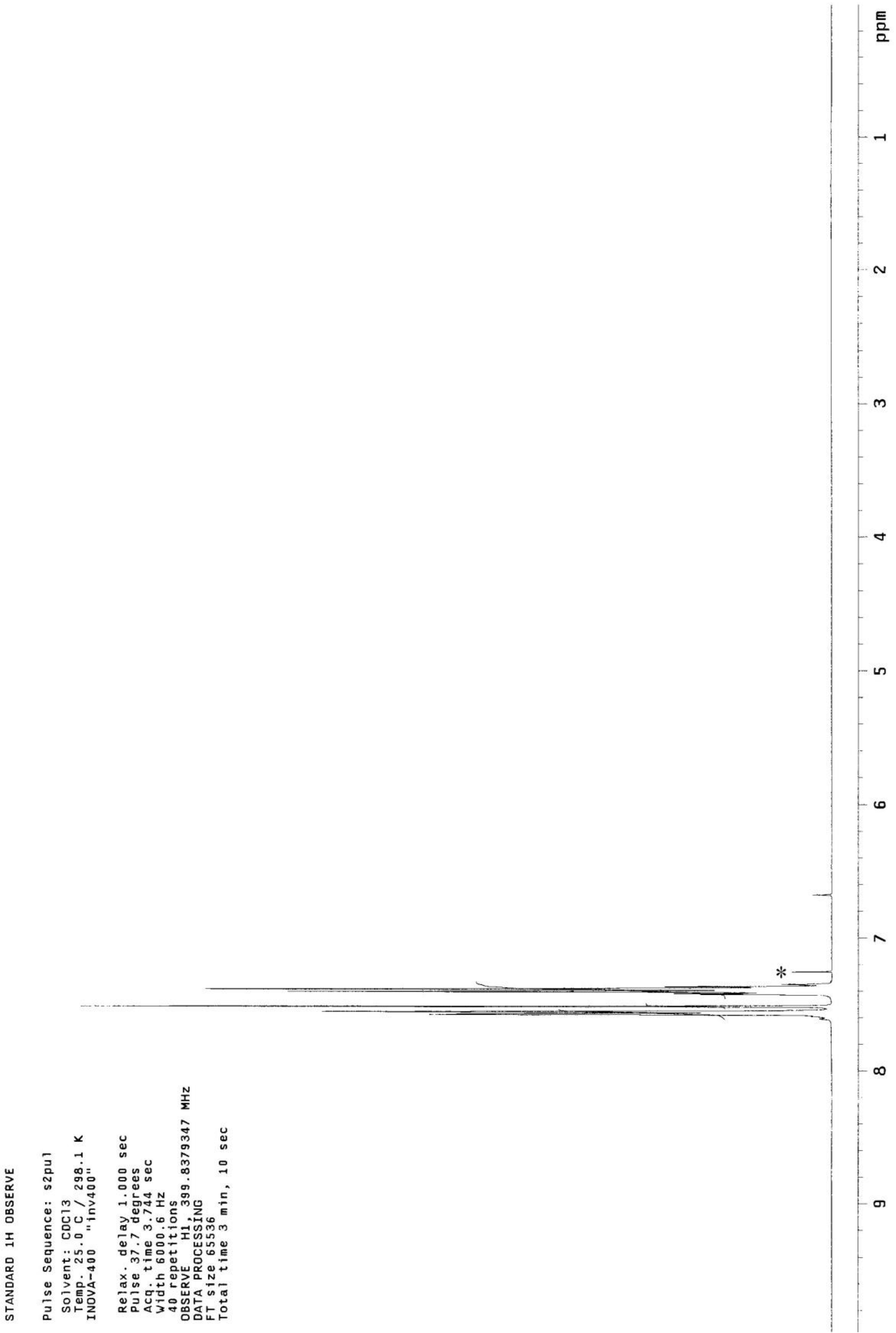
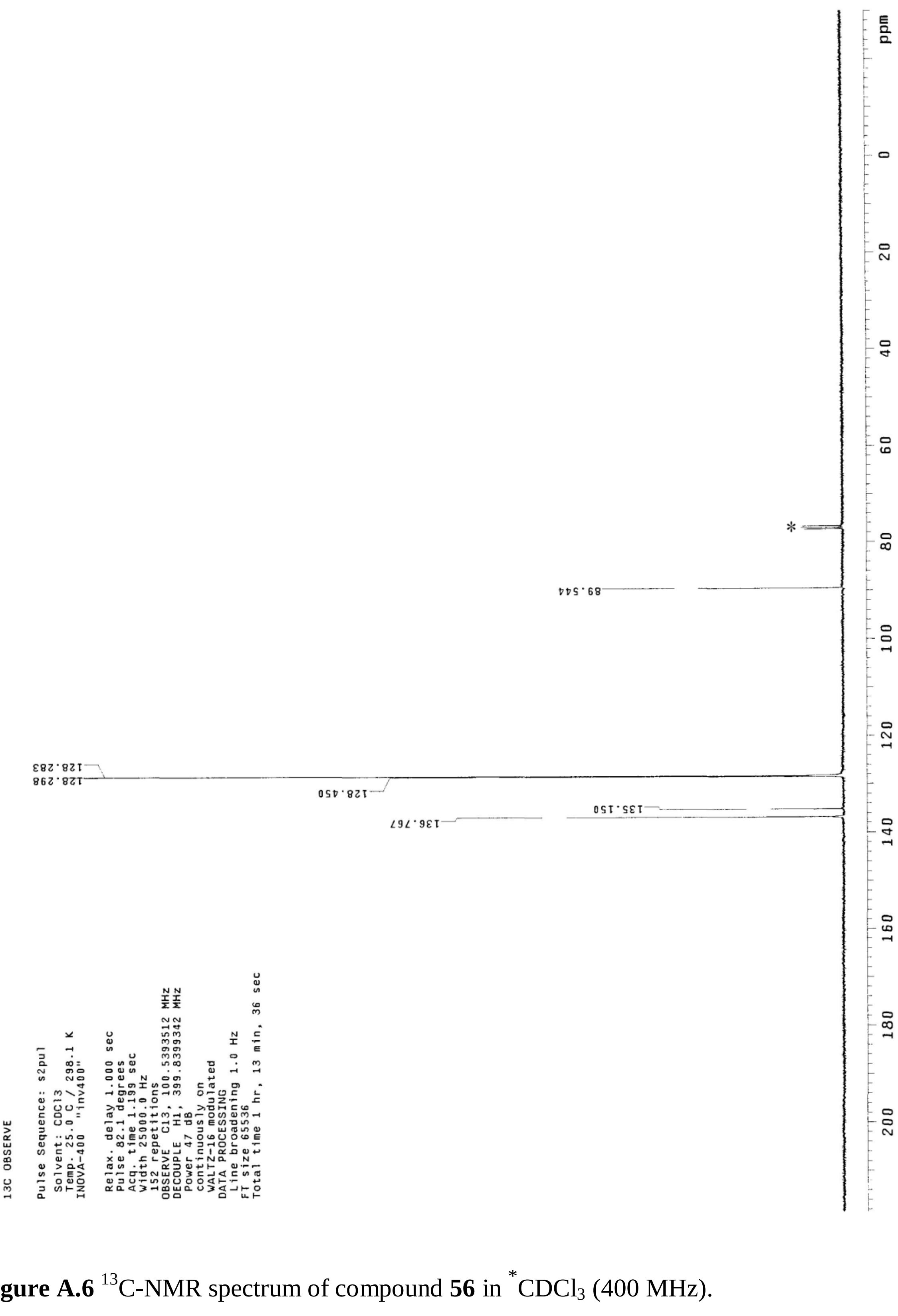


Figure A.5 ^{1}H-NMR spectrum of compound **56** in *CDCl$_3$ (400 MHz).



```
13C OBSERVE

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INOVA-400  "inv400"

  Relax. delay 1.000 sec
  Pulse 82.1 degrees
  Acq. time 1.199 sec
  Width 25000.0 Hz
  152 repetitions
OBSERVE   C13, 100.5393512 MHz
DECOUPLE   H1, 399.8399342 MHz
  Power 47 dB
  continuously on
  WALTZ-16 modulated
DATA PROCESSING
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FT size 65536
Total time 1 hr, 13 min, 36 sec
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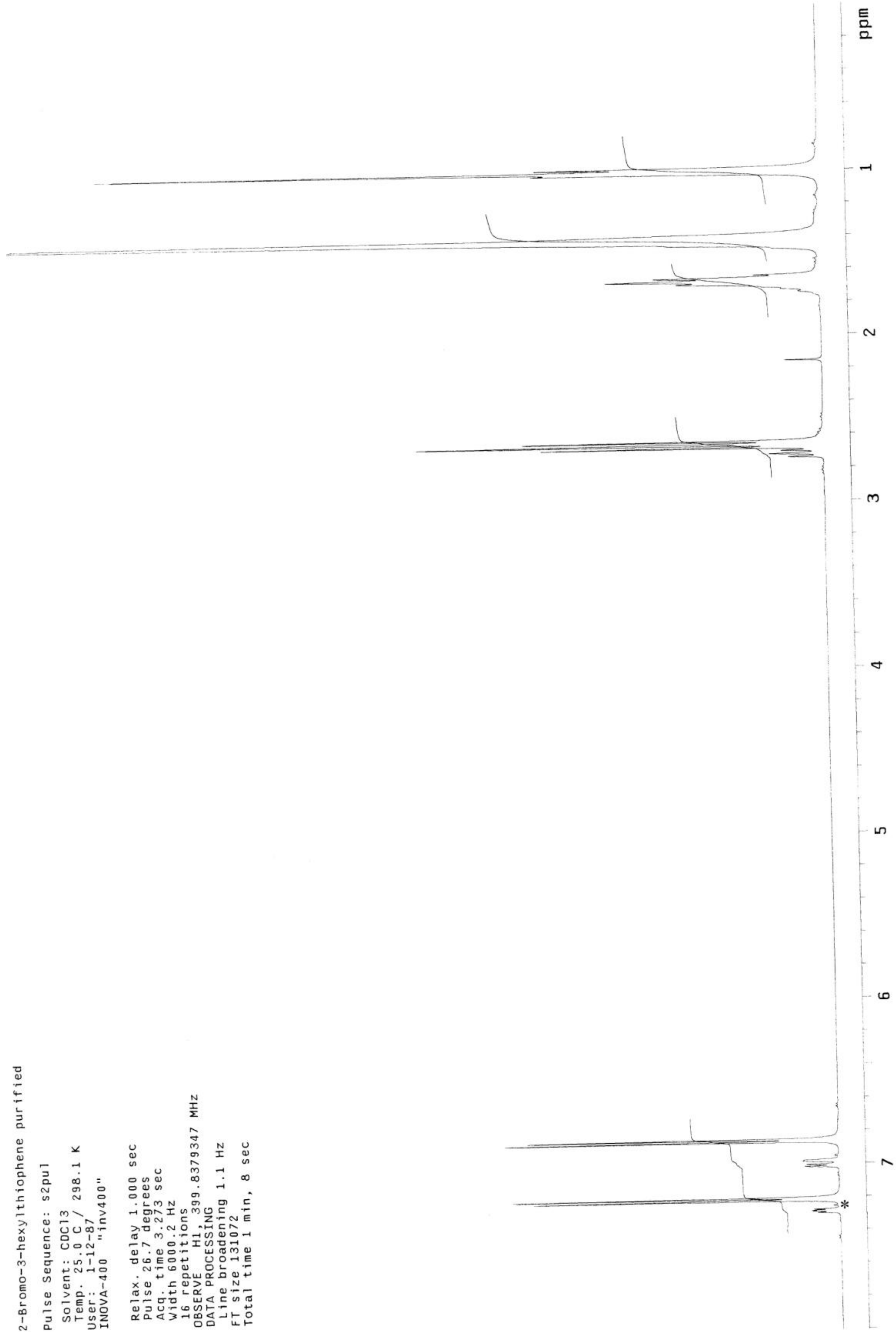
Figure A.6 ^{13}C-NMR spectrum of compound **56** in *CDCl$_3$ (400 MHz).



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2-Bromo-3-hexylthiophene purified

Pulse Sequence: s2pul

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 User: 1-12-87
 INOVA-400  "inv400"

Relax. delay 1.000 sec
Pulse 26.7 degrees
Acq. time 3.273 sec
Width 6000.2 Hz
 16 repetitions
OBSERVE   H1, 399.8379347 MHz
DATA PROCESSING
 Line broadening 1.1 Hz
FT size 131072
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Figure A.7 ^{1}H-NMR spectrum of compound **60** in *CDCl$_3$ (400 MHz).

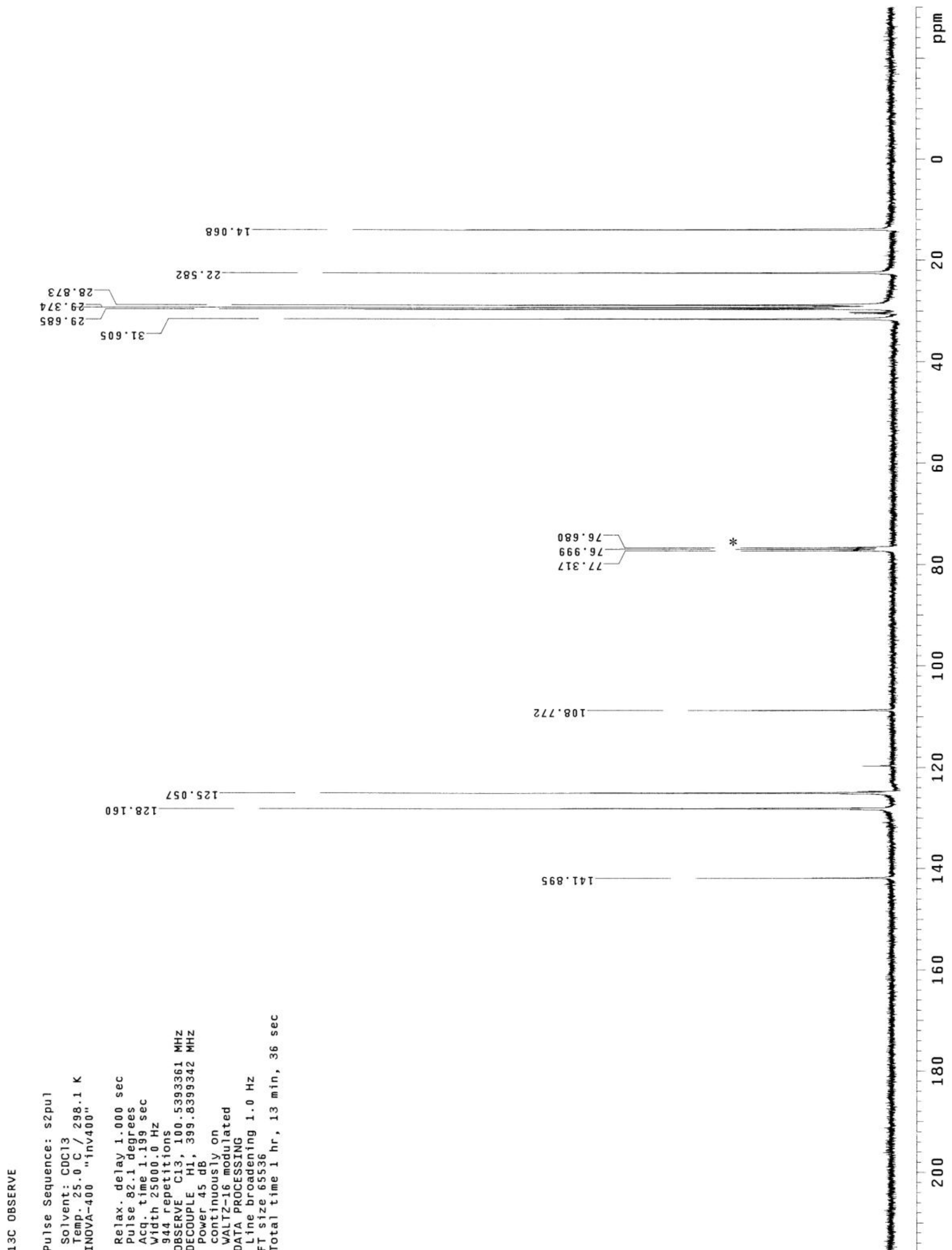
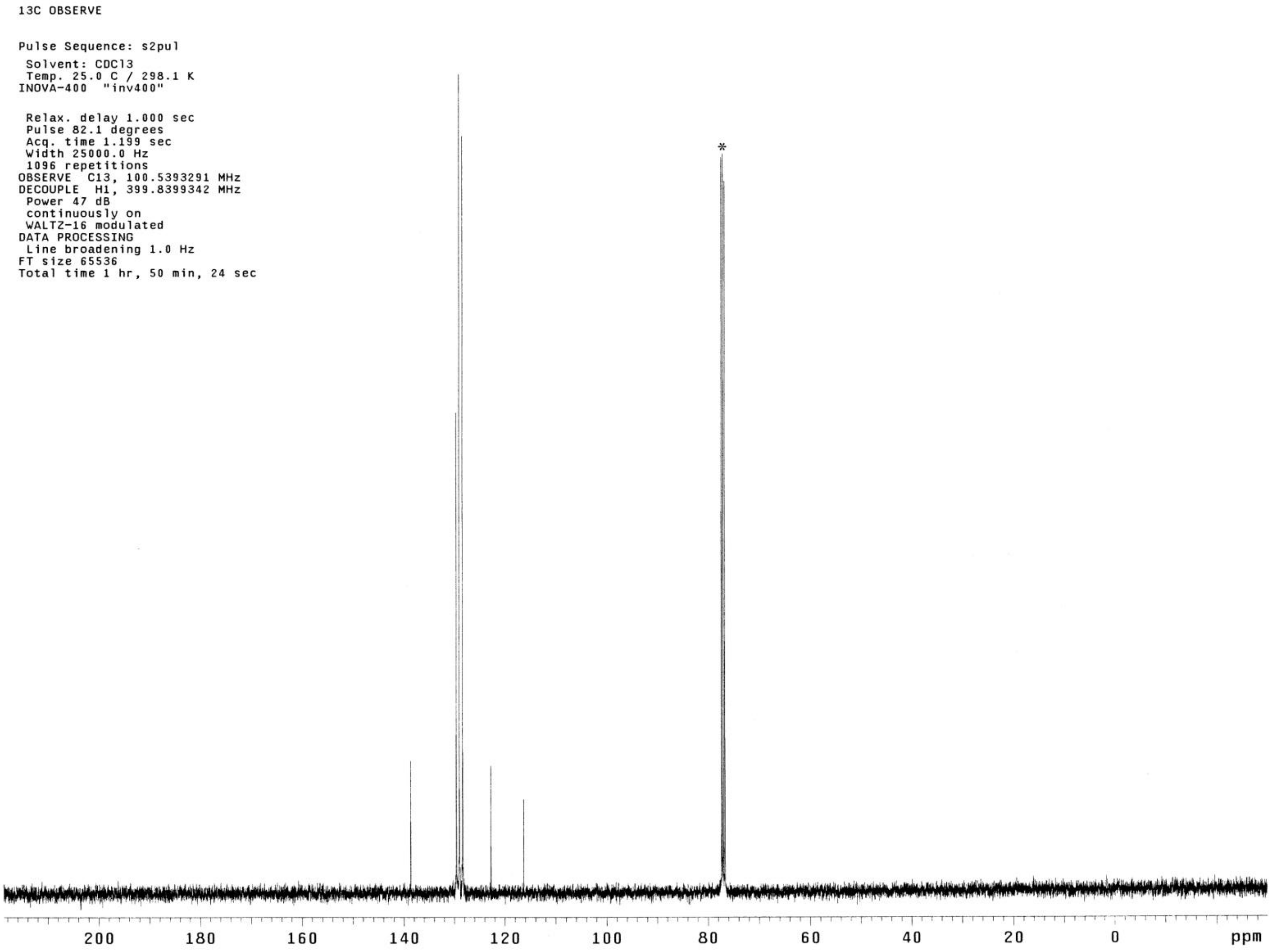


Figure A.8 ^{13}C-NMR spectrum of compound **60** in *CDCl$_3$ (400 MHz).



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13C OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1096 repetitions
OBSERVE  C13, 100.5393291 MHz
DECOUPLE  H1, 399.8399342 MHz
 Power 47 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 50 min, 24 sec
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Figure A.9 ^{13}C-NMR spectrum of compound **69** in *CDCl$_3$ (400 MHz).

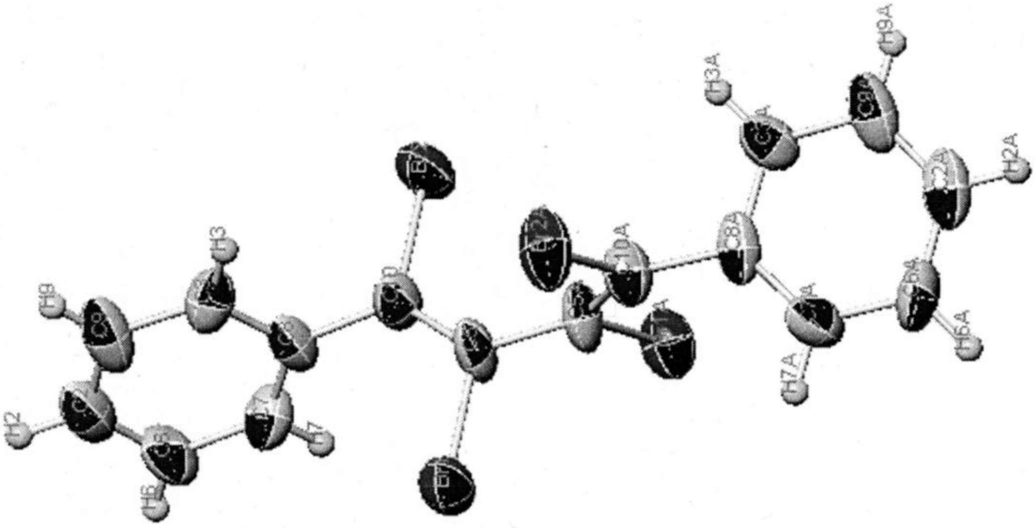


Table 1. Crystal data and structure refinement for cwbc113.

Identification code	cwbc113	
Empirical formula	C16 H10 Br4	
Formula weight	521.88	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 12.893(5) Å	α= 90°.
	b = 43.671(15) Å	β= 90°.
	c = 5.8444(19) Å	γ = 90°.

Figure A.10 Solved x-ray crystal structure of compound **69**.

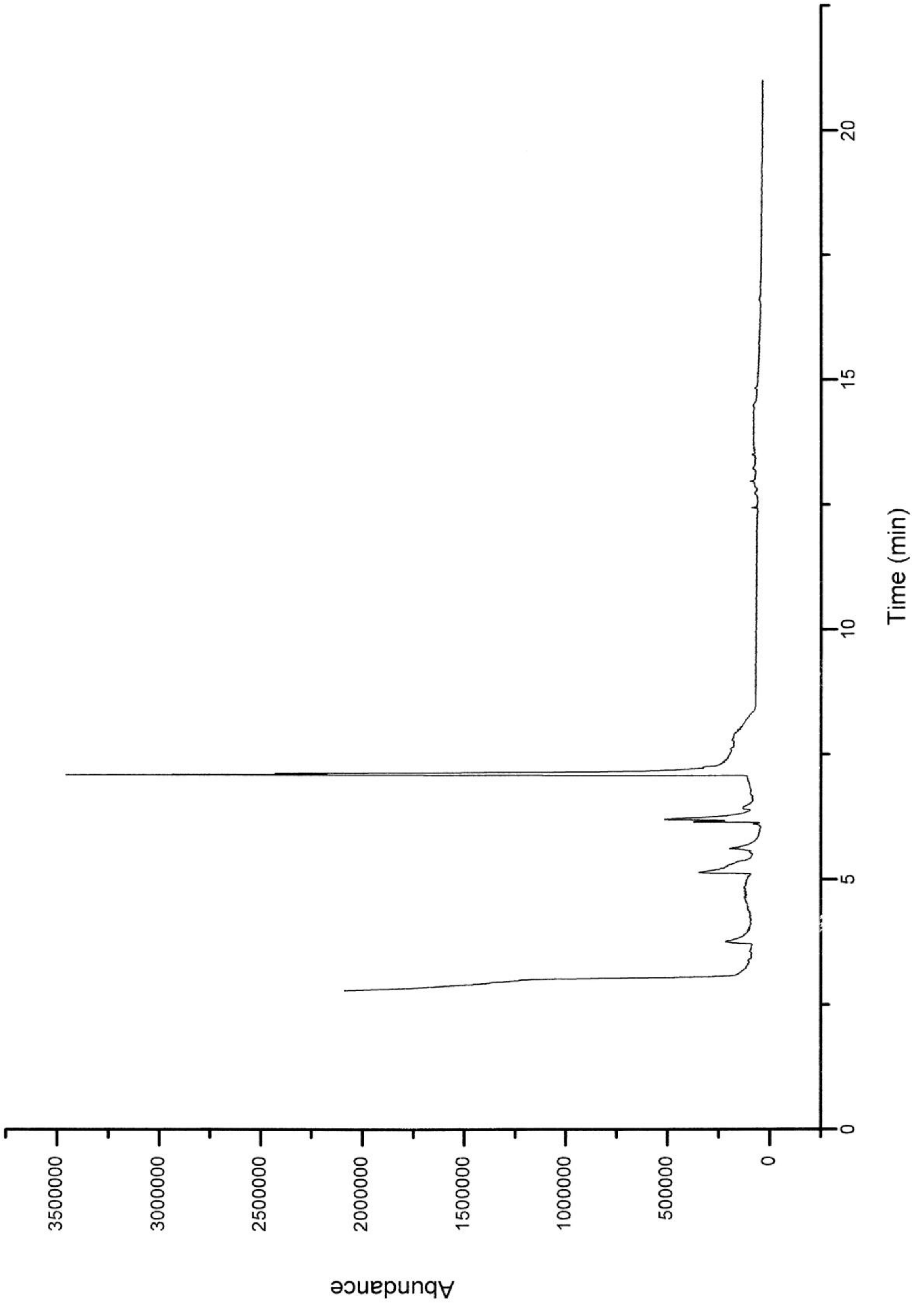


Figure A.11 Gas chromatogram of compound **38**.

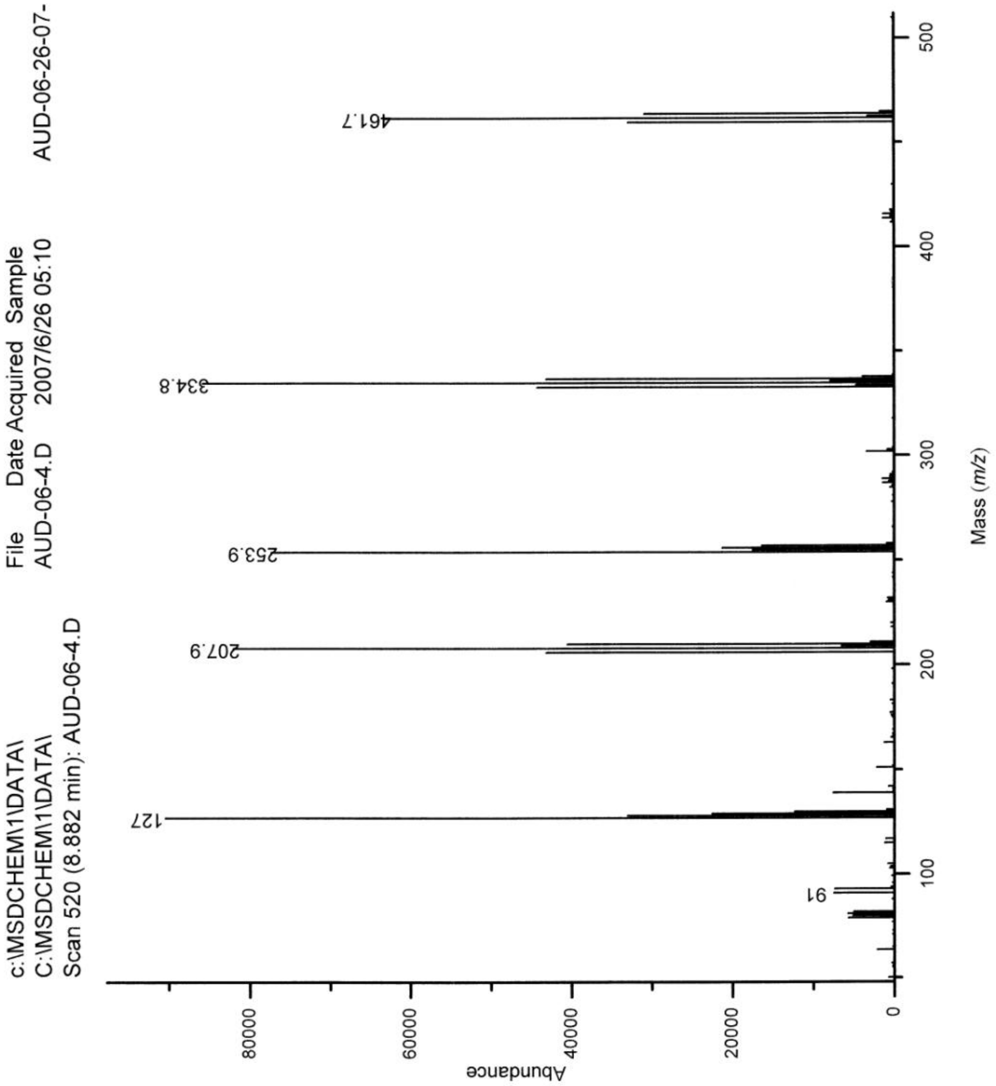


Figure A.12 Mass spectrum of compound **38**, obtained from GC (Figure A.11).

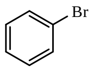
Trial	Solvent	Ph$\equiv$H mmol	*n*-BuLi mmol	$ZnCl_2$ mmol	Catalyst Co-catalyst	 mmol	Time h	%Yield	
								58	**49**
1	THF	1.2	1.25	1.35 Heated	$(PPh_3)_4Pd(0)$ 5 mol%	1.0	1	5	13
2	THF	6.0	6.0	6.5 Heated	$(PPh_3)_4Pd(0)$ 5 mol%	5.0	3	—	—
3	THF	6.0	6.0	6.0 Heated	$(PPh_3)_4Pd(0)$ 5 mol% CuI 2 mol%	5.0	3	Complex Mixture of Cmpds.	
4	THF	3.0	3.0	3.2 New Ampule	$(PPh_3)_4Pd(0)$ 5 mol%	2.5	24	19	32

Table A.1 Trials of alkynylation of **57** with phenyl ethynyl zinc chloride.

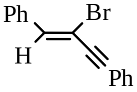
Trial	Solvent	 mmol	Base mmol	Reagent mmol	Catalyst 0.5 mol%	Time h	Product
1	THF	0.18	1 eq. LDA	$ZnCl_2$ 0.53	Ni(DPPE)Cl_2	20	Recover Starting Material
2	THF	0.18	1 eq. LDA	$ZnCl_2$ 0.35	Ni(DPPE)Cl_2	48	Recover Starting Material
3	THF	0.18	1 eq. LDA	$MgBr_2$ 0.18	Ni(DPPP)Cl_2	18	Recover Starting Material
4	THF	0.18	1 eq. LDA	$ZnCl_2$ 0.35	Ni(DPPP)Cl_2	14	Recover Starting Material
5	THF	0.18	1 eq. LDA	$MgBr_2$ 0.18	Ni(DPPP)Cl_2	18	Recover Starting Material
6	THF	0.18	1 eq. *n*-BuLi	$ZnCl_2$ 0.35	Ni(DPPE)Cl_2	18	*E* and *Z* 1,4-dipheny-1-butene-3-yne
7	THF	0.18	1 eq. *n*-BuLi	$MgBr_2$ 0.18	Ni(DPPE)Cl_2	16	*E* and *Z* 1,4-dipheny-1-butene-3-yne

Table A.2 Polymerization trials.

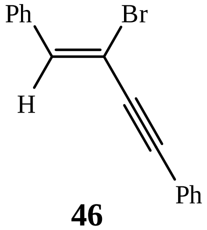
Trial	Solvent	Diene Mmol	Base M	Temp. C°	Time M	Product
1	THF (5 ml)	0.19 E/Z	1 eq. *n*-BuLi (1.6M)	-78°C warm to 0°C	30	Compound **49** and starting material **69**
2	THF (50 ml)	0. 23 E/Z	2 eq. *n*-BuLi (0.6M)	-78°C warm to 0°C	30	Compound **49** and starting material **69**
3	THF (5 ml)	0.227 E/Z	1 eq. *n*-BuLi (1.6M)	-78°C	15	Compound **49** and starting material **69**
4	THF (5 ml)	0.06	0.95 eq. *n*-BuLi (1.6)	-78°C warm to -40°C	30	Compound **49** and starting material **69**
5	THF (50 ml)	0.089	0.95 eq. *n*-BuLi (0.6)	-78°C warm to -40°C	30	Compound **49** and starting material **69**

Table A.3 Various trials exploring the selective elimination of diene **69**.

Trial	Temp.	Light Exposure	Time	Solvent	Additional Solvent	Br_2 M	C_4I_2 mmol	Characterization GC Mass Spec, m.p.
1	-20	-	2 h	CCl_4 4 mL	*n*-pentanes 15 mL	2	3.2	M.W. 462, over addition m.p. 71-75 °C
2	-20	-	2 h	CCl_4 4 mL	*n*-pentanes 15 mL	1.55 *n*-pentanes	3.2	No cumulene observed m.p 95 °C
3	-20	-	1 h	CCl_4 1 mL	*n*-pentanes 2 mL	1.55 *n*-pentanes	3.2	No cumulene observed m.p 90-95 °C
4	-20	-	1 h	-	*n*-pentanes 8 mL	2	0.8	No Cumulene observed m.p 90 °C
5	-20	very limited	2 h	-	*n*-pentanes 14 mL	2	3.2	No Cumulene observed m.p. 80-85 °C
6	-15	Very limited	2 h	CCl_4 4 mL	*n*-pentanes 15 mL	2	3.2	M.W. 462, over addition m.p. 95-97 °C
7	-15	Very limited	1 h	CCl_4 4 mL	*n*-pentanes 15 mL	2	3.2	M.W. 462, over addition m.p. 80-85 °C
8	-15	Very limited	2 h	CCl4 4 mL	n-pentanes 10 mL	2	3.2	M.W. 462, over addition m.p. 95-97 °C
9	-15	Very limited	2 h	CCl4 4 mL	n-pentanes 15 mL	2	3.2	M.W. 462 m.p 110 °C
10	-15	Very limited	2 h	CCl4 4 mL	*n*-pentanes 15 mL	2	3.3	M.W. 462 m.p 113 °C

Table A.4 Trials toward the synthesis of $C_4Br_2I_2$.

Optimized geometries (B3LYP/6-31G*)



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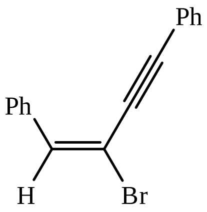
Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.390668	0.000000	-3.552804
2	6	0	0.224027	0.000000	-2.127598
3	6	0	0.081009	0.000000	-0.906413
4	6	0	-0.158360	0.000000	0.491459
5	6	0	0.697779	0.000000	-6.367747
6	6	0	0.469319	1.222626	-4.268599
7	6	0	0.469319	-1.222626	-4.268599
8	6	0	0.621467	-1.218901	-5.664695
9	6	0	0.621467	1.218901	-5.664695
10	1	0	0.407640	2.160986	-3.724040
11	1	0	0.407640	-2.160986	-3.724040
12	1	0	0.678945	-2.161426	-6.203568
13	1	0	0.678945	2.161426	-6.203568
14	1	0	0.813723	0.000000	-7.448799
15	6	0	0.828150	0.000000	1.432474
16	35	0	-2.115422	0.000000	0.912712
17	1	0	1.820683	0.000000	0.975006
18	6	0	0.875776	0.000000	2.901583
19	6	0	1.240825	0.000000	5.728727
20	6	0	-0.240185	0.000000	3.781059
21	6	0	2.175627	0.000000	3.481861
22	6	0	2.359085	0.000000	4.872075
23	6	0	-0.053407	0.000000	5.173488
24	1	0	-1.247006	0.000000	3.385358
25	1	0	3.046561	0.000000	2.828581
26	1	0	3.364510	0.000000	5.285688
27	1	0	-0.922378	0.000000	5.827334
28	1	0	1.375114	0.000000	6.807674



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Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.123645	0.000000	-2.809208
2	6	0	-0.275320	0.000000	-1.431391
3	6	0	-0.606982	0.000000	-0.246455
4	6	0	-1.083150	0.000000	1.081647
5	6	0	0.900894	0.000000	-5.531181
6	6	0	0.321358	1.223232	-3.501133
7	6	0	0.321358	-1.223232	-3.501133
8	6	0	0.706648	-1.219150	-4.851468
9	6	0	0.706648	1.219150	-4.851468
10	1	0	0.168213	2.161608	-2.975085
11	1	0	0.168213	-2.161608	-2.975085
12	1	0	0.854078	-2.161626	-5.372877
13	1	0	0.854078	2.161626	-5.372877
14	1	0	1.198614	0.000000	-6.576832
15	6	0	-0.409691	0.000000	2.265429
16	35	0	-3.095237	0.000000	1.201120
17	6	0	1.040486	0.000000	2.520348
18	1	0	-1.020564	0.000000	3.166965
19	6	0	3.796985	0.000000	3.218311
20	6	0	2.043377	0.000000	1.515236
21	6	0	1.453508	0.000000	3.879970
22	6	0	2.813338	0.000000	4.226684
23	6	0	3.402956	0.000000	1.864996
24	1	0	1.760729	0.000000	0.468936
25	1	0	0.698916	0.000000	4.664489
26	1	0	3.105306	0.000000	5.274033
27	1	0	4.157561	0.000000	1.081973
28	1	0	4.851816	0.000000	3.482031