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An Exploration of Alkyne-Alkyne Cross-Coupling Reactions and Attempts Towards Controlled Polymerization of Diiodooctatetrayne

A Dissertation Presented

by

Allison Black

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The Graduate School

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in

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Abstract of the Dissertation

An Exploration of Alkyne-Alkyne Cross-Coupling Reactions and Attempts Towards Controlled Polymerization of Diiodooctatetrayne

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Polyynes are one-dimensional rigid carbon rods composed of alternating triple and single bonds. They have attracted much interest due to their electronic, optical, and physical properties. These carbon oligomers can serve as possible precursors to polydiacetylenes or graphitic ribbons, as subjecting ordered aggregates to heat and/ or irradiation can lead to topochemical polymerization. Furthermore, polyynes can act as models for understanding conjugation, and may be used to predict the properties of carbyne, the linear allotrope of carbon. In this work, model Stille and Cadiot-Chodkiewicz coupling reactions using iodoalkyne substrates were thoroughly investigated. Once optimal conditions were determined for each system, symmetric double cross-couplings to diiodopolyynes were attempted. The Stille reaction was shown to be more effective, as poor selectivity and low overall yield continue to be issues in the Cadiot-Chodkiewicz reaction.

The topochemical polymerization of diiodooctatetrayne was also studied, applying a host-guest strategy that aligns the monomers in the proper orientation for controlled polymerization via halogen bonding interactions. Polymerization was monitored using X-ray diffraction and Raman spectroscopy. The spectroscopic data suggest that the morphology of the crystal gradually becomes disordered, as the monomer undergoes partial polymerization. The Raman spectrum of the disordered co-crystals upon irradiation with a 532 nm laser beam indicates the potential conversion of polyynes to graphitic ribbons or fragments.

In addition, a synthetic route for an asymmetric diyne with a donor (I) and an acceptor (COOH) end-group was developed, with the goal of preparing a push-pull polydiacetylene.

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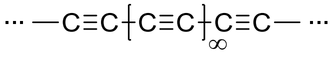
Vita, Publications and/or Fields of Study

DeCicco, R. C.; Black, A.; Li, L.; Goroff, N. S. An iterative method towards the synthesis of symmetric polyynes. *Eur. J. Org. Chem.*, **2012**, 4699-4704.

Description of Research for a Non-Scientist

Carbon is found in all living organisms and is the foundation of organic chemistry. This nonmetal can bond with a wide variety of elements such as oxygen, hydrogen, and nitrogen. Pure carbon compounds are particularly interesting to study because the arrangement of the atoms greatly affects the properties of the resulting materials. For example, diamond is the hardest known natural mineral while graphite is one of the softest substances and is used in pencils. Additionally, graphite can act as an electrical conductor and is therefore used as a component in devices such as batteries. A current synthetic challenge is carbyne, the hypothetical linear form of carbon consisting of alternating triple and single bonds (Figure 1). This material is pursued as it is expected to have interesting properties.[1]



$$\cdots -C\equiv C\left[C\equiv C \right]_{\infty} C\equiv C- \cdots$$

Figure 1 Structure of carbyne.

One-dimensional rigid carbon rods with iodine end groups (Figure 2a) have been prepared in this group.[2] A synthetic strategy was developed in which simple starting materials were used, mild conditions were employed, and the isolation of unstable intermediate compounds were avoided.[3] The stability of these iodine capped compounds decreases as the number of carbon-carbon triple bond units (n) increases. For example, when n = 4, the material becomes a shock-explosive when handled as a solid. Although it is proposed that bulkier end-groups may prevent decomposition,[4-5] iodine was chosen as this relatively small side group should have little effect on the physical properties of the resulting polymer (Figure 2b). Polymers, or compounds with a repeating unit, are interesting in their own right, as they are found in a wide range of everyday items, from synthetic plastics to natural materials such as silk, wool, and rubber. Polymer **1** is expected to conduct electricity, and therefore may be of interest for use in devices such as solar cells. Organic materials offer great potential for low cost fabrication and light, flexible substrate assembly, thus motivating research of this technology in industrial applications.

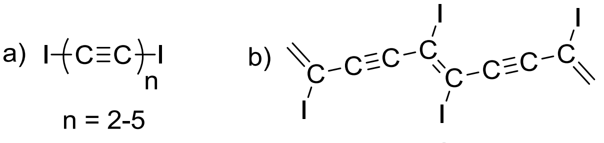


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Figure 2 (a) Structure of iodine capped carbon rods; (b) polymer.

Polymer **1** might also serve as a precursor to other conductive materials if different groups can be substituted for iodine. Additionally, it has been suggested that iodine may be eliminated with high temperatures[6] or with particular bases,[7] thus indicating the formation of carbyne or other carbon rich materials. Polymers obtained from longer iodine capped carbon rods may also be valuable. Currently, my research demonstrates that the carbon rod with 4 carbon-carbon triple bonds in length (Figure 2a) leads to a disordered polymer. This can be attributed to the instability of this carbon rod in comparison to when n = 2,[2,8-9] as well as to the increase of possible reactive C≡C sites. Interestingly, under a high energy laser beam, the polymer material resembles graphite, suggesting potential conversion of linear rods to graphitic material.

The synthesis of an asymmetric linear compound was also developed to determine the effect of the different end-groups on the polymerization behavior (Figure 3a). Two polymers are possible depending upon the alignment of the asymmetric carbon rod. To date, efforts towards either polymer shown in Figure 3b has been unsuccessful. The end-groups chosen should allow electrons to be donated and withdrawn throughout the system, making polymers **3** and **4** attractive since potential applications in optical or electronic devices can be assumed.[10-11]

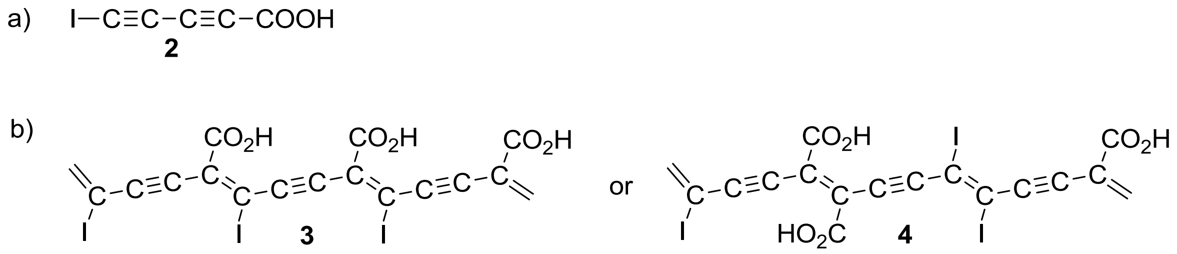

Figure 3 (a) Structure of asymmetric capped carbon rods; (b) possible asymmetric polymers.

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Chapter 1: Introduction

1.1 Polydiacetylenes

Polydiacetylenes (PDAs) are conjugated organic polymers which have attracted much attention due to their potential electronic, optical, and biological applications.[1-3] The alternating double and triple bonds that comprise their backbone allow for a highly delocalized one-dimensional π-electron system throughout the polymer chain.[1] When exposed to external stimuli such as heat, pressure, pH modifications, or organic solvents, a visible blue-to-red color transformation is observed in some PDAs, rendering them valuable in optical sensing devices.[4-6] This color change between the blue and red PDAs may be caused by either differences in the chain conformation or from the effect of the side groups that are present, such as steric interactions and packing forces.[7-9] Depending upon the nature of the side chains, the color change can be reversible.[4,10-12] Specifically, it is thought that the geometry of the red PDA chains have some degree of twisting, which ultimately can decrease or interrupt conjugation, while the blue PDA chains are planar.[8] Therefore, PDAs have been used as biosensors and incorporated into drug delivery systems[3] or to diagnose infectious diseases.[13] For example, PDA films functionalized with an analog of sialic acid have shown to be effective biosensors for the detection of the influenza virus. These films change color in response to ligand-receptor interactions (Figure 1.1).[14] PDA based sensors typically show blue-to-red colorimetric changes; however Yoon and co-workers recently reported a PDA bearing boronic acid side groups which displays unique colors upon the addition of varying cationic surfactants.[15] Furthermore, the chromatic and fluorescence characteristic of PDA networks has driven the development of chemical and thermal sensing applications.[16-19]

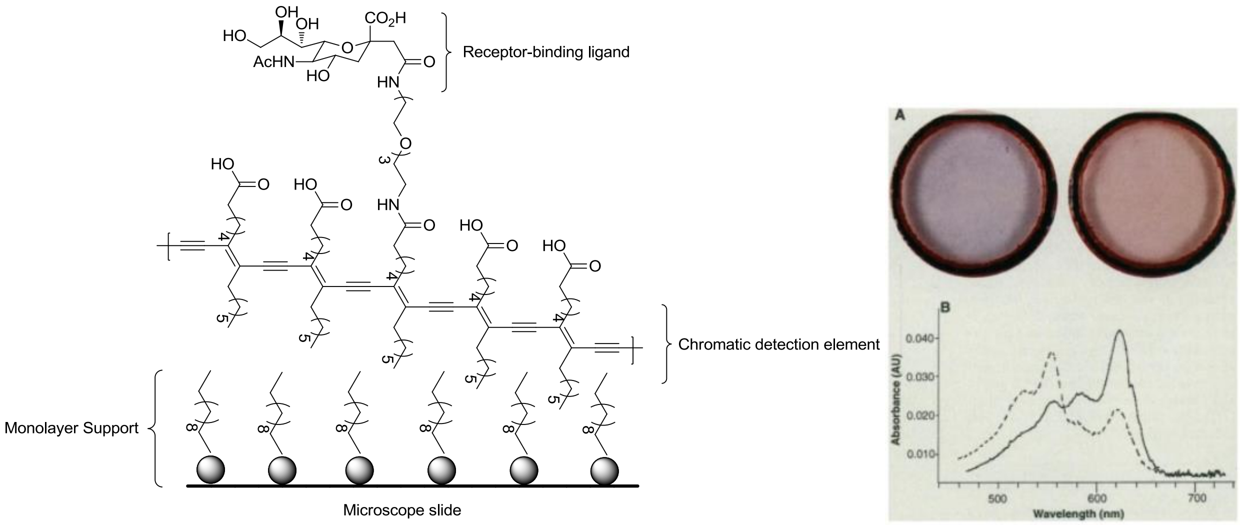


Figure 1.1 Colorimetric detection of the influenza virus. The film changes from blue to red after exposure to the virus. The UV-Vis absorption spectrum of the film prior to (solid line) and after (dashed line) viral incubation. Reproduced with permission from ref. 14, Copyright 1993, American Association for the Advancement of Science.

Experimental and theoretical calculations have shown that PDAs can serve as excellent multiphoton absorbers.[2,20-21] The interaction of light waves with matter, typically at high intensities, can result in the nonlinear generation of light at a new frequency.[22-23] Since PDAs are comprised of a polarizable π system and highly ordered conjugated backbone, these organic compounds are regarded as candidates for third-order nonlinear optical (NLO) materials.[24-25] The structure-function relationship for the third-order NLO susceptibility (χ^3) value in organic and organometallic chromophores has been reviewed.[26] In 1976, Sauteret and co-workers pioneered research in PDAs as a nonlinear medium. From third-harmonic generation (THG) measurements, these researchers determined a large χ^3 value and a subpicosecond response time for PTS [hexa-2,4-diynylene bis(toluene-*p*-sulfonate)], making this a promising material for ultrafast all-optical switches.[27] The ease of molecular tailoring for processing and stability, in addition to the inherent flexibility and low cost, give PDAs advantages over their inorganic counterparts.[25-26] However, preparation of high quality thin films is often hampered by decreased transparency, minimal solubility (processability), and structural defects of the PDAs.[25,28] Current research is underway to use PDAs, as well as other organic polymers, as promising materials for practical applications in optoelectronic devices.[1,26,29-30]

1.1.1 Preparation of Polydiacetylenes by Topochemical Polymerization

Diynes can react by either a 1,2- or 1,4-addition, therefore yielding a polymer with an irregular backbone. It is almost impossible to predict solid state assembly; however, if aligned in the solid state, diynes can undergo a controlled polymerization to form PDAs, as first demonstrated by Wegner.[31] A few years after Wegner's discovery, Baughman established the required parameters for the ordered 1,4-polymerization of diynes.[32] The ideal repeat distance (r) between the monomer units was calculated to be 4.9 Å, a separation which matches the repeat distance in the corresponding polymer (Figure 1.2). Furthermore, a 45° tilt angle (θ) between the translational axis and the diyne rod was determined to be necessary to bring the reacting carbons C1 and C4 ($d_{1,4}$) of adjacent monomers into the van der Waals contact distance of 3.5 Å.[32] These spacial requirements allow for minimal molecular motion of the reacting monomers, therefore increasing the chance of preserving the crystalline lattice during the entire transformation.[33-34] Experiments have since shown that the repeat distance is the most important parameter in determining the success of the controlled diyne polymerization.[35-36]

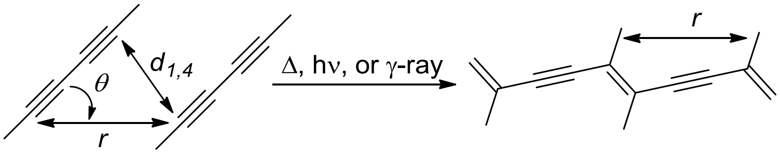


Figure 1.2 Structural parameters for 1,4-topochemical polymerization, r = 4.9 Å, θ = 45°, $d_{1,4}$ = 3.5 Å.[32,37]

Because most diynes do not assemble with the appropriate alignment in the solid state, control of crystal packing is necessary for the monomers to achieve a topochemical polymerization.[33,38] Topochemical polymerizations are reactions in which the prearrangement of the reactant monomers determines the structure of the product.[33] One approach to align diynes for an ordered polymerization is to exploit different end-group interactions. For example, Frauenrath and co-workers have utilized perfluorophenyl-phenyl networks to attain an alternating diyne copolymer that polymerizes under UV irradiation (Figure 1.3).[39-40]

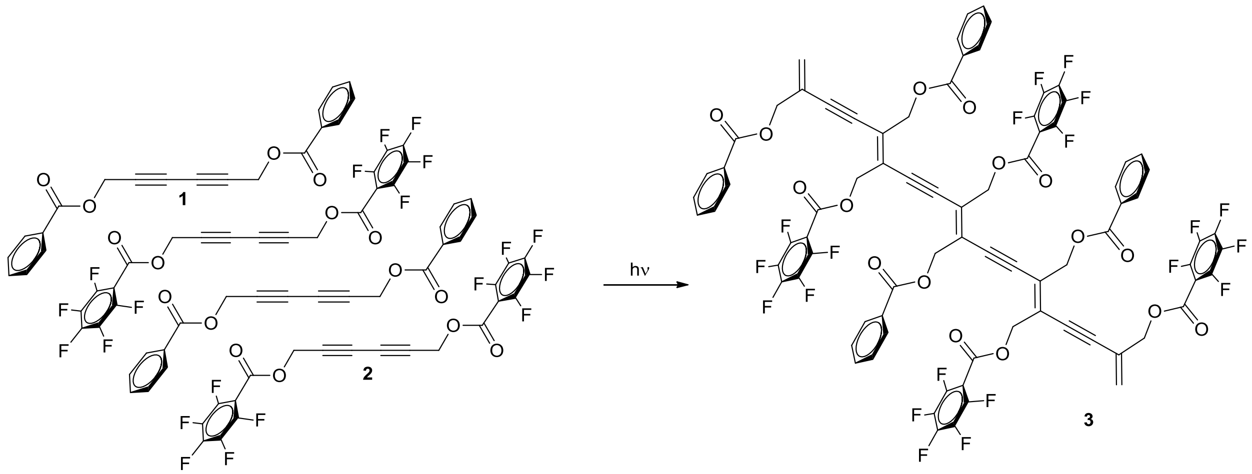
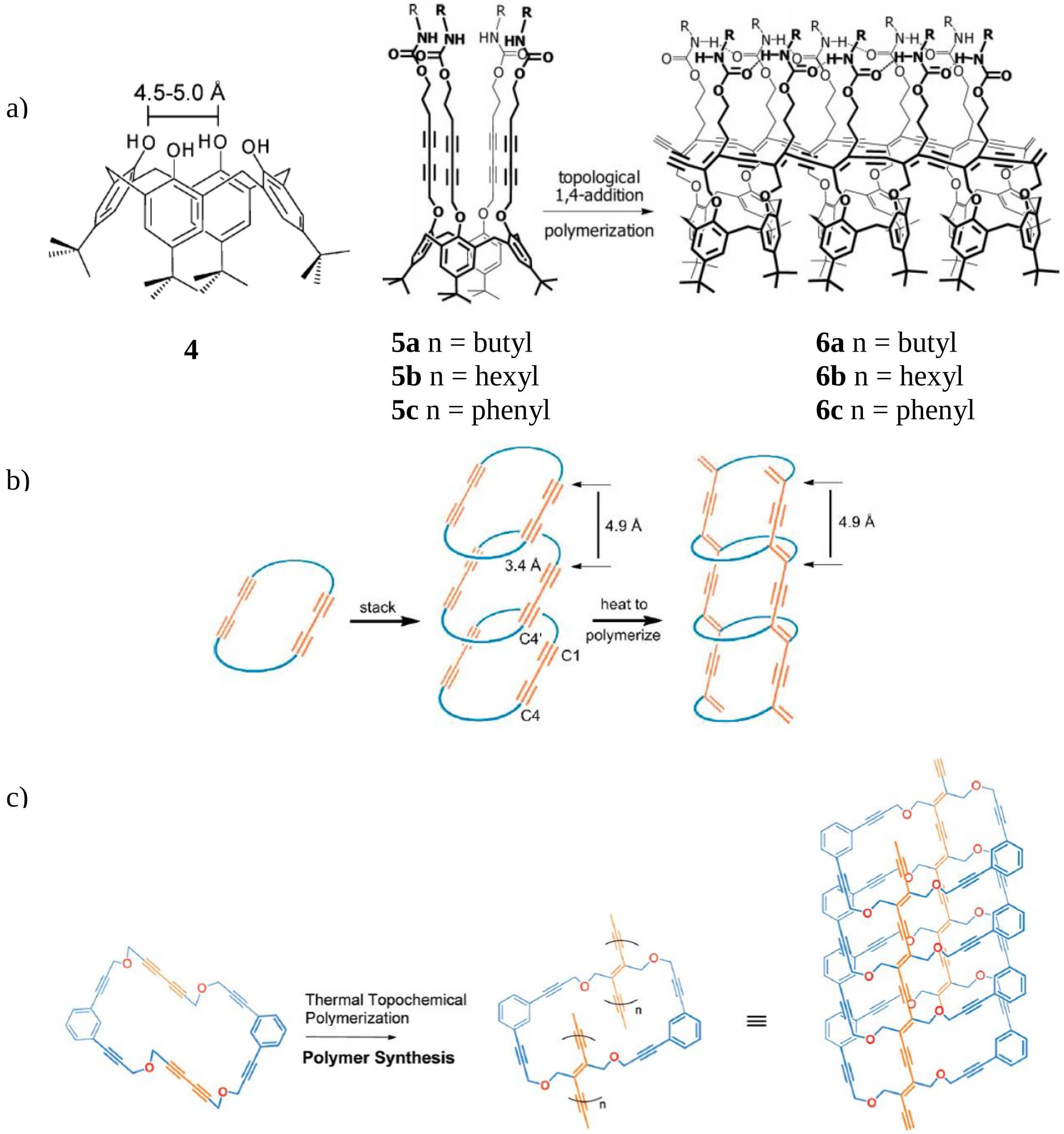


Figure 1.3 Alternating poly(diacetylene) copolymer by 1,4-topochemical polymerization.[39]

In a different system, the1,4-topochemical polymerization of diynes has been achieved intramolecularly. The neighboring hydroxyl groups in *tert*-butylcalix[4]arene are preorganized to be between 4.5-5.0 Å apart. Therefore, conversion of the hydroxyl substituents to diyne units with alkyl urethane groups allowed for a controlled photopolymerization to give PDAs containing calix[4]arene (Figure 1.4a).[41] In the same manner, a diyne functionalized macrocycle can be self-assembled into columns and upon heating or irradiation, initiate an intramolecular polymerization of the preorganized monomer units to give tubular PDAs (Figure 1.4b).[36,42-43] For example, slow annealing of a polyether macrocycle monomer for 35 days brought about a single-crystal-to-single-crystal polymerization. This is the first example of an experimentally determined structure of a tubular addition polymer (Figure 1.4c).[36]



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5a n = butyl
5b n = hexyl
5c n = phenyl

6a n = butyl
6b n = hexyl
6c n = phenyl

Figure 1.4 (a) *Tert*-butylcalix[4]arene (left) and the 1,4-topochemical polymerization of its butadiyne derivative (right). Reproduced with permission from ref. 41, Copyright 2007, American Chemical Society; (b) Overview of the preparation of synthetic nanotubes by the solid-state polymerization of a stacked column of diyne macrocycles. Reproduced with permission from ref. 36, Copyright 2011, American Chemical Society; (c) Single-crystal-to-single-crystal polymerization of a polyether macrocycle monomer. Reproduced with permission from ref. 36, Copyright 2011, American Chemical Society.

The development of a host-guest strategy by Fowler and Lauher has allowed for various diyne monomers to undergo a 1,4-polymerization that would otherwise not occur.[37] In this method, the diyne monomers function as guests, and are aligned for an ordered polymerization by the host compounds to which they are hydrogen bonded. Accordingly, the hosts are designed to self-assemble at the repeat distance outlined by Baughman. Oxalamide and urea functionalities have been shown to form hydrogen bonding networks with repeat distances of 5.0 Å and 4.6 Å, respectively, and have therefore been integrated into the host molecules (Figure 1.5).[37-38] The hydrogen bonded network formed from the molecular packing of the oxalamide moiety is linear, as opposed to the bent hydrogen bonds that are seen in the urea hosts, thus giving a longer and more favored repeat distance to the oxalamide hosts.[38] The repeat distance in the host framework translates to the spacing between the guest monomers, thus aligning the diynes in the proper orientation for a 1,4-topochemical polymerization (Figure 1.5).[37] This host-guest scaffold has been implemented for the successful single-crystal-to-single-crystal polymerization of diynes, triynes, and trienes.[37]

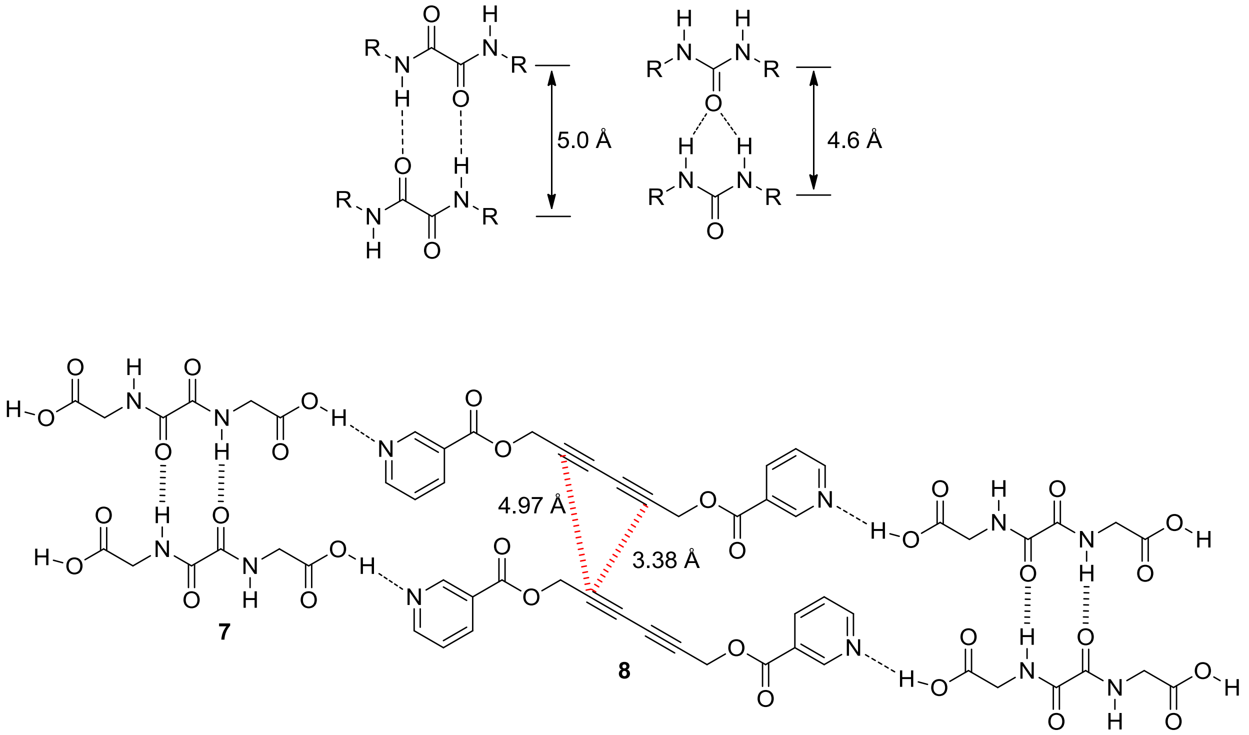

Figure 1.5 Hydrogen bonding networks for the oxalamide (top left) and urea (top right) functional groups of the host molecules,[38] and utilization of the host-guest scaffold to correctly align diyne monomers for a 1,4-polymerization (bottom).[37]

1.2 Poly(diiododiacetylene)

In collaboration with Fowler and Lauher, the Goroff group has adapted this host-guest method and as a result, successfully polymerized diiodobutadiyne (**9**).[37] Analogous to the non-covalent hydrogen bonding host-guest interactions, halogen bonding[44-45] has proven suitable for aligning monomer **9** in the proper orientation to allow for a 1,4-topochemical polymerization.[46-48] The Lewis acidic iodine atoms in guest diiodobutadiyne (**9**) and the Lewis basic nitrogen atoms in the bis(pyridyl) and bis(nitrile) oxalamide hosts **10-14** (Figure 1.6) were effective in co-crystal formation; however only hosts **12**, **13**, and **14** demonstrated spontaneous topochemical polymerization of diyne **9** to give PIDA [poly(diiododiacetylene)] **15** (Figure 1.6).[46-47,49] The sterically bulky pyridyl group presumably impedes polymerization,[33,50-51] and consequently, the crystals with hosts **10** and **11** required above 3 GPa of external pressure to overcome rearrangement barriers to afford the desired polymer **15**.[52] As estimated by ^{13}C MAS (Magic Angle Spinning) NMR, a powdered sample of **9•10** co-crystals reaches > 90% polymer after pressing to 6 GPa, while the powder of **9•11** co-crystals achieves only ~55% polymerization.[48] Evidence for a pressure-induced single-crystal-to-single-crystal transformation in the **9•10** co-crystals has recently been reported.[52] The extra methylene unit in bis(pyridyl) host **12** may offer additional flexibility to allow for the spontaneous polymerization of diyne **9**.[49-50]

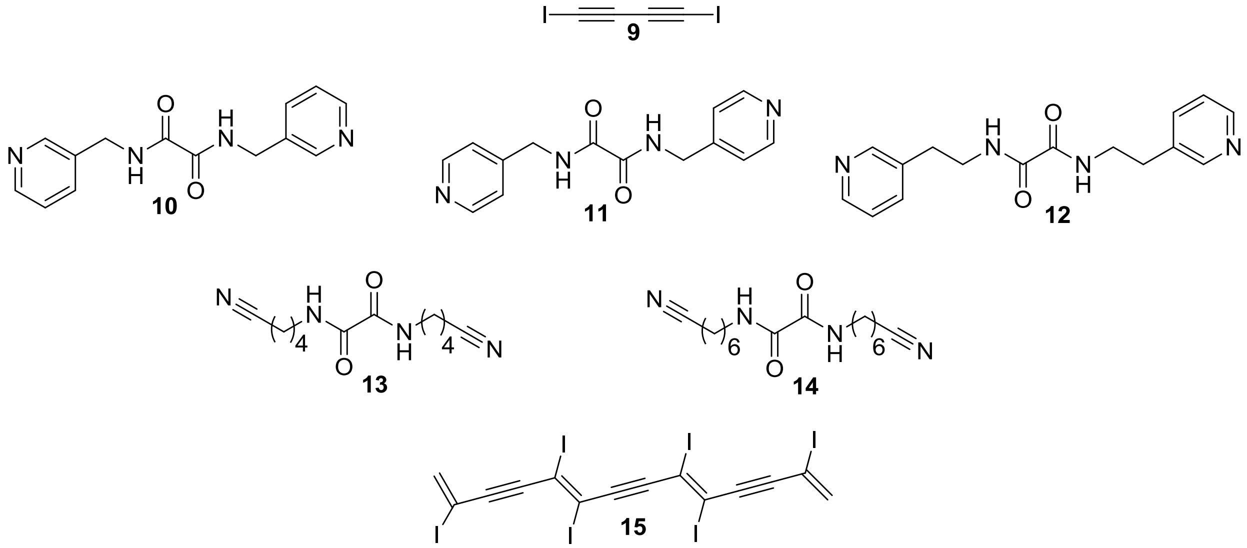

Figure 1.6 Guest **9** and hosts **10-14** employed in the host-guest scaffold; targeted polymer **15**.

PIDA **15** consists of only iodine and carbon atoms,[46] and therefore, the steric influence from the iodine side groups should have little effect on the physical properties of this polymer, which ultimately may help to offer insights into the optical and electronic properties of conjugated materials, including the chromatic changes in PDAs. Moreover, polymer **15** may serve as a precursor to carbyne, the sp-hybridized linear allotrope of carbon (Figure 1.7a), or to other PDAs via post-polymerization modification reactions.[47,53] After isolating PIDA **15** from the host compounds through repetitive rinsing and sonication with organic solvents such as chloroform, methanol, or THF,[47] addition of Lewis bases at room temperature to this aggregate suspension leads to partial (at least ~60%) dehalogenation of the polymer.[54] Furthermore, annealing isolated PIDA nanofibers **15** at 900 °C for 1 hour results in complete carbonization.[53] In both cases, after iodine elimination, an insoluble conducting material results, indicative of graphitic particle formation.[53,54] This suggests that PIDA **15** and other polymers obtained from longer diiodopolyyne analogs may be valuable precursors to graphitic materials. Consequently, the versatility of the host-guest strategy has been extended recently to diiodohexatriyne (**16**)[55-56] (Figure 1.7b) and diiodooctatetrayne (**17**)[57] (Figure 1.7c). The controlled polymerization of these diiodopolyynes has been pursued using the host compounds displayed in Figure 1.6. The polymerization of tetrayne **17** will be further discussed in Chapter 4.

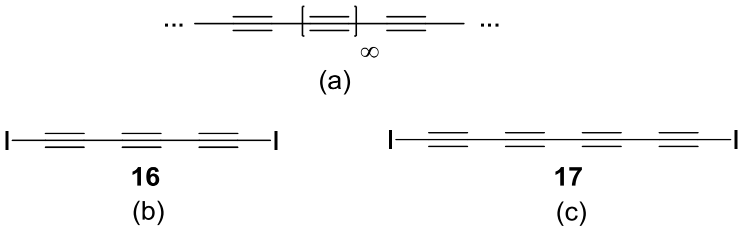

Figure 1.7 (a) Structure of carbyne; (b) Diiodohexatriyne; (c) Diiodooctatetrayne.

1.3 Exploration of Diiodopolyynes and PIDA upon Low-Energy Ion Irradiation

A collaboration with Rik Tykwinski at the Friedrich-Alexander-Universität (FAU) in Erlangen, Germany was recently begun to explore the behavior of diiodobutadiyne (**9**) under low-energy ion irradiation. In particular, this iodocarbon will be adsorbed on a HOPG (highly oriented pyrolytic graphite) surface and examined by STM (scanning tunneling microscopy).[58] The conversion of diiodobutadiyne (**9**) into carbon-rich materials will be monitored under these conditions, with the objective of finding a route for selective preparation of specific carbon allotropes. Transformation of longer diiodopolyynes and the polymer PIDA **15** into graphitic materials by ion irradiation will also be investigated and their conducting properties will be studied.

1.4 Polyynes

Polyynes are one-dimensional rigid carbon rods composed of alternating triple and single bonds, as shown in Figure 1.8. The thermodynamic stability of these compounds decreases as the number of alkyne units (n) increases. Therefore, it is important to choose an appropriate end-group (R) to aid in stability, as well as solubility, of these carbon oligomers.[59] Bulkier end-groups allow for greater chain-chain separation, which ultimately helps prevent spontaneous polymerization and decomposition.[60-61] Research in oligoyne chemistry has increased in recent years due to their electronic, optical, and physical properties.[62] Theoretical and experimental findings have shown that sp-hybridized carbon chains have large multiphoton absorption cross-sections. Additionally, the third-order NLO properties of polyynes are of specific interest.[62-68]

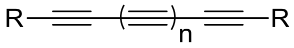

Figure 1.8 Structure of polyynes.

Triple bonds have cylindrical symmetry, and therefore, these bonds are always in conjugation with each other and with the end-groups of the polyyne, regardless of the relative orientation of these end-groups. Because conjugation along the backbone is preserved, several groups have suggested that polyynes can behave as molecular wires since charge transport through the chain is not disturbed.[69-74] Likewise, an iron-substituted molecular wire was recently synthesized which exhibits tunable redox properties due to the incorporation of Fe(II) centers along the rigid-rod structures.[75] Additionally, it has been suggested that polyynes may act as insulated molecular wires once threaded through a macrocycle to form rotaxanes or polyrotaxanes.[76-77] Polyynes have also drawn attention because they can be used as models for exploring conjugation, or more specifically, to predict the properties of linear carbon, or carbyne (Figure 1.7a).[62] Moreover, these oligomers can act as possible precursors to polydiacetylenes, nanotubes, fullerenes, graphitic materials, and other carbon-rich compounds.[60,78-84] Specifically, if stacked at an appropriate tilt angle, polyynes may serve as potential precursors to graphitic ribbons by subjecting the oligomer aggregates to heat and/or irradiation.[1,59,85-86] Polyynes are also found in many natural products with a wide range of biological activity,[87-90] as highlighted in Figure 1.9. For example, minquartynoic acid (**18**) has exhibited anti-HIV properties as well as cytotoxic activity against specific tumor cell lines, while caryoynencin (**19**) has shown antimicrobial activity against bacteria.[88] These biological properties demonstrate that polyynes are versatile compounds with applications beyond materials science.

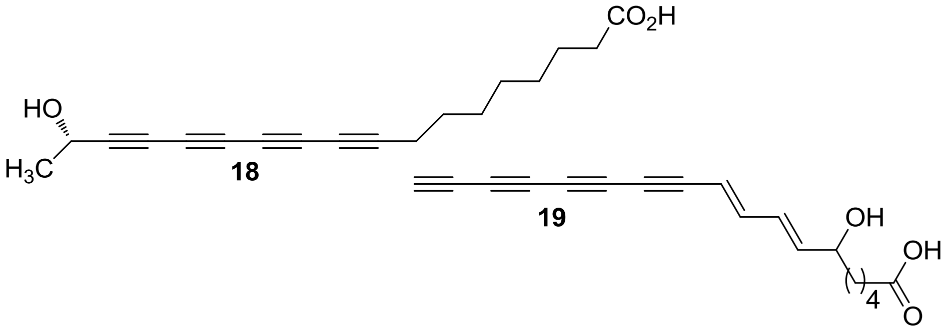

Figure 1.9 Examples of tetrayne natural products: (S)-Minquartynoic acid (**18**) and caryoynencin (**19**).[88]

1.5 Solid-state Polymerization of Triynes, Pentaynes, and Hexaynes

As previously described in Section 1.1.1, the 1,4-topochemical polymerization of diynes has been thoroughly investigated.[1,31-32,37,91-93] However, the controlled polymerization of higher oligoyne homologs has been explored in much less detail.[1,94] The ordered polymerization of longer polyynes is more complicated, commonly yielding a mixture of products or material with undefined structure. While examples for the 1,4-polymerization of triynes is limited,[94-98] the 1,6-polymerization of triynes is even more uncommon.[38,99] Okada and co-workers have claimed the controlled polymerization of tetrayne monomers,[1] although characterization of the resulting polymers is typically limited to UV-Vis and ^{13}C MAS NMR spectroscopic measurements. Changes in the powder X-ray diffraction (PXRD) patterns during the course of polymerization have also been reported with some samples; however the degree of order in these materials as well as the calculated percentage of polymerization is never discussed. The polymerization of tetraynes in the solid-state will be discussed further in Section 1.6. Okada and co-workers have also investigated the topochemical polymerization of a pentayne monomer. The ladder polymer product, composed of two PDAs connected by an acetylene spacer unit, was partially synthesized through two sequential 1,4-polymerization events, indicated by UV-Vis and solid-state NMR spectroscopy.[100] In 2010, this same group described the solid-state polymerization of triacontahexayne diol, diphenylurethane hexayne, and diphenylester hexayne under thermal conditions. Triacontahexayne diol and diphenylurethane hexayne derivatives each underwent a 1,4-polymerization, as suggested by UV-Vis spectroscopy, but only the diphenylester hexayne was believed to further undergo an irregular polymerization or oligomerization to give the ladder-type PDA.[101] Although alkyl[86] and alkylurethane[102] hexaynes have previously been prepared by Okada and co-workers, these substituents were not ideal due to their instability and insolubility, respectively, when used with longer polyyne chains.

1.6 Polymerization of Tetraynes

The topochemical polymerization of octatetraynes has been pursued for about 35 years, beginning with theoretical calculations studied by Baughman and Yee.[98] The instability of longer polyynes, along with the complexity of the polymerization process, makes the controlled polymerization of tetraynes challenging compared to diyne monomers.[85] For example, one could hypothesize that 1,4-, 1,6-, 1,8-, 3,6-, and other polymerization pathways are plausible for octatetraynes, influenced by r and θ between the adjacent polyyne rods. Recently, Tykwinski and co-workers described select octatetrayne monomers which pack in an arrangement conducive to topochemical polymerization. Although initiation using thermal, photochemical, and/or γ-irradiation offered evidence for polymer formation, the structural determination of the product(s) was elusive, highlighting the challenges involved in obtaining an ordered material from a tetrayne monomer.[85] These researchers have also exploited the supramolecular stacking interactions between the perfluorophenyl-phenyl units to arrange tetraynes in the solid-state for a topochemical polymerization. The unsymmetrical monomers stack with a center-to-center separation of 3.67 and 3.73 Å, while cocrystals of diphenyl octatetrayne and diperfluorophenyl octatetrayne (1:1) stack at 3.68 Å,[103] indicating that the packing motif is incommensurate with the corresponding polymer.

In 2006, Szafert and Gladysz summarized the crystal packing parameters for various tetraynes.[60] The monomers reviewed were not aligned for a 1,8-topochemical polymerization, possibly because the large repeat distance r (9.6 Å) required is rare in single component polyyne crystals. Several tetraynes did however appear to be plausible candidates for a 1,4- or a 1,6-topochemical polymerization.[60] For example, Lagow and co-workers discovered that bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne aligns in the solid-state with parameters favorable for 1,4-

polymerization (r = 4.5 Å, $d_{C1\text{-}C4}$ = 3.799 Å, $d_{C3\text{-}C6}$ = 3.853 Å), but the large tilt angle (θ = 69°) seemed to prevent polymerization[104] (Szafert and Gladysz had later calculated θ to equal 49.4°).[60] Tetraynes generally require bulky end-groups to aid in their stability, which may explain why the strict packing parameters necessary for a controlled polymerization have seldom been met thus far.[59] In 2012, Szafert and co-workers reported a benzoxazine end-capped tetrayne which has the potential to undergo a 1,4-topochemical polymerization. A chain-chain distance of 3.880 Å and a tilt angle of 50.2° suggest that cross-linking is possible, despite the bent conformation of the carbon chain.[105]

Okada and co-workers have been the only group thus far to claim successful topochemical polymerization of tetrayne oligoynes in the solid state. Their findings indicate the generality of the 1,4-addition pathway for octatetraynes upon γ-ray irradiation. Specifically, polymers with alkyl,[94,106] urethane,[107-109] and aromatic[110] substituents were obtained by this route. Additionally, the dialkyl-substituted derivative, hexatriacontatetrayne, was irradiated at room temperature to undergo a 1,4-polymerization which after subsequent heating, yielded a ladder polymer with parallel PDA chains (Figure 1.10).[86,111]

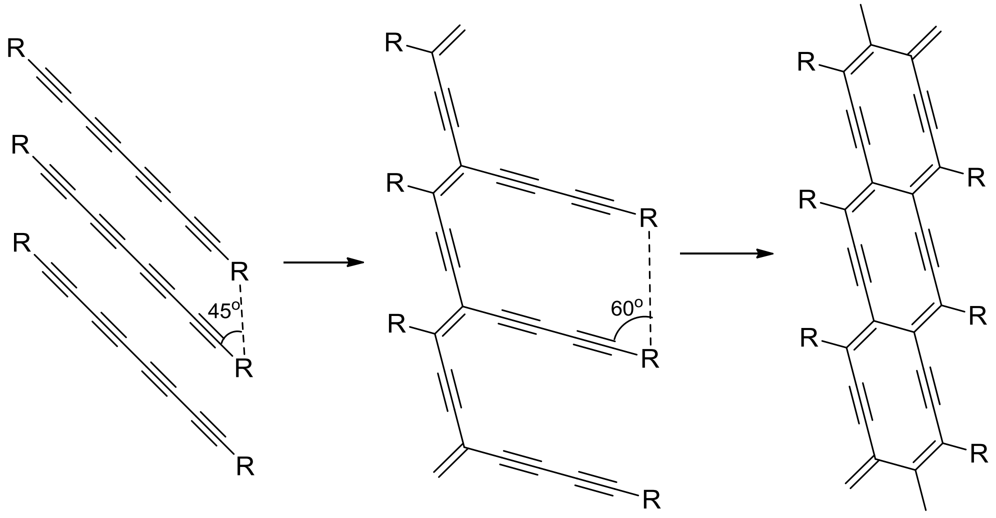

Figure 1.10 Proposed solid-state 1,4- and 5,8-polymerization of octatetrayne monomers.[86]

The bathochromic shift in the UV-Vis absorption spectra to the near IR region, as well as the formation of two broad peaks in the ^{13}C MAS NMR around 145 and 80 ppm for the olefinic and acetylenic carbons, respectively, alluded to the materialization of a laddered polymer.[86,111] This is further corroborated by the ESR (electron spin resonance) signal obtained, which is consistent with the presence of a highly conductive material.[112] The controlled polymerization of a dicarboxylic acid, diaryl ester, and dianilide tetrayne was also reported by Okada and co-workers, but spectroscopic evidence to support this claim is weak.[113] Alternatively, these researchers have suggested that dithiophene- and diquinoline-substituted tetraynes undergo a 1,2-polymerization with thermal annealing. In particular, the dithiophene monomer was obtained as a single crystal, and the large tilt angle ($\theta = 71°$) calculated led Okada and co-workers to propose that a 1,2-addition reaction was likely. The UV-Vis spectra did not correspond to a PDA π-conjugated structure and the absence of acetylenic carbon peaks in the solid state NMR further indicated that the resulting heteroaryl polymers subsequently cyclized to form an irregular aromatic material.[114] This has been the only reported example to date of a 1,2-addition reaction of a triyne, tetrayne, pentayne, or hexayne monomer in the solid state.[1]

The topochemical polymerization of tetrayne derivatives to give ladder polymers has also been explored because these polymers may serve as viable candidates for third-order NLO applications,[1] which has been supported theoretically.[115] The synthesis of novel ladder PDAs was designed according to Figure 1.11.[116] An advantage of forming ladder polymers from monomers with a spacer group (X), as opposed to the analogous polymer with only acetylene units in the backbone (Figure 1.10), is that these polymers typically remain crystalline.[1] Furthermore, the bridging moiety that is inserted may enhance the π-conjugation length or density within the polymer backbone. For instance, saturated substituents function as a spacer group to reduce strain within the crystal lattice, while unsaturated groups serve to fine tune the electronic and optical properties of the PDA chain by expanding the π-system.[1]

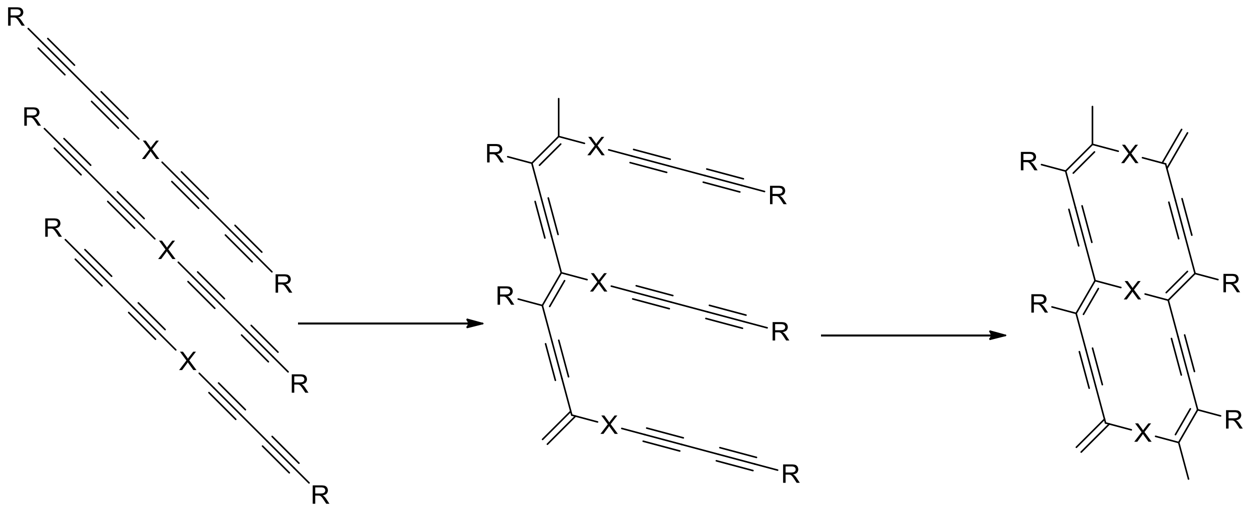

Figure 1.11 Synthesis of ladder PDAs from tetraynes with a spacer group (X).[116]

Okada and co-workers initially attempted to synthesize ladder PDAs with phenylene as a bridging unit; however once the monomer was heated above 27 °C, this cyclic spacer group experienced a flipping motion. The resulting polymerization was complex, which was attributed to the inability of the monomers to obtain proper alignment under thermal conditions.[117] Urethane side groups (R) were subsequently added to control the polymerization of the diacetylene units through hydrogen bonding. Nevertheless, only the 1,4-addition polymer was suggested by solid-state ^{13}C NMR, despite using different arylene spacer groups.[118] Substituting phenylene with a linear methylene chain led to formation of the ladder-type polymer[116,119-120] which exhibited large χ^3 values.[116] The chemical structure of the polymer was investigated by solid-sate ^{13}C NMR spectroscopy and powder X-ray diffraction before and after γ–ray irradiation. Because no monomer was extracted after dissolving the polymerized material in hot toluene or hexanes, quantitative conversion was suggested.[116,119-120] It was also shown with UV-Vis and ^{13}C MAS NMR spectroscopy that a methylene chain attached to amido groups could serve as a successful linker unit to afford ladder polymers due to intermolecular hydrogen bonding between both the bridging moiety and the side groups.[121]

Ladder polymers have also been prepared by Okuno and co-workers using an arylamine spacer group with thermal annealing above 80 °C. PXRD, UV-Vis spectroscopy, and scanning electron microscope (SEM) imaging were used to characterize the crystalline solid. Due to the small energy difference, nitrogen atoms in arylamines can bear both sp^2 and sp^3 configurations, and therefore help reduce structural strain, similar to methylene chains. The polymerized material showed high conductivity after I_2 doping, presumably due to the introduction of an electron donating linker to the one-dimensional π-system. The high regularity and conductivity of the obtained polymer is unusual for PDAs.[122] In 2013, Morin and co-workers reported the self-assembly of a soluble conjugated 1D nanowire from a star-shaped molecule with three diyne units attached to a central phenyl core (Figure 1.12). Formation of the rigid PDA from topochemical polymerization of the 1,4-diarylbutadiyne precursor is performed in the gel state, first through self-assembly of the monomer and then by cross-linking under UV irradiation. PXRD, SEM imaging, and variable-temperature ^{1}H NMR (VT-^{1}H NMR) all suggest columnar assembly of the gel. Deposition of the gel on a glass substrate followed by drying under ambient conditions afforded a xerogel, which under UV irradiation, yielded a PDA nanowire film as indicated by TEM (transition electron microscopy) analysis, UV-Vis, and Raman spectroscopy. A high degree of polymerization is indicated by the TEM images which show nanowires that are a few tens of nanometers long.[123] Exploration of the potential use of ladder polymers for applications in solid-state devices is in progress.[1,123]

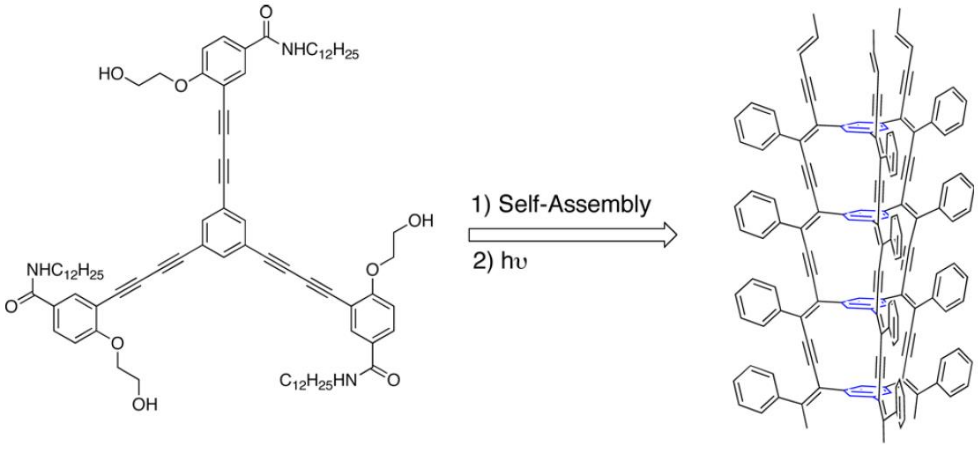

Figure 1.12 Self-assembly of a star-shaped molecule to give a conjugated 1D nanowire. Substituents on the aryl rings are omitted from the drawing of the product. Reproduced with permission from ref. 123, Copyright 2013, American Chemical Society.

The proposed polymerization pathway outlined in Figure 1.10 is rather interesting, as the ladder polymer might further cycloaromatize to a more stable planar polymer, such as graphitic ribbons or some other conductive carbon-rich material. Cycloaromatization may be driven by the in-plane repulsion of the π-orbitals at the sp-carbons in the ladder polymer, but experimental evidence to support this claim is limited.[86] On the contrary, Baughman and Yee had previously indicated that formation of a ladder polymer from cyclization of the butadiynyl substituents is not likely, as considerable displacement would be required to proceed. Additionally, the polymer product would probably exhibit sizeable intramolecular strain energy initiated by configuration changes.[98] However, if long, flexible polyyne chains were stacked at an appropriate tilt angle, formation of graphitic ribbons may then be achieved with heat and/or light, assuming the polymerization reaction will be exothermic enough to overcome rearrangement barriers.[1,59,85-86] The proposed formation of a graphitic ribbon from tetrayne monomers is shown in Figure 1.13.

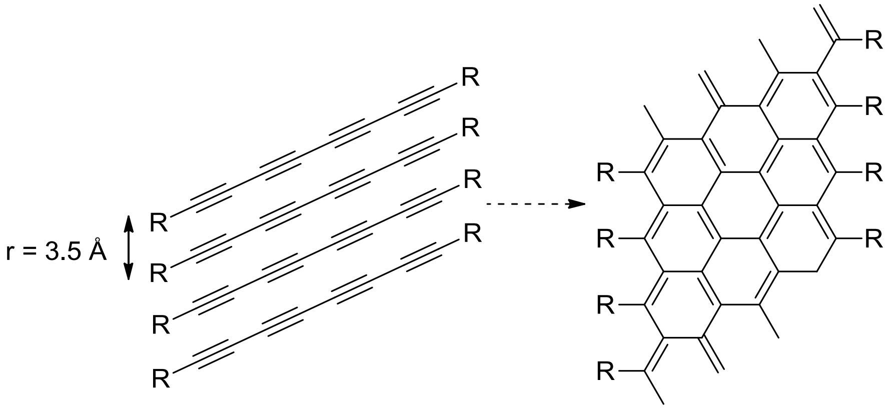

Figure 1.13 Proposed formation of a graphitic ribbon from tetrayne monomers.

According to Figure 1.13, R could not be a large, rigid end-group, as close monomer contact (van der Waals distance) would be required, and flexibility is desired to allow for small displacement and molecular mobility of the crystal lattice. Likewise, Okada and co-workers have reported that an asymmetrically-substituted octatetrayne monomer undergoes a site selective 1,4-polymerization on the side substituted by the more flexible side chain according to the observed solid-state ^{13}C NMR chemical shifts.[108] Peter Giattini, an undergraduate in this group, has previously performed molecular modeling calculations (molecular mechanics, semi-empirical, and density functional theory calculations) to determine the most successful arrangement of pentayne monomers for polymerization. He found that lining up the rods diagonally, as opposed to linearly, would be more efficient to reduce molecular motion during polymerization. A fairly recent precedent to support graphitic ribbon preparation from tetrayne monomers is the formation of carbon nanospheres from fullerene-substituted tetraynes by thermal annealing at 160 °C.[124-125] Alternatively, self-assembly of tetraynes in solution may offer more flexibility to form the desired carbon-rich materials. For example, Ding and Olesik prepared carbon nanospheres after cross-linking dihydroxymethyl tetrayne films under pyrolysis conditions at 800 °C.[126]

The topochemical polymerization diiodooctatetrayne (**17**) may undergo is of great interest for its potential applications and interesting optical properties, and will be explored in this report. If the tetrayne monomers react together with 1,4-regiochemistry (r = 4.9 Å), the 1,4- or 3,6- polydiacetylene will form, but if the polymerization takes place with 1,8-regiochemistry (r = 9.6 Å), the 1,8-polytetraacetylene will be afforded (Figure 1.14).[85] The arrangement of the monomers in the co-crystal determines which polymerization mode will occur. If a polydiacetylene is obtained, the polymer may be separated from the host to study its thermal, chemical, and optical behavior, similarly to PIDA.[47,53] Furthermore, both polydiacetylenes prepared from the 1,4- or 3,6- polymerization of diiodotetrayne **17** has pendant alkyne groups, and will therefore be less rigidly planar than PIDA, possibly increasing the solubility of the polymer and subsequently allowing for post-polymerization substitution of iodine. Alternatively, if the polytetraacetylene is obtained, addition of Lewis bases to the isolated polymer might lead to dehalogenation,[54] and consequently afford carbyne. The topochemical polymerization of diiodooctatetrayne (**17**) will be further discussed in Chapter 4.

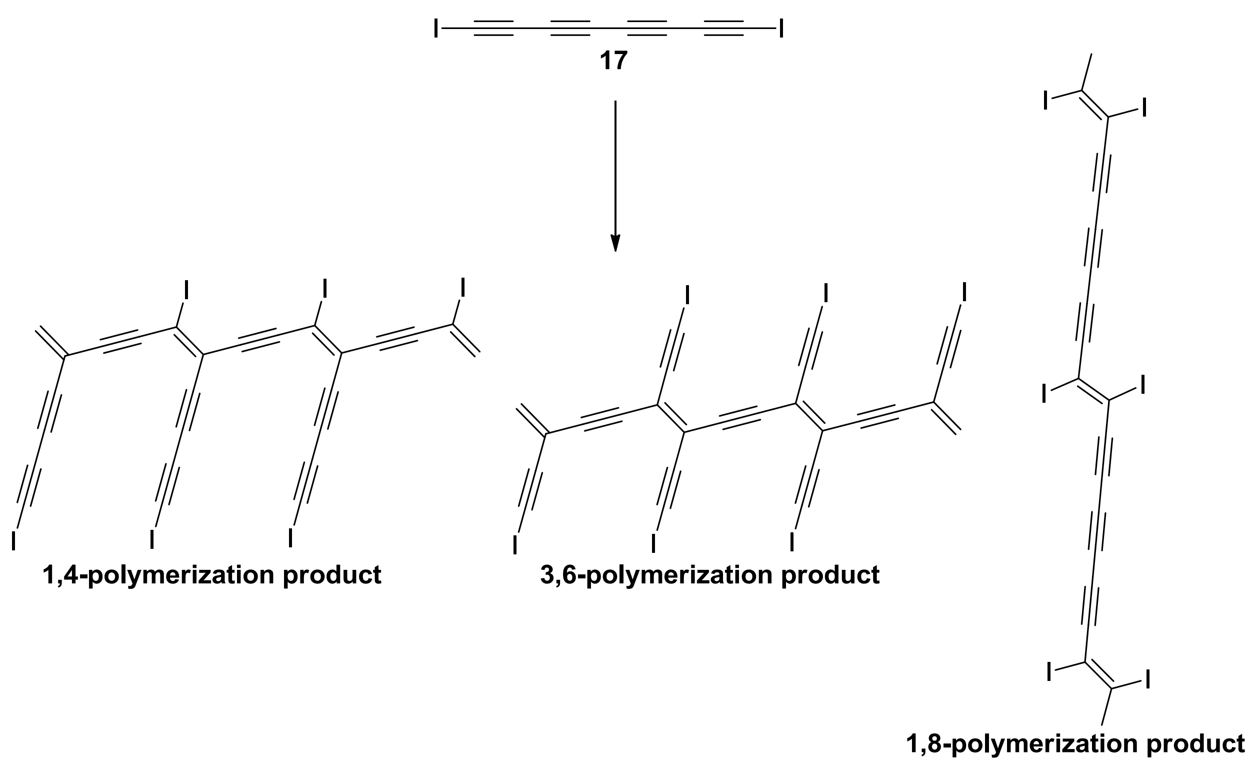

Figure 1.14 Targeted conjugated polymers from diiodooctatetrayne (**17**).

Okada and co-workers have utilized PXRD to help characterize the material formed from tetrayne polymerization in this section probably because the samples are either amorphous or exhibit poor crystal quality. Instead, the supramolecular host-guest scaffold used in our system allows for a single-crystal-to-single-crystal transformation. Therefore, single-crystal XRD, a more powerful technique for structure determination than its PXRD analog, may be used to gain further structural insights into the polymerization process of tetraynes and the formation of graphitic material.

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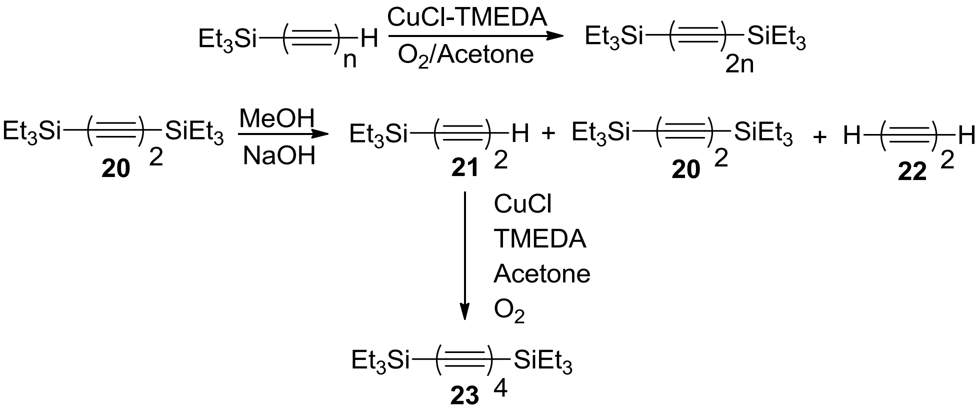
Chapter 2: The Synthesis of Tetraynes via Metal-Catalyzed Coupling Reactions

2.1 Previous Work on the Synthesis of Polyynes

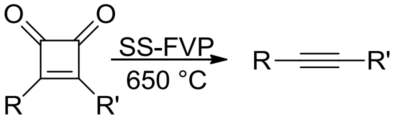
The synthesis of long polyyne chains was pioneered by Walton and co-workers in 1972.[1] By utilizing Cu-catalyzed oxidative Hay coupling reactions, triethylsilyl (TES)-capped polyynes extending from 4 to 16 C≡C bonds in length were prepared (Scheme 2.1).[1] However, due to a dramatic decrease in kinetic stability and yield, protected oligoynes with more than 8 carbon-carbon triple bonds were not isolated.[1] The product of each homocoupling reaction was mixed with sodium hydroxide to desilylate one end of the polyyne, and subsequently, this material was then used in another Hay coupling reaction. This method resulted at each step in a statistical combination of monodeprotected, protected, and completely deprotected polyyne products, which proved difficult to separate.[1] The presence of byproducts in the mixture makes this pathway challenging.



Scheme 2.1 Walton's route.[1]

Approximately 20 years later, Diederich and co-workers described the synthesis of shorter polyyne rods containing up to 5 alkyne units. These researchers employed solution-spray flash vacuum pyrolysis (SS-FVP) to obtain a wide array of polyynes in moderate to high yields from substituted 3,4-dialkynyl-3-cyclobutene-1,2-diones, as outlined in Table 2.1.[2] Although this method was effective in affording a variety of phenyl (Ph) and silyl-protected polyynes in relatively high yields, the synthesis of the cyclobutane-dione precursors is complex and the experimental setup utilized is not easily accessible.

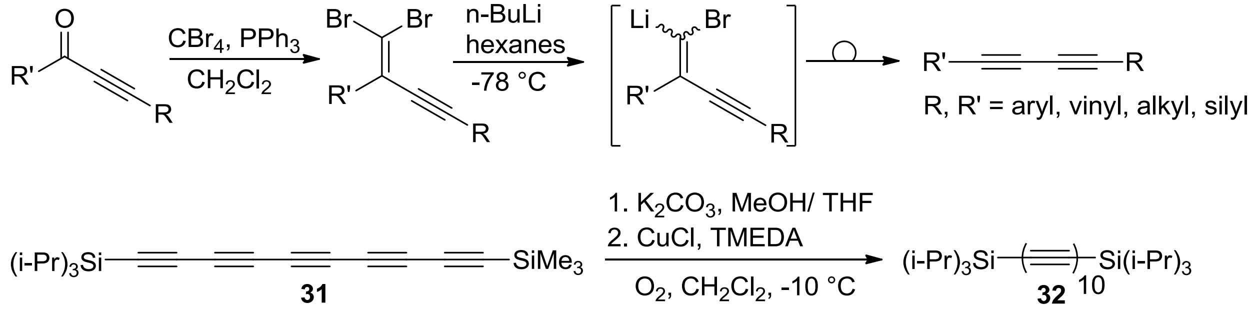
Table 2.1 Diederich's route.[2]



Compound	R	R'	% Yield
24	Ph-	Ph-	98
25	PhC≡C-	PhC≡C-	97
26	PhC≡C-C≡C-	PhC≡C-C≡C-	59
27	*n*-PrC≡C-	*n*-PrC≡C-	78
28	$Me_3SiC{\equiv}C$-	$Me_3SiC{\equiv}C$-	99
29	*i*-$Pr_3SiC{\equiv}C$-C≡C-	*i*-$Pr_3SiC{\equiv}C$-C≡C-	42
30	*i*-$Pr_3SiC{\equiv}C$-	$Me_3SiC{\equiv}C$-	71

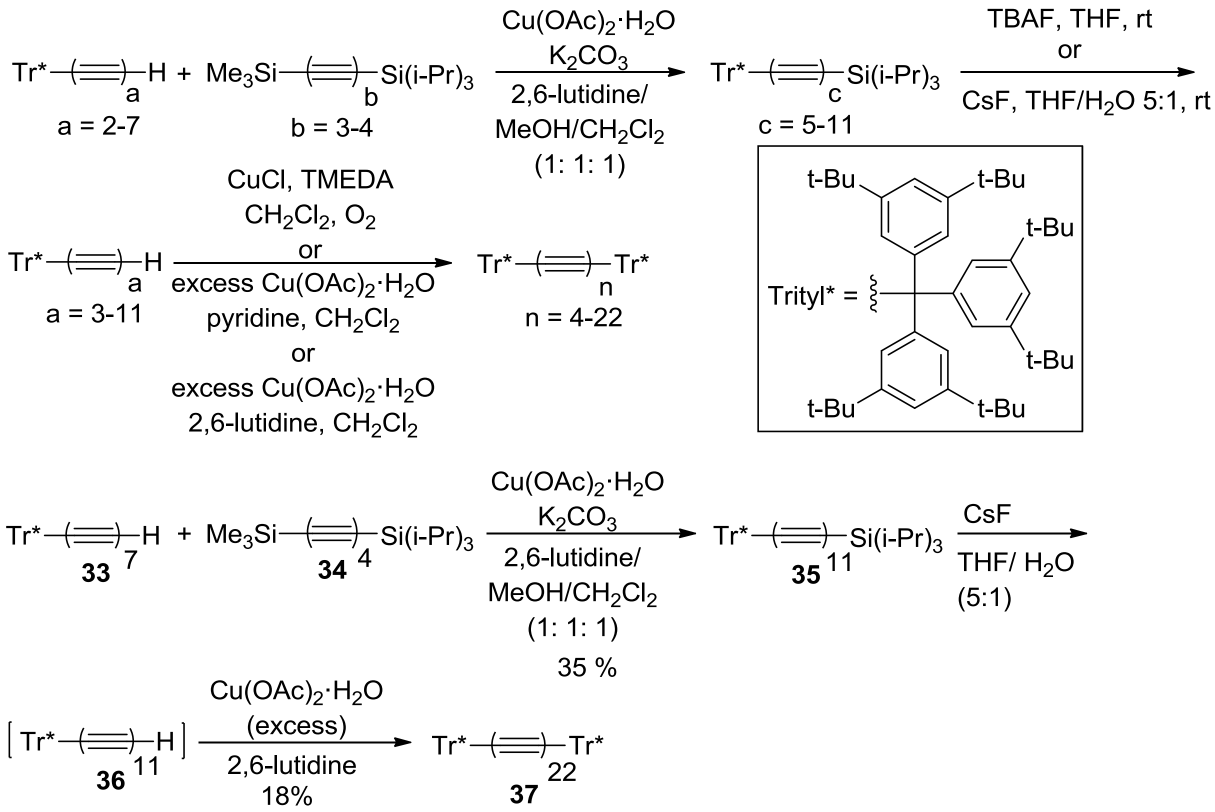
Tykwinski and co-workers used the Fritsch-Buttenberg-Wiechell (FBW) rearrangement to synthesize polyynes with various end groups ranging from 2 to 10 C≡C bonds. Additionally, since a large array of dibromoolefins can be prepared, symmetrical and unsymmetrical polyynes can be made, as highlighted in Scheme 2.2.[3-5] Bulky end-cap groups have allowed for the successful isolation of extended polyynes of at least 10 alkyne units[6-7] with dendrimer,[8] adamantyl (Ad),[9] platinum,[10-11] triisopropylsilyl (TIPS), and tert-butyl (*t*-Bu) substituents.[12] The

TIPS and *t*-Bu end-groups utilized by Tykwinski and co-workers are advantageous because they offer both stability and solubility of the sp-hybridized carbon oligomers without modifying the electronic properties of the system.[3-4] Although the FBW rearrangement is effective for chains up to nine carbon-carbon triple bonds in length, oxidative homocoupling reactions were required when pursing decaynes.[3] Therefore, higher homologs that were prepared by this route all contained an even number of triple bonds.



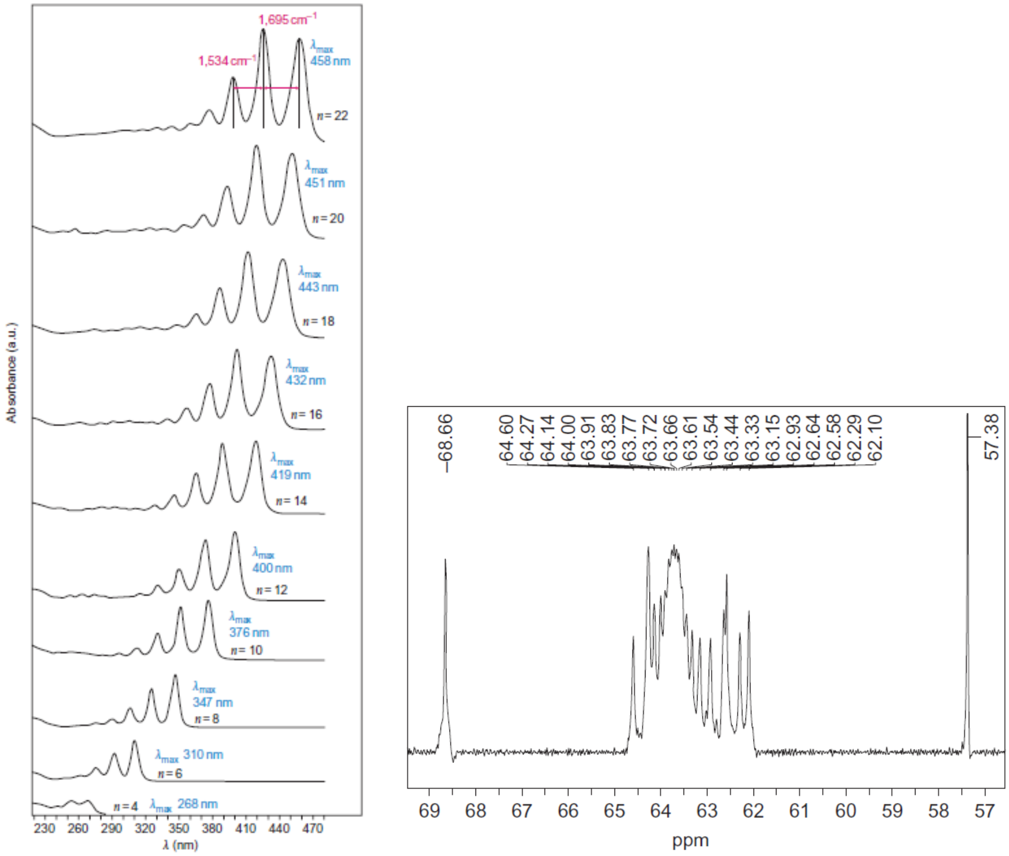
Scheme 2.2 Tykwinski's route.[3]

Using a modified Eglinton-Galbraith oxidative coupling reaction, Chalifoux and Tykwinski recently reported the synthesis of the longest isolated polyyne to date, which contains 22 alkyne units (Scheme 2.3).[13] Bulky tris(3,5-di-*t*-butylphenyl)methyl ("trityl*") protecting groups were required to stabilize the longer carbon oligomers. Specifically, terminal polyynes up to 7 C≡C bonds in length were isolated, and could be handled in the solid state because of the stabilizing effect of the Tr* end-group.[13]



Scheme 2.3 Tykwinski's synthesis of polyynes containing up to 22 alkyne units.[13]

The spectroscopic properties for polyyne **37** and shorter polyynes were examined to predict the properties of carbyne. UV-Vis spectroscopy for the series of trityl*- protected oligoynes showed a bathochromic shift in λ_{max} as a function of increasing chain length (Figure 2.1a),[13] consistent with a decrease in the HOMO-LUMO bandgap energy (E_g) as a function of increasing polyyne length. Assuming the bandgap will eventually reach an asymptotic limit, the λ_{max} and E_g values for carbyne can be predicted. [3,8,13] It is inferred from the UV-Vis spectra that an asymptotic limit of around 485 nm (2.56 eV) is reached once the chain length equals 48 alkyne units, resembling the predicted λ_{max} of carbyne.[13] A ^{13}C NMR spectrum was also obtained for polyyne **37,** and 21 unique peaks between 62.1 and 64.6 ppm along with two overlapping signals at 64.2 ppm were detected, verifying that the carbon chain is composed of alternating single and triple bonds (Figure 2.1b).[13]

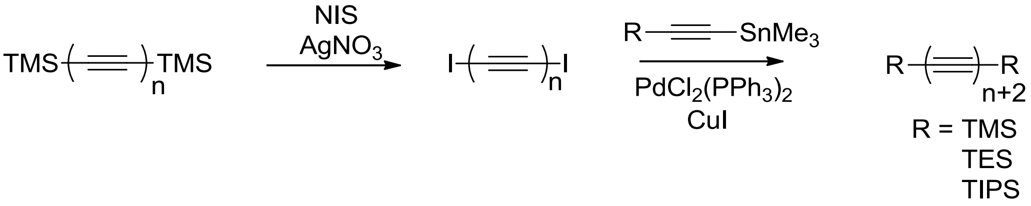


a) b)

Figure 2.1 (a) UV-Vis spectra for Tr* end-capped polyynes measured in hexanes; (b) ^{13}C NMR spectrum for polyyne **37**. Reproduced with permission from ref. 13, Copyright 2010, Macmillan Publishers Ltd: Nature Chemistry.

2.2 An Iterative Route for the Synthesis of Polyynes

While the routes developed by Walton, Diederich, and Tykwinski (Section 2.1) have proven effective for many cases, some drawbacks include the required use of unstable terminal alkynes, complicated precursor preparation, or harsh reaction conditions. Therefore, a synthetic pathway toward moderate length polyynes was developed by former group member Lei Li, in which short carbon rods are iodinated and subsequently used in a palladium-catalyzed Stille coupling reaction with silyl-protected tin acetylides.[14] The tin acetylides couple to both ends of the diiodopolyyne, ultimately resulting in a silyl-protected oligoyne, which once again can be iodinated and used in a successive Stille coupling reaction.[14] Although there are only a few examples of Stille-type alkyne-alkyne couplings in the literature,[15-18] this reaction appears to be efficient and is central to our developed pathway. Each iodination/coupling cycle symmetrically increases the length of the polyyne chain by two C≡C bonds (Scheme 2.4).[14] This iterative method is attractive because simple it uses simple starting materials, employs mild conditions, and avoids the preparation or isolation of terminal alkyne intermediates. Instead, this route incorporates diiodopolyynes, which are relatively stable in comparison to the analogous terminal or bromoalkynes. Furthermore, end group selection can be made in the final step, as phenyl- and silyl-protected tin acetylides have been successfully coupled to obtain the corresponding polyynes. Lastly, this method offers a simple route to prepare symmetric polyynes with an odd number of C≡C bonds.[19]



Scheme 2.4 Iterative synthetic method.[14]

Few examples of cross-coupling reactions with diiodopolyynes have been described in the literature. Using Cadiot-Chodkiewicz conditions, Hirsch and co-workers coupled diiodoacetylene to terminal alkynes that were connected by an alkyl tether to give the corresponding macrocycle. Products were obtained as mixtures, and the desired compound was isolated in low yield.[20] Similarly, Cataldo and co-workers reported the cross-coupling of diiodoacetylene with phenyl- or napthyl-capped copper acetylides. A mixture of diarylpolyynes of different lengths was yielded, and isolation of the individual components was not attempted.[21-22] Bruce and co-workers described the palladium-catalyzed cross-coupling of diiodoalkynes and gold(I) alkynyl complexes.[23-25] These literature examples support our method in which diiodopolyynes are coupled to tin acetylides as part of a general synthetic pathway toward symmetric polyynes. Tetraynes, pentaynes, hexaynes, and a heptayne have been prepared and isolated by this method (Table 2.2).[19]

Table 2.2 Polyyne synthesis via Stille coupling with diiodopolyynes.[19]

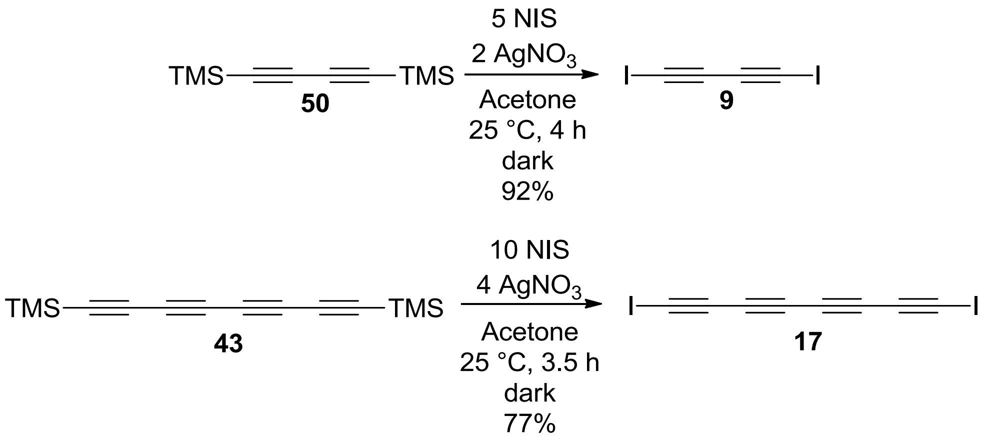
Diiodopolyyne	Sn Acetylide	Product	Temperature (º C)	% Yield[a] (isolated)
$\text{I}-\equiv-\equiv-\text{I}$ **9**	$\text{TIPS}-\equiv-\text{SnMe}_3$ **39**	$\text{TIPS}-\equiv-(\equiv)_2-\equiv-\text{TIPS}$ **42**	25	77
9	$\text{TMS}-\equiv-\text{SnMe}_3$ **40**	$\text{TMS}-\equiv-(\equiv)_2-\equiv-\text{TMS}$ **43**	0	59
$\text{I}-\equiv-\equiv-\equiv-\text{I}$ **16**	**39**	$\text{TIPS}-\equiv-(\equiv)_3-\equiv-\text{TIPS}$ **44**	0	40
16	**40**	$\text{TMS}-\equiv-(\equiv)_3-\equiv-\text{TMS}$ **45**	0	61
16	$\text{Ph}-\equiv-\text{SnMe}_3$ **41**	$\text{Ph}-\equiv-(\equiv)_3-\equiv-\text{Ph}$ **46**	0	28
$\text{I}-\equiv-(\equiv)_2-\equiv-\text{I}$ **17**	**39**[b]	$\text{TIPS}-\equiv-(\equiv)_4-\equiv-\text{TIPS}$ **47**	0	47
17	**41**	$\text{Ph}-\equiv-(\equiv)_4-\equiv-\text{Ph}$ **48**	0	16
$\text{I}-\equiv-(\equiv)_3-\equiv-\text{I}$ **38**	**39**	$\text{TIPS}-\equiv-(\equiv)_5-\equiv-\text{TIPS}$ **49**	-15	10

Conditions: Mole ratio of organostannane to diiodoalkyne 2:1; $Pd(PPh_3)_2Cl_2$ 12 mol %; CuI 23 mol %, THF, 10h. [a] All yields are for isolated product, based on diiodopolyyne starting material. [b] Excess organostannane was used, CuI 13 mol %.

Former group member Racquel DeCicco explored the synthesis of polyynes with an odd number of carbon-carbon triple bonds,[26] while my research focused on preparation of polyynes with an even number of alkyne units. The iodination of commercially available trimethylsilyl-capped diyne **50** to give diiodobutadiyne (**9**) was achieved using silver nitrate ($AgNO_3$) and *N*-iodosuccinimide (NIS) according to previously described literature procedures (Scheme 2.5).[27] Nishikawa and co-workers reported that a catalytic amount of $AgNO_3$ and 1.2-1.5 equivalents (per silyl group) of NIS was required to iodinate trimethylsilylacetylenes.[27] When DeCicco used 1 equivalent of $AgNO_3$ and 2.5 equivalents of NIS to synthesize diiodotriyne **16** from its corresponding bis(trimethylsilyl) triyne precursor, she noticed the presence of monoiodinated material in the product mixture,[26] suggesting that for compounds containing multiple triple bonds, these reagent amounts were insufficient. To ensure complete iodination, 2.5 equivalents of $AgNO_3$ and 4 equivalents of NIS were needed.[26] This reaction must proceed quickly, as the resulting diiodoalkynes are significantly less stable than their respective silyl-capped precursors, especially as the number of alkynyl units in the chain increases. Therefore, iodination of trimethylsilyl-capped tetrayne **43** was attempted at 0 °C in an effort to slow down the decomposition rate of diiodopolyyne **17**; however the lower temperature also increased the reaction time and a black insoluble solid appeared at the bottom of the flask, corroborating the need for short reaction times with longer diiodopolyynes. To compensate for this effect and to enhance the reaction rate of longer polyynes, the concentration of $AgNO_3$ and NIS was increased. Four equivalents of $AgNO_3$ and 10 equivalents of NIS were found to iodinate trimethylsilyl-capped tetrayne **43** in 3-4 hours (Scheme 2.5). The iodination of longer polyynes may proceed more slowly than shorter analogs because the silver also complexes to the internal carbon-carbon triple bonds, and therefore is less available to react with the silyl alkyne on the end.

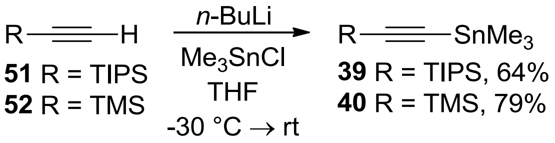
The unstable nature of tetrayne **17** presented isolation challenges since this material has been shown to be a shock explosive in the solid state, emitting an orange flash followed by black smoke, and ultimately resulting in a decomposed black insoluble solid.[28] Therefore, diiodopolyynes with 4 or more C≡C bonds should only be handled in amounts of 50 mg or less.

Furthermore, this material should be kept in solution in the dark and stored below 0 °C. At 85 °C, diiodooctatetrayne (**17**) explodes and emits molecular iodine as a red liquid.



Scheme 2.5 Iodination of C_4TMS_2 (**50**) and C_8TMS_2 (**43**).

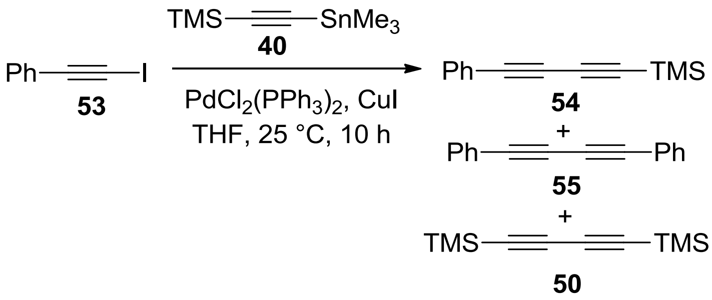
Diiodopolyynes **9** and **17** were cross-coupled with various organostannanes using Stille coupling conditions (Table 2.2).[19] The trimethylsilyl, triisopropylsilyl, and phenyl tin acetylides were prepared according the method reported by Moloney and co-workers (Scheme 2.6).[29] The demanding purification process, which requires extraction and distillation, resulted in moderate product yields. An equimolar ratio of reagents was reported for the tin acetylide synthesis,[29] although a 2: 1.5: 1 ratio of TMS-acetylene (**52**), n-BuLi, and trimethyltin chloride, respectively, has also been found to give good yields for tin acetylide **40**. Caution should also be taken when preparing and handling the tin acetylides, as trimethyltin chloride and analogous organotin compounds have been declared toxic by all means of exposure.[30] Tributyltin chloride was not pursued despite its relative stability, since isolation problems have previously arisen due to the low polarity and high solubility of this compound.[14]



Scheme 2.6 Preparation of tin acetylides.[14,29]

Lei Li initially studied the double cross-coupling reaction of diiodobutadiyne (**9**) with silyl-protected alkynes using a variety of palladium-catalyzed conditions. She found that coupling of diiodopolyyne **9** with tin acetylides under Stille coupling conditions promoted tetrayne formation, while both the Negishi and Sonogashira reactions predominantly led to homocoupling of the terminal alkyne.[14] Later, DeCicco further explored the Negishi coupling as a means to afford TMS, TIPS, and Ph capped tetraynes from the corresponding zinc acetylides. Unfortunately, preparation of the zinc acetylides proved unreliable, and the product yields were generally low.[19,26]

Therefore, model reactions with iodophenylacetylene (**53**) and TMS tin acetylide **40** were performed to optimize Stille coupling conditions for the diiodopolyyne substrates (Scheme 2.7). In this system, cross-coupled diyne **54** and both homocoupled diynes **55** and **50** (formed from the homocoupling of haloalkyne **53** and tin acetylide **40**, respectively) could be identified and quantified, unlike the polymeric material that results from the homocoupling of diiodoalkynes. Examination of catalyst ratio, solvent system, and reaction temperature was fully explored, and the results are highlighted in Table 2.3.



Scheme 2.7 Model Stille coupling reaction.

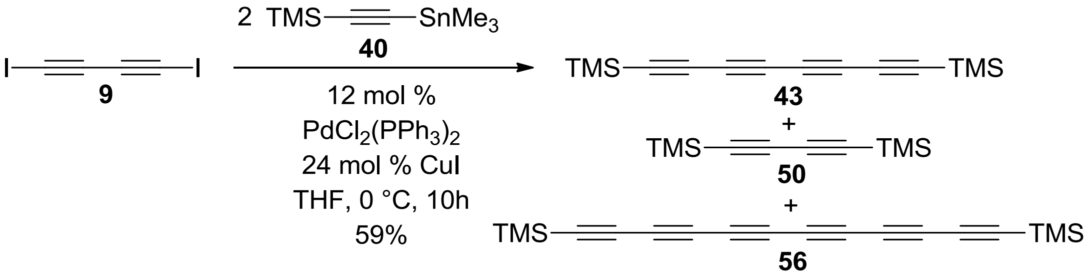
Table 2.3 Model Stille coupling reaction conditions.

% Catalyst Loading $PdCl_2(PPh_3)_2$: CuI	**Solvent**	**Crude Ratio of 54: 55: 50[a]**	**Crude Yield (%)**	**NMR Yield of 54 (%)**
12:22	THF	1: 0.55: 0.19	85	49
6:11	THF	1: 0.17: 0.43	23	17
6:15	THF	1: 0.13: 0.42	55	36
6:15	Toluene	1: 0.21: 0.48	59	35
6:15	Methanol	1: 1.1: 0.09	9	4
6:30	THF	1: 0.16: 0.41	40	26
6:15	DMF	1: 1.4: 0	14	6

Conditions: Mole ratio of organostannane to iodoalkyne 1:1. Alkynes **53** and **40** were added 3 drops/ min to the reaction mixture via cannula over 10 hours. The reaction was then allowed to stir over-night at room temperature. [a] Determined by ^{13}C NMR.

The model Stille coupling experiments indicated that methanol and DMF each limit formation of homocoupled diyne **50**; however the low crude yields obtained discouraged further studies with these solvents. Although toluene and THF gave similar product yields, THF was used in the Stille reactions with diiodopolyynes because the catalysts showed better solubility in this solvent. Additionally, the model Stille coupling experiments indicated that the reaction rate and order of reagent addition were crucial to the success of this reaction. Slow addition of haloalkyne **53** and tin acetylide **40** in solution to the catalyst mixture provided better results than when all reagents were combined in one pot, probably because the effective concentration of the catalysts are increased relative to the alkyne reactants. Adding compounds **53** and **40** to the catalyst mixture over a period of 10 hours was shown to be optimal, as shorter addition times caused increased homocoupling of the tin acetylide. Furthermore, the concentration of the copper iodide co-catalyst proved to be particularly important to promote cross-coupling in this reaction. Previously, the coupling of tin acetylides with aryl halides was studied by Farina and co-workers. Their findings suggest that a copper co-catalyst transmetalates with the organostannane to form a copper acetylide, which in turn may transmetalate with palladium at a faster rate than the stannane alone.[31-32] The presence of copper iodide therefore minimizes homocoupling of iodoalkyne **53**; however excess copper iodide can lead to undesired homocoupling of tin acetylide **40**. A catalytic amount of triphenylphosphine (PPh_3) was also added in some trials to promote the reduction of $PdCl_2(PPh_3)_2$; however CuI can act as a free ligand scavenger[31-33] and consequently, diyne **54** was obtained in yields comparable to Table 2.3. A $PdCl_2(PPh_3)_2$: CuI ratio of approximately 1:2 was determined to be the optimal catalyst loading, and consequently, 12 mol% palladium (6 mol% per iodine) and 23 mol% copper (11.5 mol% per iodine) were used for the symmetric double cross-coupling of diiodopolyynes to obtain the desired product as the major component in the crude mixture.[19]

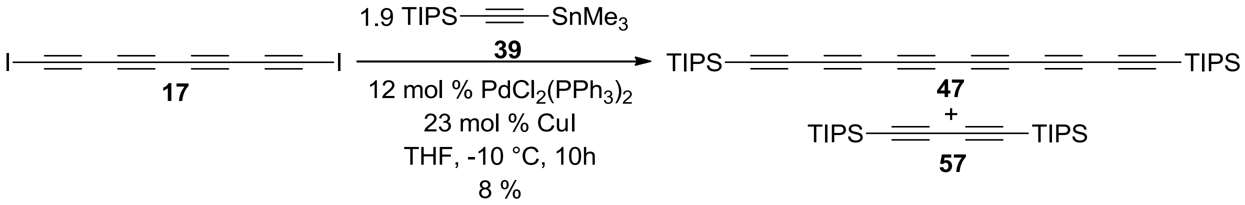
As demonstrated with the model Stille coupling reactions, addition of the diiodoalkyne and tin acetylide solution to the catalyst mixture over a period of 10 hours was shown to be optimal, as shorter addition times not only resulted in increased homocoupling of organostannane, but also the unwanted formation of longer oligomers as determined by ^{13}C NMR spectroscopy,[14,19] presumably through the homocoupling reaction of mono coupled material. Moreover, using an automated syringe pump, as opposed to a cannula, also led to increased homocoupling and longer oligomer materialization. This finding suggests that there is a significant difference in drop size between the two apparatuses, and optimization of the drip rate would first have to be performed with the syringe pump if it were to be employed. Furthermore, Li had previously observed that when all the starting materials were mixed at once, a black insoluble material formed during the reaction, possibly due to diiodopolyyne decomposition or random polymerization.[14] All the diiodopolyynes were handled with caution, as these compounds are shock explosives and have been observed to become less stable over time. Diiodopolyynes are light sensitive, and consequently, the flask containing this material was wrapped in aluminum foil. The decreased stability of the longer polyyne intermediates was addressed by lowering the temperature of the solution for the entire reaction (Table 2.2). Moreover, the diiodopolyynes were used within a week of preparation, and were washed with aqueous sodium thiosulfate ($Na_2S_2O_3$) immediately prior to use to remove any excess I_2 that may have formed *in situ*.[19] DeCicco synthesized the polyyne products with an odd number of carbon-carbon triple bonds, as well as hexayne **48**.[26] Tetrayne **42** and hexayne **47**, reported in Table 2.2, were prepared by Li.[14] 1,8-bis(trimethylsilyl)-1,3,5,7-octatetrayne (C_8TMS_2, **43**) was obtained from the coupling of diiodobutadiyne (**9**) and TMS tin acetylide **40** (Scheme 2.8).[19]



Scheme 2.8 Synthesis of tetrayne **43**.

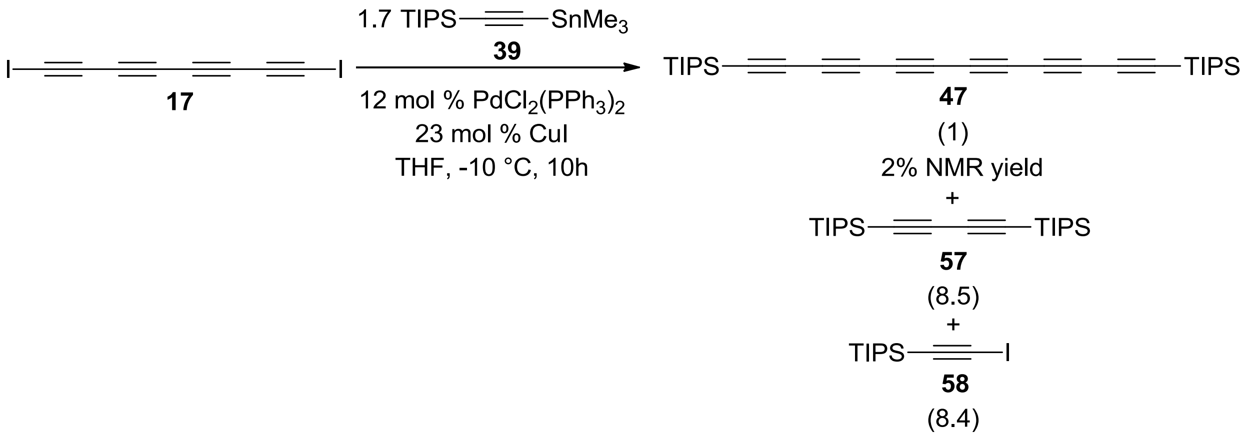
Diyne **50**, resulting from the homocoupling of the organostannane, normally formed in much smaller amounts than the desired tetrayne **43**. Compound **50** was easily separated from the product mixture using vacuum sublimation. The ability to recover diyne **50** and reuse it in future iodination reactions adds to the overall atom efficiency of this route.[14,19] 1,12-bis(trimethylsilyl)-1,3,5,7,9,11-dodecahexayne ($C_{12}TMS_2$, **56**) was also produced in some trials, but typically in low yields. Chromatographic separation of the silyl-protected tetrayne **43**, diyne **50**, and hexayne **56** proved to be difficult, as these compounds have very similar polarities and therefore move together on silica. As a result, diyne **50** was first removed from the crude mixture by vacuum sublimation, and then column chromatography was used to isolate tetrayne **43** from hexayne **56**. Many of the fractions that were collected contained both products, thus decreasing the yield of isolated tetrayne. To facilitate separation, iodination of the crude mixture was also performed to increase the polarity of the polyynes, but the instability of the longer diiodopolyynes limited the effectiveness of this approach. Despite wrapping the column in aluminum foil, black solid was noticed on the silica gel, indicative of decomposition. Isolation of diiodopolyyne **17** was achieved, but in a much lower yield than what was obtained after the iodination of pure tetrayne **43**.

Diiodooctatetrayne (**17**) was next allowed to react with tin acetylide **39**. The sterically bulky TIPS end-group was employed to aid in the stability of the resulting hexayne. Although the flask containing the diiodoalkyne was kept in an ice bath (~0 °C), only homocoupling of the organostannane resulted, suggesting decomposition of the diiodotetrayne prior to or during the course of the reaction. Therefore, diiodopolyyne **17** was prepared on the same day that it was used in the Stille coupling, and was kept in a dry ice/ acetone bath at -10 °C during the course of the reaction. Despite handling this tetrayne in the dark prior to coupling, it immediately started to turn from an orange solid to a black solid. Hexayne **47** was successfully synthesized, but a significant amount of the diiodotetrayne decomposed, and subsequently, an insoluble black precipitate formed at the bottom of the flask containing the diiodoalkyne/ organostannane mixture. Therefore, only 8 % of the hexayne was isolated (Scheme 2.9).



Scheme 2.9 Synthesis of hexayne **47**.

To avoid handling unstable tetrayne **17** as a solid, a solution of diiodopolyyne **17** dissolved in pentane was cross-coupled to tin acetylide **39** (Scheme 2.10). After iodination of tetrayne **43**, diiodooctatetrayne (**17**) was extracted with pentane, and solvent was removed *in vacuo* until about 1 mL of the pentane/ diiodotetrayne **17** mixture remained. Tin acetylide **39** and THF were then added to this flask, and this solution was subsequently added dropwise to the catalytic mixture. No black solid was observed during the reaction, but instead, the diiodoalkyne/organostannane mixture turned from orange to red, indicative of I_2 formation. This color change suggests that decomposition of diiodopolyyne **17** occurred primarily during the course of the reaction. Molecular iodine can act as an oxidizer and consequently may promote the palladium-catalyzed homocoupling of alkynylstannane **39**,[34] giving a reason for the high ratio of diyne **57** observed in Scheme 2.10. Isolation of hexayne **47** was not attempted; however the amount of alkynyl carbon adjacent to the TIPS end-group was quantified via ^{13}C NMR peak integration to determine the product ratio in the crude mixture. Furthermore, the formation of haloalkyne **58** can be explained by an *in situ* halogen-metal exchange of the copper acetylide with I_2.[35-36] To the best of my knowledge, this is the first time that haloalkyne **58** has been produced under the Stille coupling reaction conditions outlined in Scheme 2.4. The yield of hexayne **47** was calculated to be only 2% based on mass, primarily resulting from the instability of intermediate diiodotetrayne (**17**). Li had previously reported a 47% isolated yield of hexayne **47** (Table 2.2).[14,19] This moderate yield may be attributed to the excess organostannane and the similar mol % of co-catalyts that were used.



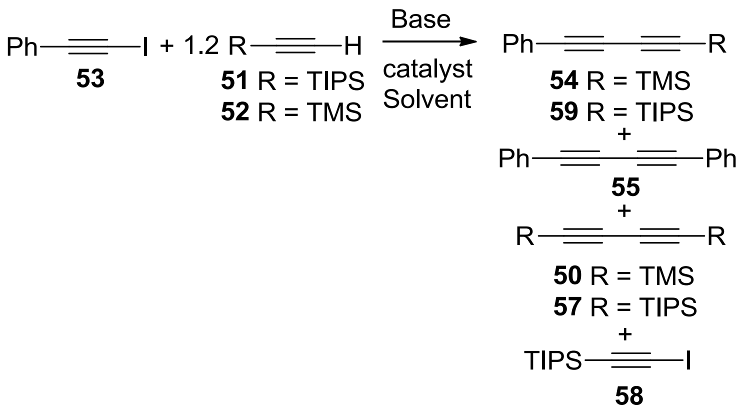
Scheme 2.10 Synthesis of hexayne **47**. The number in parentheses is the product ratio in the crude mixture determined by ^{13}C NMR spectroscopy.

2.3 Cadiot-Chodkiewicz Cross-Coupling Reaction

The potential toxicity of the tin reagents and byproducts in the Stille reaction has served as motivation for exploring alternative coupling conditions. The cross-coupling of two different terminal alkynes has been reported, although it is common to react one of the alkynes in great excess to promote the desired reaction.[37-42] Therefore, the Cadiot-Chodkiewicz reaction was studied as another route toward moderate length oligoynes. This method typically couples a 1-bromoalkyne and a terminal alkyne in the presence of a copper salt and an amine base to form unsymmetrical 1,3-diynes;[35,43-46] however copper and palladium co-catalyzed variations have been reported.[47-48] Iodoalkynes have also been successfully cross-coupled by this route with[49-51] and without[17,52-53] the addition of a palladium co-catalyst. More recently, reaction condition modifications have allowed for diiodopolyynes[20-22, 24-25] and dibromopolyynes[54] to be used. Additionally, the Cadiot-Chodkiewicz reaction has been extended to the synthesis of rotaxanes containing a polyyne chain.[55-57] One drawback to the Cadiot-Chodkiewicz conditions is the production of large amounts of homocoupled byproducts,[46] which can result from oxygen in the system,[58] halogen-metal exchange,[35,59] and poor selectivity between electronically similar reacting alkynes.[45] Typically the unwanted Glaser-type reaction results when the copper acetylides formed *in situ* subsequently undergo an oxidative homocoupling.[35,45] Therefore, this reaction can be controlled by addition of the reducing agent hydroxylamine hydrochloride ($NH_2OH•HCl$), which keeps the copper salt in its +1 oxidation state.[45] Furthermore, homocoupling of the haloalkyne is limited by adding a slight excess of the terminal alkyne to the reaction (usually 1.2 equivalents).[45]

2.3.1 Cadiot-Chodkiewicz Model Reactions

Model studies were initially conducted and thoroughly investigated to gain insight about the reactivity of iodoalkynes. Researchers originally thought that because iodoalkynes are strongly oxidizing towards copper(I) ions, they would favor homocoupling.[35,46] Although there is significantly more literature precedent for the coupling of bromoalkynes using Cadiot-Chodkiewicz conditions, it is unclear if bromoalkynes actually favor cross-coupling, or are preferred simply because these compounds are less costly to access. The studies described here focused on the reactions of iodophenylacetylene (**53**) and TIPS-iodoacetylene (**58**). The homocoupled byproducts of these haloalkynes are stable at room temperature and can be detected by NMR spectroscopy, contrary to diiodopolyynes, which are more apt to polymerize. Therefore, all three possible products—the cross-coupled diyne and both homocoupled diynes—can be identified and quantified. All reactions were conducted in the dark and under an argon atmosphere to prevent unwanted side reactions and decomposition of the iodoalkynes. Isolation of the cross-coupled diyne was not attempted, but rather the product ratio in the crude mixture was determined by NMR spectroscopy. Peak integration proved challenging when TIPS-acetylene (**51**) was used as the TIPS peaks overlap with each other in the ^{1}H NMR. As a result, the amount of alkynyl carbon adjacent to the TIPS end-group was quantified via ^{13}C NMR peak integration to determine the product ratio. It is assumed that the error associated with integrating carbon signal intensities remains consistent for all alkynyl carbons. These ratios were used to calculate the mass percent of each compound in the crude mixture. ^{13}C NMR integration was also used with TMS alkynes to keep the method for ratio assessment consistent in all model reactions. If the crude mixtures were comprised of any homocoupled products, the ratio for that compound was divided in half to account for the two identical functional groups present. To investigate the Cadiot-Chodkiewicz coupling of iodophenylacetylene (**53**) with silyl-protected alkynes, numerous bases, catalysts, temperatures, solvents and reaction times were explored (Scheme 2.11). The results are outlined in Table 2.4.



Scheme 2.11 Model Cadiot-Chodkiewicz coupling reactions.

Table 2.4 Model Cadiot-Chodkiewicz coupling reaction conditions.

Entry	**Terminal Alkyne**	**Catalyst (mol %)**	**Base/ Solvent**	**Reaction Time/ Temp. (°C)**	**Crude Ratio[c] 53: 54: 55: 50 or 53: 51: 59: 55: 57: 58**	**Crude Yield (%)**	**NMR Yield of 54 or 59 (%)**
1	**52**	CuI (10)	i-Pr$_2$NH/ THF	24 h/ 25	2: 1: 0.55: 0	47	13
3	**52**	Cu(PPh$_3$)$_2$NO$_3$ (10)	i-Pr$_2$NH/ THF	24 h/ 25	1.8: 1: 0.52: 0.09	38	11
3	**51**	CuI (10)	i-Pr$_2$NH/ THF	24 h/ 25	1.8: 0: 1: 1.3: 0: 13.5	79	4
4	**52**	CuI (5) PdCl$_2$(PPh$_3$)$_2$ (1)	i-Pr$_2$NH/ THF	3 h/ 25	0: 1: 0.25: 0.18	68	48
5	**52**	CuI (5) Pd(PPh$_3$)$_4$ (1)	i-Pr$_2$NH/ THF	3 h/ 25	0: 1: 0.33: 0.34	72	43
6	**52**	CuI (10)	Et$_3$N/ THF	24 h/ 25	1: 0: 0: 0	-	0
7	**51**[a]	CuI (5)	30% n-BuNH$_2$	30 min/ 0	0: 0: 1: 0.85: 1.2: 0	69	22
8	**51**	CuI (5)	K$_2$CO$_3$/ MeOH	90 min/ 0	1: 0.1: 0: 0: 0: 0.13	-	0
9	**51**[b]	CuI (5)	Pyrrolidine	30 min/ 0	0: 0: 1: 0: 0.92: 0	98	45

Conditions: Mole ratio of iodoalkyne to terminal alkyne is 1:1.2. All reactions were stirred under an argon atmosphere in the dark. [a] A few crystals of NH$_2$OH•HCl were added to the reaction mixture. [b] Haloalkyne washed with aqueous Na$_2$S$_2$O$_3$ immediately prior to use. [c] Determined by ^{13}C NMR.

A variety of copper catalyts were first studied in the model Cadiot-Chodkiewicz cross-coupling reactions. The coupling of iodophenylacetylene (**53**) and TMS-acetylene (**52**) with 10 mol% CuI, *i*-Pr_2NH (diisopropylamine), and THF resulted in a large amount of unreacted iodoalkyne **53** in the crude mixture after stirring for 24 h (entry 1).Terminal alkyne **52** was not detected by NMR spectroscopy because it was removed *in vacuo* after work-up. Despite additional modifications that involved stirring the reagents for 1 week at room temperature, adding iodophenylacetylene (**53**) slowly to the reaction mixture, or increasing the CuI catalyst loading to 1 equivalent, low overall conversion of the haloalkyne still resulted in all systems. After stirring for 1 week, the amount of unreacted iodoalkyne **53** decreased by 4-fold in comparison to entry 1; however the product ratio (of diynes **54** and **55**) and crude yield is comparable to entry 1, suggesting decomposition of alkyne **53** under these conditions over time. Conversely, when analogous bromophenylacetylene (**61**) was coupled to TMS-acetylene (**52**) using the conditions shown in entry 1, only 7% of unsymmetrical diyne **54** was obtained, indicating that the formation of diyne **55** in entry 1 was produced from the decomposition of iodoalkyne **53** and subsequent CuI/ I_2 mediated homocoupling *in situ*.[60-63] An advantage of using bromoalkyne **61** instead of iodoalkyne **53** is that the former haloalkyne **61** appears to be more selective; however the low product yield, along with the formation of a black insoluble solid, suggests considerable instability for the analogous bromoalkynes. These same conditions were not as effective when applied to the coupling of bromoalkyne **61** and TIPS-acetylene (**51**), implying that each Cadiot-Chodkiewicz experiment must be individually optimized.

The Cadiot-Chodkiewicz cross-coupling was further explored using several bulky copper(I) catalysts that were obtained from Dr. Dhandapani Venkataraman (University of Massachusetts, Amherst). These catalysts proved to be successful in the cross-coupling of terminal alkynes with aryl or vinyl halides.[64] Furthermore, these compounds are stable to air and moisture, which consequently may prevent homocoupled byproducts formed from the Glaser-type reaction. However, when $Cu(PPh_3)_2NO_3$ was incorporated into the model Cadiot-Chodkiewicz system with *i*-Pr_2NH and THF, a significant amount of haloalkyne **53** remained and both homocoupled diynes were observed in the crude mixture, along with the heterocoupled product (entry 2). Comparable results were obtained with $Cu(phen)(PPh_3)Br$, even after varying the catalyst concentration or including a palladium co-catalyst. Furthermore, the coupling of iodoalkyne **53** and TIPS-acetylene (**51**) using the bulky copper catalysts did not promote cross-coupling selectivity. The steric bulk of these copper catalysts were initially believed to prevent complete conversion of iodoalkyne **53**, but a similar yield of cross-coupled diyne **54** was calculated when CuI was used as the catalyst (entry 1).

Iodoalkyne **53** was also coupled to TIPS-acetylene (**51**) with CuI and *i*-Pr_2NH following the procedure shown in entry 3. An advantage of using this terminal acetylene versus trimethylsilyl analog **52** is that the former has a much higher boiling point and consequently, will not be removed *in vacuo.* Therefore, terminal alkyne **51** may help provide further mechanistic insight regarding the reactivity of the starting alkynes. In comparison to the coupling with TMS-acetylene (**52**) (entry 1), the resulting crude mixture in entry 3 contained haloalkyne **58**, the product formed presumably from an iodine-copper exchange.[35-36] Further investigation showed that stirring I_2, *i*-Pr_2NH, 10 mol% CuI, and TIPS-acetylene (**51**) in THF for 1 week affords haloalkyne **58** in 92% yield. In both entries 1 and 3, homocoupling of the terminal alkyne was averted. Employing freshly purified CuI or washing haloalkyne **53** with aqueous $Na_2S_2O_3$ immediately prior to use did not prevent the formation of iodoalkyne **58**; however diphenylbutadiyne (**55**) was completely avoided when a sodium thiosulfate rinse was performed. Although homocoupling of the reactants can be controlled, the large ratio of haloalkyne **58** in the crude mixture was discouraging.

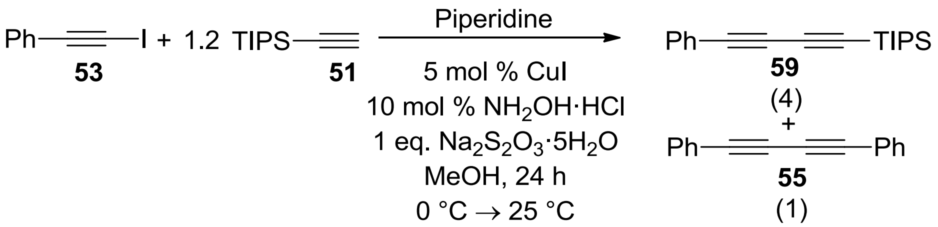
A palladium co-catalyst was added to the reaction mixture to increase product selectivity. The cross-coupling of iodophenylacetylene (**53**) and TMS-acetylene (**52**) was attempted using a CuI and $PdCl_2(PPh_3)_2$ co-catalytic system, following a procedure reported by Wityak and Chan in which diyne **54** is obtained in 91% yield.[49] Similar modified Cadiot-Chodkiewicz conditions were also described by Hwang and co-workers when coupling a bromoalkyne to TIPS-acetylene (**51**),[47] and by Ding and co-workers when coupling a silyl iodoalkyne to propargyl alcohol[50] or 1-hexyne,[51] corroborating the potential benefit of a palladium co-catalyst in this system. Nevertheless, addition of $PdCl_2(PPh_3)_2$ to the model reaction shown in Scheme 2.11 led to statistical product ratios (entry 4), even after altering the temperature and catalyst ratio. In addition, coupling under a hydrogen atmosphere did not improve the product ratio. $Pd(PPh_3)_4$ was also used (entry 5), but once again statistical yields of diynes **54**, **55**, and **50** resulted. Since $Pd(PPh_3)_4$ easily oxidizes in air,[65] it was not further pursued. Cross-coupling TIPS-iodoacetylene (**58**) and phenylacetylene (**60**), as well as iodophenylacetylene (**53**) and TIPS-acetylene (**51**), also led to statistical product ratios of unsymmetrical diyne **59** and both homocoupled diynes **55** and **57** when $PdCl_2(PPh_3)_2$ was added to the reaction mixture. Therefore, addition of a palladium co-catalyst did not appear to promote cross-coupling selectivity in this model system, and so focus was shifted to trials in which different bases were explored.

Cross-coupling with *i*-Pr_2NH consistently yielded a mixture of products. Additionally, reactant **53** was recovered in many trials, and therefore model reactions with *i*-Pr_2NH were no longer pursued. Substituting *i*-Pr_2NH, a secondary amine base, with Et_3N (triethylamine), a tertiary amine base, only afforded iodoalkyne **53** (entry 6). This outcome could be attributed to the steric bulk of Et_3N since this base has a similar pKa value as *i*-Pr_2NH. Furthermore, Alami and Ferri reported that using Cadiot-Chodkiewicz conditions, Et_3N typically gave lower yields.[52]

Unsymmetrical diynes can be obtained using Et_3N when cross-coupling two different terminal alkynes, although an excess of one of the terminal alkyne substrates is required.[39] Marino and Nguyen reported the coupling of silyl-protected terminal acetylenes with various bromoalkynes in high yields using 30% aqueous *n*-$BuNH_2$ (n-butylamine),[44] and so this base was applied to the cross-coupling of iodophenylacetylene (**53**) and TIPS-acetylene (**51)** (entry 7). Hydrolysis of the TMS moiety was described with this method,[44] thus alkyne **51** was used. Entry 7 shows that although there is no selectivity between the cross-coupled product and homocoupled byproducts, the reaction was completed in only 30 minutes. Under these conditions, catalysts CuI and CuCl gave similar results. Furthermore, when an inorganic base (K_2CO_3) with a comparable pKa value to the amine bases presented in Table 2.4 was employed (entry 8), no cross-coupling occurred. Instead, the crude mixture was composed of TIPS-iodoalkyne (**58**) and reacting alkynes **51** and **53**. This result is consistent with the hypothesis that formation of a copper-amine complex is needed to activate the deprotonation of the terminal alkynes.[35] Similarly, using inorganic bases for the oxidative dimerization of phenylacetylene **60** proved ineffective in multiple systems.[39,62,66] Changing the solvent from MeOH (entry 8) to DMF produced cross-coupled product, although the amount of heterocoupling was trivial compared to the ratio of terminal alkyne **51**, iodophenylacetylene (**53**), and TIPS-iodoacetylene (**58**) obtained in the crude mixture. Even though Wang and co-workers have described the successful cross-coupling of various terminal alkynes and 1-bromoalkynes with K_2CO_3, temperatures up to 100 °C were required.[67] These model reactions have demonstrated the importance of selecting the proper base to favor cross-coupling.

The amine base used appears to significantly affect the efficiency of the Cadiot-Chodkiewicz reaction. Alami and Ferri reported the formation of unsymmetrical diynes after 30 minutes with 10 mol% CuI in neat pyrrolidine. Specifically, iodophenylacetylene (**53**) was cross-coupled in high yields to terminal alkynes capped with an alcohol moiety.[52] Nevertheless, the coupling of iodoalkyne **53** and TIPS-acetylene (**51**) with CuI in pyrrolidine gave cross-coupled diyne **59** as well as homocoupled diynes **55** and **57**. Reducing the reaction temperature from 25 °C to 0 °C decreased homocoupling of the haloalkyne by half, while running the reaction at -25 °C yielded terminal alkyne **51**, TIPS-protected diyne **57**, TIPS-iodoacetylene (**58**), and cross-coupled diyne **59**. Formation of homocoupled diyne **55** was not observed, suggesting stabilization of the copper acetylide formed at low temperatures *in situ*.[46] Incorporating solvents such as DMF or THF, or including the reducing agent NH_2OH•HCl, did not increase product ratio, but rather yielded an undesirable mixture of compounds. When Cu(phen)(PPh_3)Br was used as the catalyst with pyrrolidine, mostly haloalkyne **53** was recovered, indicating that the rate of the coupling reaction is affected by the steric bulk of the copper catalyst in this system. Only when iodoalkyne **53** was washed with $Na_2S_2O_3$ immediately prior to use and the catalyst loading was reduced to 5 mol % CuI (entry 9) was the homocoupling of haloalkyne **53** avoided. The products of this reaction were cross-coupled diyne **59** and TIPS-protected diyne **57** in a 1 to 0.92 ratio, respectively. Since unreacted or homocoupled diiodopolyynes will polymerize and eventually decompose to an amorphous carbon material, homocoupling of the haloalkyne in these model reactions is more desirable than homocoupling of the terminal alkyne. Nevertheless, determining conditions that show controlled selectivity is still a great feat. Therefore, the conditions outlined in entry 9 were applied to the cross-coupling of diiodobutadiyne (**9**) and TIPS-acetylene (**51**), but triisopropylsilyl-capped tetrayne **42** did not form.

As base seems to play a large role in determining cross-coupling selectivity, other conditions were explored for the model Cadiot-Chodkiewicz reaction. Sankararaman and co-workers reported the synthesis of a mixture of acetylenic macrocycles ranging from dimer to octamer using a copper mediated cross-coupling reaction with piperidine.[68] Therefore, a one-pot cross-coupling of iodophenylacetylene (**53**) and TIPS-protected terminal alkyne **51** was attempted using piperidine. A 2:1 product distribution ratio of TIPS-iodoacetylene (**58**) and cross-coupled diyne **59** was calculated, respectively, when reacted with either CuCl or CuI after 5 hours. Materialization of haloalkyne **58** in both experiments suggests the formation of I_2 *in situ* primarily from iodoalkyne **53** and not from the copper iodide. However, in a separate experiment, a mixture of TIPS-acetylene (**51**), CuI, and pyrrolidine was stirred for one day to afford terminal alkyne **51**, TIPS-protected diyne **57**, and TIPS-iodoacetylene (**58**). This result indicates that the catalyst could also act as an iodine source in particular systems. Dropwise addition of haloalkyne **53** did not increase cross-coupling selectivity, as the majority of the product mixture consisted of TIPS-acetylene (**51**) and TIPS-iodoacetylene (**58**). To control the formation of molecular iodine *in situ*, sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5H_2O$) was added as a second reducing agent, resulting in approximately a 4:1 ratio of unsymmetrical diyne **59** to homocoupled diyne **55**, respectively (Scheme 2.12). To date, this method demonstrates the highest product selectivity for these model Cadiot-Chodkiewicz reactions. Similar coupling conditions with CuI in neat piperidine were reported for the cross-coupling of terminal trialkylsilyl acetylenes to both ends of a diiododiyne linked by an alkyl tether (1,6-heptadiyne),[53] suggesting that piperidine may also be effective for the double cross-coupling of diiodobutadiyne (**9**). The cross-coupling of diiodopolyyne **9** and TIPS-acetylene (**51**) was attempted according to Scheme 2.12, but triisopropylsilyl-capped tetrayne **42** was not obtained. Diyne **57** was produced in highest yield, suggesting decomposition of diiodopolyyne **9** with these conditions.

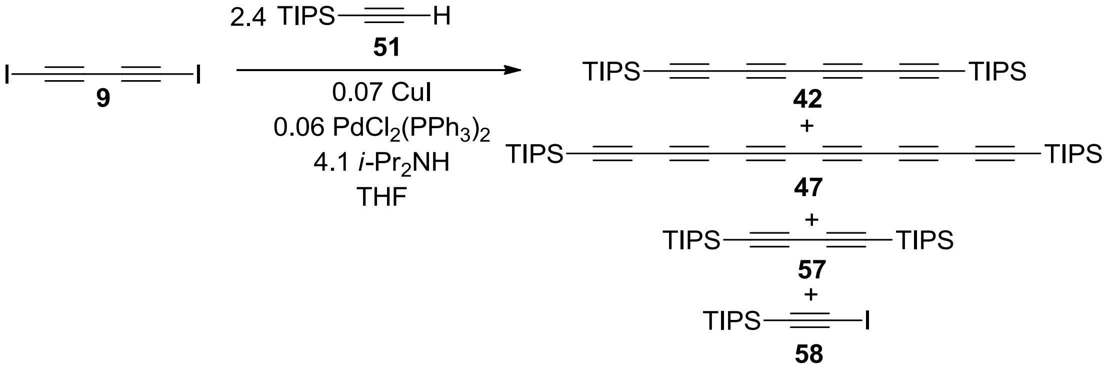


Scheme 2.12 Optimized model Cadiot-Chodkiewicz reaction. The number in parentheses is the product ratio in the crude mixture determined by ^{13}C NMR spectroscopy.

2.3.2 Cross-Coupling to Diiodobutadiyne

After altering many variables, including base, catalyst, temperature, solvent, and time, conditions for nearly complete selectivity for the unsymmetrical diyne **59** were found. Despite the high selectivity for forming product **59**, similar results were not obtained when applying these conditions to the cross-coupling of diiodopolyynes. Although diiododiyne **9** was washed with aqueous $Na_2S_2O_3$ immediately prior to use to remove any excess I_2 that may have formed *in situ*,[19] and the coupling reaction was performed in the dark at 0 °C and under an argon atmosphere, homocoupling, as well as iodination of the terminal alkyne, were uncontrollable side reactions. Tetrayne **42** was not obtained probably due to the instability of diiododiyne **9**. Alternatively, byproduct formation also suggests poor selectivity between the reacting alkynes. To account for coupling to each end of the diiodopolyyne, 2.4 equivalents of the terminal alkyne were employed.

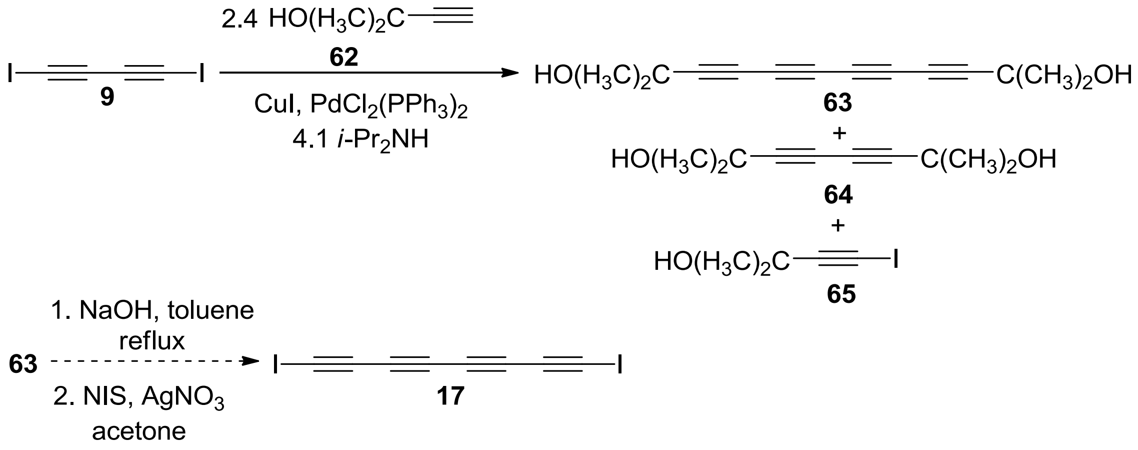
Since palladium co-catalysts have proven effective in some iodoalkyne cross-coupling reactions,[49-51] and more recently with diiodoacetylene,[20] this route was revisited for the symmetric double cross-coupling of diiodobutadiyne (**9**). While addition of palladium compounds to the model Cadiot-Chodkiewicz reaction with iodophenylacetylene (**53**) led to statistical product yields (Table 2.4), the addition of $PdCl_2(PPh_3)_2$ to the coupling of diiodopolyyne **9** and terminal alkyne **51** resulted in tetrayne **42** formation (Scheme 2.13). It is likely that the palladium co-catalyst inserts into the carbon-iodine bond at a faster rate than if the copper catalyst was used alone, thus activating transmetalation of the copper acetylide to the palladium compound. Reductive elimination to form the tetrayne **42** would consequently occur at a faster rate, reducing the amount of diiodopolyyne decomposition and ultimately promoting cross-coupling.[45]



Scheme 2.13 Cadiot-Chodkiewicz cross-coupling of diiodobutadiyne (**9**).[20]

Preparation of tetrayne **42** was attempted according to Scheme 2.13. As with the previously conducted model reactions, the alkynyl carbons adjacent to the end-groups were quantified by ^{13}C NMR peak integration to deduce the product ratios and ultimately, to calculate the product distribution in the respective crude mixtures. Diiododiyne **9** was washed with aqueous $Na_2S_2O_3$ immediately prior to use, and the reaction was always stirred in the dark for all experiments; however cross-coupled product was only observed when *i*-Pr_2NH was employed. Formation of an insoluble black solid at the bottom of the reaction flask suggested that the other amine bases used initiated decomposition of diiodobutadiyne (**9**). Once the optimized catalyst ratio was determined, the order of addition was explored. Adding both alkynes **9** and **51** dropwise (5 drops/ min) to the catalyst mixture at 0 °C prevented complete reaction of the terminal alkyne, and the product distribution of terminal alkyne **51**, tetrayne **42**, and diyne **57** was obtained in a 1.6: 1: 4 ratio, respectively. Dropwise addition of the haloalkyne has been reported to lead to an increase in cross-coupling selectivity,[46,68-70] but when diiodopolyyne **9** was added slowly to the reaction mixture, tetrayne **42**, hexayne **47**, diyne **57**, and TIPS-iodoacetylene (**58**), were afforded in a 1: 0.2: 2.6: 0.2 ratio, respectively. The formation of iodoalkyne **58** and hexayne **47** indicated *in situ* halogen-metal exchange, which has previously been described for the cross-coupling of diiodoacetylene.[21] Addition of diiodopolyyne **9** and terminal alkyne **51** to the catalytic mixture independently via two cannulas was also tried; however controlling the drip rate became too arduous. Including reducing agents $NH_2OH•HCl$ and $NH_2OH•HCl/ Na_2S_2O_3•5H_2O$ in the catalyst mixture in separate experiments was also attempted. In both cases, tetrayne **42**, diyne **57**, and iodoalkyne **58** were all detected in the crude mixture, with diyne **57** formed in the highest ratio. Overall, despite variations in the crude product ratios when coupling diiodobutadiyne (**9**) and terminal alkyne **51**, the calculated NMR yield of tetrayne **42** was only between 11-18% for all systems.

If the electronic properties of the haloalkyne and terminal alkyne are too similar, poor selectivity results, and homocoupling may never be effectively prevented.[45] Therefore, terminal alkyne **62** was explored as suggested by Dr. Jonathan Rudick, as this compound has been shown to undergo successful cross-couplings.[70-71] Furthermore, deprotection and subsequent iodination of this alcohol end-group[72-73] can be achieved to give diiodooctatetrayne (**17**) (Scheme 2.14). The palladium/ copper catalyst ratio and addition rate of diiodobutadiyne (**9**) in the Cadiot-Chodkiewicz coupling with terminal alkyne **62** was studied (Table 2.5).



Scheme 2.14 Alternative Cadiot-Chodkiewicz cross-coupling of diiodobutadiyne (**9**).

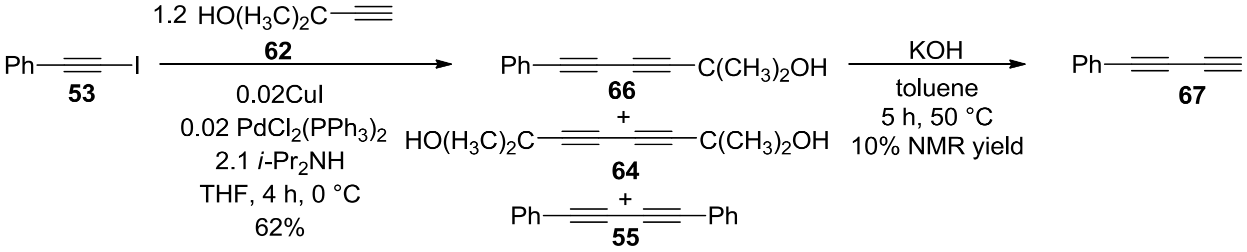
Table 2.5 Cadiot-Chodkiewicz coupling reaction conditions using terminal alkyne **62**.

Entry	**Solvent**	**Mol % Catalyst Loading[a] CuI: $PdCl_2(PPh_3)_2$**	**Drip Rate (drops/ min)**	**Addition of NH_2OH•HCl? [d]**	**Crude Ratio[e] 9: 63: 64: 65**	**Crude Yield (%)**	**NMR Yield of 63 (%)**
10	MeOH/ H_2O (2:1)	10:0	5[c]	Y	1: 0: 0: 0.11	-	0
11	MeOH/ H_2O (2:1)	7:6	5	Y	0: 1: 2.7: 0	122	40
12	MeOH/ H_2O (2:1)	7:6	20	Y	0: 1: 2.6: 0	49	16
13	MeOH/ H_2O (2:1)	7:6[b]	5	N	0: 1: 1.5: 0 + unidentified products	30	?
14	MeOH/ H_2O (2:1)	7:20	5	Y	0: 1: 4.1: 0	75	18
15	MeOH/ H_2O (2:1)	10:6	5	Y	0: 0: 0: 1	-	0
16	THF	7:6	5	Y	0: 1: 1.6: 0	83	37

Conditions: Mole ratio of iodoalkyne to terminal alkyne is 1:2.4. All reactions were stirred under an argon atmosphere in the dark. Diiodobutadiyne **9** was washed with aqueous $Na_2S_2O_3$ immediately prior to use. Diiodoalkyne **9** was then added dropwise to the reaction mixture at 0 °C unless otherwise stated. The solution was allowed to stir and warm to room temperature overnight. [a] Mole ratio of catalysts to diiodobutadiyne. [b] CuI was recently purified. [c] Solution stirred for only 1 h at room temperature after diiodopolyyne addition. [d] Twice the mol % of CuI. [e] Determined by ^{13}C NMR spectroscopy.

A palladium co-catalyst is necessary for the efficient coupling of diiodopolyyne **9** and to limit iodination of terminal alkyne **62** (entry 10). Hirsch and co-workers also used a palladium co-catalyst for the successful cross-coupling of diiodoacetylene.[20] Terminal alkyne **62** was not detected by NMR spectroscopy because it was removed *in vacuo* after work-up (Table 2.5). The rate of addition for the diiodoalkyne to the reaction mixture was explored in entries 11 and 12. In both cases, the ratio of diyne **64** to tetrayne **63** was approximately 2.5:1.The crude yield in entry 12, however, was much lower, suggesting decomposition of the diiodopolyyne when added too quickly to the mixture. Addition of the reducing agent NH_2OH•HCl to the reaction mixture increased product selectivity, but the same affect was not observed when recently purified CuI was used (entry 13). Catalyst loading was further investigated in entries 14 and 15. Nearly three times the mole percent of palladium to copper was used in entry 14, and the crude ratio of diyne **64** to tetrayne **63** increased about 2 fold when compared to the other entries in Table 2.5. Alternatively, when nearly twice the mole percent of copper was added, only iodoalkyne **65** formed (entry 15), consistent with entry 10. Once the optimized catalyst ratio of copper to palladium was determined (7:6 mol %, respectively), different solvents were explored. The ratio of diyne **64** to tetrayne **63** decreased noticeably when THF was used (entry 16) compared to MeOH/ H_2O (entry 11). Purification was also easier with THF, and therefore, the conditions in entry 16 were considered to be the most promising. The NMR yield of tetrayne **63** was determined to be 37%. Although isolated tetrayne yields obtained under Stille coupling conditions (Table 2.2) were higher, if iodination of tetrayne **63** is achieved as shown in Scheme 2.14, this method may be applied to avoid the use of tin reagents.

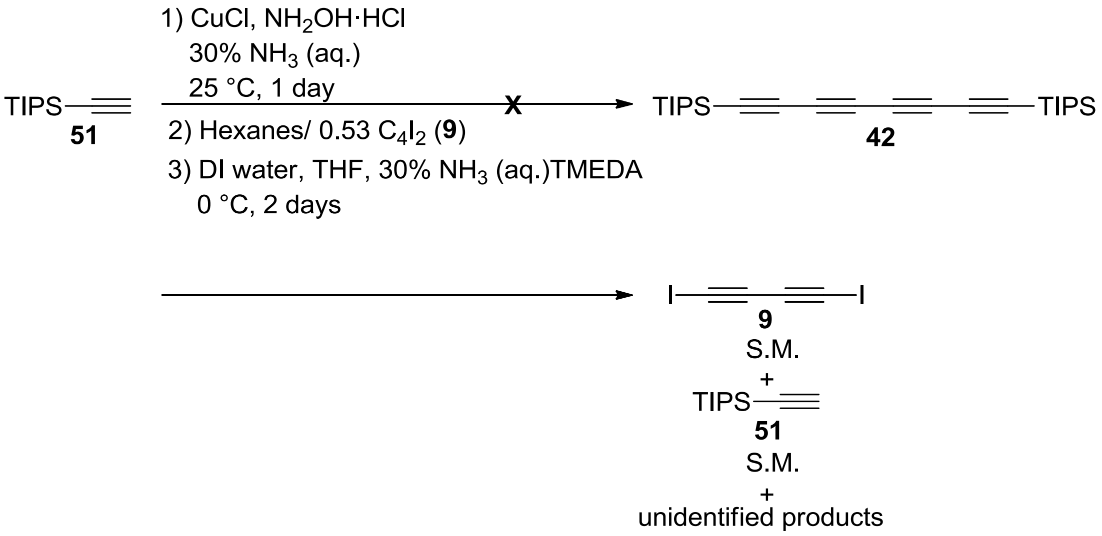
Typically at 0 °C, deprotonation of the 2-hydroxypropyl group predominates,[74] and therefore, elevated temperatures are required for cleavage of this alcohol protecting group.[70-71,75] However, high temperatures would likely lead to decomposition of tetrayne **63**, as a melting point of 150-152 °C has been reported.[76] Thus, removal of the alcohol end-group was first attempted with asymmetric diyne **66** (Scheme 2.15) since diyne **67** has been previously isolated and characterized.[70,75] Terminal alkynes are generally reactive and unstable neat, particularly as the number of conjugated carbon-carbon triple bonds increases,[75,77] and great care was taken when handling terminal diyne **67** in the solid-state.



Scheme 2.15 Overview of the synthesis of diyne **67**.

Diyne **66** was synthesized in moderate yield as shown in Scheme 2.15. A similar cross-coupling of iodophenylacetylene (**53**) and 3-butyn-l-ol [$HC{\equiv}C(CH_2)_2OH$] has been reported in 95% yield with CuI and pyrrolidine,[52] but application of these conditions to the coupling of iodoalkyne **53** and terminal alkyne **62** resulted in isolation of cross-coupled diyne **66** in only 41%. Likewise, Wityak and Chan have described the cross-coupling of iodophenylacetylene (**53**) and propargyl alcohol using CuI and $PdCl_2(PPh_3)_2$.[49] When these conditions were applied to the coupling of iodoalkyne **53** and terminal alkyne **62** (Scheme 2.15), the isolated yield of diyne **66** was increased to 62%. A higher product yield was reported for asymmetric diyne **66** by Wityak and Chan when phenylacetylene (**60**) was coupled to the iodinated propargyl alcohol compound.[49] Even though cross-coupling with the iodinated propargyl alcohol analog might lead to better product selectivity and yield, coupling with this haloalkyne was not attempted in the model experiments because it would not be able to be used for improved yield in the coupling of terminal alkyne **62** with the diiodopolyynes. Subjecting tetrayne **63** to the reflux conditions required for deprotection will probably lead to rapid decomposition. Consequently, deprotection of diyne **66** was studied using 3.1 equivalents of KOH in toluene at 50 °C. Excess KOH was added to compensate for the mild temperature. As expected, mostly diyne **66** was recovered along with deprotected terminal diyne **67** in low yield (Scheme 2.15). It was then hypothesized that addition of $AgNO_3$ and potassium tert-butoxide (t-$BuO^- K^+$) in THF might allow for deprotection of diyne **66** without the use of heat. Silver was chosen, as opposed to a copper salt, to prevent any homocoupling.[78-79] Within 5 minutes the mixture turned black, and an insoluble black solid resulted when the reaction was quenched with a few drops of water. Therefore, silver oxide (Ag_2O) may have formed from the reaction between the catalyst and base, although this solid was never characterized. From these observations, it was apparent that different conditions for synthesizing tetraynes must be employed. Diiodobutadiyne (**9**) was also coupled to propiolic acid using 10 mol % CuCl, $NH_2OH{\bullet}HCl$, and i-Pr_2NH in MeOH, but a black solid formed that could not be characterized by NMR spectroscopy. Although the synthesis of this dicarboxylic acid tetrayne has been reported, it was described as highly unstable and evidence for its formation was inconclusive.[76,80] The coupling of propiolic acid will be discussed further in Chapter 3.

Coupling of an isolated metal acetylide, such as copper[21-22,54,81] or gold[23-25] under Cadiot-Chodkiewicz conditions has been previously reported, and was explored with diiodobutadiyne (**9**) since conditions for complete selectivity of the cross-coupled tetrayne product were yet to be found. This route allows for the amount of metal acetylide to be determined quantitatively, similarly to the tin acetylide in Stille couplings, as opposed to assuming its formation *in situ*. Recently, Cataldo and co-workers have successfully cross-coupled diiodoacetylene with isolated Cu(I)-phenylacetylide[21] and Cu(I)-ethynylnaphthalide[22] to synthesize a mixture of diarylpolyynes of varying lengths. Therefore, the synthesis of tetrayne **42** was attempted, according to Scheme 2.16.

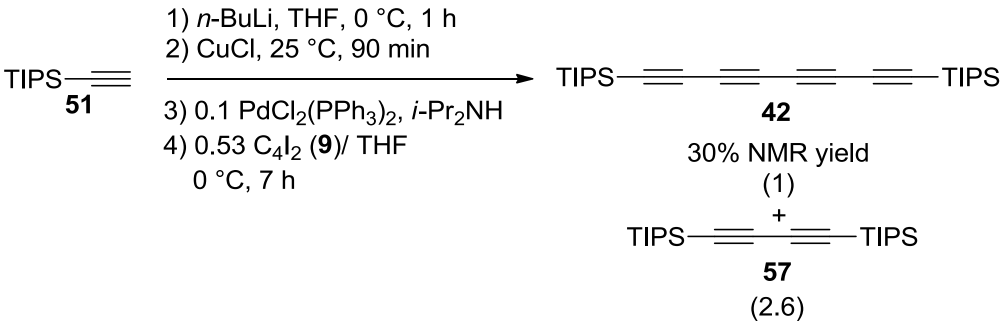


Scheme 2.16 Synthetic approach to tetrayne **42** via Cataldo's method.[21]

Starting alkyne reagents **51** and **9** were recovered, along with an unidentified product(s), indicating that these conditions were not conducive for TIPS copper acetylide formation. Isolation of this acetylide has not been reported in the literature. However, preparation of the TMS copper acetylide has been described,[82-83] but the isolated compound readily decomposes at -20 °C.[83] Stirring the mixture of CuCl, terminal alkyne **51**, NH_2OH•HCl, and aqueous ammonia over-night in the dark under an argon atmosphere resulted in formation of a brown film on the side of the reaction flask. This insoluble film may have been the decomposed copper acetylide, offering a possible explanation as to why both heterocoupling and homocoupling reactions did not occur with this method. To investigate the reproducibility of Cataldo's route, copper phenylacetylide was synthesized. Although a yellow precipitate formed, isolation of the acetylide in quantitative yield as reported by Cataldo and co-workers was not obtained.[21] Diiodobutadiyne

(**9**), phenyl-protected diyne **55**, and unidentified products were yielded, suggesting that the copper acetylide was prepared from phenylacetylene (**60**), unlike with TIPS-acetylene (**51**).

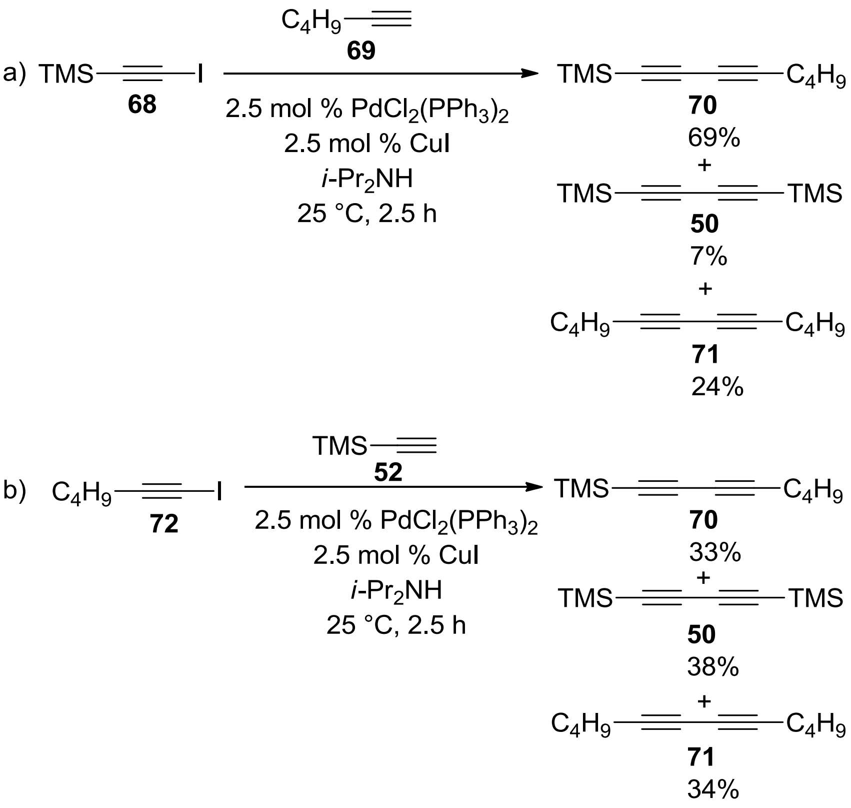
Due to the difficulty that was encountered when trying to carry out Cataldo's cross-coupling method, an alternative approach was pursued. Hirsch and co-workers have synthesized polyynes with up to 10 C≡C bonds in length by first forming a dendrimeric copper acetylide *in situ*, and then cross-coupling it with a diluted solution of bromoalkyne via slow addition.[8] Because isolation of the TIPS copper acetylide previously proved difficult, the synthesis of tetrayne **42** was attempted with this method. Unlike the cross-coupling of diiodobutadiyne (**9**) and TIPS-acetylene (**51**) described previously (Scheme 2.13), with this route, the TIPS copper acetylide is first formed *in situ* before addition of the diiodopolyyne. However, iodination of the terminal alkyne predominated to give haloalkyne **58**. Tetrayne **42** and diyne **57** were also obtained, indicating formation of TIPS copper acetylide *in situ*. This outcome parallels the previous experiment with diiodopolyyne **9** and TIPS-acetylene (**51**) when stirring CuI, *i*-Pr_2NH, and THF in one-pot (Table 2.4). These researchers have more recently described the cross-coupling of diiodoacetylene, using a copper and palladium co-catalytic system, to bridged terminal alkynes connected by an alkyl tether.[20] Therefore, $PdCl_2(PPh_3)_2$ was added to the reaction with diiodobutadiyne (**9**), as shown in Scheme 2.17. The ratio of each product in the crude mixture is shown in parentheses and is based on ^{13}C NMR peak integration.



Scheme 2.17 Synthetic approach to tetrayne **42** via Hirsch's method.[8] The number in parentheses is the product ratio in the crude mixture determined by ^{13}C NMR spectroscopy.

Incorporation of a palladium co-catalyst into the reaction mixture, along with dropwise addition of diiodobutadiyne (**9**) over 7 hours (5 drops/ min), gave polyynes **42** and **57** in a 1:2.6 ratio, respectively. The mass percent (30%) was calculated for cross-coupled tetrayne **42**, based on the product ratio in the crude mixture as determined from ^{13}C NMR peak integration. The possibility that homocoupling of terminal alkyne **51** occurred before diiododiyne **9** addition, and could therefore be limited, was investigated. Despite stirring CuCl and NH_2OH•HCl (2 equivalents) with terminal alkyne **51** for only fifteen minutes prior to diiodoalkyne addition, the same product ratio was determined, suggesting that the homocoupling reaction occurs at a quicker rate than the cross-coupling reaction. It appears that upon decomposition of the unreacted diiodopolyyne, I_2 is released into the mixture, which further promotes oxidative dimerization.[60-63] The instability of the diiodopolyyne appears to be a major limiting factor in achieving cross-coupling selectivity, despite attempts to keep the reaction mixture cold (0 °C) and in the dark. Currently, first forming the TIPS copper acetylide *in situ* and then coupling it to diiodobutadiyne (**9**) using a palladium/ copper co-catalytic system (Scheme 2.17) has given the highest calculated tetrayne **42** yield for all of the Cadiot-Chodkiewicz reactions attempted.

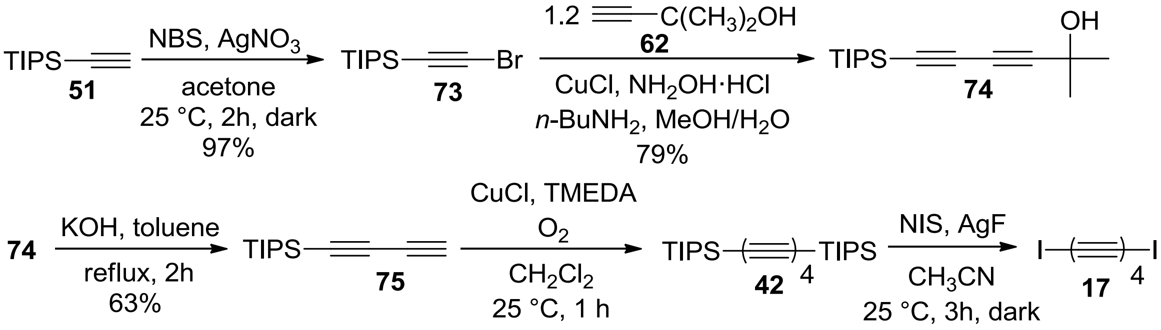
Homocoupling remains an inherent problem with Cadiot-Chodkiewicz couplings, and it is unclear from the results obtained whether this side reaction primarily stems from poor selectivity between the reacting alkynes or is due to the instability of the iodoalkyne.[46] To investigate the role the electronic properties of the reagents play on cross-coupling selectivity, TMS-iodoacetylene (**68**) and 1-hexyne (**69**), as well as 1-iodo-1-hexyne (**72**) and TMS-acetylene (**52**), were each coupled to synthesize asymmetric diyne **70**. Diyne **70** has been previously synthesized by Ding and Olesik, and therefore, the conditions reported by this group were used (Scheme 2.18).[51] Consistent with expectations, the ratio of heterocoupled and homocoupled diynes varied for each system. Isolation of diyne **70** was not attempted. Instead, the mass percent of each compound, calculated from the product ratio in the crude mixtures, is shown in Scheme 2.18.



Scheme 2.18 Overview of the synthesis of diyne **70**. The mass percent calculated from the product ratio in the crude mixtures is shown.[51]

The electronic properties of the reacting alkynes have an effect on product selectivity. The cross-coupling of iodinated silyl compound **68** with 1-hexyne (**69**) favored unsymmetrical diyne **70** (Scheme 2.18a), while the coupling of 1-iodo-1-hexyne (**72**) with TMS-acetylene (**52**) yielded statistical product ratios (Scheme 2.18b). However, iodoalkyne **72** quickly turns from a yellow oil to a reddish brown oil during the reaction, suggestive of molecular iodine formation. Therefore, it is still ambiguous whether homocoupling emanates from poor selectivity or haloalkyne decomposition. Likely, homocoupling is caused by both of these factors depending upon the reaction conditions employed. Even though cross-coupling with an iodinated silyl acetylene derivative might lead to better product selectivity and yield, coupling with this haloalkyne would be of no use for improved yield in the coupling of terminal alkynes with the diiodopolyynes under Cadiot-Chodkiewicz conditions. Therefore, the success of cross-coupling reactions with diiodopolyynes depends upon finding a terminal alkyne which when coupled, promotes product selectivity.

Diiodooctatetrayne (**17**) can also be prepared according to Scheme 2.19. In this route, the potentially toxic organostannane compounds used in the Stille coupling are avoided and the Hay homocoupling reaction is employed to extend the length of the polyyne chain. Bromination of TIPS-acetylene (**51**) and subsequent Cadiot-Chodkiewicz cross-coupling to terminal alkyne **62** gave diyne **74** in good yield. After deprotection of the alcohol end-group,[70-71] the resulting terminal diyne **75** was homocoupled using CuCl and TMEDA, following a procedure reported by Tykwinski and co-workers.[3] The desilylative bromination conditions that were described by Kim and co-workers served as the basis for the iodination of tetrayne **42** to give corresponding diiodopolyyne **17**.[84] This reaction was conducted at room temperature using excess equivalents of reagents (6 equivalents of NIS and 4 equivalents of AgF) to increase the rate of reaction while concurrently minimizing potential product decomposition. Additionally, acetonitrile was used, as this is the only organic solvent in which silver fluoride (AgF) is moderately soluble.[48,84] Diiodotetrayne (**17**) was formed in 36% over five steps.

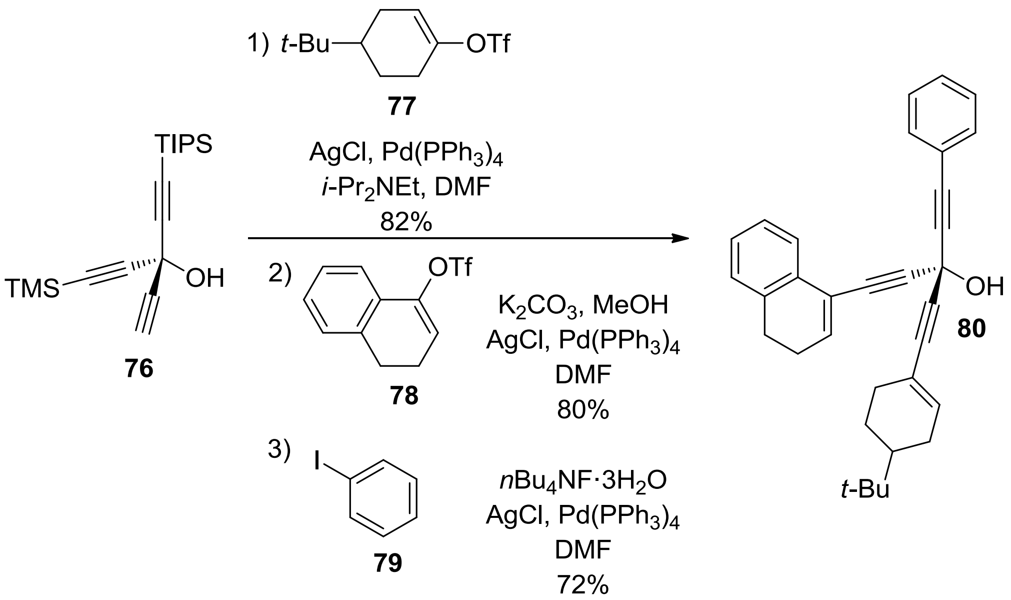


Scheme 2.19 Synthesis of tetrayne **17**.

Although this pathway is straightforward and scalable, it is a longer route than the iterative method developed by Li,[14,19] and the Cadiot-Chodkiewicz conditions employed are not conducive for TMS end-capped alkynes.[44] More importantly, potentially reactive terminal diyne **75** is isolated with this method; however this diyne has been described as a stable oil when stored at -10 °C for a few months.[71] Nonetheless, the decreased kinetic stability of higher terminal alkyne homologues probably limits this route to the synthesis of tetraynes when triisopropylsilyl is used as the end-cap group.[77] Therefore, the synthetic route shown in Scheme 2.19 is useful for the preparation of tetrayne **17** if one wants to avoid the use of organostannane compounds; however the method outlined in Scheme 2.4 allows for the successful preparation of a variety of oligoynes, ranging from four to seven consecutive carbon-carbon triple bonds.[19]

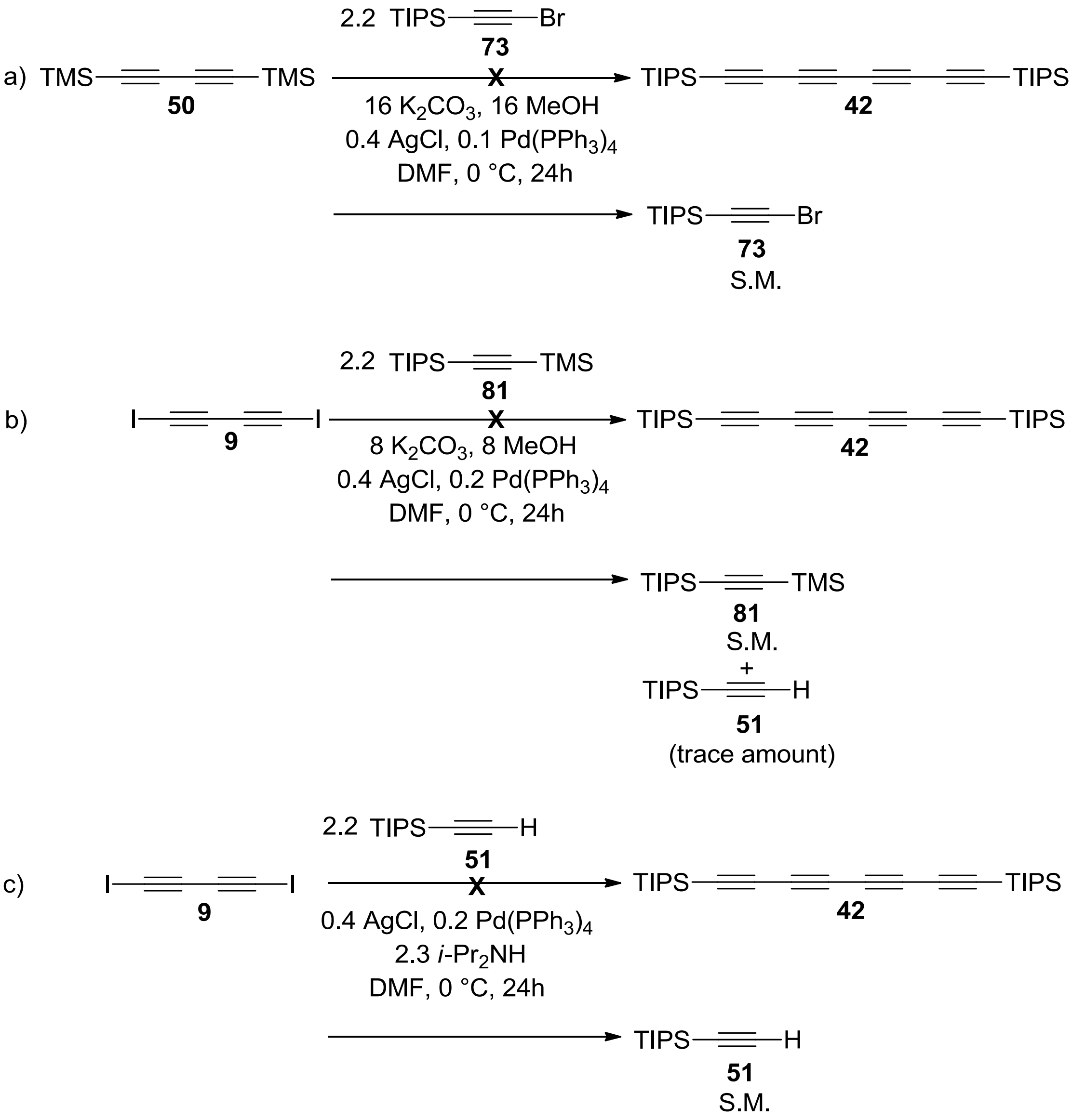
2.3.3 Silver(I) and Palladium(II) Co-catalyzed Conditions

Due to copper and palladium's tendency to produce homocoupled byproducts,[35,45] other routes towards moderate length polyynes were explored which also avoid the use of potentially toxic organostannane compounds. Pale and co-workers have developed mild sp-sp^2 cross-coupling reactions co-catalyzed by silver and palladium[85] which are thought to undergo a similar catalytic cycle as Sonogashira type reactions.[86] As outlined in Scheme 2.20, these conditions allowed for the preparation of enynes in high yields while also avoiding the formation of homocoupled byproducts,[87-91] a common side reaction that results when Cu(I) catalysts are used.[35,45] Some examples have been reported where a silver co-catalyst facilitates an acetylenic oxidative homocoupling reaction; however either copper is added to the system[92] or Ag_2O is used since it can serve as an activator as well as an oxidant.[93] Currently, there is no literature precedence for silver catalyzed alkyne-alkyne cross-coupling reactions.[78,94]



Scheme 2.20 A general route for the silver and palladium co-catalyzed coupling reactions of terminal alkynes, TMS alkynes, and TIPS alkynes.[89]

Trimethylsilyl acetylenes can be directly coupled to vinyl triflates or aryl iodides in the presence of K_2CO_3 and methanol and a catalytic amount of $Pd(PPh_3)_4$ and AgCl.[87-88] Accordingly, Fiandanese and co-workers have developed an alternative route toward unsymmetrical 1,3-diynes. Diynes with alkyl, aryl, and vinyl end groups were obtained through a selective and sequential substitution of bis(trimethylsilyl) diyne **50** using silver salts and $Pd(PPh_3)_4$.[95-96] Based on the procedure reported by Fiandanese and co-workers, a symmetric double cross-coupling reaction using AgCl and $Pd(PPh_3)_4$ was devised for diynes **50** and **9** (Scheme 2.21).[95] With this route toward tetrayne **42**, preparation and isolation of terminal polyyne intermediates is avoided.

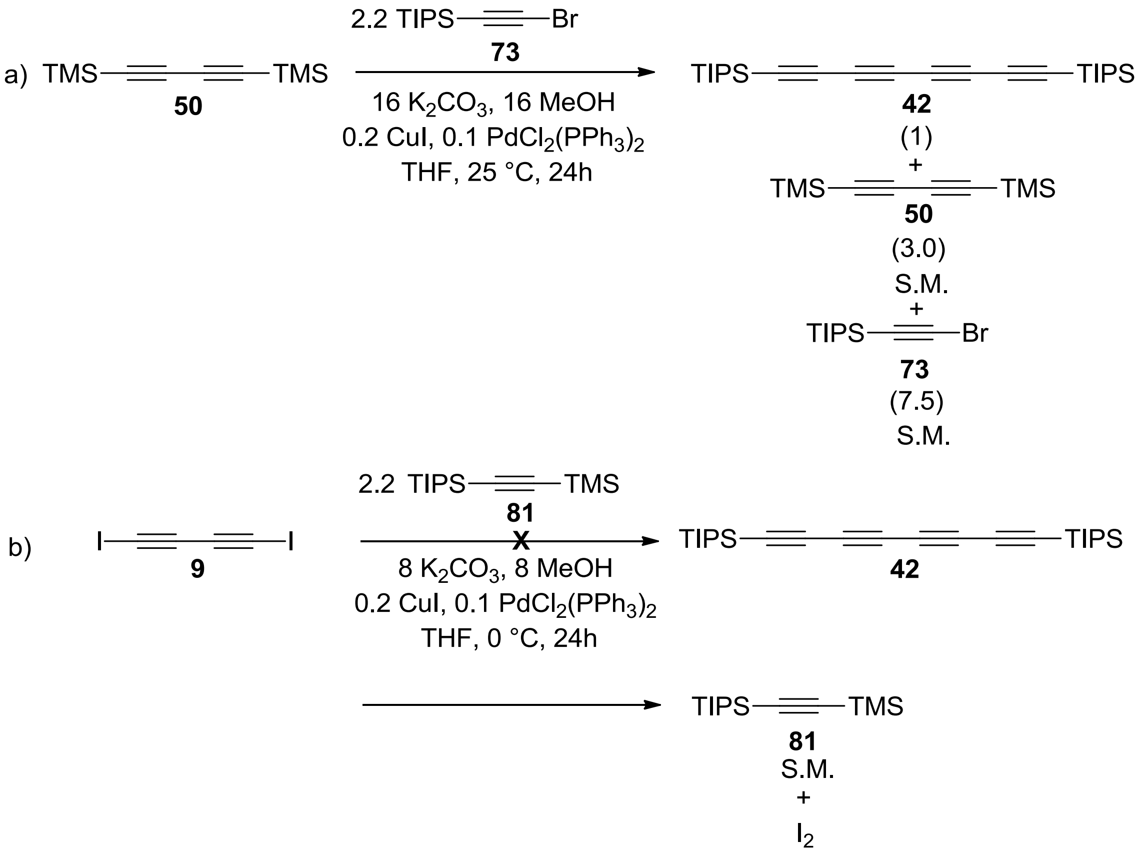


Scheme 2.21 Overview of the synthesis of tetrayne **42** via cross-coupling with silver chloride.

Alkyne-alkyne cross-coupling was not successful for either silyl-protected diyne **50** or diiodobutadiyne (**9**) when AgCl and $Pd(PPh_3)_4$ co-catalysts were employed. The recovery of only haloalkyne **73** (Scheme 2.21a) suggests that desilylation of diyne **50** occurs more rapidly than the cross-coupling between the reacting alkynes, therefore leading to formation of diacetylene gas. Also, tetrayne **42** was not obtained when coupling diiodopolyyne **9** and alkyne

81, implying decomposition of the diiododiyne. In contrast to the apparent ease of desilylation with diyne **50**, mostly silyl-protected alkyne **81** was recovered when cross-coupling to diyne **9** (Scheme 2.21b). Moreover, unlike the copper and palladium catalyzed reaction (Schemes 2.13 and 2.17), the coupling of diiodobutadiyne (**9**) to terminal alkyne **51** was ineffective using AgCl and $Pd(PPh_3)_4$ (Scheme 2.21c). Diyne **9** was added dropwise to the reaction mixture in the Cu/Pd catalyzed systems, but because only terminal alkyne **51** was recovered in the one-pot mixture in the silver catalyzed reaction (Scheme 2.21c), optimization of this coupling was not pursued any further.

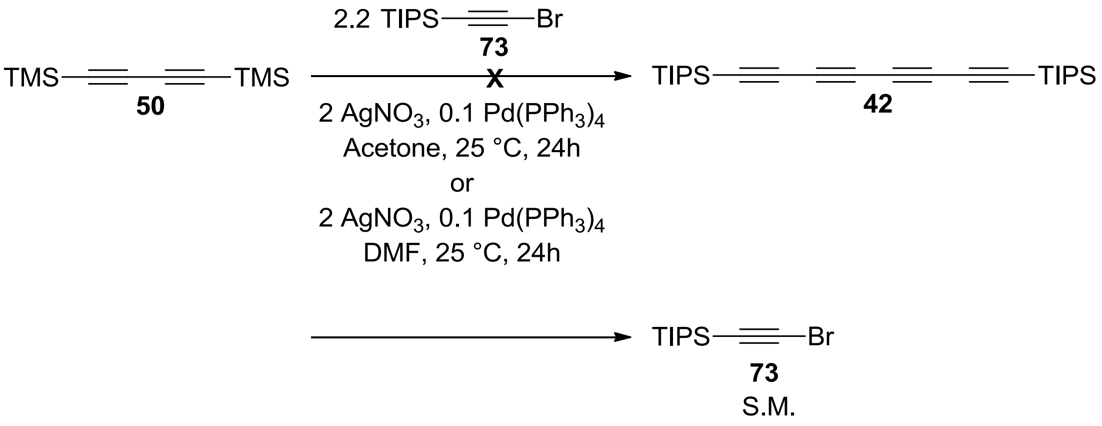
Similarly, efficient methods have been described for the *in situ* desilylation/ dimerization reaction of silyl-protected alkynes,[97-99] and therefore, the desilylation/ cross-coupling reaction with both diynes **50** and **9** were attempted (Scheme 2.22). The reaction conditions were modeled after the work of Hirsch and co-workers[20] as well as Marsden and Haley.[100] Both groups reported that the TMS capped oligoyne was first deprotected; however Hirsch and co-workers added diiodoacetylene to the resultant terminal alkyne solution to give the desired compound,[20] while Marsden and Haley added the terminal alkyne to the catalytic mixture which also contained a haloarene.[100] Because formation of diacetylene gas results from the deprotection of diyne **50**, alkynes **50** and **73** were added dropwise to the reaction mixture, and the desilylation / cross-coupling was performed in one pot (Scheme 2.22a). It has already been shown that terminal alkyne **51** can be successfully cross-coupled to diyne **9** (Schemes 2.13 and 2.17), and therefore the desilylation/ cross-coupling of alkynes **81** and **9** were also performed in one pot (Scheme 2.22b). The cross-coupling of alkynes **50** and **73** afforded tetrayne **42** in a low yield, as shown in Scheme 2.22. The ratio of each product in the crude mixture is shown in parentheses and was determined by ^{13}C NMR peak integration.



Scheme 2.22 Overview of the synthesis of tetrayne **42** via a one-pot desilylation/ cross-coupling. The number in parentheses is the product ratio in the crude mixture determined by ^{13}C NMR spectroscopy.

The desilylation of diyne **50** and subsequent cross-coupling with bromoalkyne **73** to give tetrayne **42** is successful with CuI and $Pd(PPh_3)_2Cl_2$ (Scheme 2.22a) but not with AgCl and $Pd(PPh_3)_4$ (Scheme 2.21a). The recovery of alkynes **50** and **73** in high ratios in the crude mixture indicates that the rate of desilylation is slow (Scheme 2.22a). Deprotection of diyne **50** is predicted to occur statistically; however the volatility of the fully deprotected diacetylene gas may limit the effectiveness of this route. Cross-coupling of alkynes **50** and **73** was also performed at 0 °C, but was unsuccessful. Therefore, a one-pot desilylation/ cross-coupling reaction with diyne **50** did not seem promising. Silyl-protected alkyne **81** was then prepared as there is only one TMS moiety to be cleaved, which should increase the desilylation rate of this compound relative to diyne **50**. Additionally, the resulting terminal alkyne is a relatively stable liquid. Cross-coupling of diiododiyne (**9**) and alkyne **81**, however, resulted in the recovery of silyl-protected alkyne **81** and the formation of I_2, indicated by the dark pink oil obtained, which is suggestive of diiodopolyyne decomposition (Scheme 2.22b).

Silver(I) acetylides have been prepared and isolated under mild conditions[79,86,101-102] and are relatively stable in the absence of light or heat.[103] Unlike the analogous copper acetylide, TIPS-protected alkynyl silver has been isolated.[103-104] Despite this literature report, cross-coupling to diiodobutadiyne (**9**) was not attempted as silver acetylides are shock explosive in the solid-state[79] and are insoluble in common organic solvents.[104-105] Silver acetylide preparation[101] and subsequent protiodesilylation[106-107] from 1-trimethylsilyl-1-alkynes is possible with silver nitrate. The synthesis of tetrayne **42** was attempted by the cross-coupling of silyl-protected diyne **50** and bromoalkyne **73** (Scheme 2.23) according to suggestions provided by Natalie St. Fleur of Dr. Andreas Mayr's group. Silver nitrate was used to facilitate the desilylation and cross-coupling reactions concurrently, but only haloalkyne **73** was recovered in both systems. This finding indicates that the desilylation reaction is occurring, while the cross-coupling remains ineffective, similar to the example in Scheme 2.21a with AgCl. In contrast, tetrayne **42** was obtained from the cross-coupling of alkynes **50** and **73** when a copper and palladium co-catalytic mixture was employed (Scheme 2.22a). Therefore, silver catalyts do not appear to promote alkyne-alkyne cross-coupling reactions.



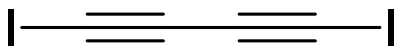
Scheme 2.23 Overview of the synthesis of tetrayne **42** via cross-coupling with silver nitrate.

2.4 Summary

The iterative route developed by Lei Li for obtaining symmetric polyynes was further investigated in this work. Model studies were used to optimize the experimental conditions including catalyst ratios, temperature, and reaction time, resulting in a straightforward method for the preparation of silyl or phenyl capped tetraynes, pentaynes, hexaynes, and heptaynes. The potential toxicity associated with the tin reagents and byproducts in the Stille reaction served as motivation to explore the synthesis of polyynes using Cadiot-Chodkiewicz coupling conditions. However, the method only favored high product selectivity in the model Cadiot-Chodkiewicz reaction. The same selectivity was not apparent when applied to the cross-coupling of diiodopolyynes as no clear trend is observed, suggesting that optimized conditions are particular to each system. Currently, the Stille reaction has shown to be more effective than the Cadiot-Chodkiewicz reaction for the symmetric double cross-coupling to diiodopolyynes; as poor selectivity along with low overall yield continues to be issues in the Cadiot-Chodkiewicz reaction.

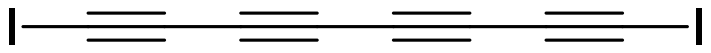
2.5 Experimental

General Methods: Reagents were purchased reagent grade from Aldrich, Fisher Scientific/Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. Tetrahydrofuran was distilled under argon from sodium/ benzophenone. Copper iodide was purified by recrystallization. High purity hexanes should be used when preparing silyl-capped polyynes, to avoid possible grease contamination caused by the low polarity of these compounds. All reactions were performed under an inert argon (Ar) atmosphere, unless stated otherwise. Iodination and coupling reactions of polyynes were carried out in aluminum foil wrapped flasks in an unlighted hood. All diiodopolyynes were washed with aqueous $Na_2S_2O_3$ immediately prior to use. Caution was taken when preparing and handling the tin acetylides, as trimethyltin chloride and analogous organotin compounds have been declared toxic by all means of exposure.[30] Column chromatography: Alumina (50-200 mesh) from Acros Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. ^{1}H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, Inova-500 MHz, Bruker-400 MHz, or Bruker-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise.



9

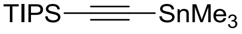
1,4-Diiodo-1,3-butadiyne (9).[108] Commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne (**50**, 0.526 g, 2.7 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.925 g, 5.5 mmol) and *N*-iodosuccinimide (3.05 g, 13.5 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 4 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **9** as a yellow solid that decomposes at 90 °C (0.753 g, 2.5 mmol, 92% yield). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 79.7, -3.3.[108]



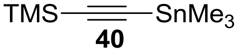
17

1,8-Diiodo-1,3,5,7-octatetrayne (17).[28] 1,8-Bis(trimethylsilyl)-1,3,5,7-octatetrayne (**43**, 0.10 g, 0.41 mmol) was dissolved in 200 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.28 g, 1.7 mmol) and *N*-iodosuccinimide (0.93 g, 4.1 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 3.5 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (2 x 100 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **17** as an orange solid that explodes at 85 °C (0.11 g, 0.314 mmol, 77% yield). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 78.9, 62.1, 58.9, 1.4.[28,109]

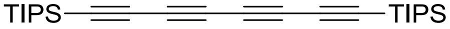
General Procedure for the Preparation of Tin Acetylides:[29]


39

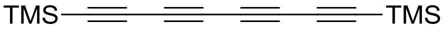
Triisopropylsilyl(trimethylstannyl)ethyne (39). Triisopropylsilyl acetylene (4.50 g, 25.0 mmol) was dissolved in 50 mL THF, and the solution was cooled to -30 °C using a dry ice/acetone bath. *n*-BuLi (1.6M/hexanes, 15.0 mL, 25.0 mmol) was added dropwise over 15 min. After stirring for 15 min at -30 °C, $SnMe_3Cl$ (1M/THF, 25.0 mL, 25.0 mmol) was added, and the mixture was stirred for an additional 30 min before warming to room temperature and stirring for 1 h. Hexanes (100 mL) was added to the reaction mixture, resulting in the formation of a white precipitate. The mixture was extracted with 25 mL H_2O, and the organic layer was dried over $MgSO_4$. The solution was filtered and solvent was removed *in vacuo*, leaving a cloudy yellow liquid. Vacuum distillation (~90 °C) was used to isolate **39** as a colorless liquid (5.50 g, 0.016 mol, 64 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.07(br, 21H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 115.1, 113.5, 18.6, 11.2, -7.6.[110]


40

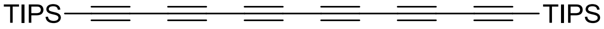
Trimethylsilyl(trimethylstannyl)ethyne (40). colorless liquid; (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.27 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 117.4, 113.1, 0.2, -7.7.[111]


42

1,8-Bis(triisopropylsilyl)-1,3,5,7-octatetrayne (42).[3] Triisopropylsilylbuta-1,3-diyne (**75**, 156 mg, 0.756 mmol) was dissolved in 5 mL CH_2Cl_2 and was added under oxygen to a solution of copper(I) chloride (71.6 mg, 0.723 mmol) and 1 mL tetramethylethylenediamine (TMEDA) in 20 mL CH_2Cl_2. Oxygen was bubbled through the mixture as it stirred for 1 h at 25 °C. The mixture was then quenched with sat. aq. NH_4Cl (20 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed once with H_2O (20 mL), and the resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in a crude mixture as a brown oil and a white solid. Purification using a short plug (SiO_2/ hexanes) afforded **42** as a white solid (0.154 g, 0.375 mmol, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.11-1.10 (m); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 89.6, 85.6, 62.2, 61.3, 18.5, 11.3.[3]

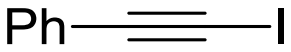

43

1,8-Bis(trimethylsilyl)-1,3,5,7-octatetrayne (43).[19] Diiodobutadiyne (**9**, 0.239 g, 0.792 mmol) and trimethylsilyl(trimethylstannyl)ethyne (**40**, 0.414 g, 1.58 mmol) were dissolved in 20 mL dry THF in a heart-shaped flask wrapped in aluminum foil. The flask was placed in an ice bath (0 °C). CuI (0.036 g, 0.19 mmol, 24 mol %) and $Pd(PPh_3)_2Cl_2$ (0.065 g, 0.093 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and the solution of **43** and **40** was added to the catalyst mixture via cannula over a period of 10 h. The mixture was stirred for 2 h after the addition, solvent was removed *in vacuo*, and excess catalyst was removed using a short plug (SiO_2/hexanes). Vacuum sublimation was used to isolate **43** as brown oil that contained solid needles (0.11 g, 0.454 mmol, 59 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.21; ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 88.01, 87.83, 62.16, 62.14, -0.57.[19]



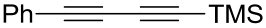
47

1,12-Bis(triisopropylsilyl)-1,3,5,7,9,11-dodecahexayne (47).[19] In a heart-shaped flask wrapped in aluminum foil, diiodotetrayne (**17,** 0.122 g, 0.348 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**39**, 0.229 g, 0.662 mmol) were dissolved in dry THF (20 mL) and kept at -10 °C. CuI (0.016 g, 0.084 mmol, 24 mol %), and $Pd(PPh_3)_2Cl_2$ (0.029 g, 0.042 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and the flask was kept in an ice bath (0 °C). The solution of **17** and **39** was added to the catalyst mixture via cannula over a period of 10 h. After addition, the mixture was stirred over-night and allowed to warm slowly from 0 °C to 25 °C. Solvent was removed *in vacuo,* and excess catalyst was removed using a short plug (SiO_2/ hexanes), which resulted in 0.111 g of a crude mixture as an orange film and a brown solid. Column chromatography (SiO_2/ hexanes) was used to isolate **47** as a yellow oil (0.013 g, 8% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.09-1.08 (m); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 89.38, 87.01, 62.68, 62.63, 62.36, 61.24, 18.48, 11.25.[19]



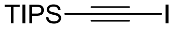
53

1-Iodo-2-phenyl-acetylene (53). Commercially available phenylacetylene (**60**, 0.499 g, 10 mmol) was dissolved in acetone (50 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.0843 g, 1 mmol), and *N*-iodosuccinimide (1.21 g, 11 mmol) were added, and the reaction mixture was allowed to stir at room temperature for 2 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting yellow solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **53** as a yellow oil (0.955 g, 4.2 mmol, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.45-7.48 (m, 2H), 7.30-7.36 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 132.1, 128.6, 128.1, 123.1, 94, 6.7.[112-113]



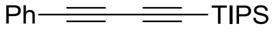
54

1-Phenyl-4-(trimethylsilyl)butadiyne (54). CuI (0.008 g, 0.042 mmol, 10 mol %) was added to a round bottom flask wrapped with aluminum foil, which was then degassed. 1-Bromo-2-phenyl-acetylene (**61**, 0.076 g, 0.42 mmol), trimethylsilyl acetylene (**52**, 0.071 mL, 0.502 mmol), THF (5 mL), and *i*-Pr_2NH (0.13 mL, 0.925 mmol) were added to the catalyst mixture, and the reaction was allowed to stir for 24 h at room temperature under a stream of argon. Excess catalyst was removed using a short plug (SiO_2/hexanes). Removal of solvent resulted in **54** as a yellow oil (0.006 g, 0.029 mmol, 7 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.48-7.49 (m, 2H), 7.31-7.33 (m, 3H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 132.7, 129.3, 128.4, 121.4, 90.6, 87.8, 74.1, -0.4.[114]



58

1-Iodo-2-(triisopropylsilyl)acetylene (58). Commercially available triisopropylsilyl acetylene (**51**, 1.03 g, 5.66 mmol) was dissolved in 50 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.097 g, 0.57 mmol), and *N*-iodosuccinimide (1.40 g, 6.24 mmol) were added and the reaction mixture was allowed to stir in the dark at room temperature for 2 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **58** as a colorless oil (1.26 g, 4.06 mmol, 72 %).^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.07-1.08 (m); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 100.7, 19.9, 18.5, 11.4.[115]



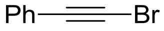
59

1-Phenyl-4-(triisopropylsilyl)butadiyne (59).

Cadiot-Chodkiewicz Procedure A. CuI (0.004 g, 0.023 mmol, 5 mol %) was added to a 2.5 mL solution of *n*-$BuNH_2$ (30%). A few crystals of hydroxylamine hydrochloride were added to remove the blue color from the solution. 1-Iodo-2-phenyl-acetylene (**53**, 0.108 g, 0.444 mmol) was added and the solution was immediately cooled in an ice-water bath. Triisopropylsilyl acetylene (**51**, 0.12 mL, 0.535 mmol) was added, the mixture was warmed to room temperature, and the flask was wrapped with aluminum foil. The reaction was stirred for 30 minutes, and the product was extracted with hexanes (3 x 50 mL) and then dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.087 g of a crude material as yellow crystals. The molar ratio of cross-coupled diyne **59** to homocoupled diyne **55** was determined by the integration of the alkynyl carbon peak at δ 75.6 ppm and δ 81.5 ppm, respectively. The molar ratio of cross-coupled diyne **59** to homocoupled diyne **57** was determined by the integration of the alkynyl carbon peak at δ 87.8 ppm and δ 81.6 ppm, respectively. This ratio of diynes **59**: **55**: **57** was 1: 0.85: 1.2, respectively, which was used to determine the mass percent of each compound in the crude mixture. Therefore, 32 % of the mixture was cross-coupled product **59**, which equates to a 22 % product yield. No further separation was attempted. The product peaks are shown in bold. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ **7.6-7.3**, **1.1-1.0**; ^{13}C NMR (500 MHz, $CDCl_3$, 25 ºC): δ **132.7**, 132.5, **129.2**, **128.4**, 121.8, **121.6**, 90.3, **89.6**, **87.8**, 81.6, 81.5, **75.6**, **74.7**, 73.9, **18.5**, **11.3**.[114]

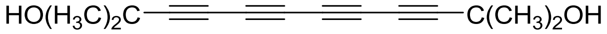
Cadiot-Chodkiewicz Procedure B. CuI (0.003 g, 0.017 mmol, 5 mol %), hydroxylamine hydrochloride (0.002 g, 0.035 mmol), and sodium thiosulfate pentahydrate (0.085 g, 0.343 mmol) were combined in a round-bottom flask wrapped with aluminum foil, and the system was degassed and backfilled with Ar. 3 mL MeOH was added to the flask, followed by 1-Iodo-2-phenylacetylene (**53**, 0.078 g, 0.342 mmol), piperidine (0.051 mL, 0.516 mmol), and triisopropylsilyl acetylene (**51**, 0.092 mL, 0.41 mmol). The reaction was stirred for five hours in an ice bath (0 °C) and then allowed to stir over-night at room temperature. Excess catalyst was removed using a short plug (SiO_2/hexanes). Removal of solvent resulted in 0.011 g of a crude material as a colorless oil. The molar ratio of cross-coupled diyne **59** to homocoupled diyne **55** was determined by the integration of the alkynyl carbon peak at δ 75.6 ppm and δ 81.5 ppm, respectively. This ratio was 1:0.25, respectively, which was used to determine the mass percent of each compound in the crude mixture. Therefore, 85 % of the mixture was cross-coupled product **59**, which equates to a 9 % product yield. No further separation was attempted. The product peaks are shown in bold. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ **7.5-7.2**, and **1.1-1.0**; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ **132.5**, **129.1**, **128.3**, 121.8, **121.5**, **89.5**, **87.8**, 81.5, **75.6**, **74.6**, 73.9, **18.5**, **11.3**.[114]

Cadiot-Chodkiewiz Procedure C. CuI (0.004 g, 0.02 mmol, 5 mol %) was added to a round-bottom flask wrapped with aluminum foil, and the system was degassed and backfilled with Ar. 1-Iodo-2-phenylacetylene (**53**, 0.095g, 0.42 mmol), triisopropylsilyl acetylene (**51**, 0.11 mL, 0.49 mmol), and pyrrolidine (1.5 mL) were added to the mixture, and the reaction was allowed to stir for 30 minutes at 0 °C. Solvent was removed under reduced pressure from the resulting light green solution, and excess catalyst was removed using a short plug (SiO_2/hexanes). Removal of solvent resulted in 0.12 g of a crude material as a colorless oil and a white solid. The molar ratio of cross-coupled diyne **59** to homocoupled diyne **57** was determined by the integration of the alkynyl carbon peak at δ 87.9 ppm and δ 81.6 ppm, respectively. This ratio was 1: 0.92, respectively, which was used to determine the mass percent of each compound in the crude mixture. Therefore, 46 % of the mixture was cross-coupled product **59**, which equates to a 45 % product yield. No further separation was attempted. The product peaks are shown in bold. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ **7.5-7.3**, and **1.1-1.0**; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ **132.7**, **129.1**, **128.4, 121.6**, 90.2, **89.5**, **87.9**, 81.6, **75.6**, **74.7**, **18.6**, **11.3**.[114]



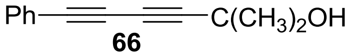
61

1-Bromo-2-phenyl-acetylene (61).[116] Commercially available phenylacetylene (**60**, 2.82 g, 27.6 mmol) was dissolved in acetone (50 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.475 g, 2.8 mmol) and recrystallized *N*-bromosuccinimide (5.40 g, 30.4 mmol) were added, and the reaction mixture was allowed to stir at room temperature for 2 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting yellow solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **61** as a yellow oil (3.43 g, 19.2 mmol, 70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.45-7.48 (m, 2H), 7.30-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 1321.9, 128.6, 128.2, 122.6, 80, 49.7.[112,116]



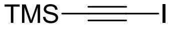
63

3, 5, 7, 9-Dodecatetrayne-2, 11-diol, 2, 11-dimethyl- (63). Diiodobutadiyne (**9**, 0.058 g, 0.192 mmol) was dissolved in 7 mL THF in a heart-shaped flask wrapped with aluminum foil. The flask was then placed in an ice bath (0 °C). CuI (0.003 g, 0.014 mmol, 7 mol %), $PdCl_2(PPh_3)_2$ (0.008 g, 0.011 mmol, 6 mol %), and NH_2OH•HCl (0.002 g, 0.027 mmol, 14 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, followed by 2-methylbut-3-yn-2-ol (**62**, 0.039 g, 0.463 mmol, 0.045 mL) and diisopropylamine (0.079 g, 0.783 mmol, 0.11 mL), and the flask was then placed in an ice bath (0 °C). The diiododiyne **9**/ THF solution was added to the catalyst mixture via cannula at a rate of 1 drop/ 12 s. After addition, the mixture was stirred over-night at room temperature. The reaction was then quenched with ice water and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed once with brine and once with a sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. After filtration and concentration, the product was purified using a short plug (SiO_2/ethyl acetate), which resulted in 0.034 g of a brown film and a black solid. The molar ratio of cross-coupled tetrayne **63** to the homocoupled diyne **64** was determined by the integration of the alkynyl carbon peak at δ 82.6 ppm and δ 83.9 ppm, respectively. This ratio was 1:1.6, respectively, which was used to determine the mass percent of each compound in the crude mixture. Therefore, 44 % of the mixture was cross-coupled product **64**, which equates to a 37 % product yield. No further separation was attempted. The product peaks are shown in bold. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ **1.53** and 1.52; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 84.0, **82.7**, **67.3**, 66.3, 65.6, **65.5**, **64.0**, **61.6**, 31.1, **31.0**. [41]



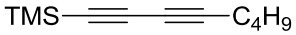
66

2-methyl-6-phenylhexa-3,5-diyn-2-ol (66). CuI (0.004 g, 0.021 mmol, 2 mol %) and $PdCl_2(PPh_3)_2$ (0.015 g, 0.021 mmol, 2 mol %) were added to a round-bottom flask and the system was degassed and backfilled with Ar. 1-Iodo-2-phenyl-acetylene (**53**, 0.24 g, 1.1 mmol), 2-methyl-3-butyne-2-ol (**62**, 0.12 mL, 1.2 mmol), diisopropylamine (0.31 mL, 2.2 mmol), and THF (15 mL) were added to the mixture, and the reaction was allowed to stir for 4 h at 0 °C in the dark. Solvent was removed *in vacuo*, and excess catalyst was removed using a short plug (SiO_2/ ethyl acetate), which resulted in 0.23 g of a crude mixture. Column chromatography (SiO_2/ 5:1 hexanes; ethyl acetate) was used to isolate **66** as white needles (0.12 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.45-7.43 (m, 2H), 7.29-7.27 (m, 3H), 2.26 (s, 1H), 1.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC):δ 132.4, 129.1, 128.3, 121.4, 86.7, 78.64, 73.1, 66.9, 65.6, 30.9.[70]



68

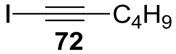
1-Iodo-2-(trimethylsilyl)acetylene (68).[117] Commercially available trimethylsilylacetylene (**52**, 4.3 mL, 31 mmol) was dissolved in 25 mL dry THF in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.52 g, 3.1 mmol) and *N*-iodosuccinimide (6.9 g, 31 mmol) were added, and the reaction mixture was allowed to stir for 2 h at room temperature in the dark. Ice water (100 mL) and diethyl ether (100 mL) were added, and the aqueous layer was extracted with 3 x 100 mL of diethyl ether. The combined organic layers were washed once with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in the formation of **68** as a colorless oil (6.8 g, 100% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 104.1, 20.3, -0.1.[117]



70

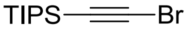
1-Butyl-4-(trimethylsilyl)-1,3-butadiyne (70).[51] CuI (0.058 g, 0.31 mmol, 2.5 mol %) and $PdCl_2(PPh_3)_2$ (0.21 g, 0.31 mmol, 2.5 mol %) were added to a round-bottom flask and the system was degassed and backfilled with Ar. 90 mL diisopropylamine, 1-hexyne (**69**, 1.0 g, 12.1 mmol), and 1-iodo-2-(trimethylsilyl)acetylene (**68**, 2.7 g, 12.2 mmol) were then added to the flask under Ar. The solution was stirred at room temperature for 2.5 h. The reaction mixture was filtered, and the resulting filtrate was concentrated *in vacuo* and then passed through a short plug (SiO_2/ hexanes). Removal of solvent resulted in 1.4 g of a crude mixture as a brown oil. The molar ratio of cross-coupled diyne **70** to the homocoupled diyne **50** was determined by the integration of the alkynyl carbon peak adjacent to the TMS end-group at δ 82.7 ppm and δ 85.7 ppm, respectively. The molar ratio of cross-coupled diyne **70** to the homocoupled diyne **71** was determined by the integration of the alkynyl carbon peak adjacent to the butyl end-group at δ 65.4 ppm and δ 65.2

ppm, respectively. The ratio of **70**: **50**: **71** was 1: 0.11: 0.35, respectively, which was used to determine the mass percent of each compound in the crude mixture. Therefore, 69 % of the mixture was cross-coupled product **70**, which equates to a 46 % product yield. No further separation was attempted. The product peaks are shown in bold.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ **2.27-2.21**, **1.49-1.47**, **1.42-1.39**, **0.91-0.87**, 0.17, **0.16**. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ **88.4**, 87.9, 85.7, **82.7**, **80.0**, 77.2, **65.4**, 65.2, 30.4, **30.1**, **21.9**, **18.8**, **13.4**, **-0.41**, -0.60.[51]



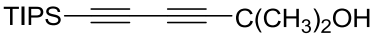
72

1-Iodohex-1-yne (72).[117] Commercially available 1-hexyne (**69**, 3.0 g, 37 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.63 g, 3.7 mmol) and *N*-iodosuccinimide (9.2 g, 41 mmol) were added, and the reaction mixture was allowed to stir for 3 h at room temperature in the dark. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in 5.8 g of a crude mixture that was further purified using a short plug (SiO_2/ hexanes). Haloalkyne **72** was isolated as a yellow oil (2.6 g, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.37-2.33 (t, 2H), 1.51-1.38 (m, 4H), 0.92-0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 94.6, 30.4, 21.8, 20.4, 13.4, -7.5.[117]



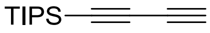
73

1-Bromo-2-(triisopropylsilyl)acetylene (73).[70] Commercially available triisopropylsilyl acetylene (**51**, 4.04 g, 22.2 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.380 g, 2.24 mmol) and recrystallized *N*-bromosuccinimide (4.34 g, 24.3 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 2 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 100 mL). The combined organic layers were washed with water (1 x 50 mL) and sat. aq. $Na_2S_2O_3$ (1 x 50 mL). The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **73** as a yellow oil (5.59 g, 21.4 mmol, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.08 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 83.5, 62.0, 18.5, 11.3.[70]



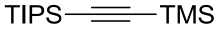
74

2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol(74).[71] *n*-Butylamine (2.31mL, 23.3 mmol), 2-methylbut-3-yn-2-ol (**62**, 1.51 mL, 15.5 mmol), copper chloride (15.2 mg, 0.154 mmol, 2 mol%), and hydroxylamine hydrochloride (163 mg, 2.34 mmol) were added in order to a solution of 2:1 methanol:water (45 mL). 1-Bromo-2-(triisopropylsilyl)acetylene (**73**, 2.03 g, 7.79 mmol) was dissolved in 20 mL methanol, and added dropwise under argon via cannula to the catalyst mixture over 30 min. The resulting mixture was left stirring at room temperature for 24 h under argon in the dark. The solution was then diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with water (1 x 50 mL) and brine (2 x 50 mL). The resulting solution was dried over $MgSO_4$ and filtered. Solvent was removed *in vacuo*, resulting in 1.81 g of a crude mixture as a yellow oil. Purification using a short plug (SiO_2/ 9:1 hexanes: EtOAc), followed by recrystallization with pentane, resulted in the isolation of **74** as a white solid (1.63 g, 6.16 mmol, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.61 (s, 1H), 1.52 (s, 6H), 1.06 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.0, 84.6, 80.7, 67.6, 65.5, 31.0, 18.5, and 11.2.[71]



75

Triisopropylsilylbuta-1,3-diyne (75).[70] 2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (**74**, 1.59 g, 6.01 mmol) was added to a solution of crushed potassium hydroxide (0.676 g, 12.0 mmol) in 45 mL anhydrous toluene, and the resulting solution was heated to 110 °C for 2 h under argon gas. The solution was then cooled and the solids were removed by filtration through a pad of Celite. After concentration, the product was purified using a short plug (SiO_2/hexanes), which resulted in **75** as an orange oil (0.781 g, 3.78 mmol, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.06 (s, 1H), 1.09 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.1, 81.9, 68.6, 65.5, 18.5, and 11.2.[70]



81

1-(Triisopropylsilyl)-2-(trimethylsilyl)acetylene (81).[118] Triisoproplysilyl acetylene (**51**, 0.51 g, 2.8 mmol) was dissolved in 10 mL THF, and the solution was cooled to -78 °C using a dry ice/ acetone bath. *n*-BuLi (1.6M/ hexanes, 1.9 mL, 3.0 mmol) was added dropwise over 10 min. After stirring for 15 min at -78 °C, the flask was warmed to room temperature, and the mixture was stirred for an additional 15 min. The mixture was then cooled to -78 °C, and TMSCl (0.48 mL, 3.1 mmol) was added, and the mixture was stirred for an additional 60 min before warming to room temperature and stirring for 2 h. Ice water (30 mL) and Et_2O (30 mL) were added, and the aqueous layer was extracted with 3 x 30 mL of Et_2O. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in the formation of **81** as a colorless oil (0.64 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.08-1.07 (m, 21H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 116.2, 110.1, 18.6, 11.1, 0.03.[118]

CuCl Purification.[119] Copper chloride (5.35 g, 54.0 mmol) was dissolved in 60 mL 0.1M HCl and stirred for 10 min. Deionized water was added to the blue/green suspension, causing a white precipitate to form which was isolated using vacuum filtration. The solid was washed with 20mL portions of methanol, ethanol, acetone, and diethyl ether, and dried in the vacuum oven. The purified compound was stored in a desiccator in the dark.

CuI Purification.[26] Potassium iodide (18.2 g, 109 mmol) was dissolved in 32 mL H_2O and 1.25 g CuI (6.54 mmol) was added. After stirring under argon for 1 h, 1.27g (106 mmol) charcoal was added and the mixture was stirred with moderate heat for 30 min. The mixture was cooled to room temperature and filtered under argon. 30 mL H_2O was added and the white precipitate that formed was isolated after 45 min using vacuum filtration (under Ar). The solid was washed with water, ethanol, and ether (10 mL portions) and dried over-night in the vacuum oven (~100°C). The purified compound was stored in a Schlenk flask that had been degassed and filled with Ar, and was placed in a desiccator.

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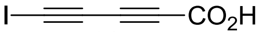
Chapter 3: Attempts Towards the Synthesis of Diynes with Carboxylic Acid End-Groups

3.1 5-Iodo-penta-2,4-diynoic Acid

Push-pull diynes are of interest for their potential low band-gap properties. By incorporating a donor (I) and an acceptor end-group (COOH), asymmetric diyne **82** makes for an interesting target (Figure 3.1). Theoretical studies by Jain and Chandrasekhar have suggested that integrating donor and acceptor groups, such as I (or Br) and CN, respectively, increases the hyperpolarizabilities of the polyynes studied.[1] Therefore, the likely push-pull nature of diyne **82** could allow for interesting optical properties.[1-3]



82

Figure 3.1 Asymmetric diyne **82**.

Furthermore, conjugated polymers **83** (head-to-tail) and **84** (head-to-head) may be formed from diyne **82** via topochemical polymerization, depending upon how the monomers are aligned in the co-crystal (Figure 3.2). The head-to-head arrangement in polymer **84** is expected to be less stable, however, due to the alternating symmetric alkene units. These polymers are also attractive since the presence of both donor and acceptor groups could enable charge transfer throughout the polydiacetylene (PDA) backbone, reducing the energy difference between the ground and excited state. Thus, potential applications in optical or electronic devices are suggested for this polymeric material.[4-5]

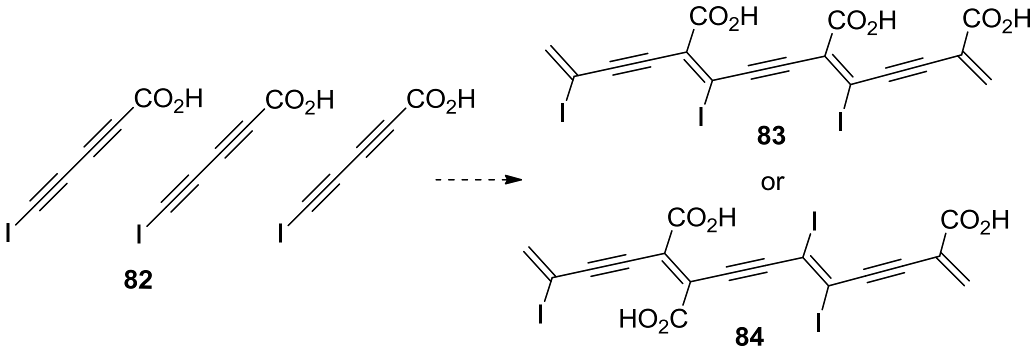
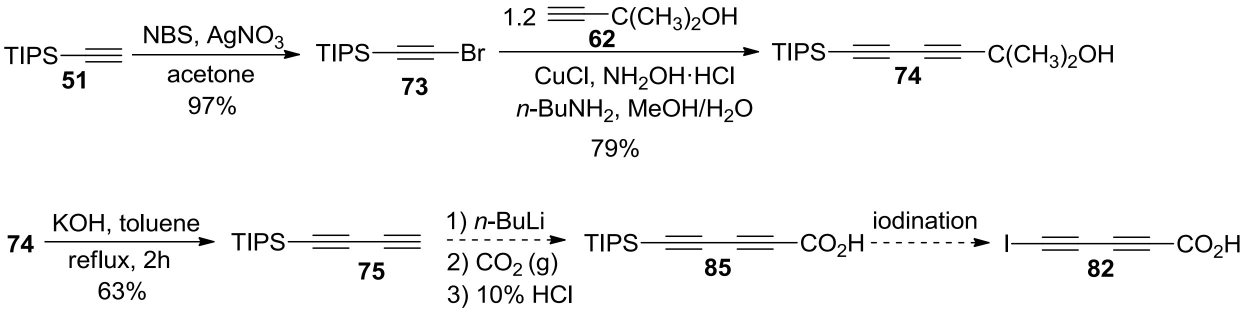


Figure 3.2 Possible 1,4-topochemical polymerizations of diyne **82**.

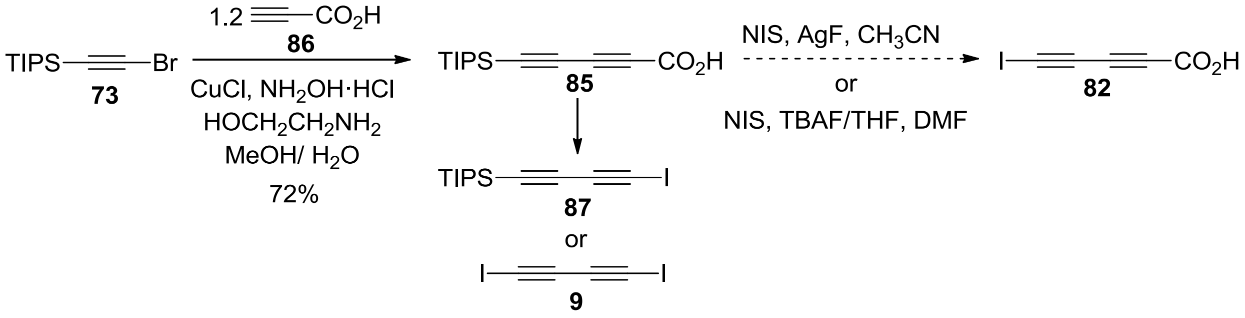
An advantage of synthesizing push-pull diyne **82**, as opposed to cyanoiodobutadiyne,[6] is that both ends are Lewis acidic, and therefore, a symmetric host can be used to form polymer **83** or **84** via the host-guest strategy developed by Fowler and Lauher.[7] Previous co-crystallization experiments with cyanoiodobutadiyne have suggested that the asymmetric hosts employed came out of solution independently of the monomer, possibly due to the low solubility of the host compounds.[6] In addition to its polymerization behavior, synthesis of diyne **82** is also appealing since both the iodine and carboxylic acid substituents may be easily eliminated once polymerized, similarly to the behavior of the iodine substituents on PIDA [poly(diiododiacetylene)],[8] making polymers **83** and **84** potential precursors to carbyne or a carbon rich material. Moreover, without side groups to apply twisting to the backbone, like PIDA, polymers **83** and **84** should result in a planar structure. Lastly, post-polymerization modification of the polymer will allow for a variety of PDAs to be synthesized.

3.1.1 Synthetic Efforts Towards 5-Iodo-penta-2,4-diynoic Acid

There are no previous reports for the synthesis of diyne **82** reported in the literature, thus the preparation of this diyne was initially attempted according to Scheme 3.1.


Scheme 3.1 First attempted synthesis of diyne **82**.

Terminal diyne **75**, which has been described as stable for several months in the freezer at -10 °C,[9] was prepared according to literature procedures.[9-10] Tykwinski and co-workers reported the synthesis of diyne **85,**[11-12] but attempts to repeat this synthesis proved challenging. Despite using a new bottle of *n*-BuLi, a mixture of products was yielded after CO_2 gas was bubbled through the reaction, including unreacted terminal diyne **75**. Therefore, a new route toward diyne **82** was devised, and is depicted in Scheme 3.2.


Scheme 3.2 Second attempted synthesis of diyne **82**.

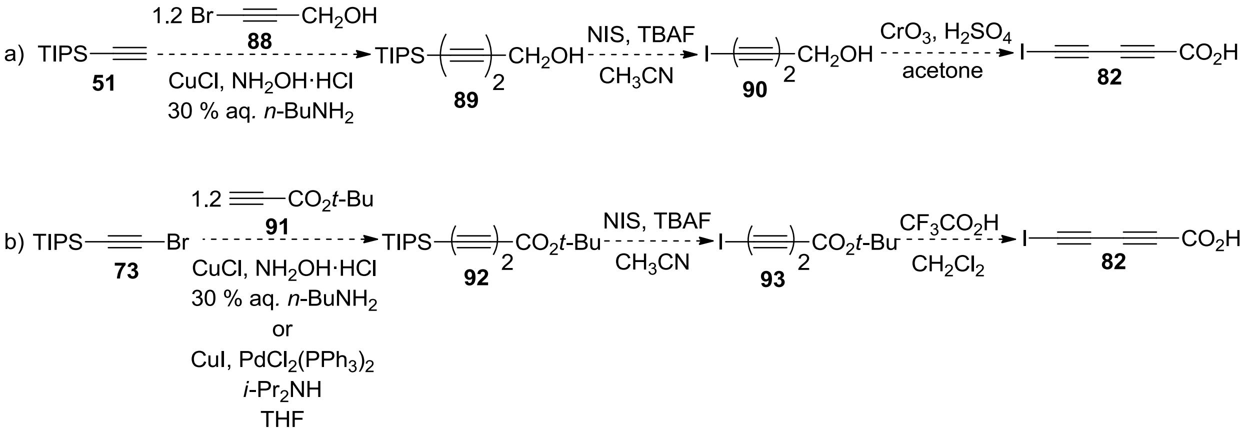
Propiolic acid (**86**) has been successfully cross-coupled to the haloalkyne 1-iodoeicosyne in 80 % yield,[13] as well as to various bromoalkynes in moderate yields via Cadiot-Chodkiewicz cross-coupling reaction conditions.[14] Diyne **85** was synthesized from the coupling reaction between haloalkyne **73** and terminal alkyne **86** without formation of byproducts when following the reported procedure by Dikusar and co-workers (Scheme 3.2).[14] Because alkynyl acid derivatives can also undergo copper or palladium catalyzed decarboxylative cross-coupling reactions, heat was avoided.[15-18]

The final step in the synthetic route is desilylative iodination of the TIPS end-group. Kim and co-workers reported the successful desilylative bromination of 1-triisopropylsilyl acetylenes with *N*-bromosuccinimide (NBS) and silver fluoride (AgF).[19-20] But the addition of *N*-iodosuccinimide (NIS) and AgF to unsymmetrical diyne **85** resulted largely in the iodination of both end groups to form diyne **9**. Novel diyne **87** was also obtained but in a much lower ratio (3.7:1, respectively). Formation of diynes **9** and **87** involves an undesirable decarboxylation, which seems to be faster than the desired desilylation/ iodination reactions. Because optimal conditions were determined by Kim and co-workers to require 1.2 equivalents of both NBS and AgF,[20] decreasing the amounts of NIS and AgF used in Scheme 3.2 was not attempted, and this pathway toward diyne **82** was abandoned. These researchers also achieved desilylative bromination of 1-triisopropylsilyl acetylenes with NBS and tetrabutylammonium fluoride (TBAF). Interestingly, a large excess of NBS (4 equivalents) was required to give the desired bromoacetylene and simultaneously limit protiodesilylation.[20] Based on these results, desilylative iodination of TIPS-protected diynoic acid **85** was tried using NIS and TBAF, which solely produced diiodobutadiyne (**9**).

In order to gain a better understanding regarding the ease of the halodecarboxylation reaction, 1.2 equivalents of NIS and 0.05 equivalents of TBAF were mixed with diyne **85**. After only 30 minutes, decarboxylated diyne **87** was produced in 26% yield, confirmed by NMR, FT-IR, and mass spectrometry. The low yield is due the numerous purification techniques employed, as initially, it was believed a byproduct, such as TIPS-F, was in the product mixture. There are examples in the literature of successful desilylation reactions of 1-trialkylsilyl acetylenes;

however the carboxylic acid substituent also present is adjacent to an alkyl chain as opposed to an alkynyl moiety, as seen with diyne **85**.[21-23] An alkynyl anion is much more stable than an alkyl anion, which suggests a reason for the ease of this Hunsdiecker-like reaction exhibited in Scheme 3.2. The literature was explored in an effort to determine the feasibility of halodecarboxylation of propiolic acids. Roy and co-workers have shown that halodecarboxylation is possible with tetrabutylammonium trifluoroacetate (TBATFA) and NIS (or NBS)[24] and also with triethylamine (TEA) and NIS (or NBS).[25] Furthermore, Tykwinski and co-workers reported that when TIPS-protected diynoic acid **85** reacted with TBAF and benzyl azide, cycloaddition occurred at both ends of the diyne, suggesting decarboxylation was promoted under these conditions.[26] Moreover, Cohen and McNelis described the oxidative decarboxylation of propiolic acids with iodine and iodine pentoxide.[27] Consequently, it appears that iodination of diyne **85** to form iodo diynoic acid **82** is not possible, as my results imply that halodecarboxylation occurs much more quickly and easily than the desilylation/iodination reaction.

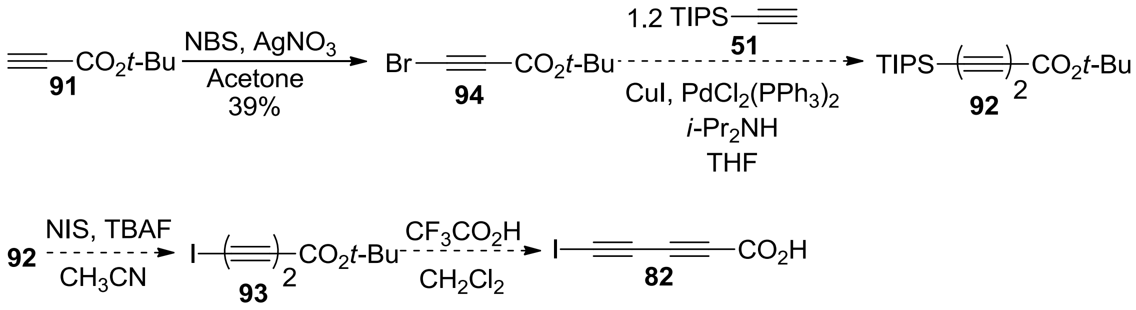
At this point, it is believed that halodecarboxylation of diyne **85** is driven by the reactivity of the alkynyl acid in the base-catalyzed reaction. Therefore, new pathways for the preparation of diyne **82** have been developed. Iodination of diyne **89** and a subsequent oxidation reaction (Scheme 3.3a) or iodination of diyne **92** followed by an ester deprotection under acidic conditions are possible routes to afford diyne **82** (Scheme 3.3b).



Scheme 3.3 Possible synthetic routes towards diyne **82**.

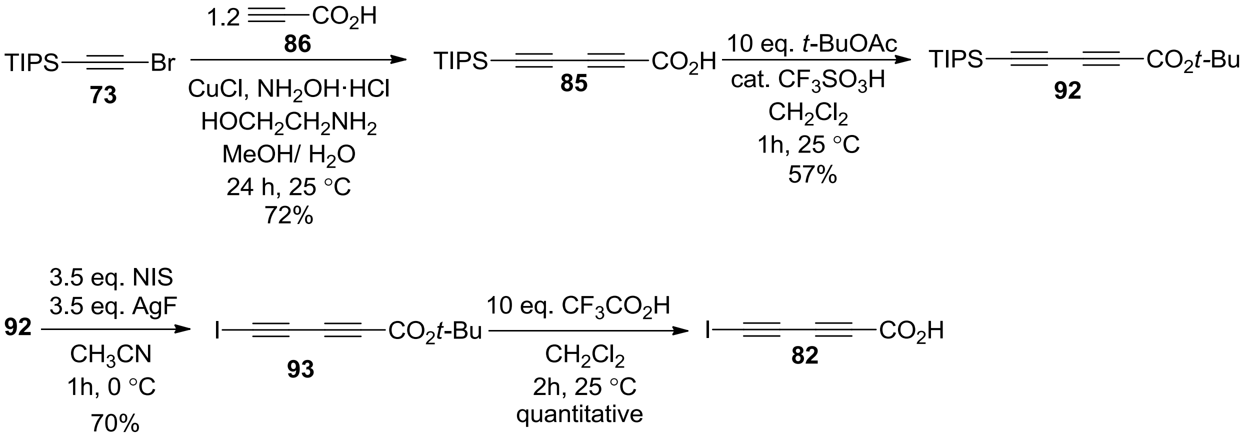
Diyne **89** has been reported,[28] as well as the conversion of propargyl alcohol to propiolic acid via Jones oxidation conditions.[29] Additionally, there is a literature example of a bromo alkynyl acid synthesized from the corresponding bromo alkynyl alcohol;[30] however, there are no reports of an iodoalkyne used in a Jones oxidation. Therefore, iodo alcohol **90** may not be stable to chromium oxidants, and the synthesis of diyne **82** was not attempted by this route. Alternatively, the preparation of diyne **82** under acidic conditions seems straightforward, even though diynes **92**, **93**, or **82** have not been reported. If desilylative iodination of the TIPS end-group is feasible for diyne **92**, the *t*-Bu ester can be cleaved under acidic conditions with either TFA (trifluoroacetic acid)[31] or TMSOTf (trimethylsilyl trifluoromethanesulfonate) and 2,6-di-*t*-butylpyridine.[32,] Formation of diyne **93** is crucial for the successful synthesis of compound **82**, as cleavage of a methyl or ethyl ester would require basic conditions,[33] which my results have indicated to promote decarboxylation.

Following reported conditions for the reaction of trialkylsilyl acetylenes and bromo alkynyl alcohols,[28] the coupling of TIPS-bromoacetylene (**73**) and terminal alkynyl ester **91** was attempted with CuCl, NH_2OH•HCl, and 30% aq. *n*-$BuNH_2$ (Scheme 3.3b). The NMR spectrum showed the presence of multiple products which contained peaks in the ester (142-171 ppm), alkynyl (60-96 ppm), alkyl (27-32 ppm), and TIPS regions (11-19 ppm). The successful cross-coupling of *tert*-butyl propiolate (**91**) under copper and palladium co-catalyzed Sonogashira conditions has been described,[31,34-35] and therefore similar conditions were applied to the coupling with bromoalkyne **73** (Scheme 3.3). The NMR spectrum included multiple peaks in the ester (152-164 ppm), alkynyl (64-92 ppm), and alkyl (27-28 ppm) regions, but just 2 peaks in the TIPS region (18.4 and 11.1 ppm), suggestive of only one compound obtained with this end-group. Because unreacted TIPS-bromoacetylene (**73**) and homocoupled TIPS-protected diyne **57** were previously removed with a short plug (SiO_2/ hexanes), the crude mixture probably contained the desired product. The synthesis of diyne **92** was inconclusive with these experiments, and a new route toward this diyne was devised (Scheme 3.4).



Scheme 3.4 Third attempted synthesis of diyne **82**.

The results described in Chapter 2, as well as in the literature,[36] indicate that cross-coupling selectivity can be controlled by altering the electronic properties of the haloalkyne. Subjecting terminal alkyne **91** to bromination conditions using Leroy's method afforded haloalkyne **94** in low yield.[37] The coupling of alkynes **94** and **51** gave a mixture of products, determined by NMR spectroscopy, with multiple peaks in the ester (151-171 ppm), alkynyl (60-103 ppm), alkyl (20-36 ppm), and TIPS regions (11-19 ppm). Additionally, unidentified peaks were noticed, and product formation was inconclusive. This route toward diyne **92** was therefore abandoned, and a new pathway was developed (Scheme 3.5).



Scheme 3.5 Synthesis of diyne **82**.

Diyne **85** was previously synthesized according to Dikusar's conditions, as described above.[14] Addition of *tert*-butyl acetate and a catalytic amount of triflic acid in dichloromethane resulted in the formation of novel *tert*-butyl ester diyne **92** in 57% yield.[38] Conditions that were reported for the bromination of TIPS groups by Kim and co-workers were used with diyne **92**,[20] except NBS was replaced with NIS. Subjecting diyne **92** to these iodination conditions afforded novel diyne **93** in 70% yield. An excess of both NIS and AgF were used (3.5 equivalents), and the reaction was stirred at 0 °C to increase the rate of the reaction while simultaneously minimizing possible product decomposition. Cleavage of ester **93** using TFA in dichloromethane was quantitative to form iodo diynoic acid **82** as a white film. A procedure described by Tam and co-workers served as the basis for the synthesis of this novel diyne.[31] Compound **82** decomposes and turns black at 98-99 °C, suggesting its stability is similar to diiodobutadiyne (**9**), which decomposes at 90 °C.

3.1.2 Co-crystallization Experiments with 5-Iodo-penta-2,4-diynoic Acid

Fowler and Lauher's host-guest strategy (Section 1.1.1) was applied to explore the co-crystallization of monomer **82**. This method has been implemented for the successful single-crystal-to-single-crystal polymerization of diynes, triynes, and trienes.[7] As discussed in Chapter 1, Baughman determined that the ideal parameters for a 1,4-polymerization of diacetylenes include a repeat distance (r) of 4.9-5.0 Å between the monomer compounds, a C1-C4 distance ($d_{1,4}$) of 3.5 Å, and a tilt angle (θ) of 45°. Current group member Xiuzhu Ang recently reported that co-crystals formed from iodo benzoic acid diyne **95** and symmetric bis(pyridyl) oxalamide host **11** in a 1:1 ratio (Figure 3.3). She found that the carboxylic acid group and the Lewis acidic iodine functionality of guest **95** could form hydrogen bond and halogen bond interactions, respectively, with the Lewis basic pyridyl nitrogen in host **11**. However, the hydrogen bonding network for the oxalamide groups did not properly align for a 1,4-polymerization.

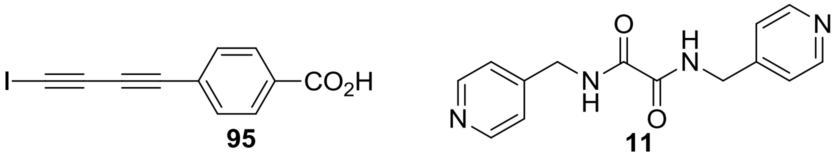


Figure 3.3 Guest **95** and bis(pyridyl) oxalamide host **11**.

Because the pyridyl oxalamide host was able to form a co-crystal with guest **95**, this host was employed for the polymerization of asymmetric diyne **82**. In an analogous manner to the procedure used for growing co-crystals of diiodobutadiyne (**9**) and bis(nitrile) or bis(pyridiyl) oxalamide hosts,[39-40] **82•11** co-crystals were prepared. The host and guest were dissolved in methanol, and the mixture was subjected to sonication to ensure that both components dissolved and to break up any possible aggregation of the monomer. Centrifugation was used to remove any excess solid that did not go into solution, and the supernatant layer was decanted into crystallization dishes. The dishes were covered with foil that contained small holes to allow for slow evaporation of the solvent while blocking any light. As per Ang's suggestion, a 1:2 ratio of host: guest was used, and the solvent was allowed to evaporate at room temperature. The resulting product is shown in Figure 3.4.

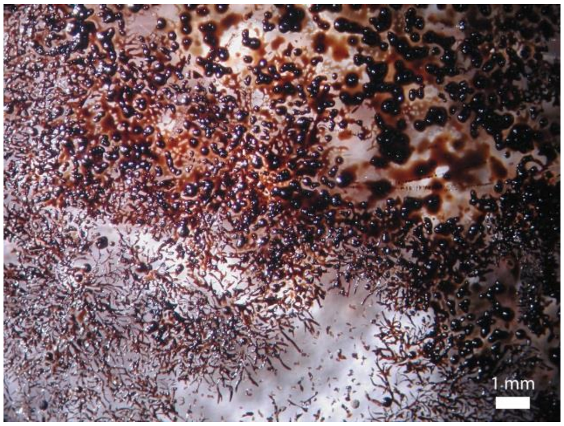


Figure 3.4 Optical microscope images of **82•11** co-crystals.

A brown film and a black solid resulted, and no further analysis could be performed. It is believed that the halogen bonding interaction between the pyridyl nitrogen in the host and the iodine in the guest, as opposed to a weaker nitrile-iodine interaction, may be conducive to co-crystal formation, and other bis(pyridyl) hosts will be initially tried. However, this group has had much success with nitrile hosts for preparing polymer **15**,[39-40] and consequently, these hosts may also be employed. Additionally, because iodo diynoic acid **82** is more electrophilic than iodo benzoic acid **95**, there is a greater chance of decomposition by nucleophilic attack. Future experiments will therefore include variations in concentration and host: guest ratio.

3.2 2,4-Hexadiynedioic Acid

Dicarboxylic acid diyne **96**, displayed in Figure 3.5, was also pursued as a precursor to polymer **97**. With the acid end-group acting as a strong electron acceptor, and its likely electronic absorptions in the visible range, this polymer will be interesting to study for its promise in electronic and optical applications.

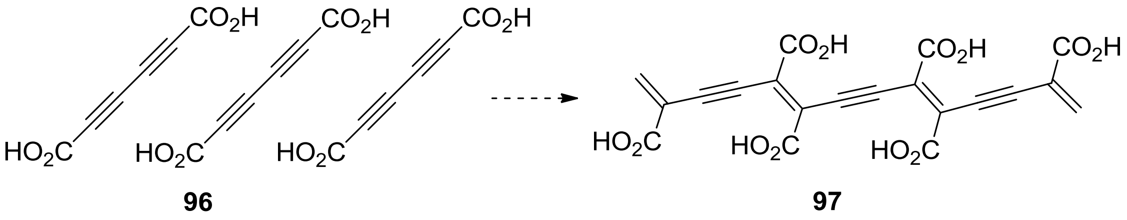
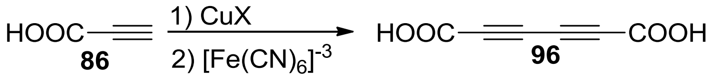


Figure 3.5 Possible 1,4-topochemical polymerization of diyne **96**.

Like diyne **82**, symmetric Lewis basic hosts can be used with symmetric diyne **96** to form polymer **97** via the supramolecular host-guest scaffold developed by Fowler and Lauher.[7] This material will be particularly electron-poor once isolated from the co-crystal, and could possibly react with external atoms, such as oxygen. For this same reason, it will be interesting to investigate the electronic behavior of polymer **97** when doped with electron donor materials.

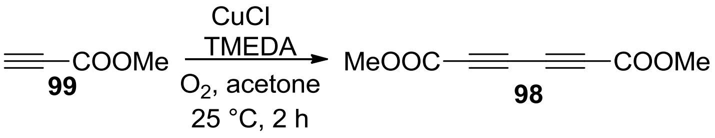
3.2.1 Synthetic Efforts Towards 2,4-Hexadiynedioic Acid

The synthesis of dicarboxylic acid **96** was first prepared by Baeyer in 1885, and was reported as the monohydrate.[41] About 60 years later, Dunitz and Robertson described diyne **96** as the dihydrate, which was determined by X-ray analysis.[42] A more recent exploration of the crystal structure for diyne **96** is reported by Dunitz.[43] According to Scheme 3.6, oxidation of the copper intermediate with ferricyanide afforded diacid **96** in very low yields; specifically only a few milligrams of product were obtained from about 2 grams of propiolic acid (**86**). Diyne **96** was described as pale yellow sword-like needles which became purple when exposed to light, and black when exposed to X-rays, therefore suggesting decomposition.[42]



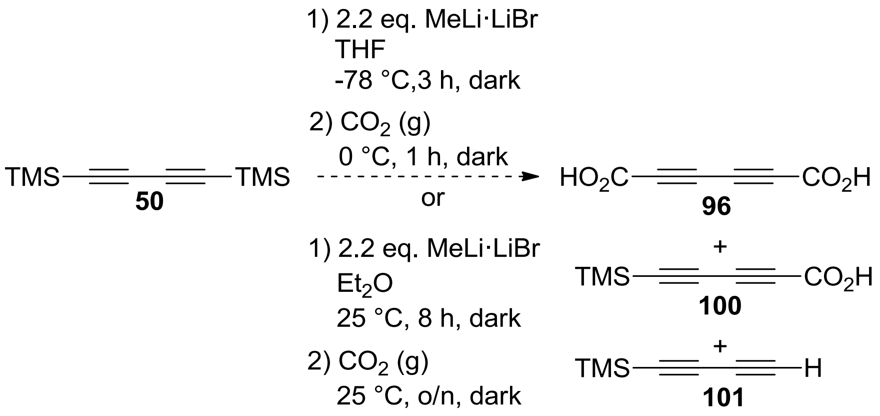
Scheme 3.6 Dunitz and Robertson's synthesis of diyne **96**.[42]

Dicarboxylic acid **96** has also been synthesized using homocoupling,[41-42,44] oxidation,[45-49] and cross-coupling conditions.[50] The most recently reported synthesis of diyne **96** is by Homsi and Rousseau in 1999, but experimental conditions are not given.[51] The instability of diynedioic acid **96** is suggested, as low yields[42] and a noticeable color change of this solid when kept cold and in the dark have been described.[47] Moreover, decomposition of the more stable diyne ester analog **98** from a clear to dark oil has been reported (Scheme 3.7).[52]



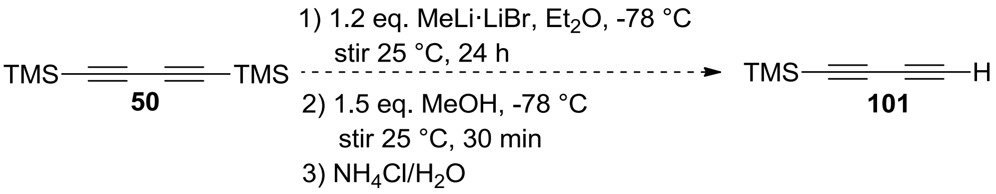
Scheme 3.7 Varela's synthesis of diyne **98**.[52]

Despite the possible inherent instability of compound **96**, a new route toward this diacid was developed (Scheme 3.8). Jones and co-workers described the conversion of the Grignard derivative of diacetylene gas to diyne **96** upon addition of CO_2 gas.[49] Additionally, the one-pot synthesis of phenyl-protected diynoic acid has been reported from the respective lithium acetylide followed by a carboxylation reaction *in situ*.[11] Therefore, deprotection and subsequent electrophilic addition of commercially available bis(trimethylsilyl) capped diyne **50** was studied as an alternative pathway toward dicarboxylic acid **96**.



Scheme 3.8 Alternative route toward diyne **96**.

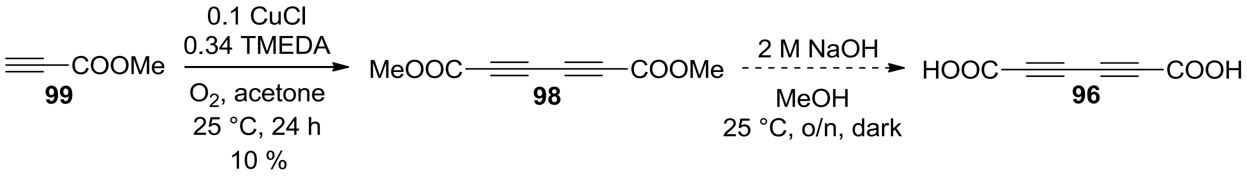
Diyne **50** was first stirred for 3 hours with MeLi•LiBr at -78 °C to allow enough time for the desilylation reaction to occur on both ends.[53] The reaction mixture was then subjected to electrophilic addition conditions, modeled after Tykwinski's route toward TIPS-protected diynoic acid **85** (Scheme 3.1).[11-12] Immediately after the addition of CO_2 gas, the solution turned from orange to black. After stirring the reaction mixture for 1 h at 0 °C, the FT-IR and NMR spectra both showed mostly precursor **50**.[54] The additional peaks in the ^{13}C NMR spectrum were difficult to interpret, although product formation was not indicated. Recovery of diyne **50** in high yield suggests that the MeLi•LiBr did not react with this compound. Alternatively, if water was present, diacetylene gas would therefore be formed *in situ* and volatilize before the carboxylation reaction was performed. However, the high yield of diyne **50** suggests otherwise. Despite increasing the reaction time and the temperature, diyne **96** was never detected by ^{13}C NMR spectroscopy, and instead, the spectrum indicated mostly precursor **50**. Additionally, trimethylsilyl capped diynoic acid **100** (suggested by the peaks reported for diyne **85**[11-12]), terminal diyne **101**, and inconclusive peaks in the alkyne (72-88 ppm) and TMS (-0.9-1 ppm) regions were observed. To determine if the pathway outlined in Scheme 3.8 is feasible, the synthesis of terminal diyne **101** was explored (Scheme 3.9) as described by former group member Lei Li.[55]



Scheme 3.9 Attempted route toward terminal diyne **101**.[55]

Although terminal diyne **101** has previously been prepared and isolated in this group,[55] difficulties were encountered when trying to repeat this synthesis. It appears that the volatility of diyne **101** significantly limits its isolation, as reported by Li.[55] Vacuum distillation resulted in a mixture of diynes **50** and **101**, while removal of solvent *in vacuo* at 0 °C afforded only starting diyne **50**. Compound **101**, as well as diacetylene, which is formed statistically, are removed under reduced pressure. In a separate experiment, solvent was allowed to evaporate at room temperature from a round-bottom flask that contained a crude mixture of products, but predominantly diyne **50** was detected by NMR spectroscopy. Even though experimental conditions for the isolation of terminal diyne **101** are found in the literature[56-58] the volatility of this diyne has been described.[9] Alternatively, deprotection of a silyl capped triyne and subsequent electrophilic addition *in situ* was reported by Rubin and co-workers.[53] Addition of CO_2 gas and MeLi•LiBr to a crude mixture of diynes **50** and **101** gave a complicated mixture of products, suggested by the complex ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum showed unreacted diynes **50** and **101**, along with unidentifiable peaks in the alkynyl (67-88 ppm) and TMS (-1.0 to -0.5 ppm) regions. A peak at 153.3 ppm was also observed, which probably corresponds to diyne **100**. The inability to form diyne **85** from the more stable TIPS-protected analog **75** (Scheme 3.1) and the high yield of diyne **50** recovered in the crude mixture, despite using a new bottle of MeLi•LiBr and dry solvents, indicates a new pathway toward diyne **96** is needed.

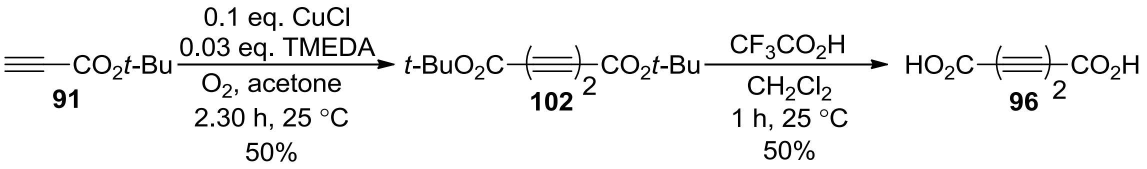
Further investigation of the protodesilylation reaction without using MeLi•LiBr was studied. Silver nitrate (5 mol %) was stirred with TMS-protected diyne **50**, based on the procedure reported by Orsini and co-workers.[59] After quenching the reaction mixture with aqueous ammonium chloride (NH_4Cl), diyne **50** was recovered in 61%. Deprotection of diyne **50** is predicted to occur statistically, and the ineffectiveness of this route is suggested. Therefore, preparation of diyne acid **96** from methyl ester **98** was attempted to avoid unstable terminal diyne intermediates (Scheme 3.10).



Scheme 3.10 Attempted route toward diyne **96**.[52,60]

Hay coupling of methyl propiolate (**99**) gave product **98** in low yield. Further, a significant amount of black insoluble material developed during formation of this diyne ester, despite attempts to keep the reaction mixture cold and in the dark. Subsequent ester cleavage of diyne **98** with 2 M NaOH provided ^{1}H and ^{13}C NMR spectra that were particularly complex, though there was no indication of precursor **98**. Multiple peaks in the ^{13}C NMR spectrum between 150-160 ppm are suggestive of alkynoic acid compounds. Likewise, the FT-IR spectrum contains OH, C≡C, and C=O stretches around 2853, 2170, and 1675 cm^{-1}, respectively.

Because the results described in this chapter indicate that decarboxylation is driven by basic conditions (Section 3.1.1), homocoupling of *tert*-butyl ester **91** and subsequent deprotection under acidic conditions was attempted to afford diacid **96**. Conditions for the homocoupling of methyl propiolate (**99**)[52] and for the *tert*-butyl ester cleavage of an alkynyl ester[31] have been reported, and a new synthetic pathway for diyne **96** was developed (Scheme 3.11). Ang has pursued this route, and successfully isolated diyne **96** in 25% yield over 2 steps. The carboxylic acid functionality appears to be relatively stable as an end-group, as diyne **96** has a melting point of 170 °C, about 100 °C higher than diiododiyne **9**. Furthermore, the white solid does not appear to change color in light as previously reported,[42,47] indicative of decomposition. Co-crystallization experiments with diynedioic acid **96** will be pursued by Ang.



Scheme 3.11 Synthesis of diyne **96**.

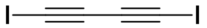
3.3 Summary

The synthesis of iodo-penta-2,4-diynoic acid (**82**) was attempted using several different approaches, as there are no previous reports of this diyne in the literature. Carboxylation of terminal diyne **75** to the corresponding acid **85** was not accomplished, but alternatively, the cross-coupling method described by Dikusar and co-workers was adapted to successfully obtain diyne precursor **85**. However, desilylation and subsequent iodination to yield desired diyne **82** proved challenging, as the halodecarboxylation reaction appeared to occur much more quickly, thus resulting in novel diyne **87**. The basicity of TBAF and AgF leads to decarboxylation of the alkynyl acid functional group. A successful route toward diyne **82** was developed after iodination of *tert*-butyl ester **92** and cleavage of diyne **93** using acidic conditions were discovered. Novel push-pull diyne **82** was used in a co-crystallization experiment with symmetric bis(pyridyl) host **11** in an effort to achieve ordered 1,4-topochemical polymerization. Unfortunately, no evidence of co-crystal formation was found for this experiment. Xiuzhu Ang will further study this system to determine the ideal co-crystallization conditions required to allow for an ordered polymerization of asymmetric monomer **82**.

Desilylation and subsequent carboxylation of TMS-protected diyne **50** did not afford 2,4-hexadiynedioic acid (**96**), but instead, mostly diyne precursor **50** was recovered. Desilylation of diyne **50** is predicted to occur statistically; however the volatility of both monodeprotected diyne **101** and fully deprotected diacetylene gas, which can form if water is in the flask, may limit the effectiveness of the subsequent carboxylation reaction. Moreover, diynedioic acid **96** was not obtained from methyl ester diyne **98**, probably because basic conditions drive the decarboxylation of alkynyl acids. Exploring ester cleavage reactions using acidic conditions allowed for the development of a pathway toward diynedioic acid **96**. Isolation of diyne **96** was performed by Ang, and she will additionally employ this symmetric diyne monomer in co-crystallization experiments with symmetric oxalamide hosts in an attempt to achieve an ordered 1,4-topochemical polymerization.

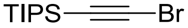
3.4 Experimental

General Methods: Reagents were purchased reagent grade from Aldrich, Fisher Scientific/ Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. Tetrahydrofuran (THF) was distilled under argon gas from sodium/benzophenone. Copper iodide and copper chloride were purified by recrystallization. All reactions were performed under an inert argon (Ar) atmosphere, unless stated otherwise. All iodination and coupling reactions were performed at 0 ºC and in the dark to prevent decomposition, unless noted otherwise. $MgSO_4$ was used as the drying agent after aqueous work-ups. Column chromatography: Alumina (50-200 mesh) from Acros Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. . ^{1}H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, Inova-500 MHz, Bruker-400 MHz, or Bruker-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise. EI-Mass spectra were measured in the Stony Brook Mass Spectrometry Facility, located in the Chemistry Building.



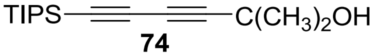
9

1,4-Diiodo-1,3-butadiyne (9).[40] Commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne (**50**, 0.526 g, 2.7 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.925 g, 5.5 mmol) and *N*-iodosuccinimide (3.05 g, 13.5 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 4 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **9** as a yellow solid that decomposes at 90 °C (0.753 g, 2.5 mmol, 92% yield). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 79.7, -3.3.[40]



73

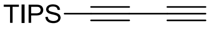
1-Bromo-2-(triisopropylsilyl)acetylene (73).[10] Commercially available triisopropylsilyl acetylene (**51**, 4.04 g, 22.2 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.380 g, 2.24 mmol) and recrystallized *N*-bromosuccinimide (4.34 g, 24.3 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 2 h. Ice water (100 mL) and hexanes (100 mL) were added, and the aqueous layer was extracted with hexanes (3 x 100 mL). The combined organic layers were washed with water (1 x 50 mL) and sat. aq. $Na_2S_2O_3$ (1 x 50 mL). The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **73** as a yellow oil (5.59 g, 21.4 mmol, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.08 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 83.5, 62.0, 18.5, 11.3.[10]



74

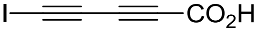
2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol(74).[9] *n*-Butylamine (2.31mL, 23.3 mmol), 2-methylbut-3-yn-2-ol (**62**, 1.51 mL, 15.5 mmol), copper chloride (15.2 mg, 0.154 mmol, 2 mol%), and hydroxylamine hydrochloride (163 mg, 2.34 mmol) were added in order to a solution of 2:1 methanol:water (45 mL). 1-Bromo-2-(triisopropylsilyl)acetylene (**73**, 2.03 g, 7.79 mmol) was dissolved in 20 mL methanol, and added dropwise under argon via cannula to the catalyst mixture over 30 min. The resulting mixture was left stirring at room temperature for 24 h under argon in the dark. The solution was then diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with water (1 x 50 mL) and brine (2 x 50 mL). The resulting solution was dried over $MgSO_4$ and filtered. Solvent was removed *in vacuo*, resulting in 1.81 g of a crude mixture as a yellow oil. Purification using a short plug

(SiO_2/ 9:1 hexanes: EtOAc), followed by recrystallization with pentane, resulted in the isolation of **74** as a white solid (1.63 g, 6.16 mmol, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.61 (s, 1H), 1.52 (s, 6H), 1.06 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.0, 84.6, 80.7, 67.6, 65.5, 31.0, 18.5, and 11.2.[9]



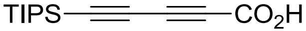
75

Triisopropylsilylbuta-1,3-diyne (75).[10] 2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (**74**, 1.59 g, 6.01 mmol) was added to a solution of crushed potassium hydroxide (0.676 g, 12.0 mmol) in 45 mL anhydrous toluene, and the resulting solution was heated to 110 °C for 2 h under argon gas. The solution was then cooled and the solids were removed by filtration through a pad of Celite. After concentration, the product was purified using a short plug (SiO_2/hexanes), which resulted in **75** as an orange oil (0.781 g, 3.78 mmol, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.06 (s, 1H), 1.09 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.1, 81.9, 68.6, 65.5, 18.5, and 11.2.[10]



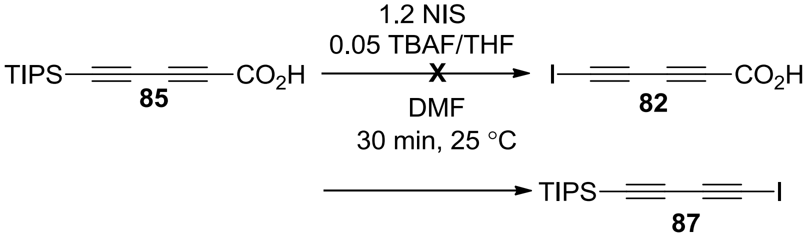
82

5-Iodo-penta-2,4-diynoic acid (82). *tert*-Butyl-5-iodopropiolate (**93**, 47.1 mg, 0.171 mmol) was dissolved in dichloromethane (1 mL) in a round-bottom flask wrapped with aluminum foil. Trifluoroacetic acid (194 mg, 1.70 mmol, 0.13 mL) was added and the reaction mixture was allowed to stir at room temperature in the dark for 2 h. Removal of solvent in vacuo resulted in 39.1 mg of an orange solid. The compound was purified by column chromatography (SiO_2), using a solvent gradient starting with 19:1 hexanes: EtOAc and progressing to 100% EtOAc and finally to MeOH. No UV active product was observed until MeOH was used. Compound **82** was formed as a white solid film that becomes light orange when exposed to light and decomposes at 98-99 °C (52.1 mg, 0.237 mmol, 139%). ^{13}C NMR (100 MHz, MeOD, 25 °C): δ 159.5, 77.6, 70.4, 66.1, and 10.2; IR (neat) 3342 (br), 2198 (m), 1568 (s), 1352 (s) cm^{-1}; EIMS *m/z* 126.9 ($[M - I]^+$, 90). Additionally, peaks at *m/z* 254 ($[I_2]^+$, 100), 302 ($[C_4I_2]^+$, 90), and 350 ($[C_8I_2]^+$, 80) indicate the presence of oligomers. These compounds are not noticed using NMR spectroscopy, and will be further explored.

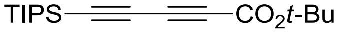


85

5-Triisopropylsilyl butadiynoic acid (85). 1-Bromo-2-(triisopropylsilyl)acetylene (**73**, 156 mg, 0.598 mmol) dissolved in 2 mL methanol was added dropwise under argon over 15 min. to a solution of propiolic acid (**86**, 0.045 mL, 0.728 mmol), 5 mL methanol, 2-aminoethanol (0.32 mL, 5.30 mmol), 1 mL water, hydroxylamine hydrochloride (63.4 mg, 0.912 mmol), and copper chloride (6.26 mg, 0.063 mmol, 10 mol%). This mixture was then allowed to stir for 24 h at 25 °C under argon in the dark. Hexanes (10 mL) was added, and the hexanes extracts were rejected. 10 % HCl (25 mL) was added, and the aqueous layer was extracted with hexanes (3 x 25 mL). The combined organic layers were washed once with water (25 mL). The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in the formation of **85** as a pale yellow oil (109 mg, 0.433 mmol, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.57 (s, 1H), 1.09-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 157.0, 94.3, 87.0, 73.8, 65.0, 18.4, and 11.1.[12]

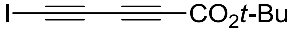


1-Iodo-4-(triisopropylsilyl)buta-1,3-diyne (87). 5-Triisopropylsilyl butadiynoic acid (**85**, 134 mg, 0.535 mmol) was dissolved in 10 mL dry DMF in a round-bottom flask wrapped with aluminum foil. *N*-iodosuccinimide (145 mg, 0.644 mmol) and TBAF/THF (1M, 0.027 mL, 0.027 mmol) were added, and the reaction mixture was allowed to stir at room temperature in the dark for 30 min. The mixture was then quenched with sat. aq. NH_4Cl (20 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine (1 x 30 mL), H_2O (4 x 30 mL), and sat. aq. $Na_2S_2O_3$ (1 x 30 mL). The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.056 g of a crude mixture as a yellow oil and solid. Purification by column chromatography (SiO_2/ hexanes) afforded **87** as a colorless solid with an oil like consistency (0.047 g, 0.14 mmol, 26%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ1.08 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 90.4, 80.5, 79.3, 18.5, 11.2, and -2.5; IR (in $CHCl_3$, cast KBr) 2958 (s), 2926 (s), 2874 (s), 1463 (w), 1379 (m) cm^{-1}; EIMS *m/z* 288.8 ([M – *i*-Pr]$^+$, 60), 260.8 ([M – Si(*i*-Pr)]$^+$, 40), 246.8 ([M – (*i*-Pr)$_2$]$^+$, 30), 232.8 ([M – Si(*i*-Pr)CC]$^+$,60), 218.7 ([M – Si(*i*-Pr)$_2$]$^+$, 100).



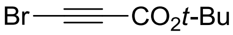
92

***tert*-Butyl-5-(triisopropylsilyl)propiolate (92).** 5-Triisopropylsilyl butadiynoic acid (**85**, 133 mg, 0.530 mmol) was dissolved in dichloromethane (10 mL) in a round-bottom flask. *tert*-Butyl acetate (619 mg, 5.32 mmol, 0.72 mL) and trifluoromethanesulfonic acid (1 drop) were added, and the reaction mixture was allowed to stir at room temperature for 1 h. The mixture was then quenched with 2M KOH (10 mL) and extracted with diethyl ether (3 x 40 mL). The combined organic layers were washed with water (40 mL). The resulting solution was dried over $MgSO_4$ and filtered to give an orange oil. After concentration, the product was purified using a short plug (SiO_2/hexanes), which resulted in **92** as a colorless oil (0.093g, 0.303 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.47 (s, 9H), 1.07-1.06 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 151.5, 91.3, 87.6, 84.2, 69.0, 67.1, 27.9, 18.4, and 11.1; IR (in $CHCl_3$, cast KBr) 2946 (s), 2868 (s), 2203 (m), 2101 (m), 1708 (s), 1289 (s), 1112 (s) cm^{-1}; EIMS *m/z* 263.3 ([M – *i*-Pr]$^+$, 100).



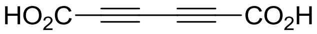
93

tert-Butyl-5-iodopropiolate (93). *tert*-Butyl-5-(triisopropylsilyl)propiolate (**92**, 0.093 g, 0.303 mmol) was dissolved in acetonitrile (50 mL) in a round-bottom flask wrapped with aluminum foil. *N*-iodosuccinimide (239 mg, 1.06 mmol) and AgF (135 mg, 1.07 mmol) were added, and the reaction mixture was allowed to stir at 0 °C in the dark for 1 h. The aqueous layer was then extracted with 2:1 hexanes: diethyl ether (3 x 75 mL). The combined organic layers were washed with water (1 x 50 mL) and sat. aq. $Na_2S_2O_3$ (1 x 50 mL). The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.103 g of a crude mixture as a yellow oil. Purification by column chromatography (SiO_2/ 19:1 hexanes: ethyl acetate) afforded **93** as a yellow solid (0.057 g, 0.206 mmol, 70%). Mp 109 °C. ^{1}H NMR (400 MHz, MeOD, 25 °C): δ1.48 (s); ^{13}C NMR (100 MHz, MeOD, 25 °C): δ 152.6, 85.7, 76.5, 69.8, 65.2, 28.3, 16.5; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ1.48 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 151.1, 84.6, 77.0, 69.0, 65.0, 27.9, 7.7; IR (neat) 2981 (w), 2932 (w), 2201 (m), 1667 (s), 1308 (s), 1114 (s) cm^{-1}; EIMS *m/z* 276.1 ([M]$^+$, 10), 220 ([M – *t*-Bu]$^+$, 25), 203 ([M – O*t*-Bu]$^+$, 100),175 ([M – CO_2*t*-Bu]$^+$, 15).



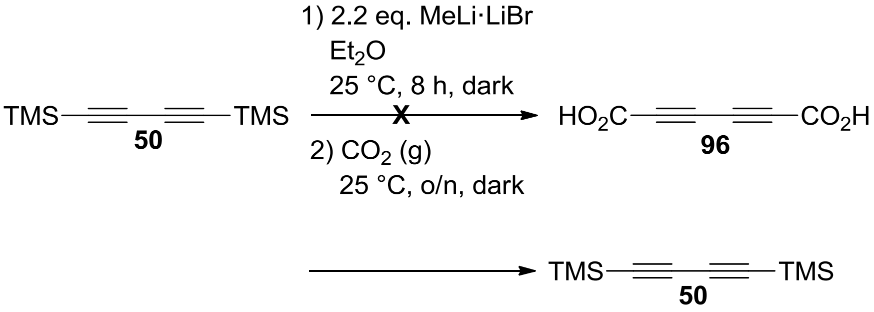
94

***tert*-Butyl 3-bromopropiolate (94)**.[37] Commercially available *tert*-butyl propiolate (**91**, 0.158 g, 1.25 mmol) was dissolved in acetone (50 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.022 g, 0.127 mmol) and recrystallized *N*-bromosuccinimide (0.244 g, 1.37 mmol) were added, and the reaction mixture was allowed to stir in the dark at room temperature for 2 h. Ice water (30 mL) and diethyl ether (30 mL) were added, and the aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$ and filtered to give a colorless oil and a white solid that crashed out at -10 °C. The oil was then decanted, washed with water, and dried over $MgSO_4$. Filtration and removal of solvent resulted in **94** as a yellow oil (0.101 g, 0.493 mmol, 39 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.48 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 151.4, 84.1, 74.0, 50.0, 27.9.[37]

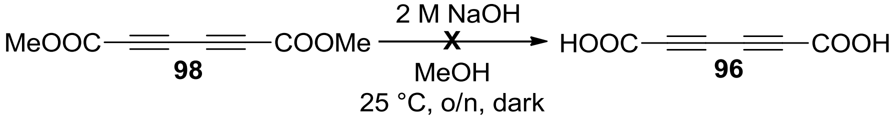


96

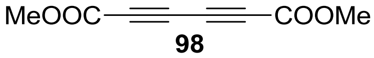
2,4-Hexadiynedioic acid (96).



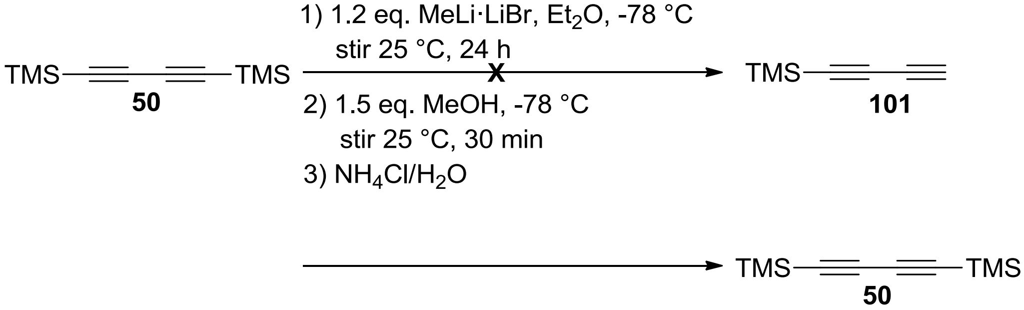
Procedure A. Commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne (**50**, 0.404 g, 2.08 mmol) was dissolved in 12 mL dry diethyl ether in a round-bottom flask wrapped with aluminum foil. The solution was cooled to -78 °C and MeLi•LiBr (2.2M/ Et_2O, 2.08 mL, 4.58 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred for 8 hours. CO_2 (g) was bubbled through the solution via a syringe needle over-night. 10% HCl (20 mL), ice water (20 mL), and Et_2O (30 mL) were added, and the aqueous layer was extracted with 3 x 30 mL of Et_2O. The combined organic layers were washed with 2 x 10 mL of 10 % HCl. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in a complex mixture that was mostly unreacted diyne **50**. Additionally, trimethylsilyl capped diynoic acid **100**, terminal diyne **101**, and peaks in the alkyne (72-88 ppm) and TMS (-0.9-1 ppm) regions were observed. The NMR and FT-IR spectra were difficult to interpret.



Procedure B. Dimethyl 2,4-hexadiyndioate (**98**, 0.096 g, 0.578 mmol) was dissolved in 25 mL methanol, and 5 mL of 2M NaOH was added. The reaction mixture was stirred at room temperature over-night in the dark. Solvent was removed, and the residue was dissolved in 25 mL water and washed with diethyl ether (2 x 50 mL). 1 M HCl (50 mL) was added to the aqueous layer, and this layer was then extracted with 2 x 100 mL diethyl ether. The organic layer was dried over $MgSO_4$. Filtration and removal of solvent resulted in crude material that was a brown and an orange solid. The ^1H NMR and ^{13}C NMR spectra were complex, but the FT-IR spectrum suggested product formation.



Dimethyl 2,4-hexadiyndioate (98).[52] CuCl (0.120 g, 1.20 mmol) was dissolved in 4 mL acetone, and TMEDA (0.06 mL, 0.40 mmol) was added. Oxygen was bubbled through the solution for 2 h, and the catalyst mixture turned dark green. A solution of methyl propiolate (**99**, 1.1 mL, 12 mmol) in 7 mL acetone was added, and oxygen was bubbled through the reaction mixture for an additional 5 h. The reaction was allowed to stir under oxygen over-night. Solvent was removed *in vacuo*, and 25 mL of diethyl ether was added. The organic layer was washed with 2 x 25 mL of 5% HCl, and dried over $MgSO_4$. Filtration and removal of solvent resulted in the formation of **98** as a brown oil (0.096 g, 0.578 mmol, 10% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.81 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.0, 72.2, 67.9, 53.4.[52]



Trimethylsilylbuta-1,3-diyne (101).[55] 1,4-Bis(trimethylsilyl)-1,3-butadiyne (**50**, 1.00 g, 5.17 mmol) and 30 mL of anhydrous diethyl ether were added to a flask purged with argon gas for 5 min. The mixture was cooled to -78 °C and MeLi•LiBr (2.2 M/ Et_2O, 2.8 mL, 6.16 mmol) was added dropwise. The solution was then allowed to warm up slowly to room temperature and stirred for 24 h under argon atmosphere in the dark. Methanol (0.31 mL, 7.65 mmol) was added to the orange solution at -78 °C and the reaction mixture was stirred at room temperature for another 30 min. The mixture was poured into 30 mL of sat. aq. NH_4Cl and the aqueous phase was extracted with pentane (3 x 50 mL). The combined organic layer was washed with 50 mL of water, dried over $MgSO_4$, and filtered. The product was further purified by vacuum distillation under reduced pressure at room temperature to give mostly precursor **50** along with small amounts of product **101** as observed by ^1H and ^{13}C NMR. Removal of solvent in vacuo at 0 °C afforded only diyne **50**.

General Method for Preparing 82•11 Co-Crystals. 5-iodo-penta-2,4-diynoic acid **82** was synthesized according to the procedure described above and used within 24 h of preparation. Host **11** was prepared by former group member Lei Li according to literature procedures.[61] To a 0.05 M solution of guest in MeOH (2 mL) was added 0.5 equivalents of host (2:1 guest to host ratio), and the solution was sonicated briefly to prevent monomer aggregation. The resulting solution was subjected to centrifugation for 10 min to remove any undissolved particles. The supernatant layer was decanted into a 50 mL crystallization dish, which was covered with aluminum foil. The foil was punctured 12-15 times using a needle. Solvent was allowed to evaporate slowly at room temperature to afford crystals. A brown film with a black solid was afforded.

3.5 References

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Chapter 4: Topochemical Polymerization of Diiodooctatetrayne

Polymerization of tetraynes in the solid state has previously been explored, as outlined in Section 1.6.[1-3] In our group, the topochemical polymerization of diiodooctatetrayne (**17**) was pursued by applying a host-guest strategy that aligns the monomers in the proper orientation for controlled polymerization via halogen bonding interactions, analogous to the preparation of poly(diiododiacetylene) (PIDA).[4] Formation of PIDA was successful with bis(pyridyl) oxalamide hosts[5-7] and bis(nitrile) oxalamide hosts.[8-9] Therefore, these hosts were used in the co-crystallization experiments with tetrayne **17**.

4.1 Co-crystallization Experiments and Results with Bis(pyridyl) Oxalamide Hosts

Hosts **10** [N, N’-bis(3-pyridylmethyl) oxalamide], **11** [N, N’-bis(4-pyridylmethyl) oxalamide], and **12** [N, N’-bis(3-pyridylethyl) oxalamide] were employed to form co-crystals with guest tetrayne **17** (Figure 4.1). The halogen bonding interaction between the Lewis acidic iodine atom in the guest and the Lewis basic pyridyl nitrogen in host should be stronger than the halogen bonding interaction between monomer **17** and the Lewis basic nitrile hosts.[5] Therefore, the stronger interaction with bis(pyridyl) oxalamide hosts may be conducive to co-crystal formation as monomer **17** is more unstable than previously polymerized diiodobutadiyne (**9**).

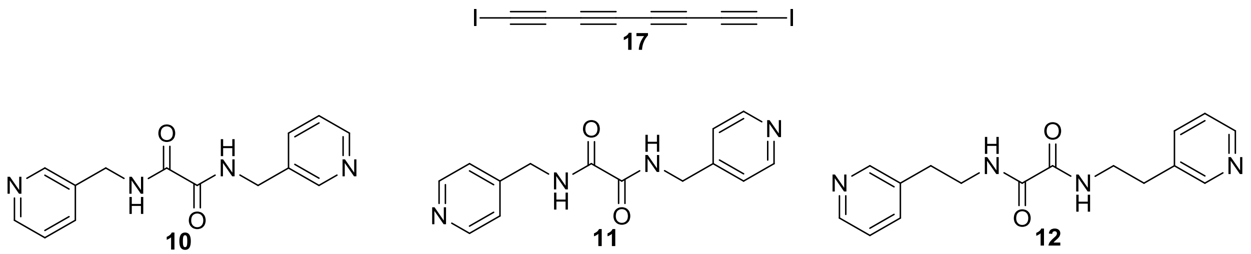


Figure 4.1 Guest **17** and bis(pyridyl) oxalamide hosts **10**, **11**, and **12**.

The diiodotetrayne co-crystals were prepared in a similar fashion to the methods that were described in Chapter 3. The **17•10** co-crystal can be grown in a 1:1 ratio of host to guest at 0 °C, 4 °C, or -20 °C in methanol, and in each case, green crystals initially appear. When heated to near 100 °C, these crystals turn black and do not melt. This result indicates co-crystal formation, as tetrayne **17** explodes at 85 °C.[10] The **17•11** and **17•12** co-crystals have been grown at 4 °C. Lower temperatures were used than with diiodobutadiyne **9** to prevent decomposition of monomer **17**. Additionally, tetrayne **17** is less stable than diyne **9**, and so greater care is taken when preparing co-crystals with this guest. At room temperature, **17•10** co-crystal turns from green to blue and after an extended period of time, the material turns dark and gradually loses crystallinity, which may be indicative of a polymerization reaction (Figure 4.2).

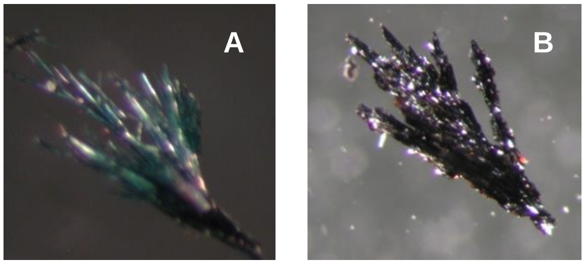


Figure 4.2 Optical microscope images of **17•10** co-crystals obtained by former group member Liang Luo. A: The co-crystals after 1 min. at room temperature; B: The co-crystals in A after 1 week at room temperature.

Conversely, **17•12** co-crystals are comprised of two different crystal morphologies (Figure 4.3), suggested by development of reddish yellow and blue crystals from the same experiment. Both types of crystals turn dark quickly at room temperature and lose crystallinity.

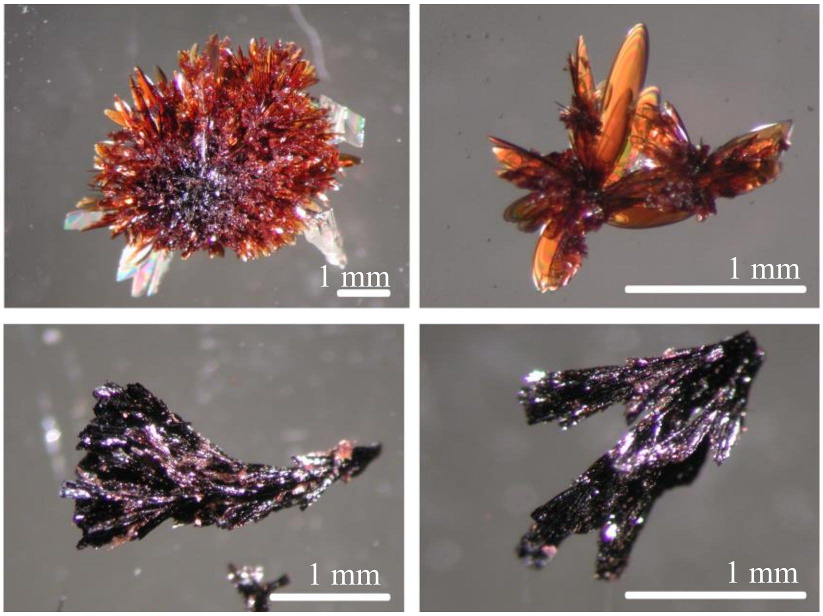


Figure 4.3 Optical microscope images of **17•12** co-crystals obtained by Luo. The top two pictures show co-crystals with a reddish yellow color, while the bottom two pictures display co-crystals with a dark blue appearance.

The unique crystal colors have precedent, since previous group member Christopher Wilhelm and current group member Margarita Milton have each discovered a different PIDA crystal morphology with diiodobutadiyne (**9**) and host **12**, confirmed by single-crystal XRD (X-ray diffraction). Wilhelm reported a monoclinic structure of coppery colored crystals in a 1:1.5 ratio of host to guest,[6] while Milton observed a triclinic structure of reddish purple crystals in a 1:1 ratio of host to guest. Furthermore, the red and blue phases of co-crystal **17•12** may indicate a twisted or planar polydiacetylene (PDA) backbone, respectively.[11] This color change has been observed in other systems (Section 1.1), caused by the steric interactions and packing effects on the side chains.[5] Although **17•12** co-crystal was never characterized by XRD, it is likely that multiple polymerizations occurred and consequently, the different crystal colors are instead due to different polymorphs.[12-13]

. The scanning electron microscope (SEM) images of the blue **17•12** co-crystals (obtained by Jim Quinn of the Material Sciences department at Stony Brook University) suggest good electron transport at the surface of the material. A conductive surface is indicated, as these images were produced without coating the sample with gold. The accelerating voltage used for this experiment was 20 kV, which allows for increased resolution on the surface (Figure 4.4).[14] Additional characterization must be performed to gain further insight regarding the polymerization process of guest **17** with host **12**.

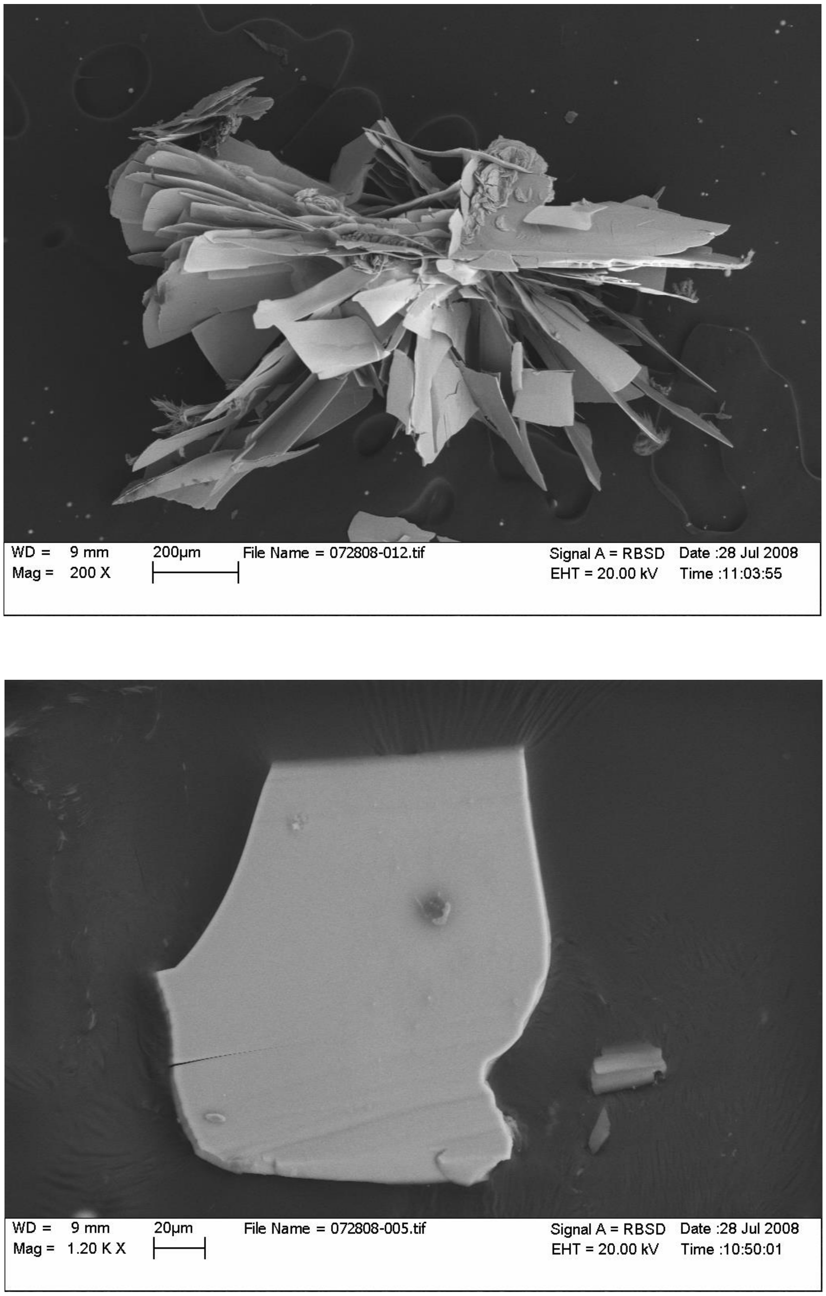


Figure 4.4 SEM images of the **17•12** blue co-crystals.

Former group member Liang Luo solved the crystal structure for both **17•10** and **17•11** co-crystals.[14] The repeat distance (r) of monomer **17** in the **17•11** co-crystal is 4.98 Å, which is favorable for a 1,4-polymerization. This result is expected as the translational distance that results from the self-complementary hydrogen bond network created by the oxalamide functionalities is 5.1 Å.[15] However, the tilt angle (θ) is 60° and the C1-C4 contact distance ($d_{1,4}$) is 4.30 Å, making the desired polymerization difficult to continue (Figure 4.5). A large θ is also seen with **9•10** and **9•11** co-crystals, perhaps owing to the steric bulk in the side groups of the bis(pyridyl) hosts.[16] Pressures as high as 10 GPa were required for the successful single-crystal transformation of diiodobutadiyne (**9**).[5-7] The bulkiness of host **11** may lead to a spatial mismatch with the rod-shaped tetrayne, resulting in curvature of monomer **17** as well as a large tilt angle.

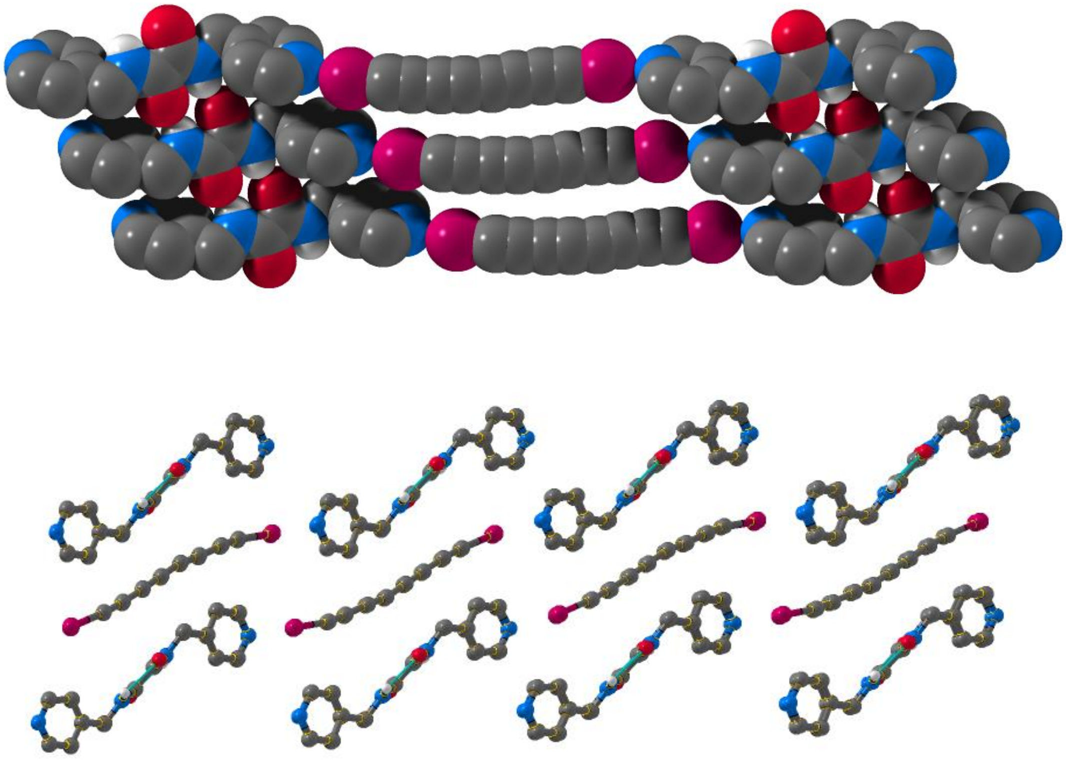


Figure 4.5 Crystal structure of a **17•11** co-crystal immediately after solvent evaporation. Unit cell parameters: Space group: P -1; Unit cell dimensions: a = 4.9867(18) Å, b = 9.624(4) Å, c = 24.076(10) Å; α = 83.165(8)°, β = 89.947(9)°, γ = 80.875(10)°, Volume = 1132.54 Å^3. Top: side view; Bottom: top view.

The geometry parameters for the **17•10** co-crystal, on the other hand, are near the ideal values for a 1,4- or 3,6-polymerization of monomer **17**.[1] The more favorable spatial arrangement may due to an increase in conformational flexibility resulting from nitrogen in the meta position in the pyridine ring[17] when forming halogen bond interactions between the host and guest compound. The repeat distance of tetrayne **17** is 5.02 Å, the C1-C4 distance is 3.71 Å, the C3-C6 distance is 3.63 Å, and the tilt angle is 47°. It is evident from Figure 4.6 that host **10** is highly disordered, with two different orientations within **17•10** co-crystal. One possible explanation is that host **10** is stacked in two different directions throughout the co-crystal, and their positions have been averaged by the diffraction scattering of the X-ray beams.

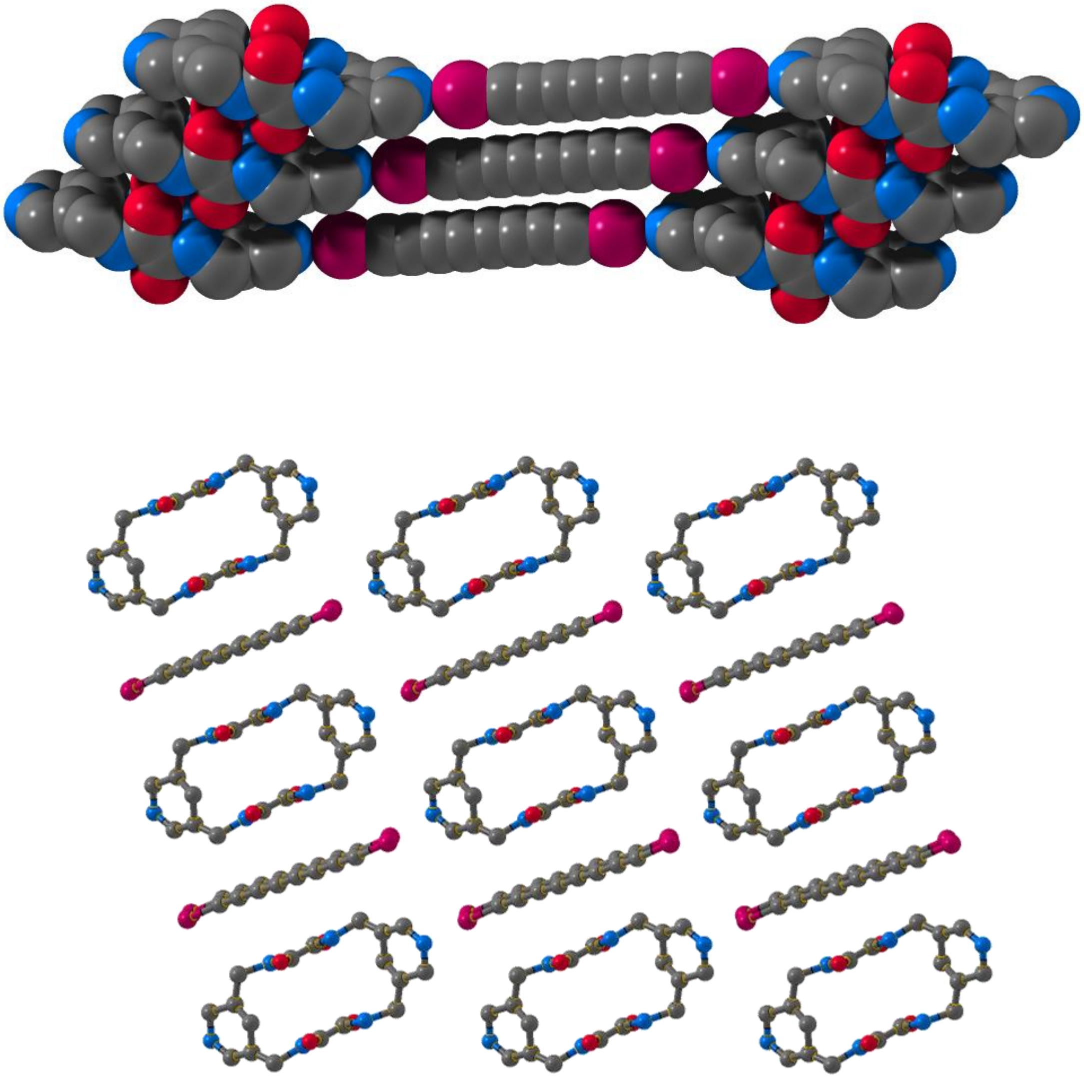


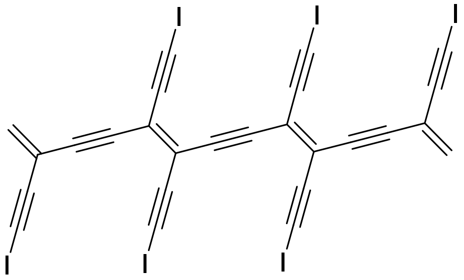
Figure 4.6 Crystal structure of a **17•10** co-crystal immediately after solvent evaporation. Host **10** appears to be disordered within the crystal. Unit cell parameters: Space group: P -1; Unit cell dimensions: a = 5.0134(14) Å, b = 10.514(3) Å, c = 12.549(3) Å; α = 74.880(5)°, β = 81.217(5)°, γ = 83.558(4)°, Volume = 629.264 Å^3. Top: side view; Bottom: top view.

A **17•10** co-crystal was kept at room temperature for 20 days, and the repeat distance (*r*) of the monomers continued to decrease, as monitored by XRD. The change in *r* indicates reaction between the monomers as this value becomes closer to the ideal repeat distance (4.9 Å) required for a 1,4-polymerization (Table 4.1).

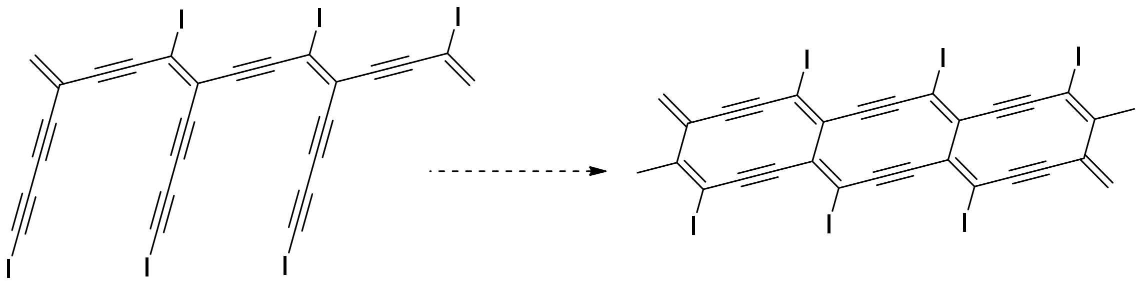
Table 4.1 Unit cell dimensions for the **17•10** co-crystals.

Time (day)	a (Å)	b (Å)	c (Å)	α (^{o})	β (^{o})	γ (^{o})	V (Å^3)
0	5.019	10.529	12.557	74.871	81.26	83.59	631.28
4	4.988	10.510	12.611	74.85	80.98	83.86	628.65
6	4.971	10.482	12.619	74.84	80.95	83.98	625.41
7	4.964	10.474	12.626	74.81	80.89	84.10	624.30
8	4.959	10.485	12.683	74.80	80.86	84.16	626.98
12	4.855	10.465	12.748	74.35	80.90	85.16	609.93
20	4.807	10.344	12.794	74.11	80.66	85.80	603.47

Even though the sample retained crystallinity over time, the crystal structure slowly became disordered, suggesting monomer **17** underwent several polymerization modes simultaneously. From the structural information obtained and the tetrayne polymerization pathways described in the literature (Section 1.6), Luo suggested that the co-crystals contained monomer **17** with a mix of partial 1,4- and 3,6-polymerization products (Figure 4.7).[14] The 3,6-polymerization product results from the interaction between the two middle triple bonds of adjacent monomers, while the 1,4-polymerization product is formed from the interaction between the triple bond adjacent to the iodine atom of one monomer and the middle triple bond (closest to the same iodine atom) of the neighboring monomer. Additionally, a laddered PDA polymer may form from a 1,4-polymerization and a subsequent 5,8-polymerization of the resulting diacetylene side chains.



3,6-polymerization product



1,4-polymerization product **1,4- and 5,8-polymerization product**

Figure 4.7 Intermediate PDA structures of decomposed **17•10** co-crystals deduced from one set of XRD results.

The Raman spectrum (obtained by Christopher Young of Gary Halada's group in the Material Sciences Department) of polymerized **17•10** co-crystal, collected at 785 nm, resembles the expected spectrum of a PDA backbone[9] with peaks around 1000 cm^{-1}[ν(C-C)], 1500 cm^{-1}[ν(C=C)], and 2000 cm^{-1}[ν(C≡C)] (Figure 4.8a). The multiple peaks in the double-bond stretching region [ν(C=C)] near 1500 cm^{-1} may suggest that several polymerization modes proceed at the same time within the co-crystal. Another possible explanation for the multiple peaks might be due to different degrees of polymerization or oligomerization, although there are no calculations to support these theories currently. The same co-crystal under irradiation at 532 nm resembles the spectrum for commercial graphite, indicating the potential conversion of polyynes to graphitic ribbons or fragments under the Raman laser (Figure 4.8b). The formation of graphitic materials is further supported by the shiny appearance of the decomposed co-crystals and a conductive surface suggested by the SEM results. Irradiating this sample again at 785 nm does not revert the Raman signal to the previously observed spectrum, suggesting that the 532 nm laser irradiation induces an irreversible structural transformation in the co-crystal to sp^2-hybridized carbon structures.[14] A different sample of **17•10** co-crystals were allowed to sit out at room temperature for one month, and when compared to the spectrum of the co-crystals taken immediately after solvent evaporation under a 785-nm laser beam, the peaks appear similar but the intensity is lower and the electroluminescence is greater (Figure 4.8c). Heating a freshly prepared sample of **17•10** co-crystals for 3 days at 40 °C immediately after solvent evaporation gave a spectrum which contained no vibrational peaks.

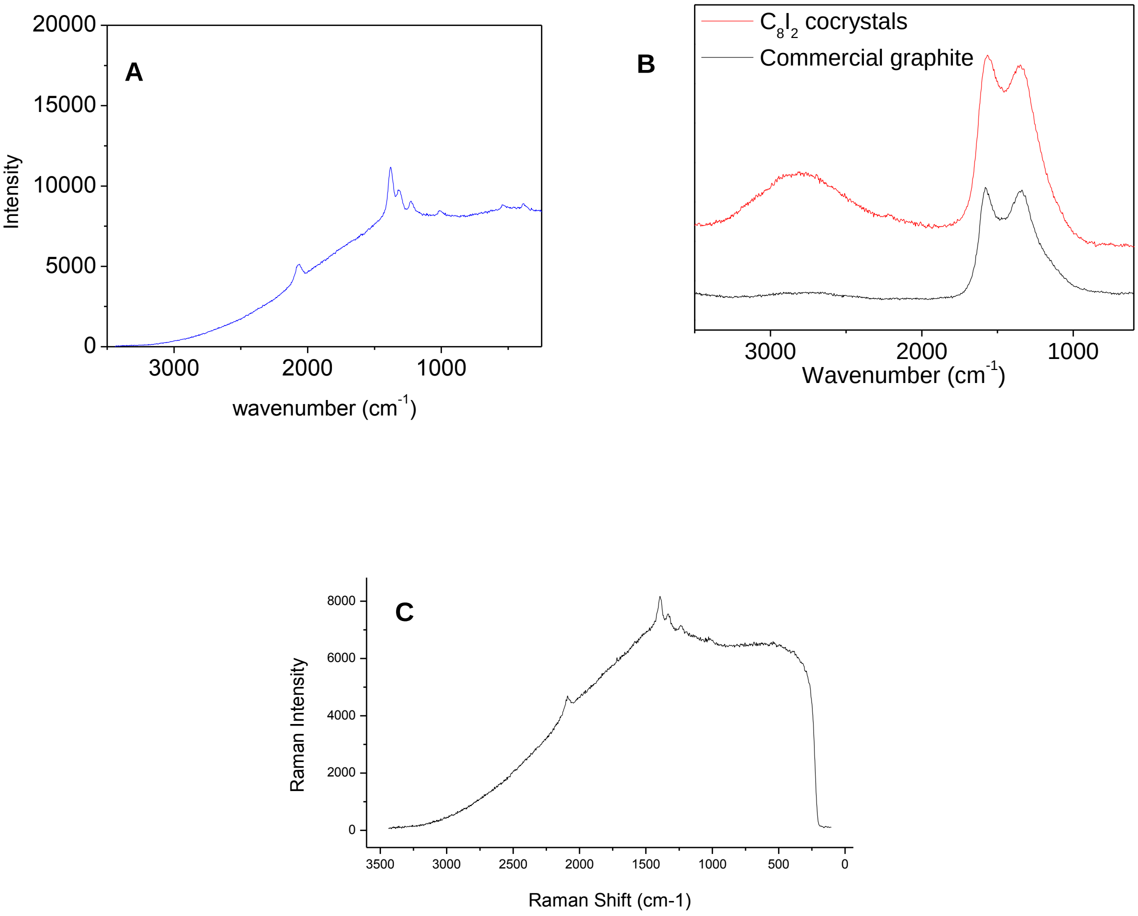
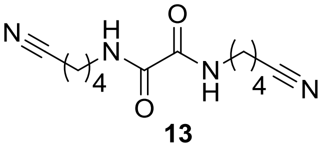


Figure 4.8 Raman spectra of **17•10** co-crystals. A:785 nm laser, 10% power; B: 532 nm laser, 10% power;[14] C: 785 nm laser, 10% power 1 month after solvent evaporation.

4.2 Co-crystallization Experiments and Results with Bis(nitrile) Oxalamide Hosts

Nitrile hosts **13** [*N,N'*-(bispentanenitrile) oxalamide] and **14** [*N,N'*-(bisheptanenitrile) oxalamide] were also used in the host-guest scaffold with tetrayne **17** to add flexibility and decrease steric bulk of the side groups (Figure 4.9).



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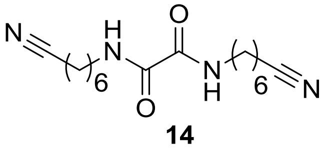


14

Figure 4.9 Bis(nitrile) oxalamide hosts **13** and **14**.

According to the optimized conditions determined by current group member Daniel Resch when studying the crystallization of diiodobutadiyne **9**, **17•13** and **17•14** co-crystals were grown in acetonitrile. Furthermore, a 1:2 ratio of host to guest was used to account for any guest that may decompose during solvent evaporation, and to incorporate the odd-even effect that has been observed with polymerization of monomer **9** and nitrile hosts.[9] Luo had found that the alkyl chain length between the oxalamide and nitrile functionality in the host affects the topochemical polymerization of diiodobutadiyne (**9**). A 1:2 host to guest stoichiometry was observed for the nitrile hosts with an even number of methylene units (4 or 6) whereas hosts with an odd number of methylene units (3 or 5) formed co-crystals in a 1:1 ratio. Monomer **9** spontaneously polymerizes at room temperature only with the nitrile hosts that contained an even number of methylene units.[9]

The **17•13** and **17•14** co-crystals were grown at 0 °C to prevent decomposition of the monomer. Once crystals began to form, the dish was moved to room temperature. These co-crystals were green and needle-like upon solvent evaporation; however, under polarized light from the microscope, the crystals appear iridescent (Figure 4.10). The highly reflective crystals are expected for a low band-gap material. Since the **17•14** co-crystals were produced in a higher yield and showed better crystal quality than the **17•13** co-crystals, host **13** has not been pursued further. However, growing the crystals at lower temperatures should be tried with nitrile host **13** to prevent decomposition of monomer **17** and to potentially increase the yield and quality of the **17•13** co-crystals. After a few days at room temperature, the **17•14** co-crystals turn from green to purple, and a bend in the crystal develops (Figure 4.10). When left at room temperature for one month, these crystals show considerable bending, but do not appear to lose crystallinity or their shiny appearance.

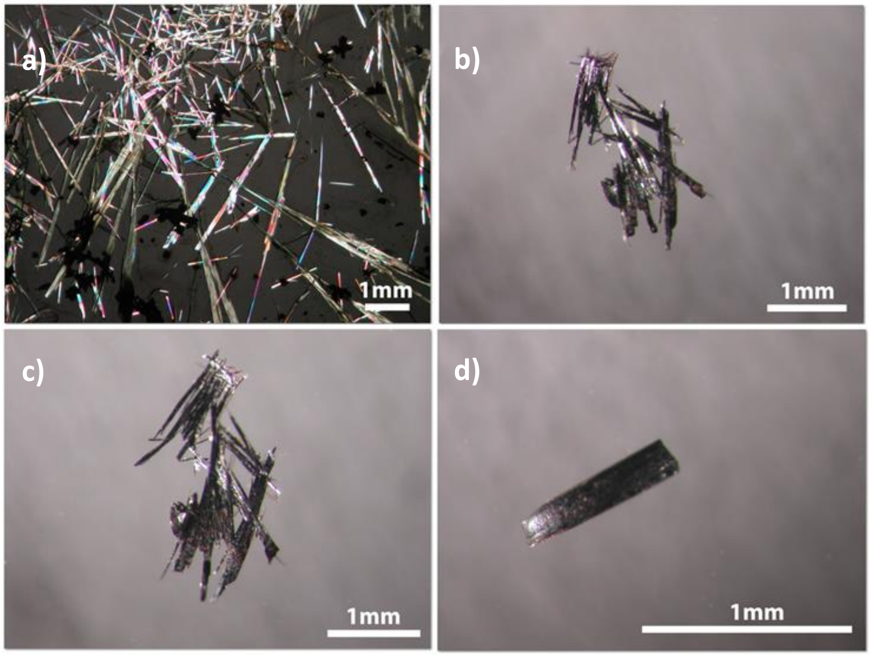


Figure 4.10 Optical microscope images of **17•14** co-crystals. A: The co-crystals after 1 day at room temperature; B: The co-crystals after 4 days at room temperature; C: The co-crystals after 14 days at room temperature; D: The co-crystals after 14 days at room temperature followed by 3 days at 40 °C.

XRD was used to obtain the crystal structure of the green **17•14** co-crystals prior to polymerization, and the structure was solved by Resch (see Appendix for complete crystal data and structure refinement). The crystal structure shows that monomer **17** forms ordered co-crystals with host **14** and acetonitrile in a stoichiometry of 2: 1: 1, respectively, via halogen bonding. This structure is the first co-crystal to be solved in this group with solvent incorporated into the crystal lattice. The repeat distance of monomer **17** is 5.14 Å, the C3-C6 distance is 3.53 Å, and the C1-C4 distance is 3.60 Å from one end (θ = 45°) and 3.64 Å from the other (θ = 47°). Therefore, similar to **17•10** bis(pyridyl) co-crystals, tetrayne **17** is aligned for a 1,4- or 3,6-polymerization as illustrated by the side view (in space-filling representation) in Figure 4.11.[1] The top view (in ball-and-stick representation) indicates that bis(nitrile) host **14** is aligned with two different orientations within **17•14** co-crystal. The thermal ellipsoids for the crystal were spherical, indicating no major signs of disorder (Figure 4.11).

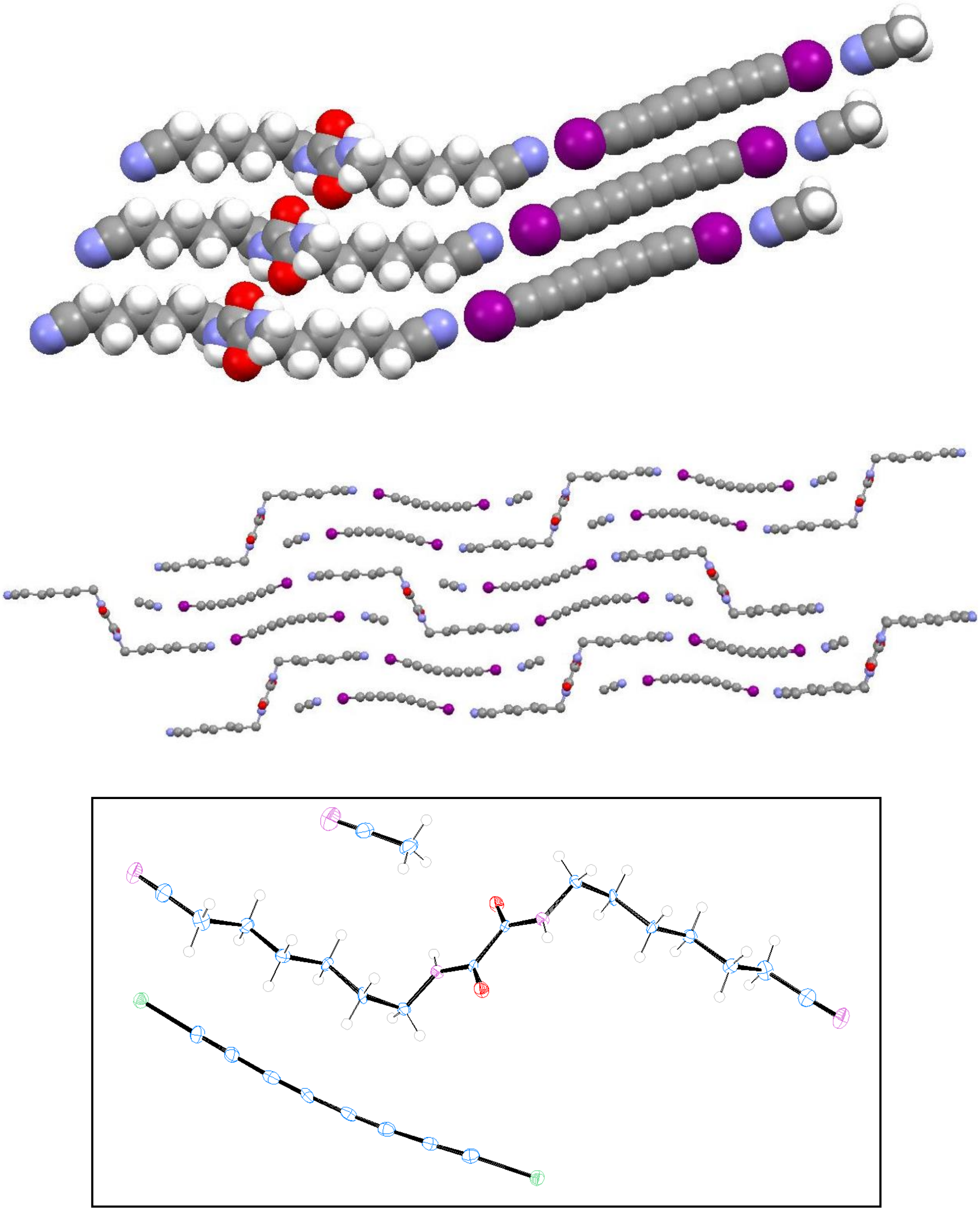


Figure 4.11 Crystal structure of a **17•14** green co-crystal immediately after solvent evaporation. Unit cell parameters: Space group: P 2_1/c; Unit cell dimensions: a = 5.1350(2) Å, b = 14.4430(5) Å, c = 26.4860(10) Å; α = 90°, β = 92.351(3)°, γ = 90°, Volume = 1962.68 $Å^3$. Top: side view; Middle: top view; Bottom: ORTEP drawing of thermal ellipsoids at the 50 % probability level.

The polymerization of **17•14** co-crystals was monitored by XRD. When the same crystals were kept at room temperature for as little as 3 days, the structure could no longer be solved, as the crystals became weakly diffracting. The same result was seen after the crystals were allowed to sit at room temperature for up to one month. Separate crystals were kept at room temperature for two weeks and then heated for 3 days at 40 °C to push the polymerization further, but once again, a crystal structure could not be determined. Acetonitrile likely adds to the flexibility required for polymerization of monomer **17**, but if this volatile solvent escapes from the crystal, alignment of the monomer will be disrupted throughout the material, suggesting a reason for the weakly diffracting crystal. This disorder would also offer a possible explanation for the bending in the crystal. Interestingly, even after heating, the **17•14** co-crystals remain crystalline and shiny. Between 95-100 °C, the green **17•14** co-crystals turn dark and acquire a bend in the structure, which remains when heated above 200 °C. The unit cell parameters obtained for crystals that were stored in the freezer (-10 °C) for 3 weeks immediately after solvent removal were very similar to the values for the green crystals in Figure 4.11. However, the crystal structure could not be solved, indicating either uncontrolled polymerization or decomposition of guest tetrayne **17**. Therefore, XRD will be taken daily of **17•14** co-crystals stored either at -10 °C or 0 °C in an effort to monitor its polymerization.

While XRD depends on the average electron density to generate a molecular structure, Raman spectroscopy identifies the strongest scatterer, and is used to further gain insight regarding the degree of polymerization for the **17•14** co-crystals. PDAs are highly polarizable materials, and therefore produce intense Raman scattering peaks. If the color transformation from green to purple is indicative of polymerization, strong peaks around 1000 cm^{-1}[ν(C-C)], 1500 cm^{-1}[ν(C=C)], and 2000 cm^{-1}[ν(C≡C)] should be detected. Still, peak shifts may vary slightly depending on the conjugation length of the PDA chain.[9] Figure 4.12 shows the gradual change in the Raman spectra for **17•14** co-crystals, obtained by Young, when left at room temperature and also after heating.

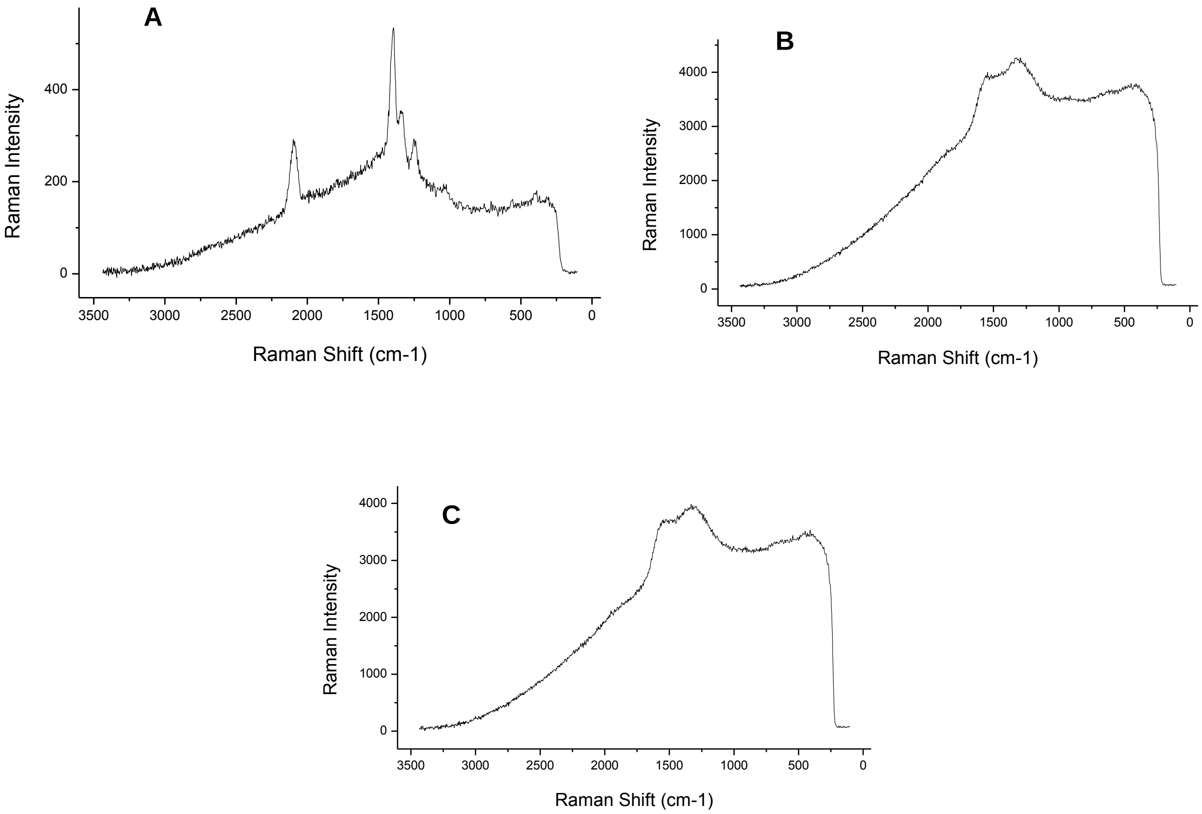


Figure 4.12 Raman spectra of **17•14** co-crystals with 785 nm laser, 10% power. A: immediately after solvent evaporation; B: 2 weeks at 25 °C; C: 2 weeks at 25 °C and successive heating at 40 °C for 3 days.

Remarkably, the laser burned a hole through the green co-crystals obtained immediately after solvent evaporation (Figure 4.12a), and only 8 scans were run on the sample to prevent background noise. A dark area formed around the hole. The peaks in Figure 4.12a are consistent with the alternating ene-yne structure of PDAs; however additional peaks in the C=C stretching range may be attributed to oligomers of varying lengths or multiple polymerizations. Currently, there are no calculations to support this claim. Furthermore, the low scattering intensity suggests a low degree of polymerization, though the amount cannot be quantified.[18] The Raman spectrum of co-crystals allowed to sit at room temperature for two weeks immediately following solvent evaporation no longer indicated the presence of polymer. But, at 100x magnification (around 1 micron surface area), the spectrum shows that disordered graphitic material forms at the surface of the crystal (Figure 4.12b). Slightly heating these crystals for 3 days gave a similar spectrum at the same magnification (Figure 4.12c). For all the spectra shown in Figure 4.12, the signal to noise is poor. Interestingly, with these bis(nitrile) co-crystals, it appears that formation of an amorphous graphitic like material is thermally induced. Conversely, the Raman spectrum for the **17•10** bis(pyridyl) co-crystals resembles commercial graphite only when a 532-nm laser beam is used (Figure 4.8b). If acetonitrile evaporates while **17•14** co-crystals sit at room temperature, heating will only further disrupt the alignment of the monomer throughout the crystal. Therefore, in an effort to better regulate polymerization, the **17•14** co-crystals were stored at 0 °C for 3 days following solvent evaporation. The flat needle-like crystals turned dark green, and the Raman spectrum of this material (Figure 4.13a) looked very similar to the spectrum obtained of the crystals immediately after solvent removal (Figure 4.12a).

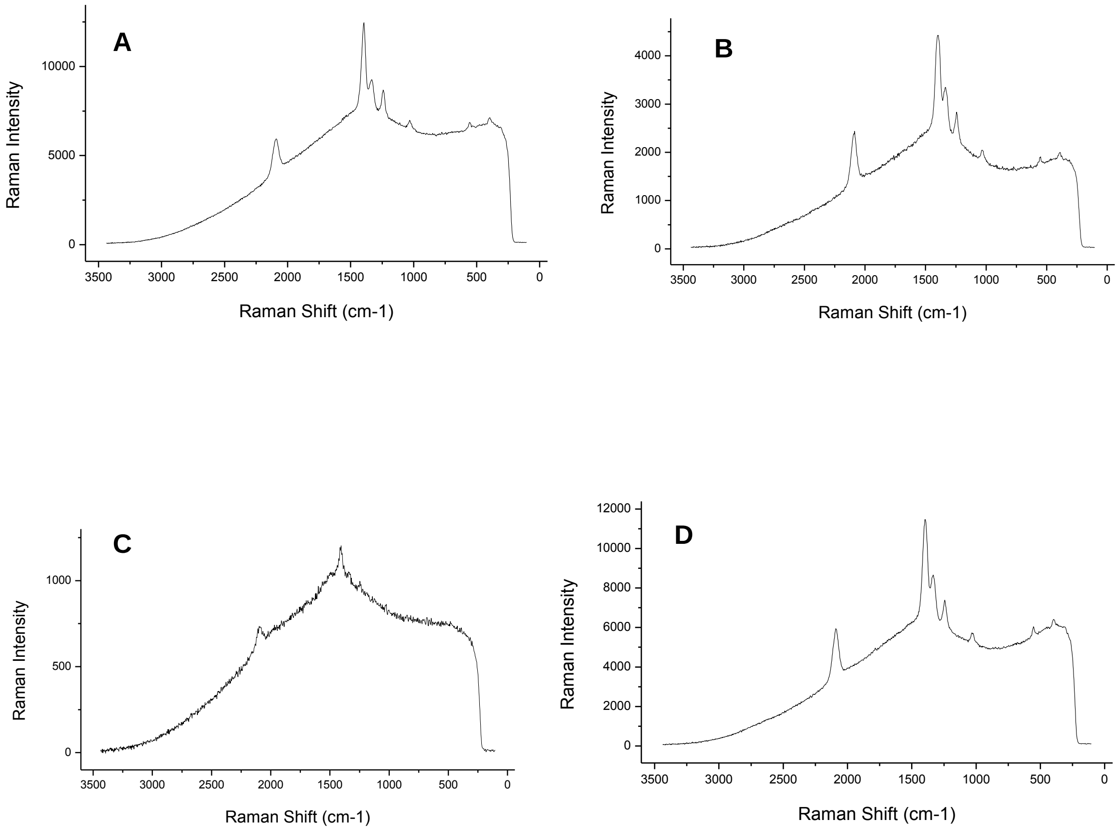


Figure 4.13 Raman spectra of **17•14** co-crystals with 785 nm laser, 10% power. A: 3 days at 0 °C immediately after solvent removal; B: 3 days at 0 °C immediately after solvent removal and successive warming to 25 °C over 1 day; C: 3 days at 0 °C immediately after solvent removal and successive warming to 25 °C over 7 days; D: 7 days at 0 °C immediately after solvent removal.

Following this experiment, these crystals were then kept at room temperature for one day. Although less intense, the Raman peaks indicating the PDA backbone remained unchanged (Figure 4.13b). The material turned dark even though a bend in the structure did not develop, suggesting that acetonitrile may still be incorporated into the crystal lattice, and consequently, a more controlled polymerization or oligomerization may be attained. The decrease in intensity of the polymer peaks can therefore be attributed to thermal damage caused by the laser, as a hole was quickly burned through the sample. This result is also suggestive that unreacted monomer **17** might still in the material as this effect was not noticed previously with the more stable PIDA polymer. After the **17•14** co-crystals were left out at room temperature for an additional 6 days, the polymer backbone signal decreased (Figure 4.13c). Additionally, thermal damage on the surface of the crystals was noticed since a crater formed upon irradiation. But, when the **17•14** co-crystals were allowed to polymerize for 1 week at 0 °C immediately after solvent removal, the PDA backbone was observed in the spectrum and the signal was intense and well defined (Figure 4.13d). Thus, a more controlled polymerization or oligomerization seems to result if the co-crystal is kept at 0 °C, and the polymerization of tetrayne **17** will be studied by XRD. This crystal is dark with clear areas that appear reflective under polarized light from the microscope. In short, the Raman spectra of **17•14** co-crystals indicate that acetonitrile evaporates from the crystal quicker than monomer **17** is able to completely undergo an ordered oligomerization or polymerization when stored at 25 °C or 40 °C. Conversely, at 0 °C, a more controlled polymerization of diiodopolyyne **17** seems likely, although multiple peaks in the C=C stretching range suggests that a single-crystal-to-single-crystal topochemical polymerization is unlikely.

Lastly, Fourier transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-Vis) were utilized to gain additional information regarding the polymerization process of the **17•14** co-crystals. Initially, peaks at 1633, 2246, and 3295 cm^{-1} in the spectrum, corresponding to the C=O, C≡N, and N-H stretches of the bis(nitrile) host **14**, were observed. A separate nitrile stretch for acetonitrile was not present, although it is unclear if one nitrile peak masks the other. Additionally, a peak at 2173 cm^{-1} indicates the presences of the C≡C bond in tetrayne **17**.[19] The intensity of this peak gradually decreases as the **17•14** co-crystals are kept at room temperature, and after two weeks, only host is detected (Figure 4.14). Since the intended polymer is a weak infrared absorber, it is unclear if polymerization or decomposition of monomer **17** occurs over time.

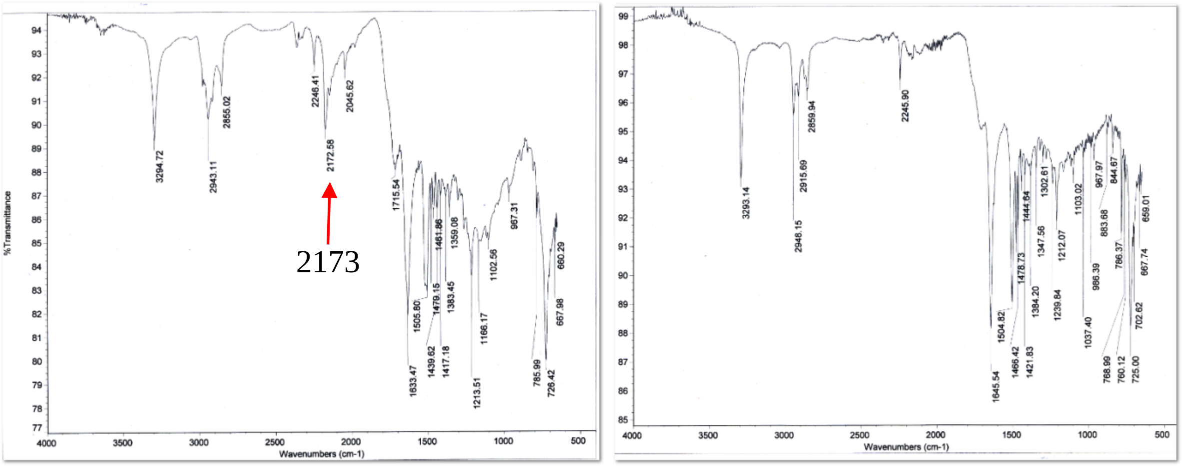


Figure 4.14 FT-IR spectrum of **17•14** co-crystals after 3 days (left) and after 2 weeks (right).

Luo has shown that both the unpolymerized and polymerized **9•13** and **9•14** co-crystals can form suspensions in water when subjected to sonication.[9,14] Similarly, green co-crystals with tetrayne **17** and host **14** were dispersed into water to form a quasi-homogeneous suspension. A brown suspension formed after sonication for 1 hour (Figure 4.15), and a dark solid immediately crashed out of solution once the sonicator was turned off. The spectrum contained a broad shoulder around 600 nm, which is less defined compared to the spectrum of Luo's **9•14** co-crystal suspension,[9] possibly due to a lower concentration of oligomers or polymer chains. The suspension was stored at room temperature for 3 days, and no color change was observed. The UV-Vis spectrum became even broader. In comparison, the UV-Vis absorption spectra obtained for solutions of tetrayne **17** dispersed in hexanes show a large absorbance at 247 and 259 nm in dilute samples, while more concentrated samples show 5 distinct peaks at 332, 356, 383, 416, and 440 nm. Absorbance at longer wavelengths in the more concentrated solution suggests an increase in polyyne aggregation, although more data is needed before any assumptions are drawn.

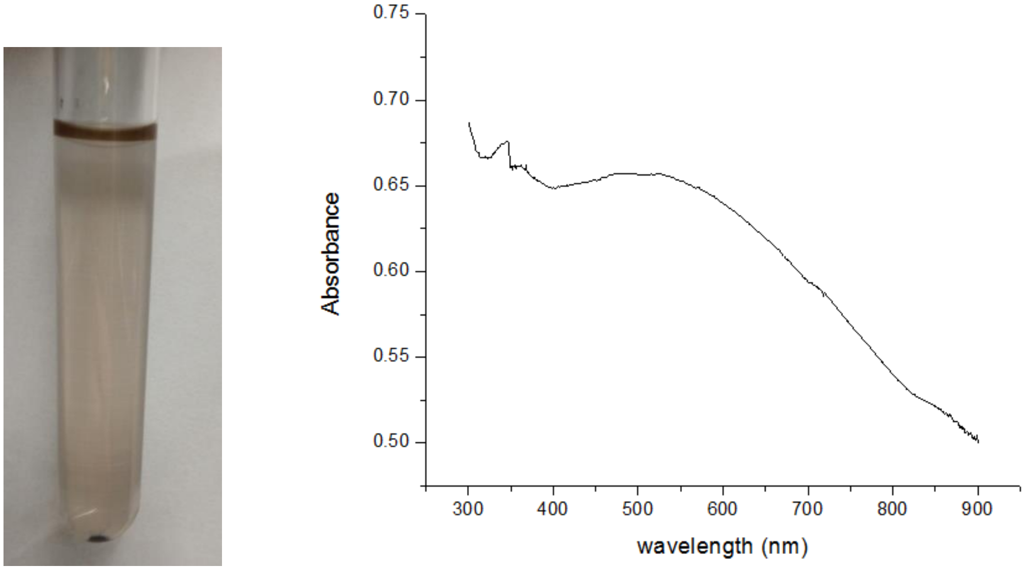


Figure 4.15 Green **17•14** co-crystals dispersed into water. (a) Color change observed after sonication for 1 hour at room temperature; (b) Corresponding UV-Vis absorption spectrum.

Experimental results for the **17•14** co-crystals are indicative of structurally disordered polymerizations of diiododooctatetrayne (**17**) to form graphitic species. Solid-state ^{13}C Magic-Angle-Spinning NMR (MAS-NMR) can be used as an alternative method to determine the presence of polymer and the effect of the incorporated acetonitrile on polymerization. Co-crystals with diiodohexatriyne (**16**) and nitrile host **14** have recently been grown in CH_2Cl_2,[20,21] therefore offering an alternate system to try with diiodooctatetrayne (**17**). Unlike acetonitrile, CH_2Cl_2 will probably not be incorporated into the crystal via halogen bonding, providing a more rigid crystal structure, and orienting monomer **17** in a fixed position to allow for a 1,4-topochemical polymerization. Initial attempts to grow the **17•14** co-crystals in CH_2Cl_2 resulted in the formation of blue shiny needle-like crystals (Figure 4.16a). Similarly to the co-crystals grown in acetonitrile, a 2:1 ratio of guest to host was used, and the crystals were grown at 0 °C over-night and then allowed to slowly warm to room temperature over one day. However, in an attempt to mount the blue crystals for XRD, the crystals exploded and bright light and black smoke was emitted (Figure 4.16b). This result suggests either weak halogen bonding to host **14** or excess monomer on the surface of the crystals because diiodooctatetrayne (**17**) is a shock explosive when neat. The **17•14** co-crystals were grown again in CH_2Cl_2, and the crystals that formed upon solvent evaporation were rinsed with pentane to remove any unreacted diiodotetrayne (**17**). The crystals once again exploded, indicating the potential benefit for using a solvent which can participate in halogen bonding with monomer **17**. Alternatively, to aid in the isolation of the crystals from the glass dishes, Teflon liners may be used.

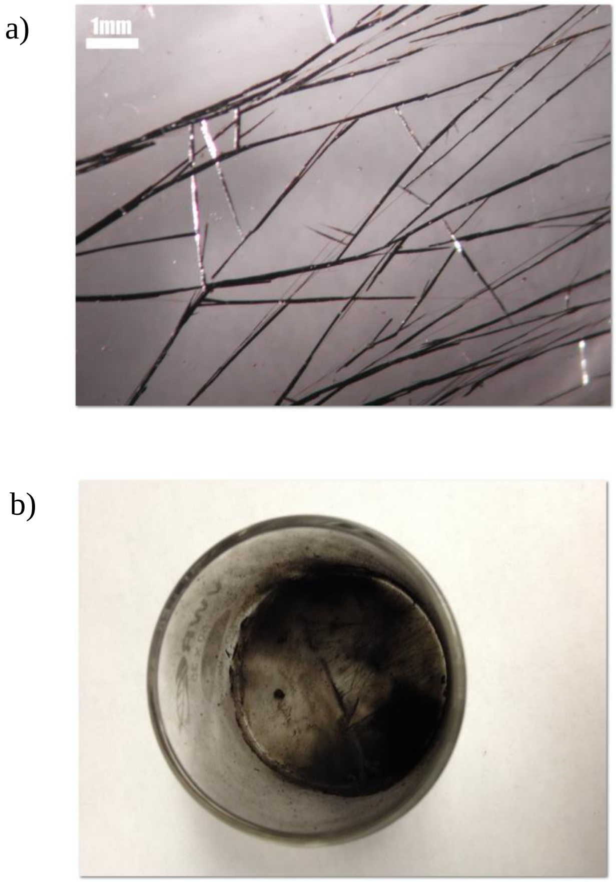
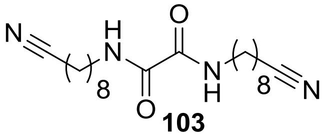


Figure 4.16 Optical microscope images of **17•14** co-crystals. A: The co-crystals after 1 day at room temperature; B: The co-crystals after explosion.

4.3 Summary

Co-crystals with diiodooctatetrayne (**17**) were successfully prepared by means of halogen bonding interactions with both bis(nitrile) oxalamide and bis(pyridyl) oxalamide hosts. A crystal structure was achieved for both the **17•10** bis(pyridyl) co-crystals and the **17•14** bis(nitrile) co-crystals, suggesting a 1:1 host: guest stoichiometry and a 1: 2: 1 host: guest: solvent stoichiometry, respectively. Although **17•10** and **17•14** co-crystals each appear to align in the proper orientation for controlled topochemical polymerization, XRD and Raman spectroscopy suggest the monomer undergoes several competing reactions concurrently at room temperature. Unfortunately, the complexity of the polymerization process makes the ordered polymerization of tetraynes challenging compared to diyne monomers, as one could hypothesize that a 1,4-, 3,6-, and other modes are plausible for octatetraynes (Section 1.6).[1]

The synthesis of bis(nitrile) oxalamide host **103** (Figure 4.17) may be necessary to facilitate the single-crystal transformation of tetrayne **17** compared to the shorter analogs **13** and **14** because of the added flexibility in the methylene chain tether. Additionally, the 1,8-topochemical polymerization of tetraynes has not yet been reported.[2] Dr. Joseph Lauher has suggested the synthesis of asymmetric hosts **104** and **105** (Figure 4.17) to attain the polytetraacetylene product. The head to tail stacking between the host compounds should align the matching hosts in the required repeat distance (9.6 Å) for a 1,8-polymerization. Once controlled polymerization of diiodooctatetrayne (**17**) is achieved, removal of host to gain insight about the polymer aggregation behavior and the capability to form carbon-rich polymeric material will be examined.[22] Studying the effect of aggregation may offer information about the bulk material properties. Post-polymerization substitution of iodine will also be studied to synthesize a variety of PDAs, including couplings to either the alkyne or the alkene moiety, depending on the polymer formed.



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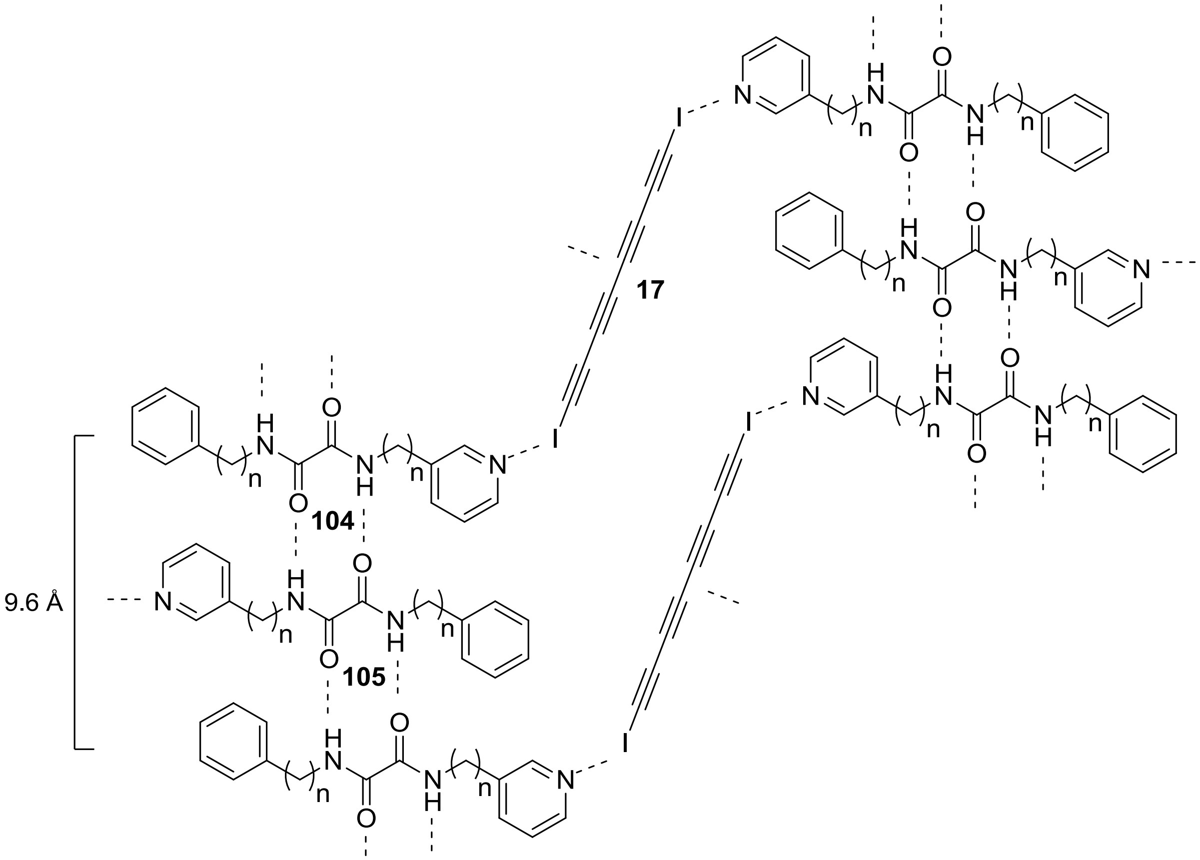

Figure 4.17 Host compounds not yet synthesized. Top: Bis(nitrile) oxalamide host predicted to be required for a 1,4-polymerization of monomer **17**; Bottom: Asymmetric bis(pyridyl) oxalamide host(s) predicted to be required for a 1,8-polymerization of monomer **17**.

4.4 Experimental Procedures and Instrumental Methods

General Methods: Reagents were purchased reagent grade from Aldrich, Fisher Scientific/Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. All reactions were performed under an inert argon atmosphere, unless stated otherwise. The iodination of polyynes was carried out in aluminum-foil wrapped flasks in an unlighted hood. All diiodopolyynes were washed with aqueous $Na_2S_2O_3$ immediately prior to use. Column chromatography: Alumina (50-200 mesh) from Acros

Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. ^{1}H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, Inova-500 MHz, Bruker-400 MHz, or Bruker-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise.

General Method for Preparing Co-Crystals with Bis(pyridyl) Oxalamide Host. Diiodooctatetrayne (**17**) was synthesized according to the procedure described in Chapter 2 and used within 1 day of preparation. Host **10** was prepared by former group member Liang Luo,[5,15] while hosts **11**[16] and **12**[6] were prepared by former group member Christopher Wilhelm according to literature procedures. To a 0.02 M solution of guest in MeOH (3 mL) was added 1 equivalent of host (1:1 guest to host ratio), and the solution was sonicated briefly to prevent monomer aggregation. The resulting solution was subjected to centrifugation for 10 min to remove any undissolved particles. The supernatant layer was decanted into a 50 mL crystallization dish, which was covered with aluminum foil. The foil was punctured 12-15 times using a needle, and the dish was placed in a refrigerator (4 ^{o}C). Solvent was allowed to evaporate slowly to afford crystals. Yields typically ranged from 60-70%. Co-crystals were stored in the freezer at -10 °C to prevent polymerization.[16]

General Method for Preparing Co-Crystals with Bis(nitrile) Oxalamide Host. Diiodooctatetrayne (**17**) was synthesized according to the procedure described in Chapter 2 and used within 1 day of preparation. Host **14** was prepared by current group member Daniel Resch, while host **13** was prepared by current group member Matthew Freitag according to literature procedures.[8] To a 0.03 M solution of guest in CH_3CN (1.5 mL) was added 0.5 equivalents of host (2:1 guest to host ratio), and the solution was sonicated briefly to prevent monomer aggregation. The resulting solution was subjected to centrifugation for 10 min to remove any undissolved particles. The supernatant layer was decanted into a 50 mL crystallization dish, which was covered with aluminum foil. The foil was punctured 12-15 times using a needle, and the dish was placed in an ice bath (0 ^{o}C). Once crystals began to form, the dish was moved to room temperature. Solvent was allowed to evaporate slowly to afford green crystals. Yields typically ranged from 60 -70%. Co-crystals were stored in the freezer at -10 °C to prevent polymerization.[9]

The same procedure was used for the preparation of **17•14** co-crystals grown in CH_2Cl_2. To a 0.02 M solution of guest in CH_2Cl_2 (3 mL) was added 0.5 equivalents of host (2:1 guest to host ratio), and the solution was sonicated briefly to prevent monomer aggregation. The resulting orange solution was subjected to centrifugation for 10 min to remove any undissolved particles. The supernatant layer was decanted into a 50 mL crystallization dish, which was covered with aluminum foil. The foil was punctured 12-15 times using a needle, and the dish was placed in an ice bath (0 ^{o}C). Once crystals began to form, the dish was moved to room temperature. Solvent was allowed to evaporate slowly to afford blue crystals and brown solid. The crude yield was 72%, but only about 1/3 of this material was the blue crystals. Co-crystals were stored in the freezer to prevent polymerization.[9]

Raman Spectroscopy. Raman spectroscopy was performed by Christopher Young of the Halada group in the Material Sciences Department at Stony Brook University. A Thermo Nicolet Almega dispersive Raman spectrometer coupled with an infinity-corrected, confocal design microscope was used. A 785-nm class I laser was used, and the data were collected in the reflection mode of the microscope at a slit width of 25 μm. The data were analyzed using the Origin Pro 8 SRO Software (OriginLab Corporation, USA).

UV-Vis Spectroscopy. The electronic absorption spectra of the co-crystal suspensions were collected using a Cary-100 UV/Visible Scan Spectrophotometer, scanning from 800 nm to 200 nm with a resolution of 1 nm. Suspensions of fresh **17•14** co-crystals were prepared by placing 0.020 g in 5 mL H_2O and subjecting the mixture to sonication for 1 hour. About 1mL of the suspension was used to obtain UV-Vis spectra. The suspension immediately turned brown, and dark solid crashed once sonication ceased. The suspension was stored at room temperature for 3 days, and no color change was observed. Additional UV-Vis spectra were obtained.

Scanning electron microscopy (SEM): SEM images were taken by James Quinn in the Material Sciences Department at Stony Brook University. A field emission scanning electron microscope (SEM, Leo 1550) was used, which operated at accelerating voltages of 20 kV and was equipped with Energy Dispersive X-ray Analysis (EDAX) capabilities.

Single crystal X-ray diffraction (XRD). Crystals were selected and mounted on glass fibers using epoxy adhesive. Each crystal was centered, and the X-ray intensity data were measured on an Oxford Gemini A Enhance diffractometer by using graphite-monochromated Mo radiation. The experiments were conducted at low temperature, using a CryojetHT. The data was collected using the Crysalis Pro 171.34.44 software.[23] WinGX 1.80.0511,[24] SIR97,[25] and SHELXL 97[26-27] were used to process the data.

Microscopy. Optical microscope images were taken under polarized light with a Nikon SMZ800 optical microscope (Nikon Instruments, Incorporated, Melville, New York).

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Chapter 1

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Chapter 2

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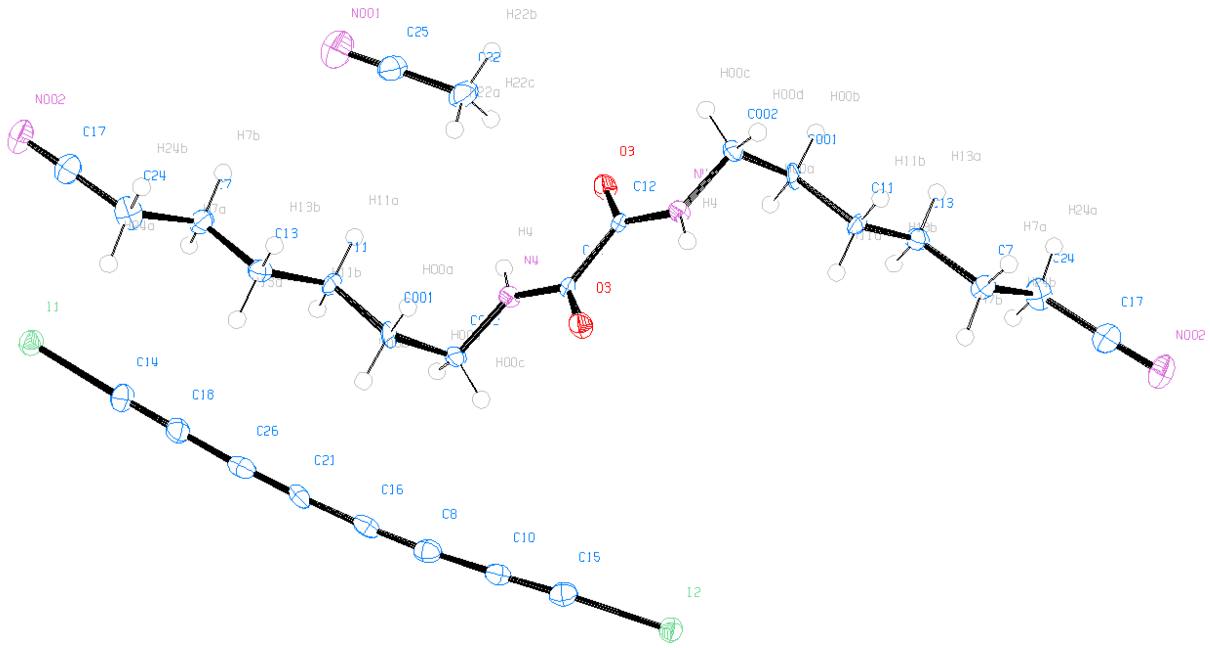


Figure: Crystal structure for **17•14** co-crystals immediately after solvent evaporation

Table 1. Crystal data and structure refinement for **17•14** co-crystals

Identification code	C8I2_6MO_CH3CN
Empirical formula	$C_{24}H_{21.333}I_{2.667}N_4O_{1.333}$
Formula weight	725.54
Temperature/K	N/A
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.1350(2)
b/Å	14.4430(5)
c/Å	26.486(1)
α/°	90
β/°	92.351(3)
γ/°	90
Volume/Å^3	1962.68(13)
Z	3
ρ_{calc}mg/mm^3	1.8414
m/mm^{-1}	3.213
F(000)	1032.5
Crystal size/mm^3	N/A × N/A × N/A
2Θ range for data collection	6.42 to 59.46°
Index ranges	$-7 \le h \le 6$, $-19 \le k \le 18$, $-35 \le l \le 34$
Reflections collected	22765
Independent reflections	4993[R(int) = 0.0769]
Data/restraints/parameters	4993/0/216
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	$R_1 = 0.0628$, wR_2 = N/A

Final R indexes [all data]	$R_1 = 0.0965$, $wR_2 = 0.1758$
Largest diff. peak/hole / e Å^{-3}	2.85/-2.29

Table 2. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times10^3$) for **17•14** co-crystals. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I1	829.4(10)	5597.9(4)	7525.6(2)	21.73(17)
I2	17620.1(9)	6619.4(4)	4109.26(19)	19.44(17)
O3	12724(10)	9339(4)	5194(2)	21.3(13)
N4	8421(11)	8997(5)	5228(2)	14.2(13)
C001	9134(14)	8080(6)	6018(3)	15.9(16)
C002	8882(15)	8079(5)	5445(3)	17.3(16)
C7	4454(15)	8170(6)	7142(3)	20.0(17)
C8	11837(16)	5920(6)	5309(3)	21.2(17)
N002	1008(15)	8075(6)	8266(3)	30.0(18)
C10	13637(15)	6131(6)	4970(3)	18.5(16)
C11	6541(14)	8189(6)	6283(3)	16.8(16)
C12	10417(14)	9538(5)	5119(3)	12.4(15)
C13	6951(15)	8078(6)	6855(3)	17.9(16)
C14	3283(16)	5565(6)	6966(3)	21.1(17)
C15	15168(15)	6334(6)	4648(3)	20.8(17)
C16	10165(15)	5775(6)	5613(3)	19.5(17)
C17	2789(16)	8059(7)	8021(3)	23.4(18)
C18	4864(17)	5571(6)	6641(3)	22.1(18)
C21	8330(16)	5657(6)	5962(3)	19.6(17)
C22	6372(18)	10996(7)	6027(3)	28(2)
N001	2598(17)	10680(7)	6618(4)	41(2)
C24	5065(15)	8013(7)	7706(3)	24.8(19)
C25	4253(19)	10829(7)	6360(4)	27(2)
C26	6709(16)	5593(6)	6277(3)	21.2(17)

Table 3. Anisotropic Displacement Parameters (Å$^2\times10^3$) for **17•14** co-crystals. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{12}}$	$\mathbf{U_{13}}$	$\mathbf{U_{23}}$
I1	20.3(3)	23.1(3)	22.1(3)	-1.0(2)	3.9(2)	0.1(2)
I2	19.4(3)	20.8(3)	18.1(3)	1.4(2)	1.99(19)	1.6(2)
O3	15(3)	22(3)	27(3)	5(2)	3(2)	9(3)
N4	10(3)	14(3)	18(3)	-1(2)	0(2)	1(3)
C001	9(3)	18(4)	21(4)	-4(3)	5(3)	8(3)

C002	17(4)	11(4)	24(4)	-2(3)	6(3)	1(3)
C7	19(4)	22(4)	18(4)	2(3)	2(3)	-1(3)
C8	25(4)	19(4)	20(4)	3(3)	-3(3)	-3(3)
N002	28(4)	41(5)	21(4)	0(4)	7(3)	2(3)
C10	18(4)	14(4)	24(4)	2(3)	0(3)	-1(3)
C11	13(4)	20(4)	18(4)	4(3)	8(3)	2(3)
C12	14(4)	13(4)	10(3)	0(3)	5(3)	0(3)
C13	18(4)	16(4)	20(4)	0(3)	1(3)	-1(3)
C14	16(4)	26(5)	21(4)	-3(3)	1(3)	1(3)
C15	21(4)	20(4)	21(4)	2(3)	-1(3)	-4(3)
C16	18(4)	13(4)	27(5)	2(3)	-5(3)	3(3)
C17	23(4)	29(5)	17(4)	-1(4)	-4(3)	-2(4)
C18	29(4)	16(4)	21(4)	-5(3)	2(3)	-1(3)
C21	25(4)	12(4)	22(4)	-1(3)	0(3)	5(3)
C22	34(5)	30(5)	20(5)	7(4)	3(4)	-4(4)
N001	35(5)	51(6)	38(5)	-1(4)	7(4)	0(4)
C24	14(4)	31(5)	29(5)	-2(3)	-4(3)	7(4)
C25	33(5)	24(5)	26(5)	4(4)	3(4)	-4(4)
C26	26(4)	14(4)	24(4)	3(3)	-6(3)	0(3)

Table 4. Bond Lengths for **17•14** co-crystals**.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C14	1.985(8)	N002	C17	1.142(11)
I2	C15	1.985(8)	C10	C15	1.219(11)
O3	C12	1.227(9)	C11	C13	1.530(11)
N4	C002	1.461(10)	C12	C12[1]	1.529(14)
N4	C12	1.330(10)	C14	C18	1.208(12)
C001	C002	1.517(11)	C16	C21	1.359(12)
C001	C11	1.538(10)	C17	C24	1.465(12)
C7	C13	1.522(11)	C18	C26	1.379(13)
C7	C24	1.532(12)	C21	C26	1.204(12)
C8	C10	1.349(12)	C22	C25	1.450(13)
C8	C16	1.219(12)	N001	C25	1.132(12)

[1] 2-X,2-Y,1-Z

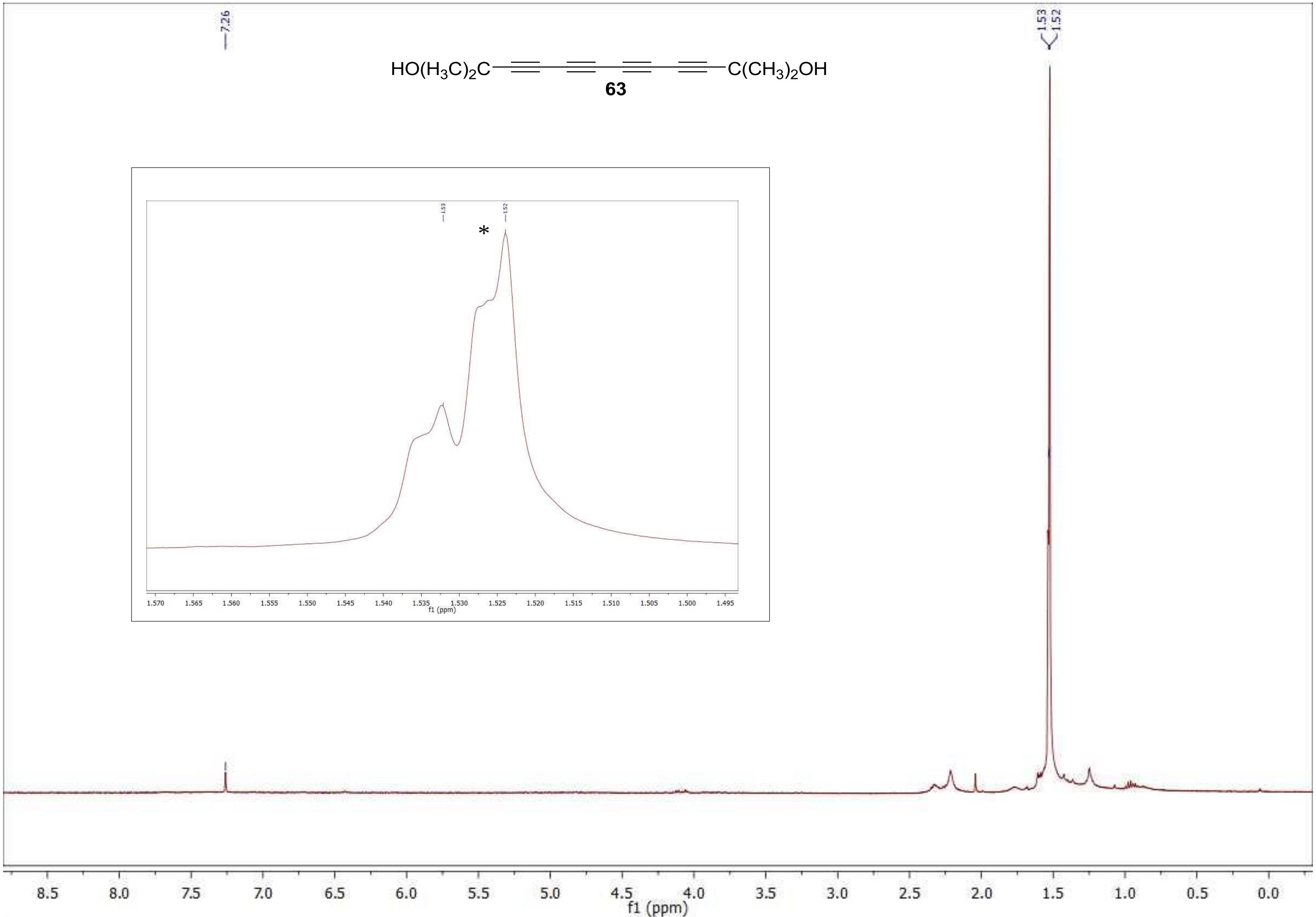
Table 5. Bond Angles **17•14** co-crystals**.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N4	C002	120.3(6)	C11	C13	C7	113.6(6)
C11	C001	C002	114.6(6)	C18	C14	I1	176.7(8)
C001	C002	N4	113.5(7)	C10	C15	I2	177.7(7)
C24	C7	C13	109.3(7)	C21	C16	C8	177.1(9)
C16	C8	C10	176.6(9)	C24	C17	N002	178.6(10)
C15	C10	C8	177.0(9)	C26	C18	C14	178.5(9)
C13	C11	C001	110.8(6)	C26	C21	C16	177.2(9)
N4	C12	O3	125.1(7)	C17	C24	C7	114.4(7)
C12[1]	C12	O3	121.5(8)	N001	C25	C22	178.6(10)
C12[1]	C12	N4	113.4(8)	C21	C26	C18	176.8(9)

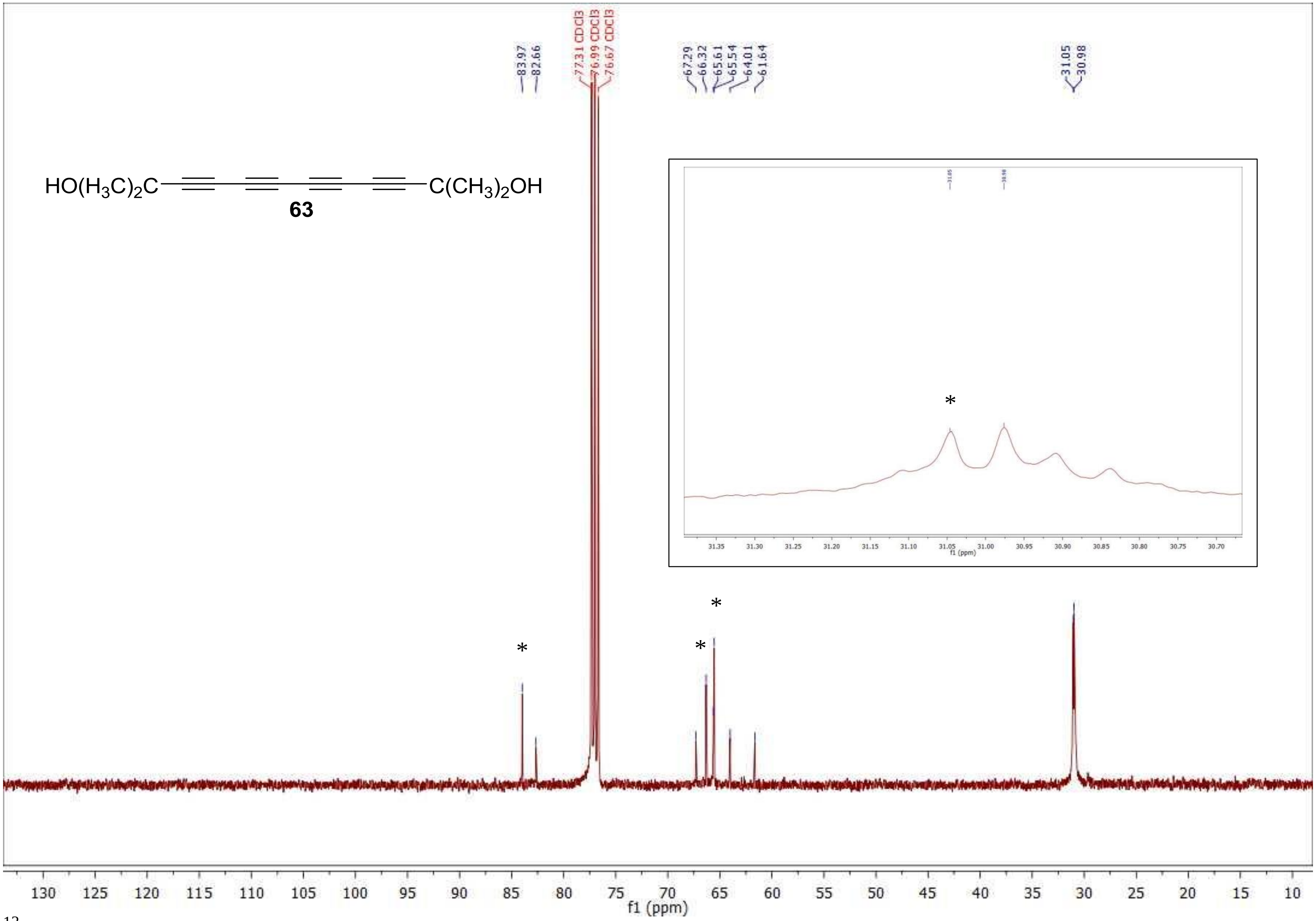
[1] 2-X,2-Y,1-Z

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **17•14** co-crystals**.**

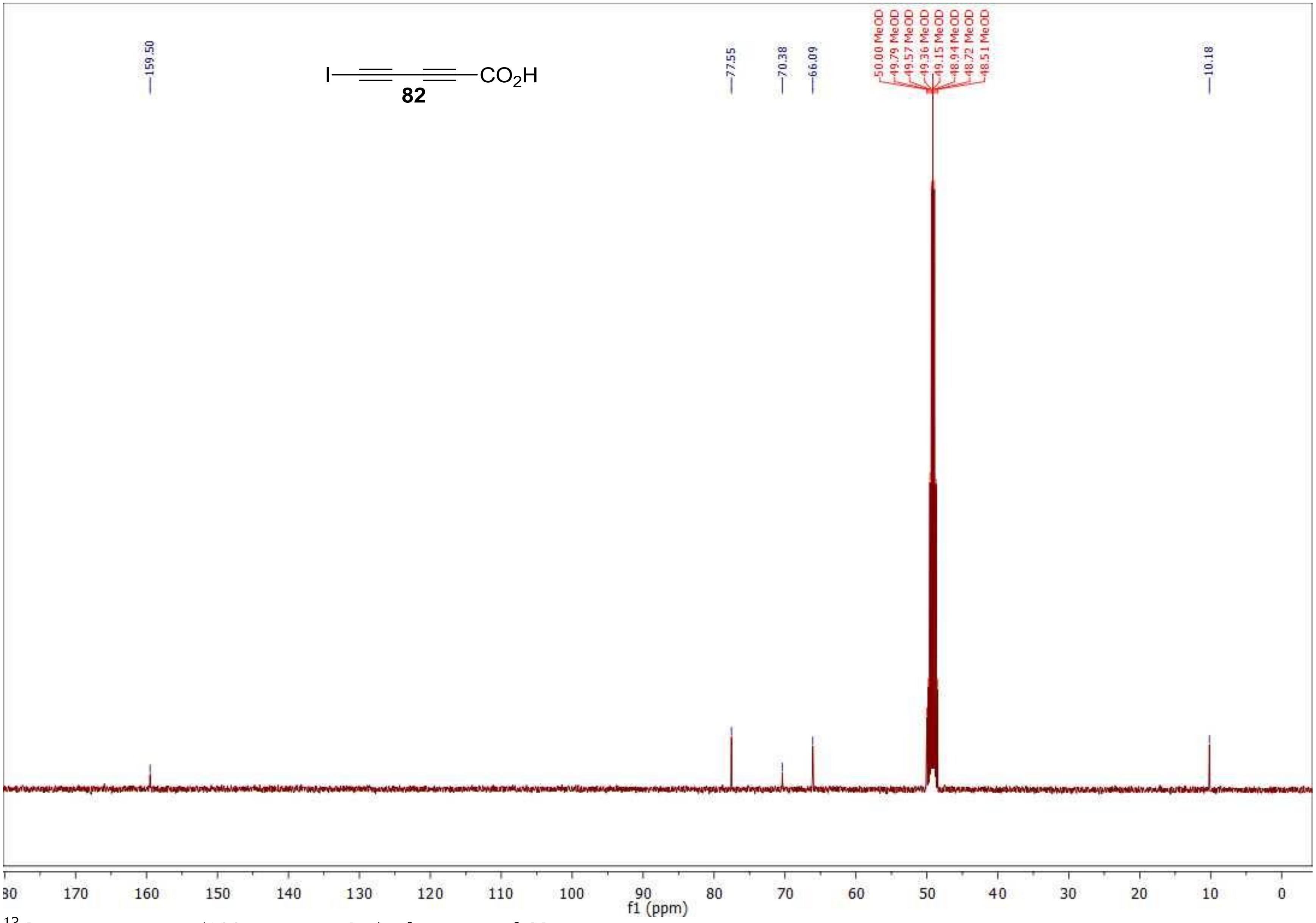
Atom	*x*	*y*	*z*	U(eq)
H4	6853	9189	5172	17
H00a	10272	8585	6126	18
H00b	9950	7507	6129	18
H00c	10442	7826	5313	19
H00d	7428	7682	5340	19
H7a	3183	7718	7018	23
H7b	3712	8783	7088	23
H11a	5811	8787	6208	20
H11b	5338	7717	6157	20
H13a	7706	7476	6928	22
H13b	8175	8544	6978	22
H22a	7856	10645	6138	43
H22b	6770	11643	6030	43
H22c	5835	10813	5687	43
H24a	5868	7416	7754	29
H24b	6300	8481	7827	29



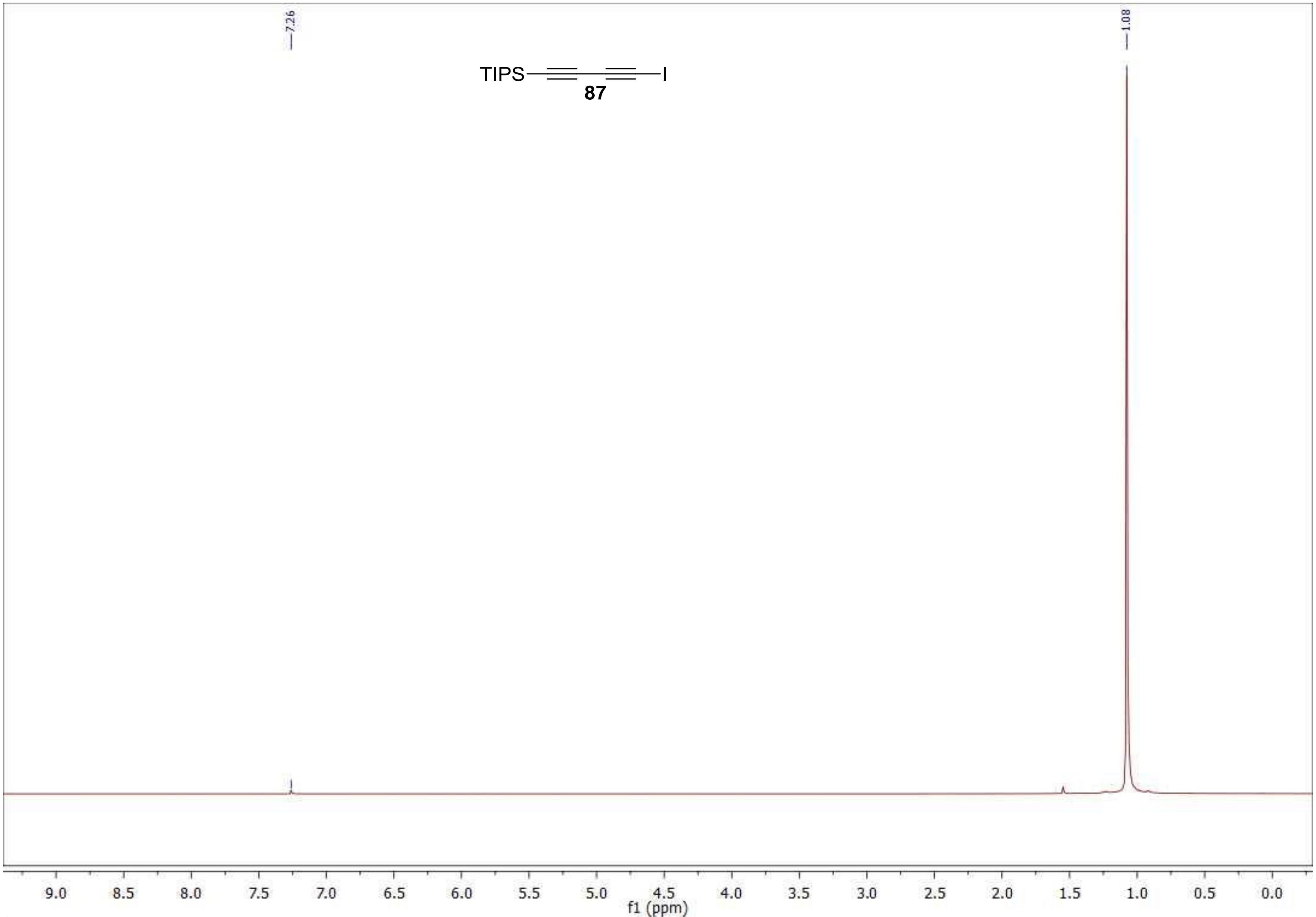
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **63**. Diyne **64** (*) denoted.



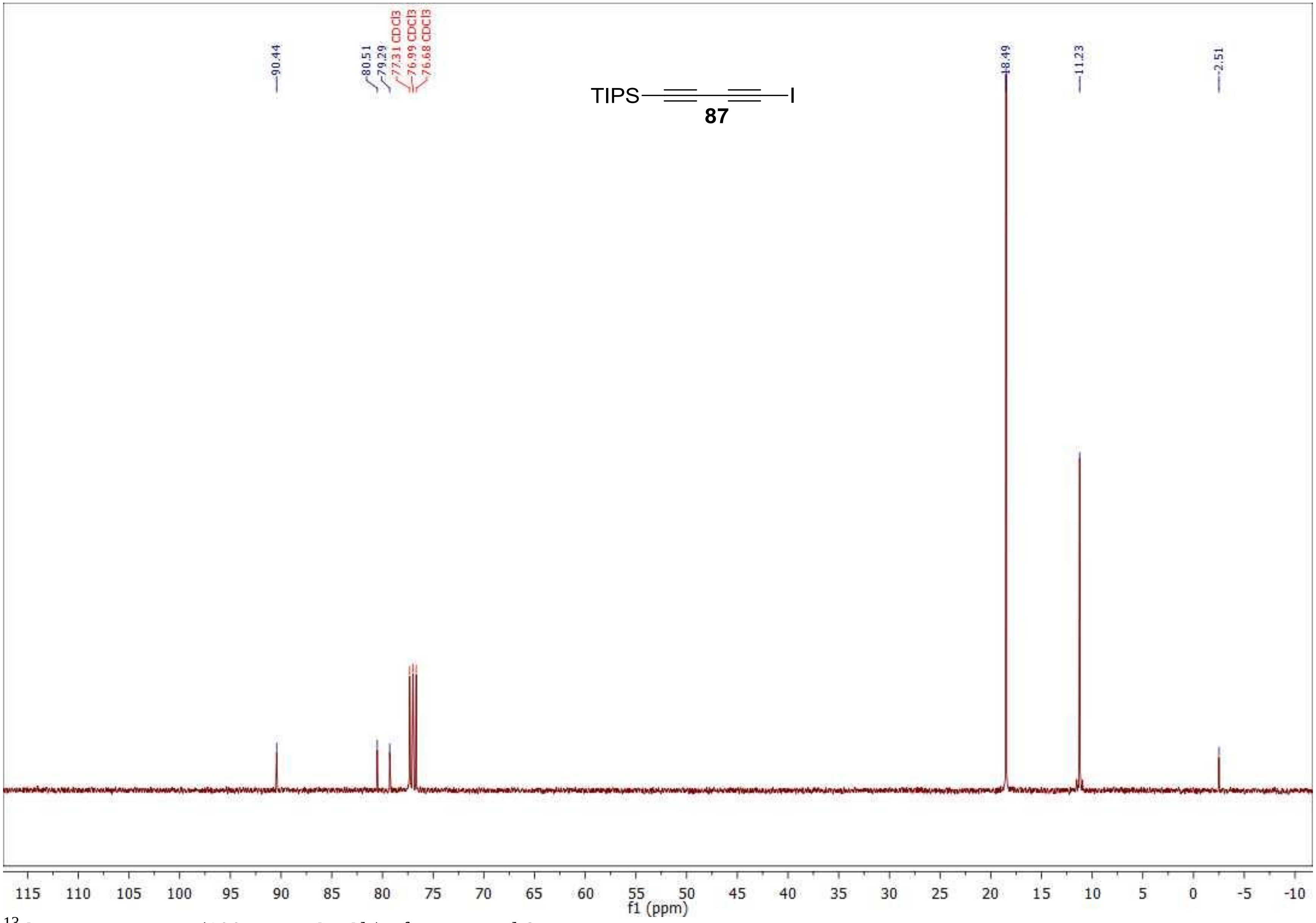
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **63**. Diyne **64** (*) denoted.



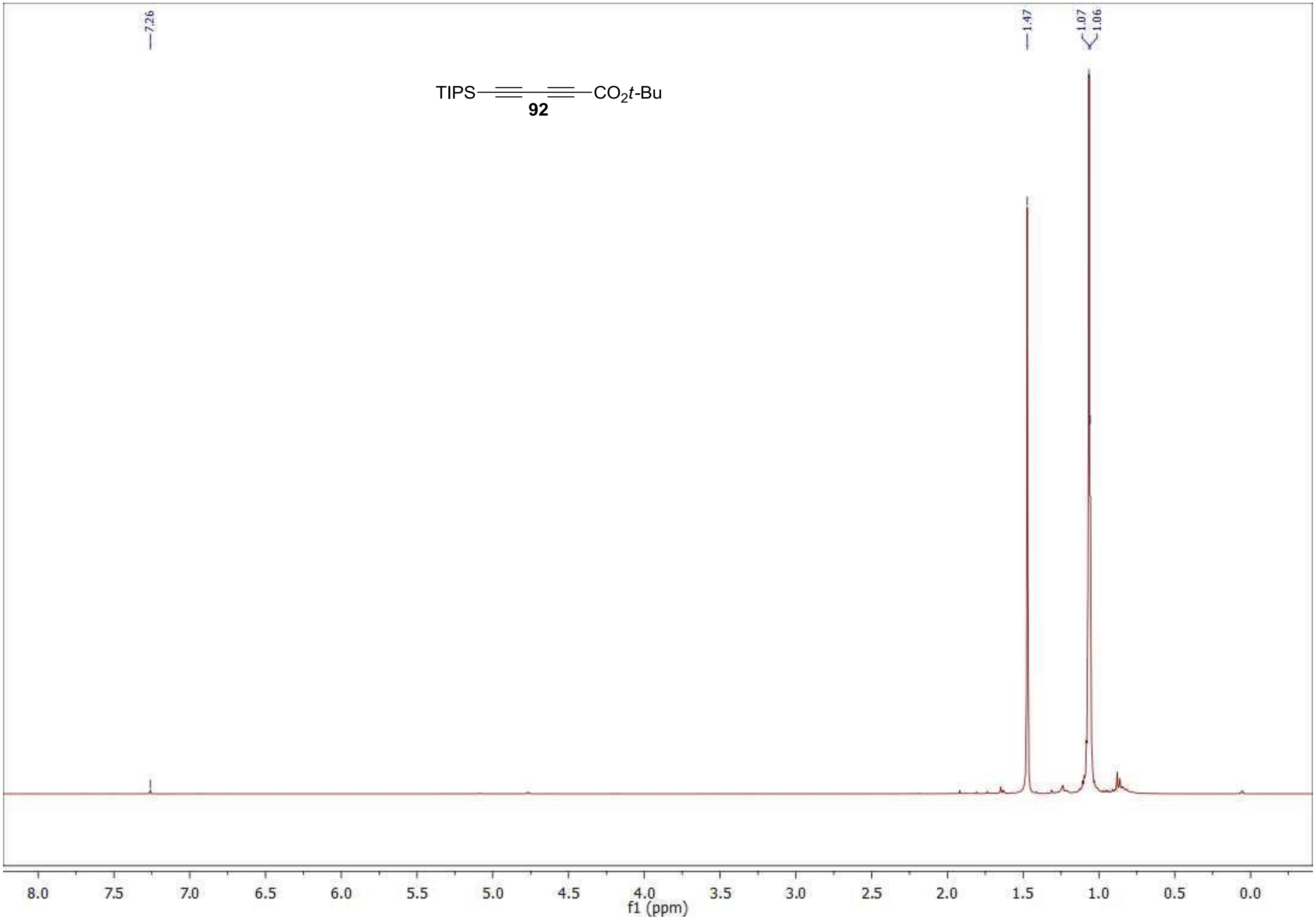
^{13}C NMR spectrum (100 MHz, MeOD) of compound **82**.



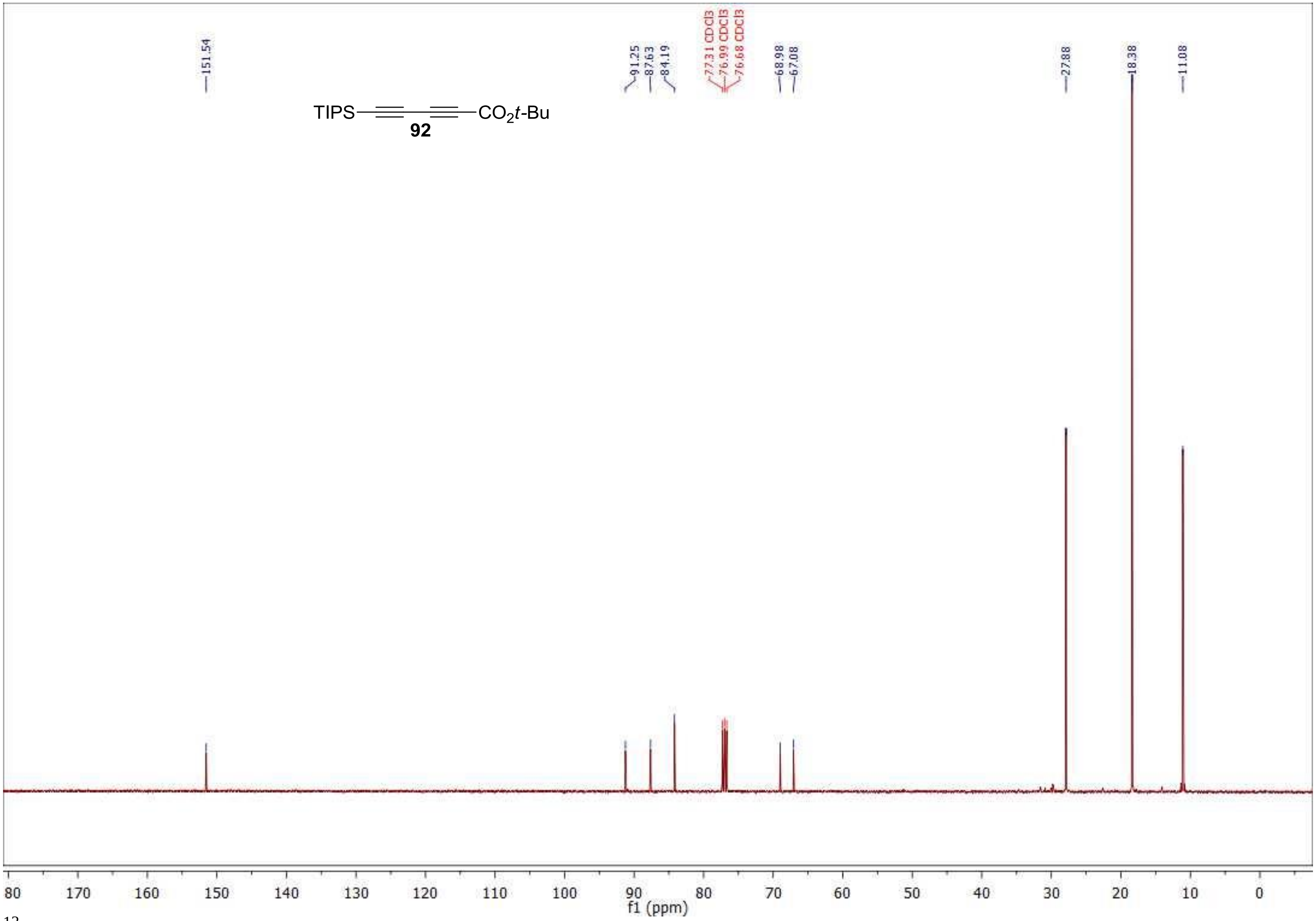
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **87**.



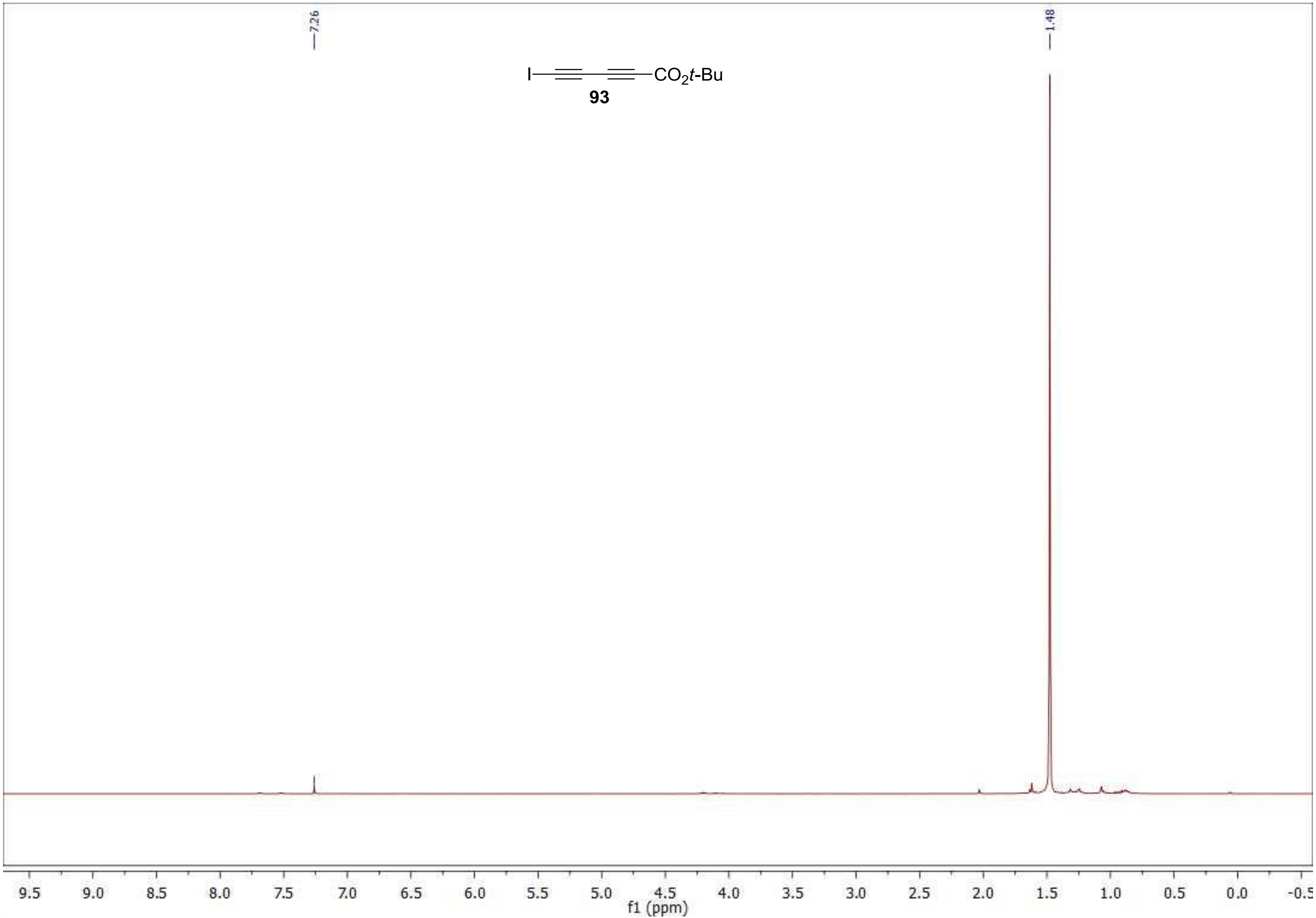
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **87**.



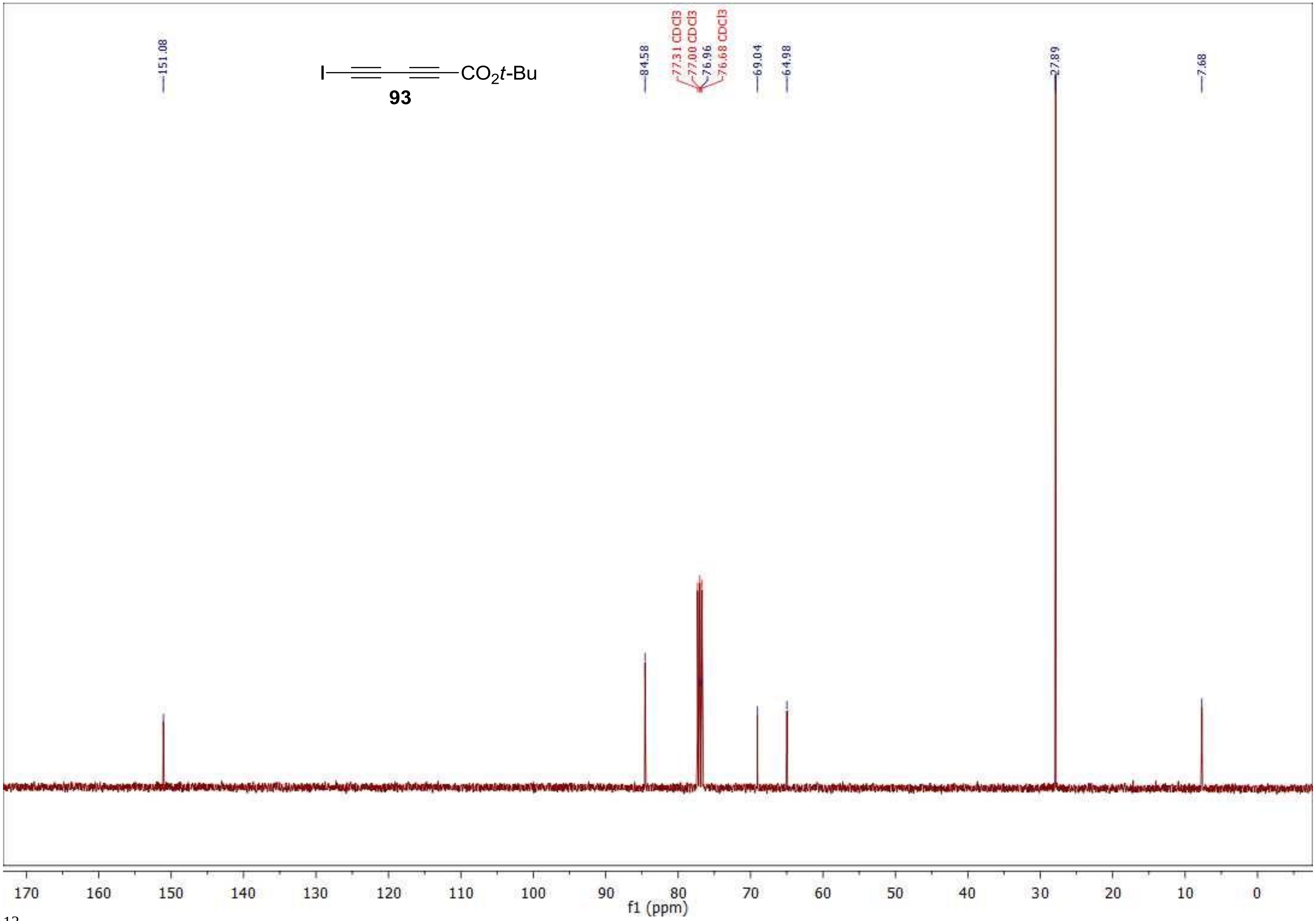
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **92**.



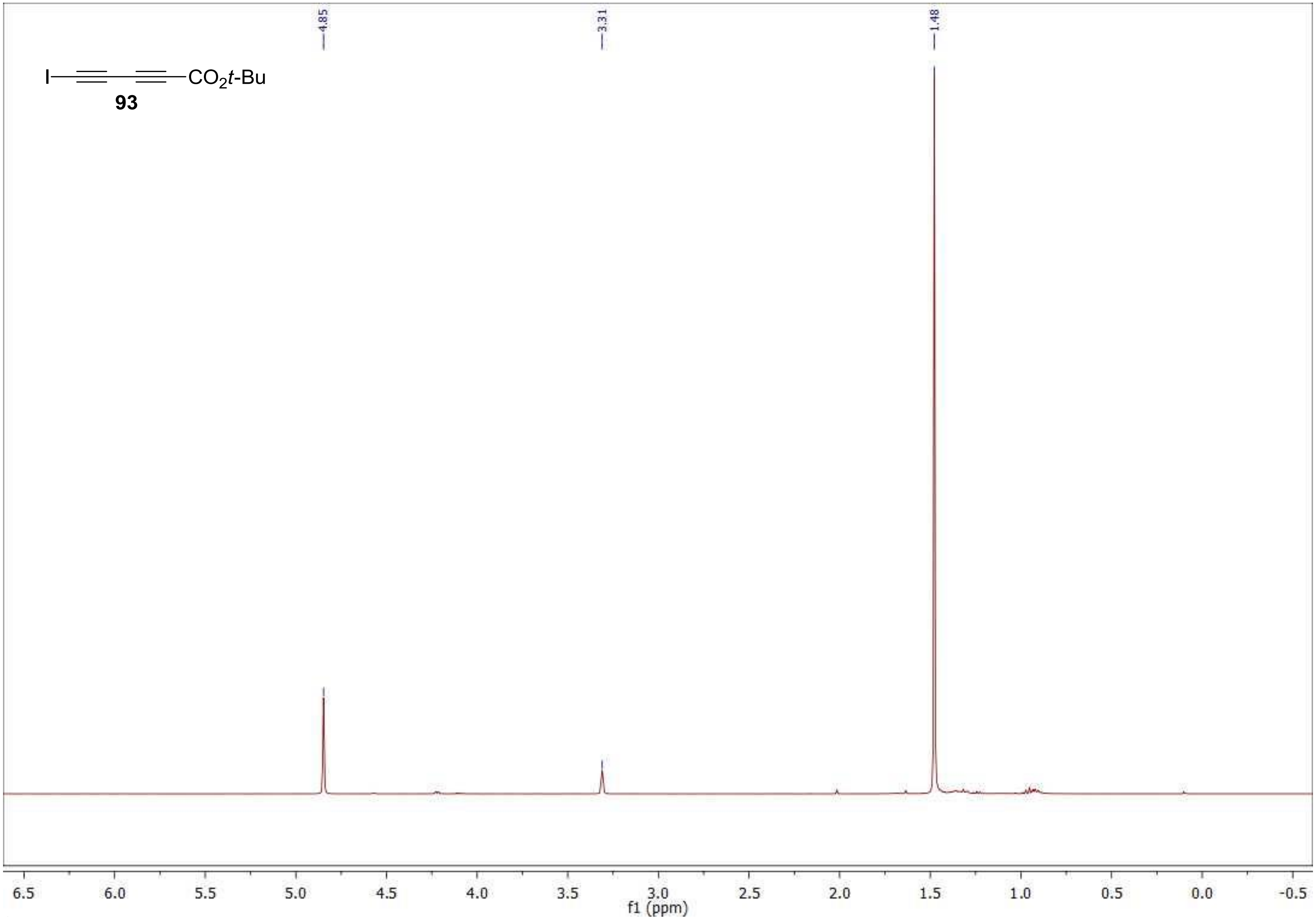
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **92**.



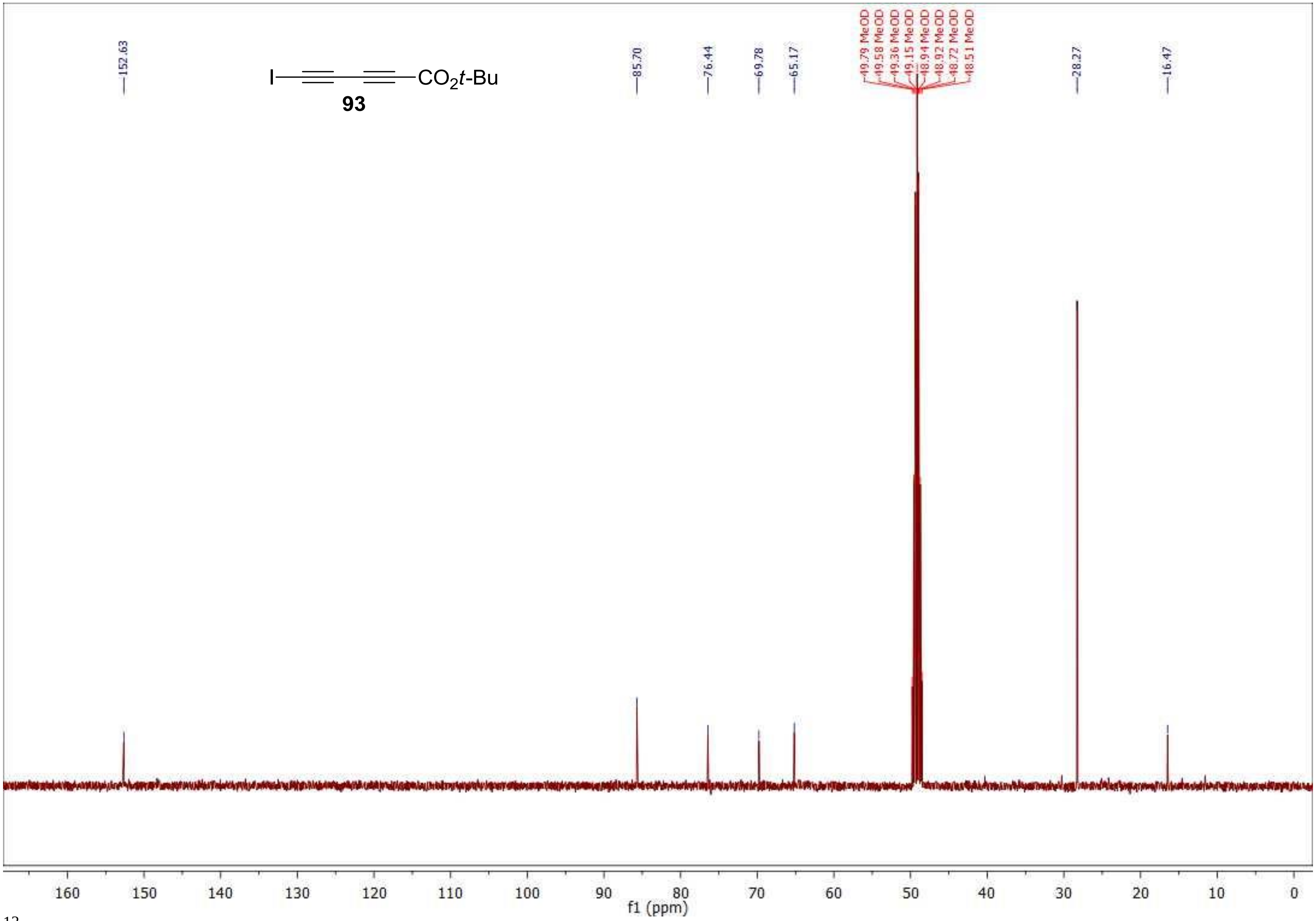
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **93**.



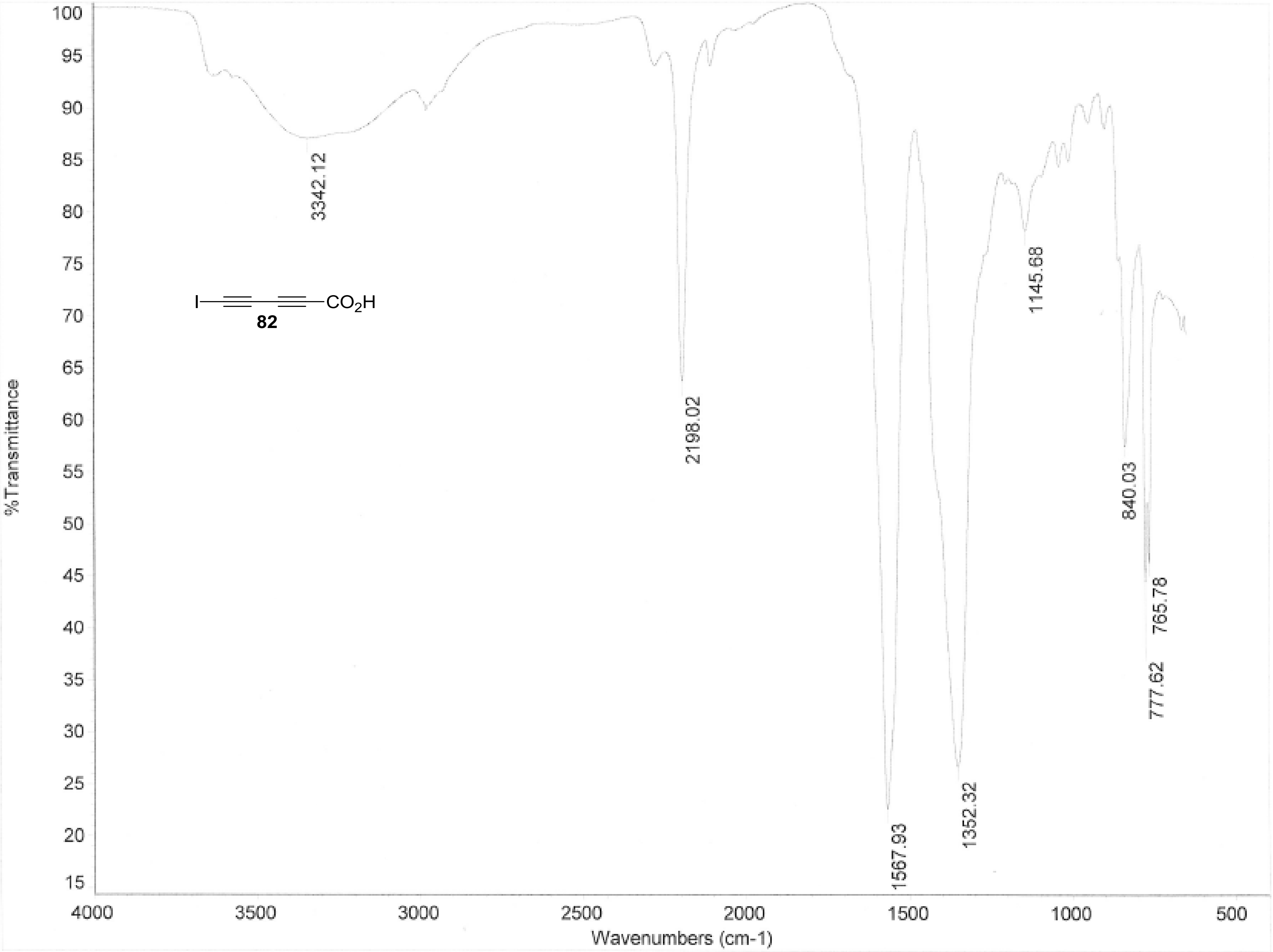
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **93**.



^{1}H NMR spectrum (400 MHz, MeOD) of compound **93**.



^{13}C NMR spectrum (400 MHz, MeOD) of compound **93**.



100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
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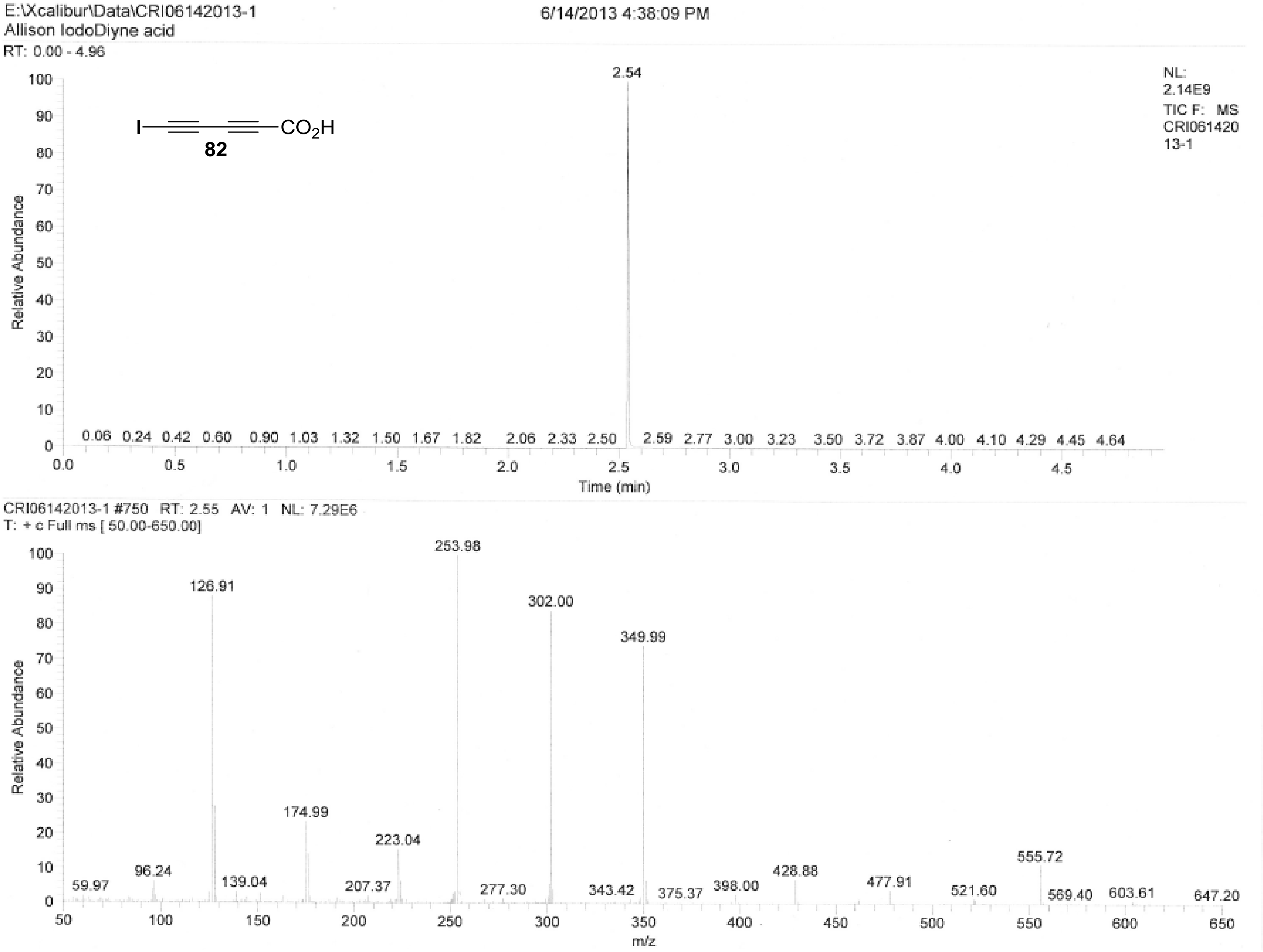
1567.93
1352.32
1145.68
840.03
777.62
765.78
I—≡—≡—CO2H
82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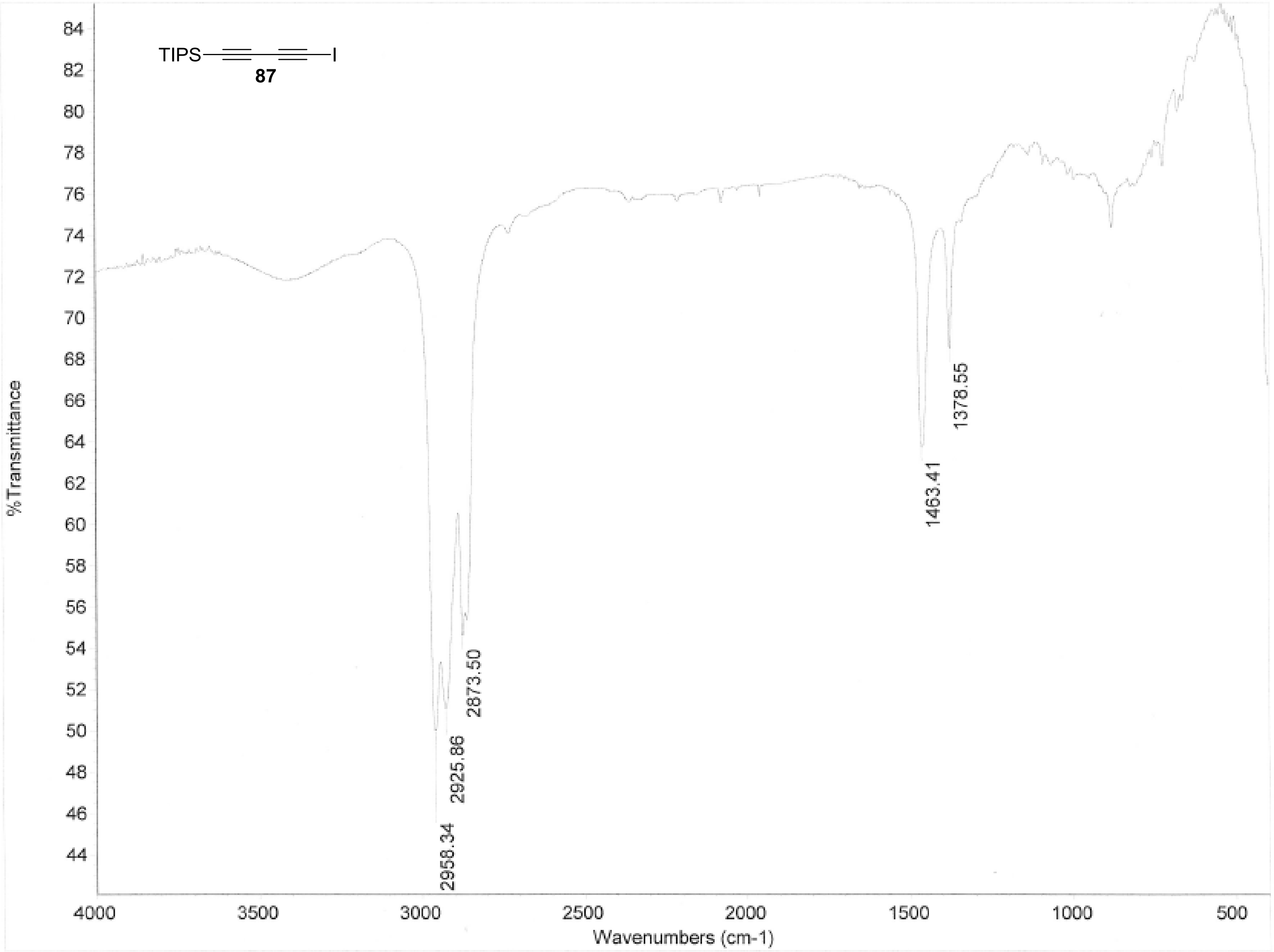
TIPS
I
87
%Transmittance
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
2958.34
2925.86
2873.50
1463.41
1378.55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

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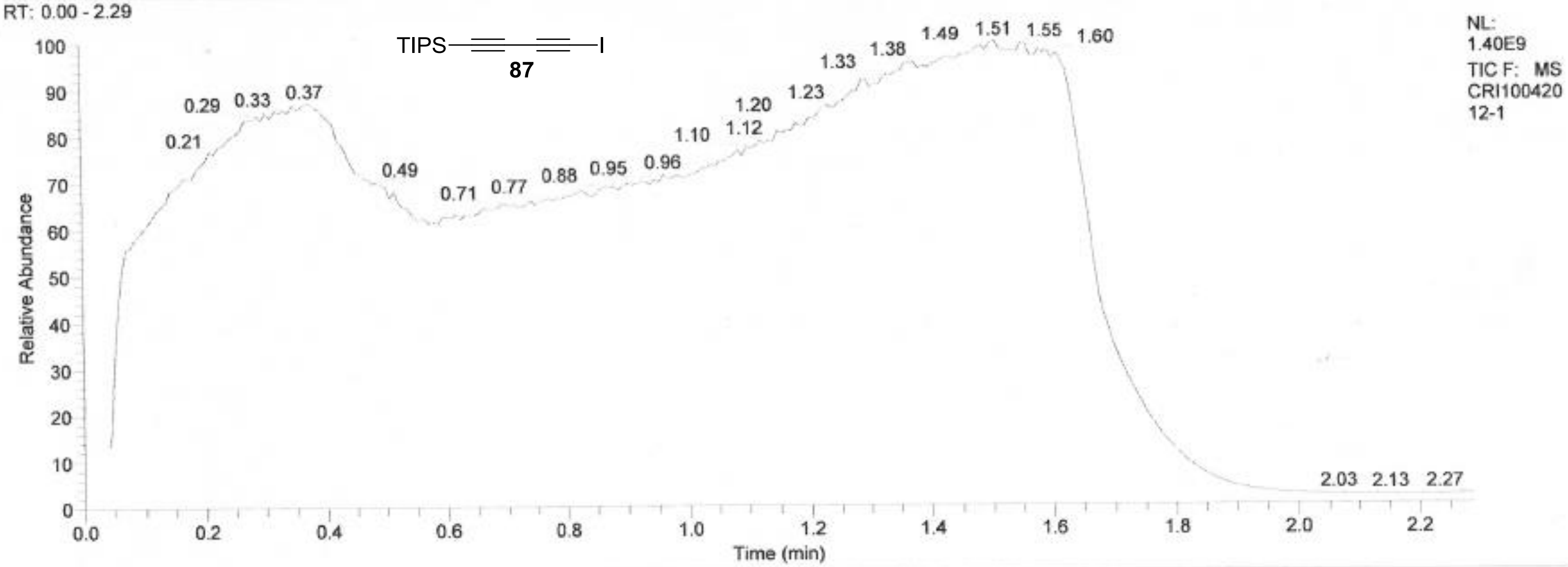
TIPSiodo diyne
RT: 0.00 - 2.29



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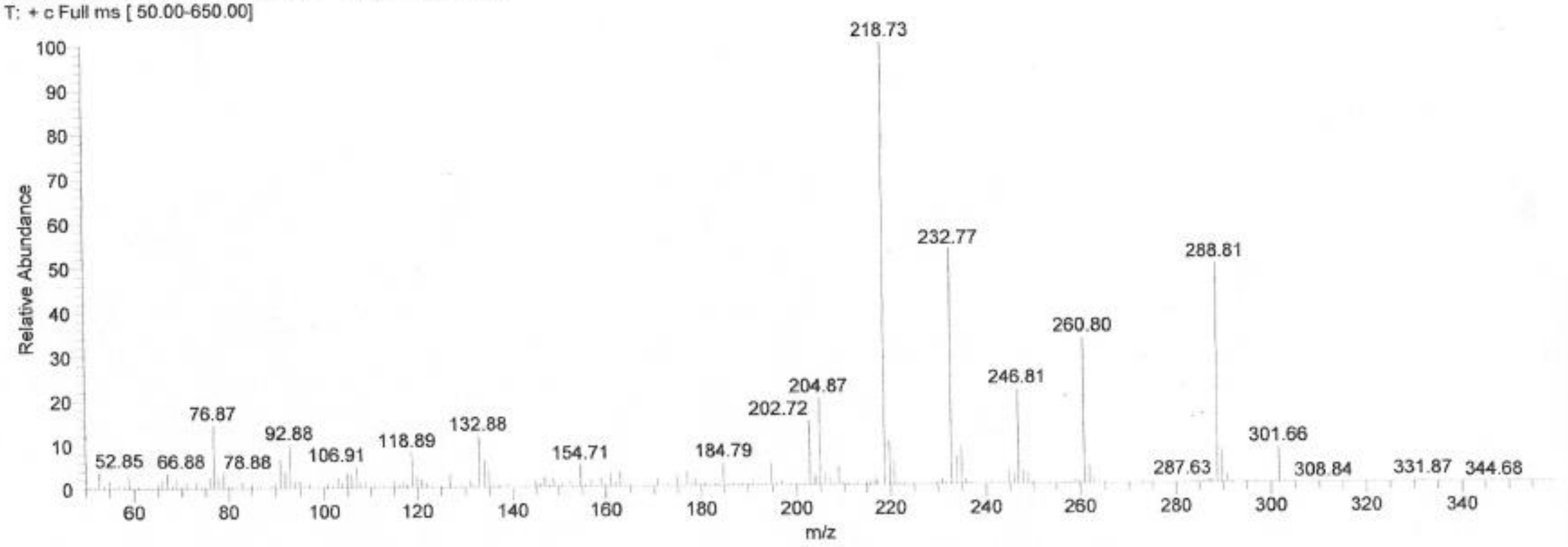
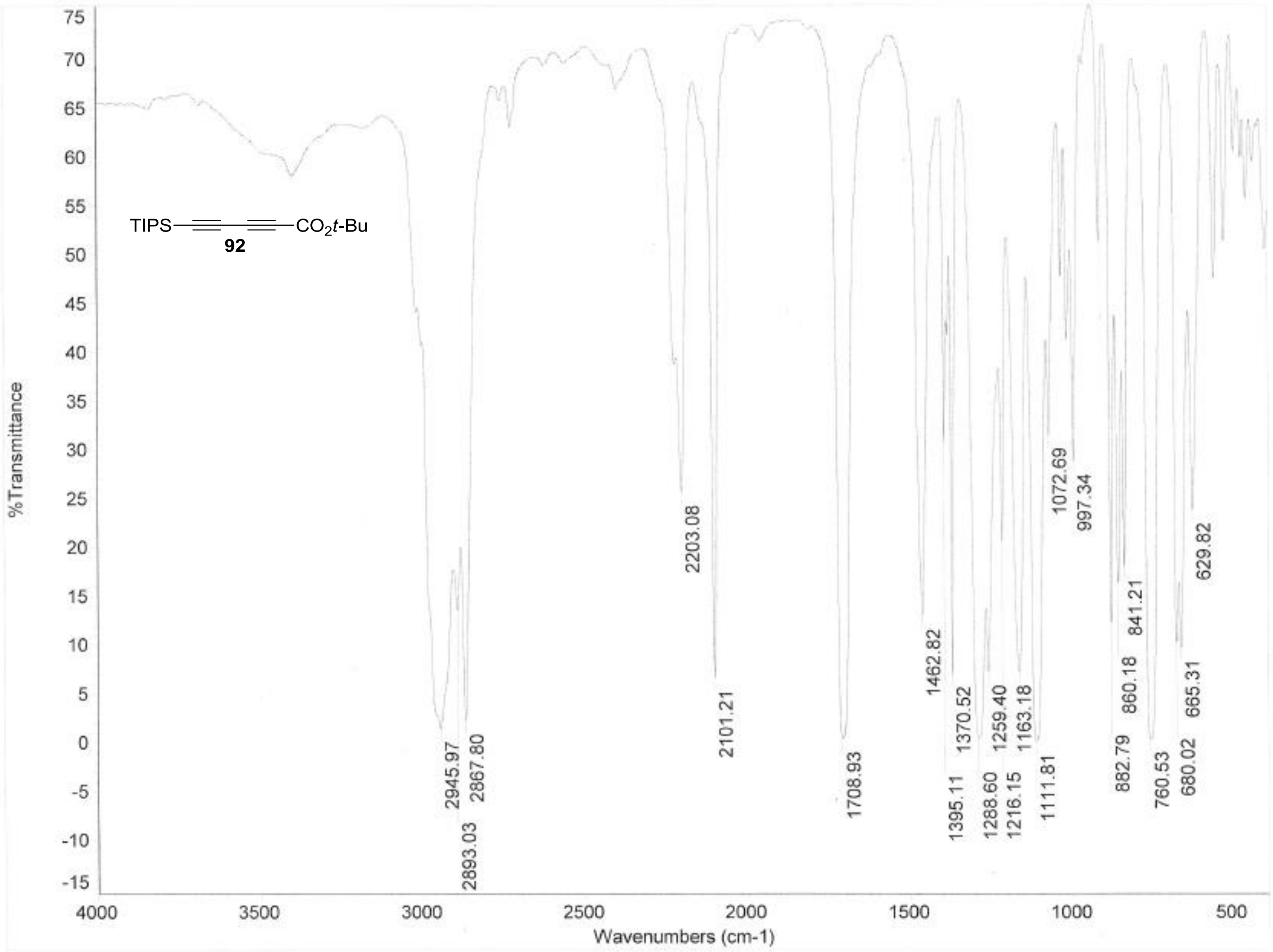
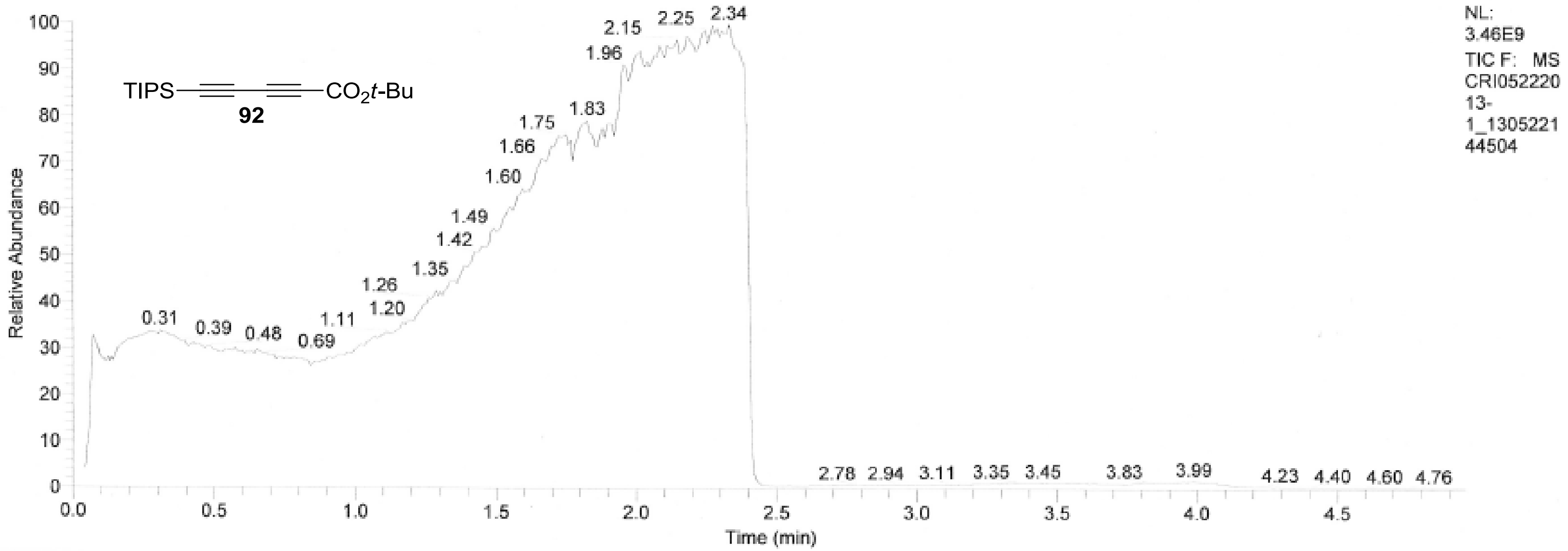



TIPS—≡—≡—CO2t-Bu
92
%Transmittance
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
2945.97
2893.03
2867.80
2203.08
2101.21
1708.93
1462.82
1395.11
1370.52
1288.60
1259.40
1216.15
1163.18
1111.81
1072.69
997.34
882.79
860.18
841.21
760.53
680.02
665.31
629.82

CRI05222013-1_130522144504 5/22/2013 2:45:04 PM
Allison
RT: 0.00 - 4.96



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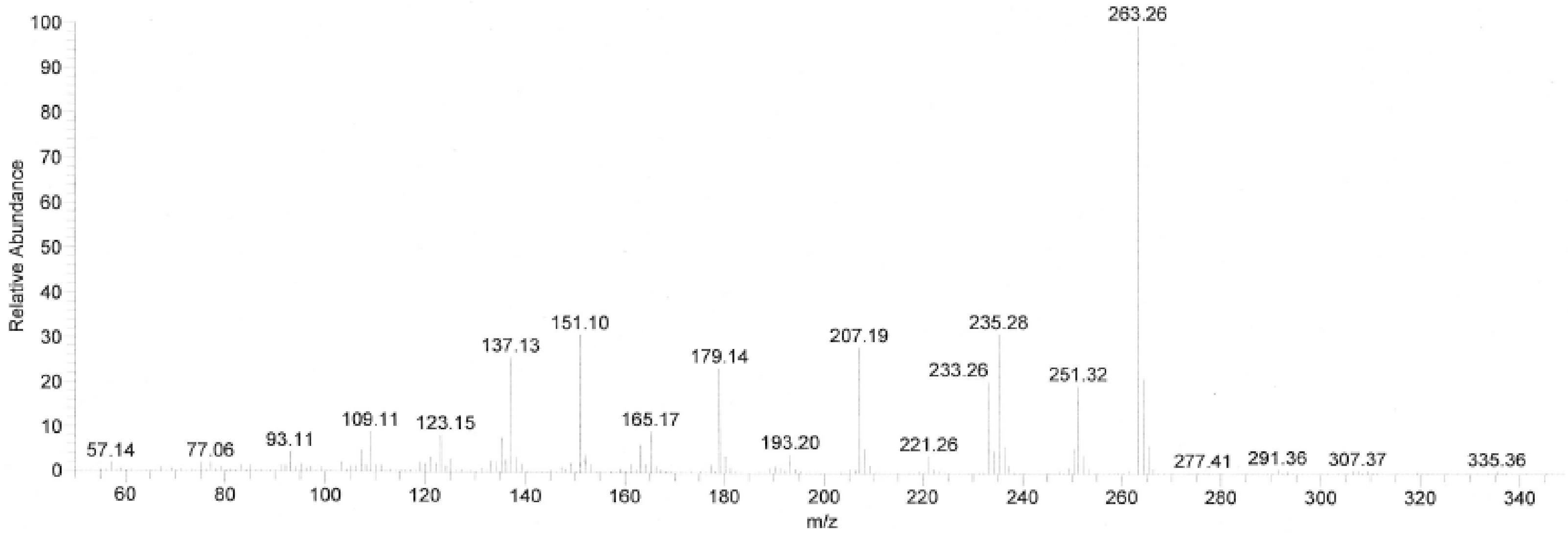
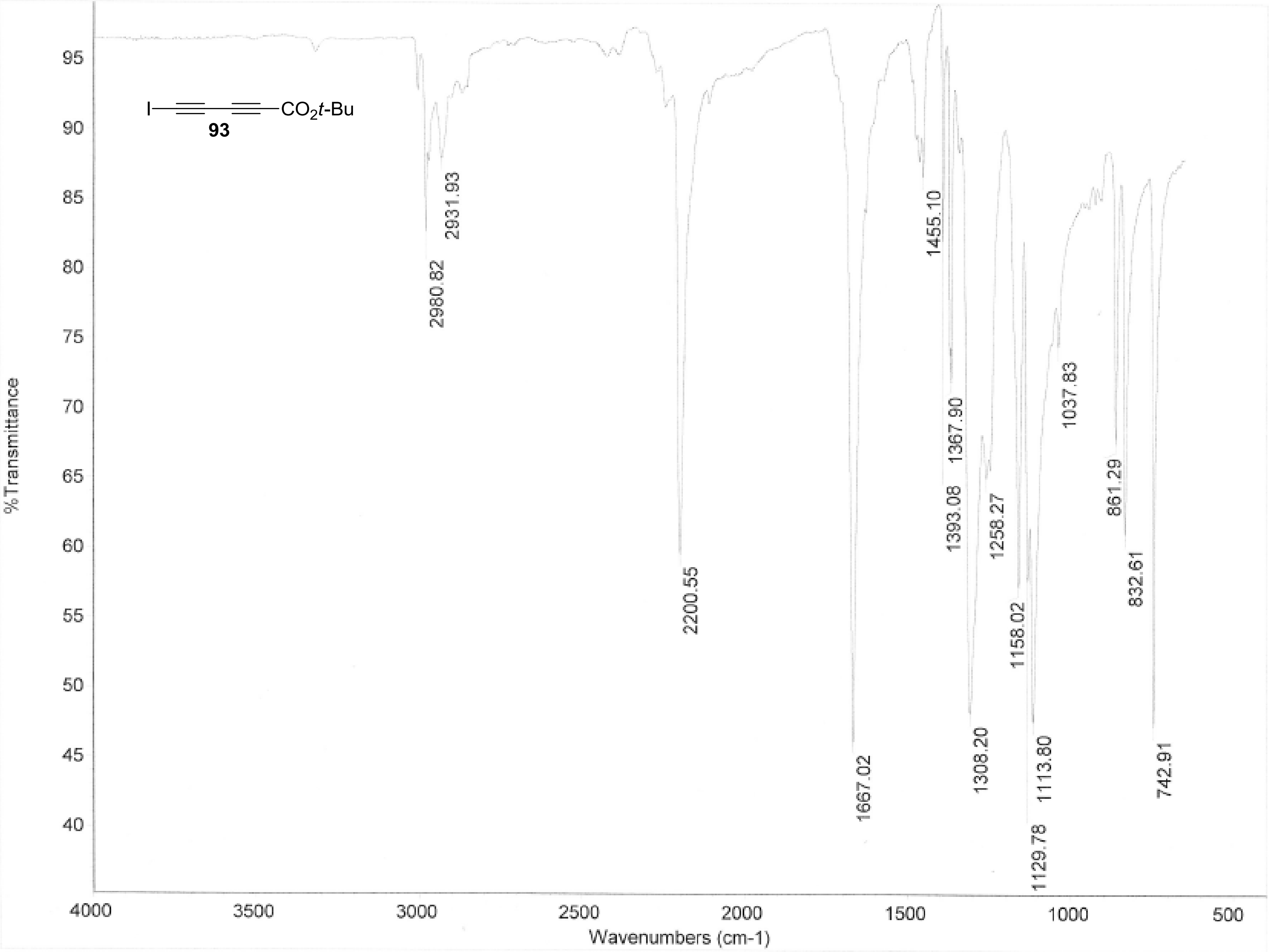
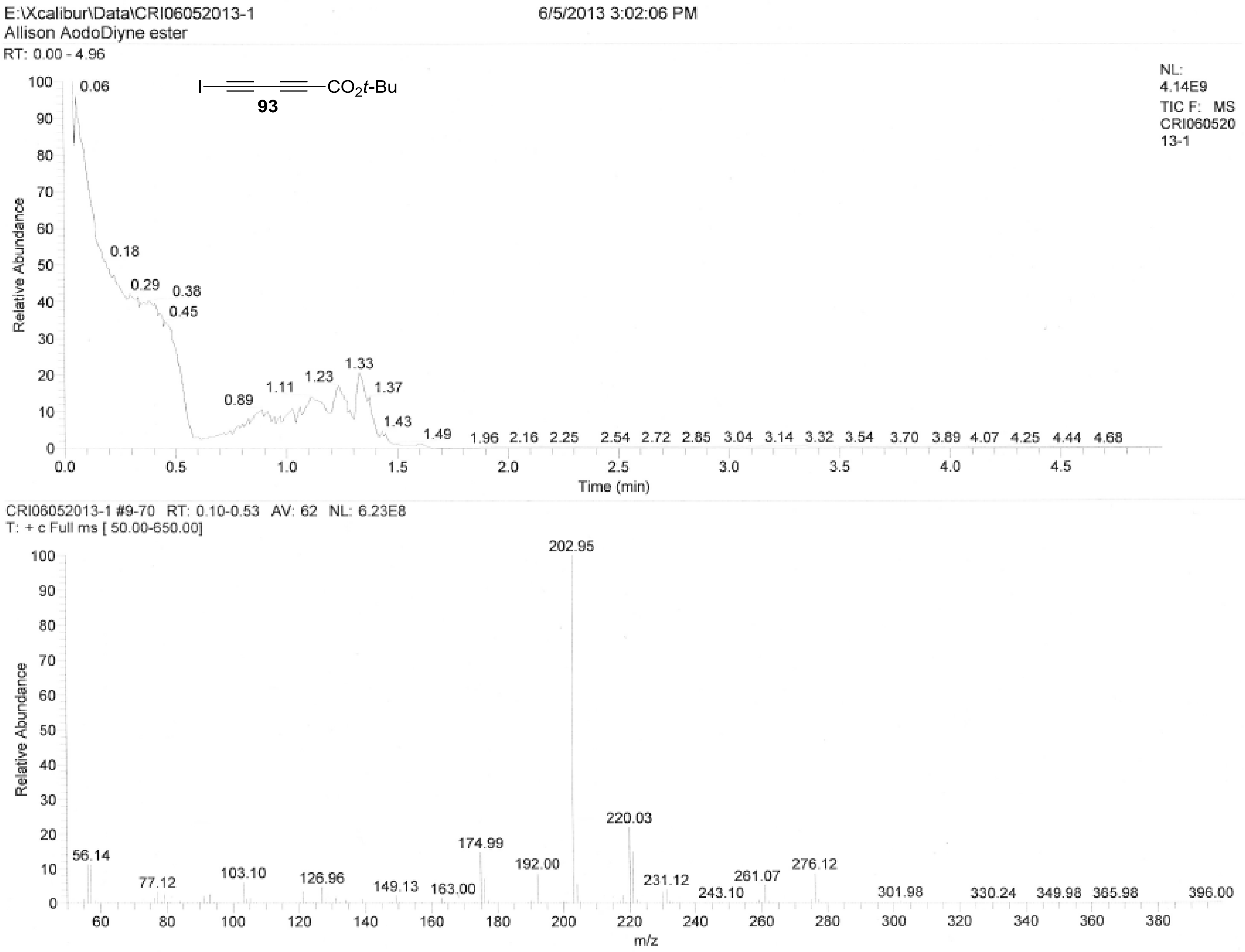



I—≡—≡—CO$_2$t-Bu
93
% Transmittance
95
90
85
80
75
70
65
60
55
50
45
40
2980.82
2931.93
2200.55
1667.02
1455.10
1393.08
1367.90
1308.20
1258.27
1158.02
1129.78
1113.80
1037.83
861.29
832.61
742.91
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


E:\Xcalibur\Data\CRI06052013-1
6/5/2013 3:02:06 PM
Allison AodoDiyne ester
RT: 0.00 - 4.96
I—≡—≡—CO2t-Bu
93
NL:
4.14E9
TIC F: MS
CRI060520
13-1
Relative Abundance
0 10 20 30 40 50 60 70 80 90 100
0.06
0.18
0.29
0.38
0.45
0.89
1.11
1.23
1.33
1.37
1.43
1.49
1.96 2.16 2.25 2.54 2.72 2.85 3.04 3.14 3.32 3.54 3.70 3.89 4.07 4.25 4.44 4.68
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5
Time (min)
CRI06052013-1 #9-70 RT: 0.10-0.53 AV: 62 NL: 6.23E8
T: + c Full ms [50.00-650.00]
Relative Abundance
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192.00
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56.14
103.10
126.96
77.12
149.13
163.00
231.12
261.07
243.10
301.98
330.24
349.98
365.98
396.00
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380
m/z