MONASH University

Polyynes to Polycycles: The Synthesis of π-Rich Molecules *via* Domino Electrophilic Cyclisation of Polyynes

Annaliese Selina Dillon

B. Pharm. Sci. Hons

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Medicinal Chemistry, Monash Institute of Pharmaceutical Science

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Abstract

π-Rich acenes and heteroacenes are ubiquitously employed within materials science research due to their electronic and photonic activity. These properties have allowed this class of compounds to be utilised as organic semiconducting materials for application within organic light emitting diodes, field effect transistors, photovoltaic cells, and as biomedical imaging agents. These π-rich materials also exhibit structure property relationships whereby variation in important structural features of the organic molecules will lead to change in electronic and photonic activity. These features can include heteroatom incorporation, ring fusion pattern and planarity. Opportunity to vary these features allows the materials scientist to 'fine tune' the organic molecule to develop the optimal set of electronic/photonic properties as they pertain to a particular device application. Unfortunately, there are limited synthetic methodologies that afford polycyclic systems, therefore restricting organic materials research. Of the methodologies available, few also address the requirement to afford structurally diverse π-rich molecules again limiting research efforts that seek to develop optimised electronic/photonic materials.

This thesis increases the synthetic access of diverse π-rich materials through the development of atom economical domino cyclisation reactions, referred to as poly-electrophilic cyclisations (PEC) (Fig. i). The one step reaction cascade has been shown to readily incorporate chalcogens (S, Se, and Te), afford varied ring fusion patterns (five and six membered rings) and furnish both planar and non-planar (twisted-spiral shaped) materials. As these cyclisation reactions require polyyne starting materials (consecutive or non-consecutive) this thesis also details the optimised synthesis of all required polyynes so as not to reduce the utility of the domino reaction.

Chapter 2 of this thesis details the use of an ambiphilic reagent (MeACl, A = S, Se, Te) that when added to a consecutive polyyne promotes a reaction cascade of electrophilic cyclisations. This novel reaction incorporates the S, Se or Te atoms from the ambiphilic reagent to afford poly-fused chalcogenophenes in moderate-high yield. Chapter 3 presents the bi-directional application of the previously reported double-electrophilic cyclisation (DEC) by Gupta and Flynn. This chapter expanded the scope of the DEC reaction but also made significant findings as to its limitations, affording heteroacene products featuring seven aryl rings. Finally, in Chapter 4 of this thesis poly-electrophilic cyclisation was explored to afford acenes featuring

up to ten aryl rings. These acenes were also found to be non-planar, exhibiting a twisted-spiral conformation.

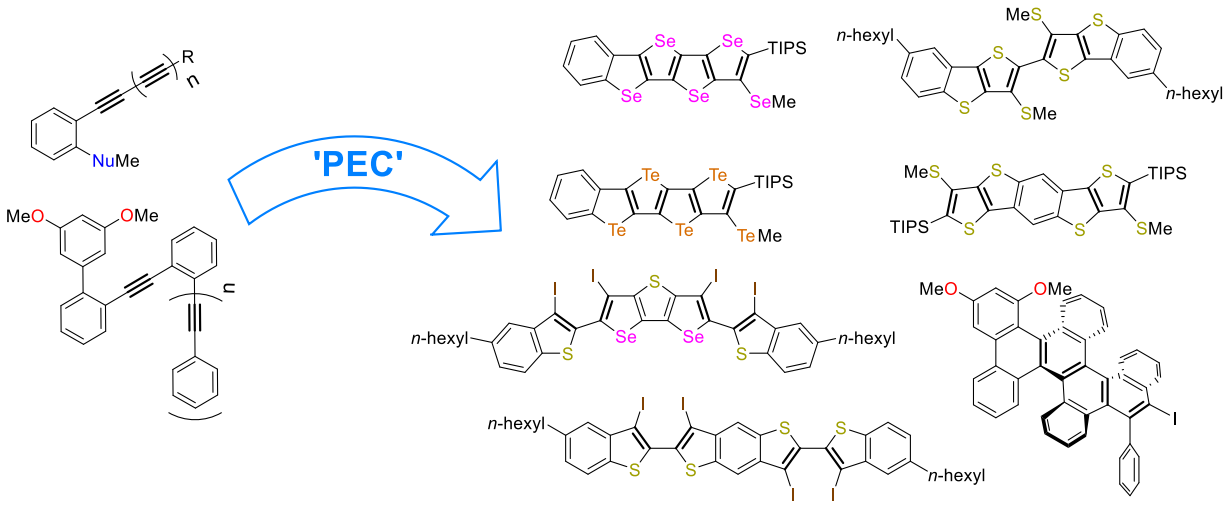

Figure i: Graphical representation of the one step conversion from polyynes to polycycles through Poly-Electrophilic Cyclisation (PEC).

Declaration

This thesis is an original work of my research and contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Print Name: Annaliese Selina Dillon

Date: 8th of October 2021

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Abbreviations and acronyms

[O]	oxidation
α	alpha
β	beta
σ	sigma
π	pi
μL	microlitres
μM	micromolar
δ	chemical shift
°C	degrees Celsius
®	registered trademark
^{13}C NMR	carbon nuclear magnetic resonance
^{1}H NMR	hydrogen (proton) nuclear magnetic resonance
^{31}P NMR	phosphorus nuclear magnetic resonance
^{77}Se NMR	selenium nuclear magnetic resonance
^{19}F NMR	fluorine nuclear magnetic resonance
2D NMR	two-dimensional nuclear magnetic resonance
3D	three dimensional
1°	primary
2°	secondary
3°	tertiary
4°	quaternary
aq.	aqueous
Ac	acetyl
ACN	acetonitrile
br	broad
Boc	tert-butoxycarbonyl
Bu	butyl
Calcd.	calculated
d	doublet
dd	doublet of doublets
ddd	doublet of doublet of doublets

DCE	1,2-dichloroethane
DCM	dichloromethane
DEC	Double Electrophilic Cyclisation
DFT	density functional theory
DIPA	diisopropylamine
DIPEA	N,N-diisopropylethylamine
DMF	dimethylformamide
DMP	Dess-Martin Periodinane
DMSO	dimethylsulfoxide
DPPF	1,1′-ferrocenediyl-bis(diphenylphosphine)
e^-	electron
EDG	electron donating group
eq.	equivalence
Et	ethyl
EWG	electron withdrawing group
g	grams
(g)	gas
h	hour
hex	*n*-hexyl
HMBC	Heteronuclear Multiple Bond Correlation
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
HSQC	Heteronuclear Single Quantum Coherence
Hz	hertz
i-Pr	iso propyl
LCMS	Liquid Chromatography Mass Spectrometry
LDA	lithium diisopropylamide
LiMHDS	lithium bis(trimethylsilyl)amide)
LRMS	Low Resolution Mass Spectrometry
LUMO	Lowest Unoccupied Molecular Orbital
mg	milligram

Min	minute
mL	millilitre
mmol	millimoles
M	molar (moles/litre)
Me	methyl
MHz	Megahertz
mp	melting point
Ms	mesyl
n-	normal substitution pattern
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
NPA	Non-Planar Acenes
Nu	nucleophile
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
O	ortho
OFET	Organic Field Effect Transistor
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
OTf	trifluoromethanesulfonate
PEC	Poly Electrophilic Cyclisation
Ph	phenyl
Pr	propyl
ppm	parts per million
q	quartet
RBF	round bottom flask
rt	room temperature (22 °C)
R_f	retention factor
s	singlet
s-Bu	*sec*-butyl
sext	sextet
SPR	Structure-Property-Relationship

t	triplet
t-Bu	*tert*-butyl
t_R	Retention time
TBAF	tetra-*n*-butylammonium fluoride
TBS	tert-butyldimethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMS	trimethylsilyl
TS	transition state
UV	Ultraviolet

Nb. All chemical reagents are given by standard chemical formulas

1.0 Introduction

1.1 Why the fabrication of electronically and photonically active π-rich compounds requires improvement

π-Rich organic molecules possess inherent functionality that relates to their ability to delocalise π-electrons across conjugated systems for both intra- and inter-molecular purposes. Materials science researchers are acutely aware of this unique functionality and have harnessed it to create the fields of organic electronics and photonics.[1] Chemists, physicists, and engineers collaborate in this space to utilise the unique ability of π-rich organic materials to convert energy between light and electrical. This field has given rise to applications in organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs) for use in devices such as phones and TVs. OLED and OFET employment have provided superior performance to previous technologies and reduced the cost of fabrication. Another important contribution of π-rich materials in organic electronics is organic photovoltaics (organic solar cells).[2] In these devices, π-rich compounds are utilised due to their capacity to mobilise electrons to convert solar energy to electrical. The applications of this field are enhancing our ability to rely on renewable power sources to reduce global carbon emissions and the effects of global warming.[3] π-Rich material's distinctive ability to interact with light has also been applied to biomedical imaging as organ or tumour targeted fluorophores that aid in the treatment of various diseases such as cancer.[4]

In the field of drug discovery there is an understood requirement for medicinal chemists to manipulate organic compounds to incorporate varied pharmacophores. This variation is commonly performed to confer better ligand-binding site interaction or explore structure-activity relationships (SARs). This concept is common to materials science where variation in molecular structure is necessary to investigate changes in π-functionality. This functionality in turn effects device and fluorophore performance. In this space it is understood that changes in heteroatom incorporation, ring size, 2D and 3D symmetry and molecular size can effect change in electronic/photonic properties. These properties include but are not limited to, the energetics of the HOMO-LUMO gap, crystallinity, conductivity, donor and acceptor interaction, and interaction with varying wavelengths of light. Each of these properties are important within materials science as they dictate application performance. Therefore, just as medicinal chemists require diverse methods for affording small molecules and peptides, organic materials chemists require synthetic methods that afford diverse π-rich molecules. Accordingly, these synthetic

methods must also provide opportunity to optimise structure and function to better explore new properties and applications. Of course, there are π-rich compounds that have been previously afforded and applied to organic electronic devices successfully. However, there remains a great limitation as to bespoke synthetic methods that appropriately address the requirements of organic materials chemists more broadly.

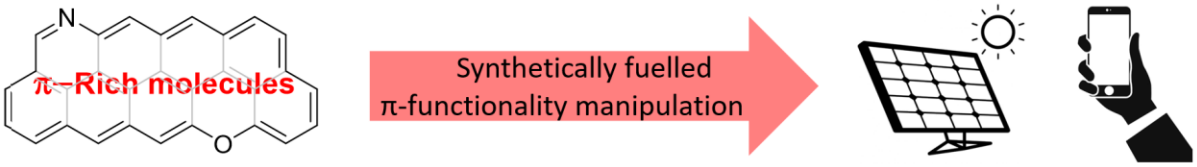


Figure 1: Graphical representation of the applications of functionally manipulated π-rich molecules.

When discussing π-rich materials, we refer to organic compounds that have an increased presence of π-orbitals. These orbitals are present across arene, alkene and alkyne covalent bonds. In a conjugated system, these orbitals can overlap allowing electrons to move laterally between π-bonds in the molecule, acting as semi-mobilised electrons.[5-7] When this mobilisation phenomenon occurs in cyclic aromatic materials, the π-electrons mobilise in a doughnut-like shape (Fig. 2, top diagram). Within this diagram, the light purple ring indicates areas of electron density and the yellow arrow represents electron movement. Also shown is how this electron density is extended in aryl polycyclic systems to provide a material that has a very high level of electron mobility. In the polycyclic diagram, the electron density 'doughnuts' link up, allowing electrons to flow between the far ends of the molecule. This demonstrates how polycyclic organic systems provide the source of π-richness that is required in materials science applications.

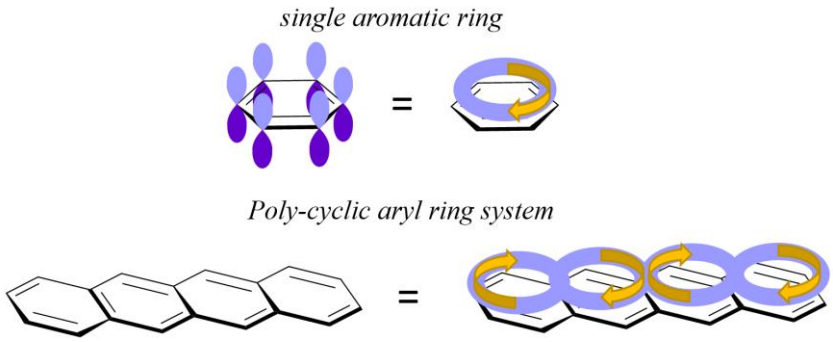
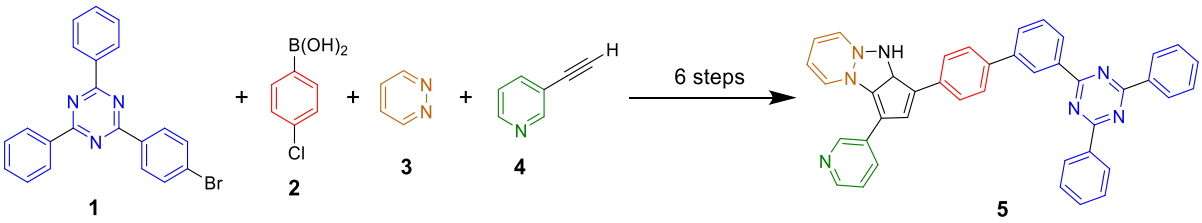


Figure 2: Graphical representation of the π-cloud of electrons that exists above conjugated cyclic systems. Purple rings represent electron density and yellow arrows represent directions of electron movement.

Despite their proven utility, the synthesis of polycyclic materials can be inefficient and cumbersome. Ring forming reactions are often capricious and don't have opportunity for variation of atom incorporation. When multiple fused rings are required, the limitations of ring forming reactions (low yield, high number of steps or stages) can multiply and lead to an inefficient and intractable synthesis. Alternatively, the required rings can be incorporated from commercially available starting materials as shown in Scheme 1.[8] This method although useful in limited cases, severely limits the diversity of the π-rich products as structural features are dictated by reactant commercial price and availability.

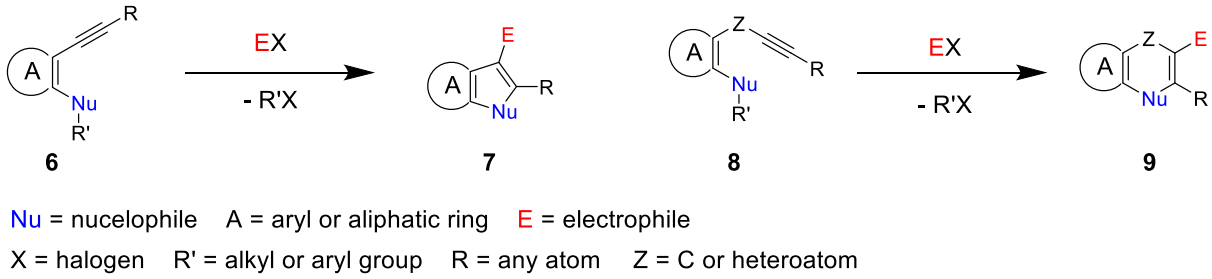


Scheme 1: Described synthesis of a product utilised in an organic electroluminescence device. Starting materials are coloured to show that all coloured rings in the product are sourced from commercially available reagents, limiting opportunity for diversity.

We view this current situation as unacceptable and believe there must be a concerted effort to develop synthetic methodologies that efficiently afford polycyclic π-rich materials with good opportunity for diversification. There are often two main objectives in developing new synthetic methodologies: enhancing the synthesis and accessibility of known materials with

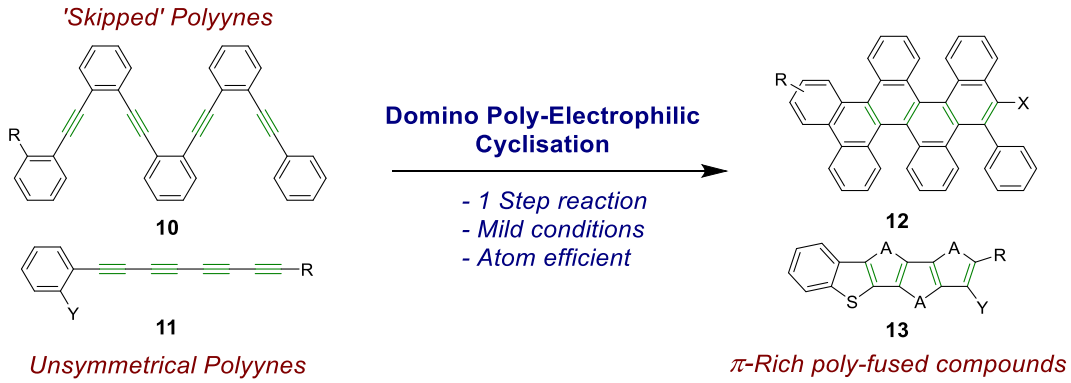
known functions and providing synthetic access to previously inaccessible materials for the development of new functions. Both require exploration in the π-rich methodology space.

Electrophilic cyclisation affords small polycyclic products in a one-step atom efficient reaction from simple materials that feature an activated alkyne (Scheme 2). This reaction has historically served the fields of both drug discovery and organic electronics very well. Particularly iodocyclisation (E = I) has provided enhanced access to benzo-thiophenes, -furans and -indoles for direct applications. There have been some preliminary developments in the electrophilic cyclisation space whereby larger polycyclic compounds are afforded by electrophilic activation and cyclisation of polyyne starting materials.[9-13] Although currently focused on the cyclisation of diynes to form two or three new rings, this concept presents fantastic potential to afford larger polycyclic π-rich compounds.



Scheme 2: Electrophilic cyclisation of an activated alkyne to form new five or six membered rings.

It is therefore the broad strategy of this project to explore the access of polycyclic π-rich materials *via* electrophilic activation and cyclisation of polyynes in a one-step domino reaction (Scheme 3). This exploration will require encountering the predicted limitations surrounding polyyne synthesis. This will be an important aspect to the work as developments in polyyne→polycycles will be inherently limited by poor access to starting materials. Once suitably afforded, these polyyne precursors will be subject to various forms of 'poly-electrophilic cyclisation' where a cascade of electrophilic cyclisations will potentially occur within a single step. If successful, this work aims to develop multiple bespoke methods of forming π-rich materials that will have great potential for application in providing better opportunity to manipulate the π-functionality of the desired compounds of organic electronic chemists.



Scheme 3: Graphical broad summary of the proposed work of this project. A = any element except C or H, X = any halogen and Y = Any element.

1.2 Applications of acenes and heteroacenes in materials science

Materials science is an interdisciplinary field that covers the formation and use of new materials and solids from a chemical and/or engineering viewpoint. Research within the field has led to discoveries surrounding electronics, aerospace, telecommunications, information processing and energy conversion.[14] Within materials science, the exploration of electronics at its core is the study of energy conversion, with almost all modern technology requiring electrical energy from a power point to, for example, light-up a display (light energy) or heat an element (heat energy). Since the technology age began, electronics has clearly been an area of great innovation, as such, research is always ongoing to improve upon the technology that's available and invent what is not. Organic chemists began to enter the electronics space in the 1970s with the first experimental reports of organic materials able to carry an electric charge and function as semiconductors.[15-17] It was already known at this time that aromatic compounds had unique potential to interact with light and perform differently in chemical reactions as a function of their π-molecular orbitals, yet these were the first reports of their electrical applications being realised.[18, 19] Utilising organic materials in electronics provides potential for improved flexibility, reduced production cost and the overall manufacture of a better performing device. Since their development, organic semiconductors have been utilised in OLEDs, OFETs and organic photovoltaics (OPVs).[2] In each of these applications, π-rich molecules were developed into their corresponding applicable materials through measured manipulation of their structure-property relationship.[20-22] This work allows materials scientists to develop better performing electronic devices through variation of the chemical structure of the π-rich materials and therefore π-functionality. Here we present a summary of the contributions of organic π-rich materials to organic electronics applications.

1.2.1 Organic light emitting diodes (OLEDs)

In the last few decades OLEDs have positioned themselves as a light source that is competitive with the current technology. The advantages OLEDs being their physical flexibility and transparency, lower cost of production and better environmental compatability.[23, 24] Diodes were the first device to use semiconducting materials to facilitate the flow of electrical current in one direction. This was an important contribution to the field as semiconducting materials can act as both conductors and insulators of electrical current, preventing the flow of current in one direction, and allowing it in the other. This can be a particularly useful feature if components within a circuit would be damaged if electrical current was to flow through them in the 'wrong' direction. But how do diodes achieve this uni-directional flow of current?

The semiconducting materials within diodes are made up of **p-type** and **n-type** materials that are fundamentally, low energy and high energy materials respectively (Figure 3). A 'junction' exists between these materials (shown as where the green and blue squares meet), for a semiconducting material to conduct electricity, there must be electron flow in both directions to each material (shown as yellow arrows).

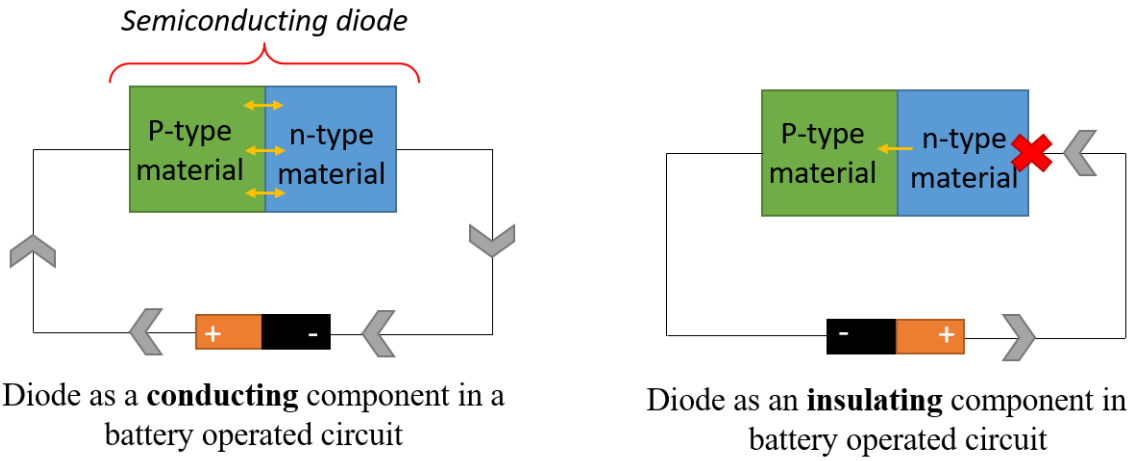


Figure 3: Graphical representation of diodes acting as either conductors (left) or insulators (right), both due to the presence of semiconductors within the p-type and n-type materials. NB: The grey arrows indicate the flow of positive charge in this figure. This can also be depicted as a negative charge due to electrons being negatively charged themselves.

Electrons can naturally flow from a high energy material (n-type) to a low energy material (p-type) with no assistance, but electron flow from low energy to high energy requires an energy supply. A common analogy for this principle is how rolling a ball down a hill requires no effort

(as high to low energy) but pushing it up a hill requires effort (low energy to high energy). As it is shown in Figure 3, current (electrical energy) must flow to the lower energy material (p-type) to overcome the energetic barrier and allow electrons to flow between the semiconducting materials (pictured left). If current is supplied to the n-type material (pictured right), there is no electron flow from the p-type material to conduct current across the 'junction'.

Light emitting diodes perform as traditional diodes as shown above, but also utilise changes in energy levels that take place at the junction between the n-type and p-type material to produce photons (light energy). It was described that electron flow between the n- and p-type materials conducts current. This electron 'flow' is many electrons moving between low and high energy states. The high energy state is known as the 'conduction band', when an electron is in this state it is referred to as 'free-flowing' (Fig. 4). The low energy state is known as the 'valence band', when electrons are in this state, they are referred to as 'holes'. When an electron is promoted from the valence band to the conduction band by electrical current it is known as 'generation'. When the electron *falls* from the conduction band back down to the valence band this process is referred to as 'recombination', this process releases energy. In a light emitting diode, the energy released upon recombination is converted to light energy or photons that can be perceived as visible light being emitted from the device. The electrical current supplied to the OLED device provides the energy for 'generation' to occur, completing the cycle of excitation (↑) and relaxation (↓) of electrons.

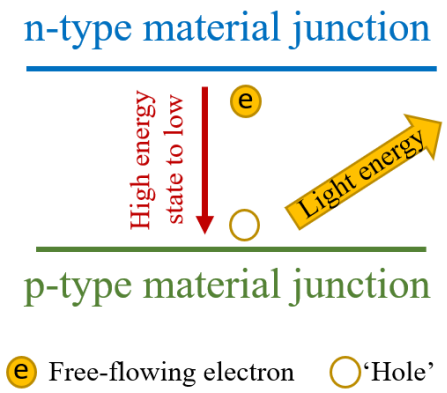


Figure 4: Graphical representation of recombination at the interface between the n-type and p-type material junction.

Within OLEDs, the wavelength of light emitted upon recombination relates to the energy difference between the p- and n-type materials. This can be modified by techniques such as

‘doping’ (introducing impurities) or variation of the chemical structures utilised. Light emitting diodes are a form of solid-state lighting, that includes traditional inorganic light emitting diodes (LEDs), polymer LEDs (PLEDs) and organic LEDs (OLEDs). Broadly, solid-state lighting presents itself as a more environmentally conscious method of converting electrical energy to light energy due in part to increased lifetime and improved light output to energy consumption ratio. Although the electricity used to light our buildings, streets and technology displays may seem insignificant, it in fact accounts for around 20-30% of global electricity consumption.[25] When comparing forms of solid-state lighting, LEDs are seen as the more outdated devices as OLEDs and PLEDs have evidenced better colour contrast than LEDs and have the physical flexibility that is increasingly important to the current consumer market.[26] Accordingly, by utilising the unique benefits of OLEDs to develop devices and lighting systems, materials scientists can address both an enhancement in product performance and cost of production, but also reduce the environmental impacts of traditional lighting.

Figure 5 shows a summary of reported π-rich compounds utilised in OLED applications. Heteroacenes **14**-**16** were reported prior to and including the year 2000, and compounds **17**-**22** were reported in the last 10 years. Both sections show useful polycycles, however the more recent materials have better representation of heteroatom diversity. This is perhaps a function of material availability but also improved synthetic methods that have paved the way for materials scientists to diversify their compounds. In the time frames described in the figure, OLEDs have also progressed from academic explorations to commercial use within smartphones and other displays.

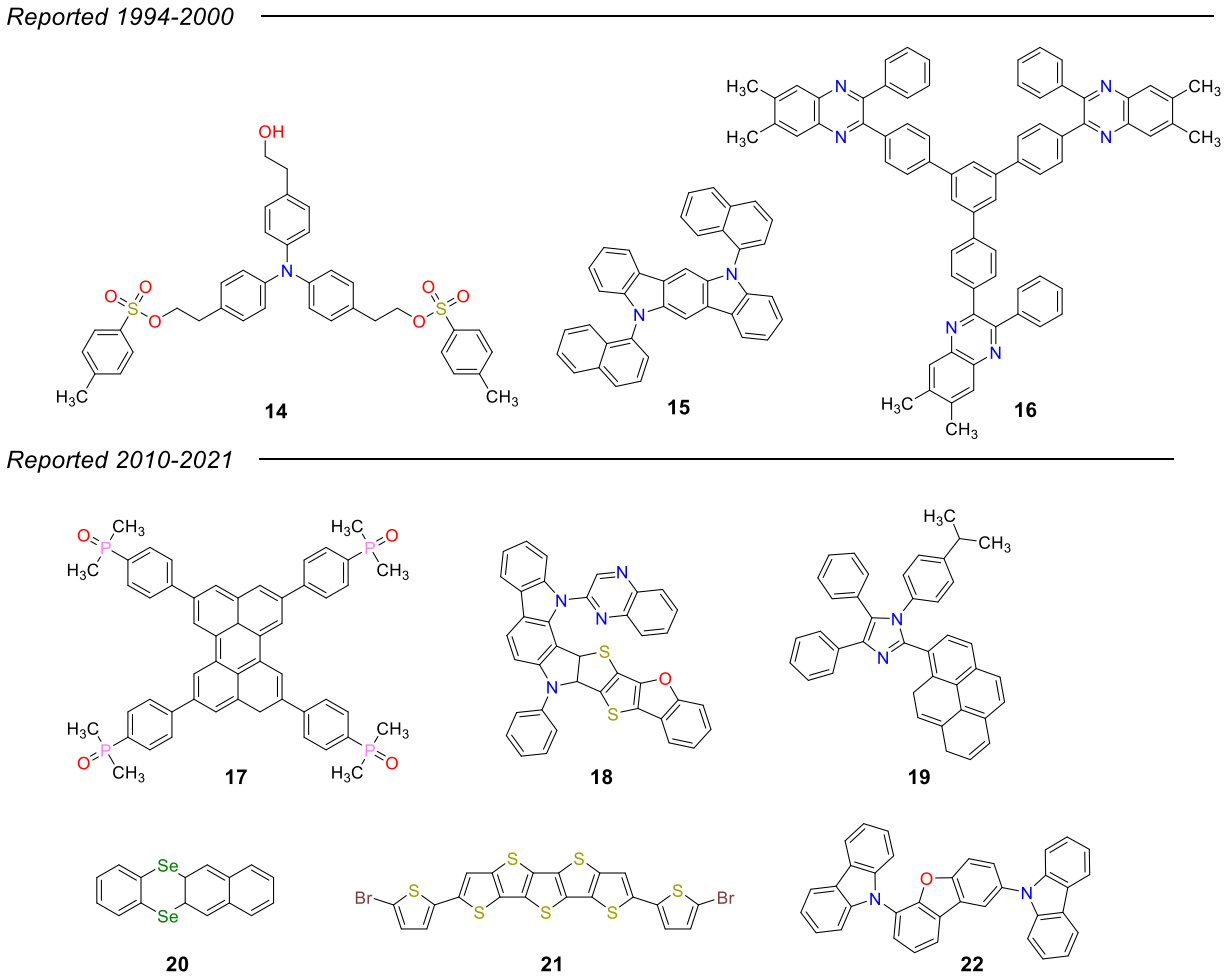


*Figure 5: Historical and recent examples of π-rich materials applied to OLED devices (**14**[27], **15**[28], **16**[29], **17**[30], **18**[31], **19**[32], **20**[33], **21**[34] and **22**[35])*

1.2.2 Organic field effect transistors (OFETs)

Field effect transistors are an integral part of modern electrical engineering.[36, 37] The first reports of field effect transistors (also referred to as solid-state transistors) occurred in the 1940s, with multiple physicist and engineers from across the globe solving different aspects of their application. These devices use an electric field (controlled by a 'gate') to control the flow of electrical current from one electrode (the 'source') to another (the 'drain') through a semi-conducting channel (Fig. 6). Identically to LEDs, the semiconducting materials in FETs feature p-type and n-type materials that when in contact with each other facilitate current flow *via* continuous 'recombination' and 'generation'. However, this current flow only occurs when the 'gate' supplies the necessary electrical energy to turn the transistor 'on'. This explains the utility of FETs in that current flow through them is controlled by a mechanism that is electronically controlled. Therefore, unlike the mechanical switches in our homes, this switch

can be turned off and on at very high speeds. This is an important feature for technology that works on a binary system (computers, TVs, phones) as the 0s and 1s of binary communication is translated by many FETs being continually switched 'off' and 'on'. In 1986 the first working organic FET was reported by Tsumura and co-workers, utilising poly-thiophene.[38] Similarly to OLEDs, OFETs have found application in modern electronics due to their performance in devices but also in the advantageous manufacturing process that is predicted to be cheaper, faster and more environmentally benign than utilising precious metals or silicon.[39]

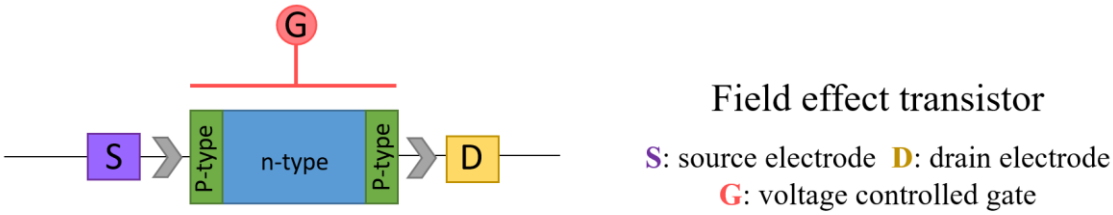


Figure 6: Graphical representation of a field effect transistor.

Figure 7 shows a summary of both historical (prior to and including 2000) and recent reports of employing π-rich compounds in OFETs. From humble beginnings of utilising simple acenes and heteroacenes (**23**[40] and **25**[41]) materials scientists have progressed to the use of more complex materials, pioneered by work such as **24** by Hu and co-workers[42] in 1999. Since their first implementation, OFETs have been developed to demonstrate a 1000-fold increase in performance, owing to all the research and developmental work by materials scientists.

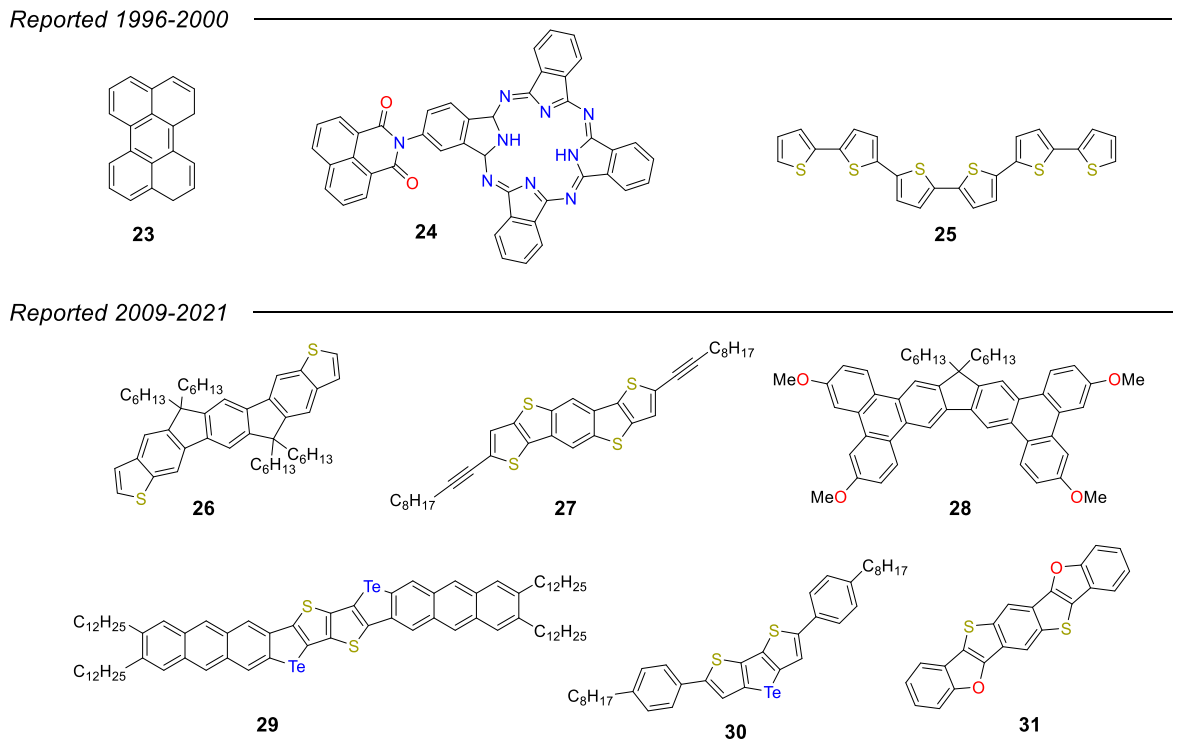


*Figure 7: Recent examples of π-rich materials applied to OFET devices (**23**[40], **24**[42], **25**[41], **26**[43], **27**[44], **28**[45], **29**[46], **30**[47] and **31**[48]).*

1.2.3 Organic photovoltaics (OPVs)

The requirement for renewable power sources is ever increasing, due to energy market instabilities, cumulative effects of climate change and the harmful effects on fauna and flora from the toxic fumes attributed to burning fossil fuels.[49] The implementation of renewable power systems is however limited by the fundamental requirement for efficient power conversion, something organic-electronic chemists and engineers are extremely familiar with.[50] Solar power is a vital area of research that seeks to convert the suns light or to a lesser extent heat energy (thermal solar panels) into electrical energy for direct use or storage. Photovoltaic cells are the units within solar panels that absorb photons (light energy) from the sun to excite electrons within a semiconducting material from the lower energy 'valence band' to the higher energy 'conduction band'. Once at this high energy level the free-flowing electrons can conduct an electrical current and thus, electricity is successfully converted from photons. Just as with OLEDs and OFETs, organic π-rich materials have been utilised within photovoltaic cells to improve upon device performance in a more environmentally conscious manner.

The first functioning OPV was reported in 1996 by Halls and co-workers with a 1% power conversion efficiency (PCE).[51] 25 years later, a record-breaking power conversion efficiency of 18% was recently achieved by Bryon Larson and co-workers.[52] Figure 8 presents **38**, the compound of which was utilised (in combination with three other π-rich polymers) by Larson to achieve the excellent results described. Accompanying **38** are a selection of other π-rich materials recently employed in OPV cells. Even from this small summary figure, it can be seen why variation in chemical structure is so necessary to the advancement of materials science. Each of these vastly structurally diverse materials having found success in application to OPVs. Continued method development studies in this space are necessary to ensure all opportunities of diversification are available to organic electronic engineers. This will ensure that materials scientists can continue to pursue improved PCEs unencumbered by synthetic limitations.

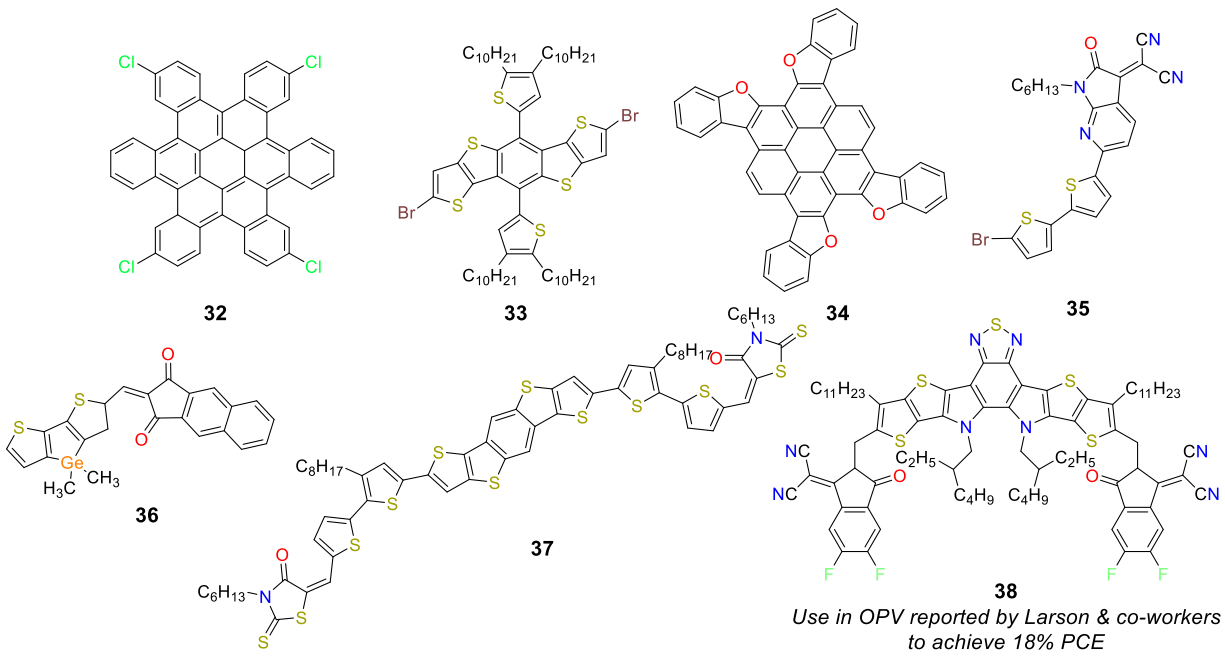
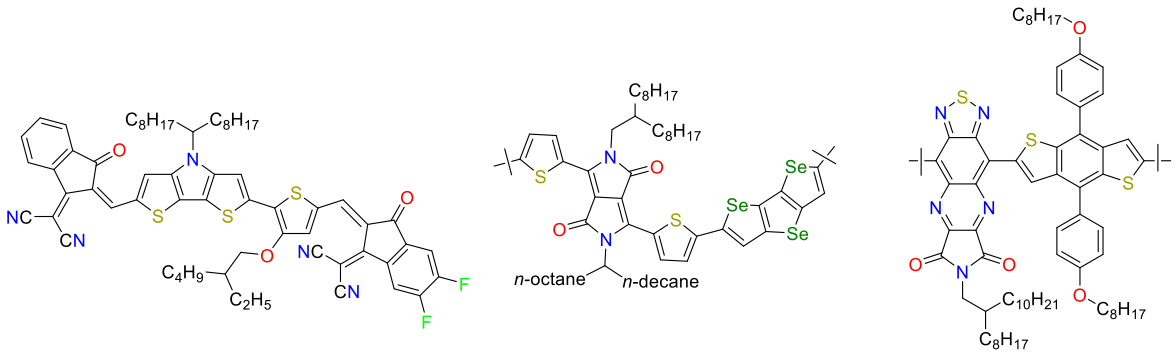


*Figure 8: Recent examples of π-rich materials applied to OPV devices (**32**[53], **33**[54], **34**[55], **35**[56], **36**[57] and **37**[58]).*

1.3 Applications of heteroacenes in biomedical imaging

Biomedical imaging plays an important supporting role to clinical treatment, aiding in diagnosis, disease mapping and pathology mechanism research.[59] π-Rich materials have long been utilised in this field as imaging agents due to their ability to act as fluorophores, emitting quantitively measurable light energy upon activation. There have been great developments in

the biomedical imaging space regarding both instrumentation and the underlying principle of imaging. In recent times the emergence of near-infrared fluorescence imaging has positioned itself as a superior technique for quick and long-term imaging. Heteroacenes utilised have even demonstrated superior activity when compared to commonly employed commercial standards such as indocyanine green.[60] This technique has been successfully utilised in tumour targeting applications to aid cancer diagnosis and treatment.[61] As an extension of this work photothermal therapy (PTT) has recently emerged as an effective method of treating cancer. This technique employs photo-thermal agents (PTAs), photoactive organic compounds or nanoparticles that are near-infrared absorbent and previously shown to bind to tumours. Upon binding and light activation, these PTAs will convert light energy to heat in the presence of the malignant tumour cells.[62, 63] This heat energy then increases the temperature of the tumour cells, ultimately inducing cancer cell apoptosis. This non-invasive technique has been shown to be safe, very effective and have particular applications in brain tumours due to the complex nature of brain cancer treatment.[64] This exciting therapy is an excellent example of researchers utilising the unique ability of π-rich organic compounds to absorb light energy and convert it to other forms of energy for meaningful applications. Figure 9 shows three select examples of near-infrared imaging agents **39**[65], **40**[66] and **41**[67]. Heteroacenes **39** and **41** have even been patented for their application, demonstrating the commercial value these heteroacenes possess within the biomedical imaging space.



39
Near-infrared fluorescence imaging agent

40
Near-infrared absorbing polymer with potential application in cancer phototheranostics

41
Near-infrared absorbing polymer with potential for photothermal therapy

Figure 9: Examples of heteroacenes employed in near-infrared fluorescence imaging techniques.

1.4 Helicenes

Helicenes are helical-shaped acenes that are traditionally quite large and have seen great utility and development in recent times.[68] Due to their unique shape and properties, these non-planar acenes make up their own chemical class aside from other acenes. From humble beginnings in 1903 the first helicene was discovered by Meisenheimer and Witte containing four-five fused aryl rings.[69] However, despite synthetically affording these examples, further method development in the space was slow to follow with few notable contributions in the 50 years following this discovery. This trend was then changed by important contributions from the likes of Newman, Wynberg, Martin, Laarhoven, and Katz.[68] The Diels-Alder reaction also proved beneficial in affording helicenes on large scale. Direct applications of the materials were not yet explored or proposed, fortunately for the field this did not limit synthetic efforts. This approach proved advantageous as the development of better crystallography and computational chemistry efforts allowed for the diverse applications of helicenes to be both investigated and posited. Since then, helicenes have found applications in dyes[70], Langmuir–Blodgett film[71], DNA interaction[72-74] and organic electronics[75] (Fig. 10).

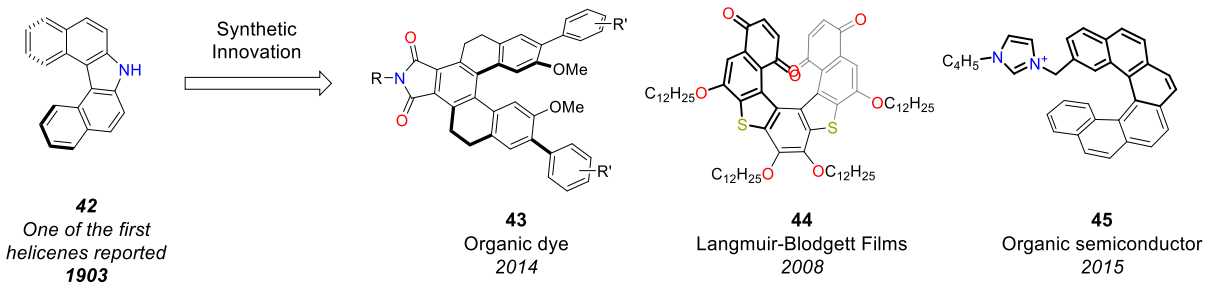


*Figure 10: Development from one of the first helicenes reported to recent applications (**42**[69], **43**[76], **44**[77] and **45**[78]).*

Due to the successful applications and ever-growing interest in these materials, there is a keen interest in diversification so that more 3D conformations can be explored. Variation in 3D conformation can result from the pattern of fused aryl rings and incorporation of different size and atom incorporating rings.

1.5 π-Rich synthetic methodology innovation: unburdening future organic electronics research

Oligo-acenes and -heteroacenes have clearly shown that they exhibit great utility, finding applications across various areas of organic chemistry. The benefits of these applications ranging from improving medical practices and treatment to environmentally focused applications that could reduce reliance on non-renewable power sources. However, the utility of these π-rich materials is still emerging, with many application-based publications occurring in that last 10 years. A major limitation of the field is the difficulty surrounding synthetic access. Larger molecules have common synthetic issues of solubility, long syntheses and therefore ultimately low yield and efficiency. When this is combined with the very limited number of synthetic methods available that form multiple new aromatic rings, organic electronic chemists simply do not have the plethora of methods that they require. The only solution for these researchers is to incorporate less diversity into their studies of organic electronic properties and application. A study of relevant literature shows the direct relationship between developments in the synthetic preparation of a class of compounds and publications reporting their applications (Fig. 11, generated from SciFinder® search). The data below illustrates that in the context of a unique and diverse class of compounds such as fused heteroacenes (**46**), to get an increase in applications, you must also have an increase in synthetic procedures available. The trend lines also demonstrate the complexity of π-rich materials as with smaller and simpler compounds, only a few publications that uncover their synthetic access being published would allow them to be utilised in applications for years to come. Clearly in this case, constant synthetic development in the space is required.

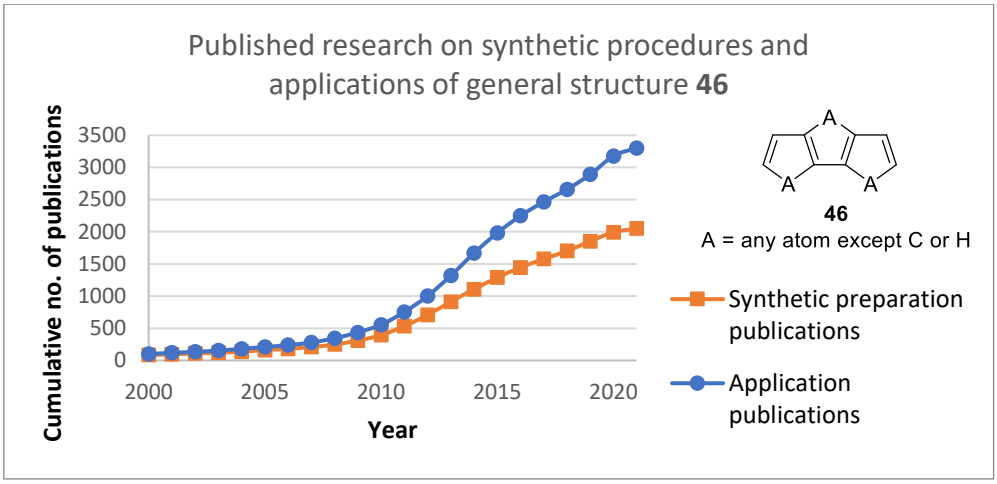


Figure 11: Cumulative published research from 2000-2021 referring to the synthetic preparation of ***46*** *(orange square) or applications of* ***46*** *(blue circles). Source: Scifinder®.*

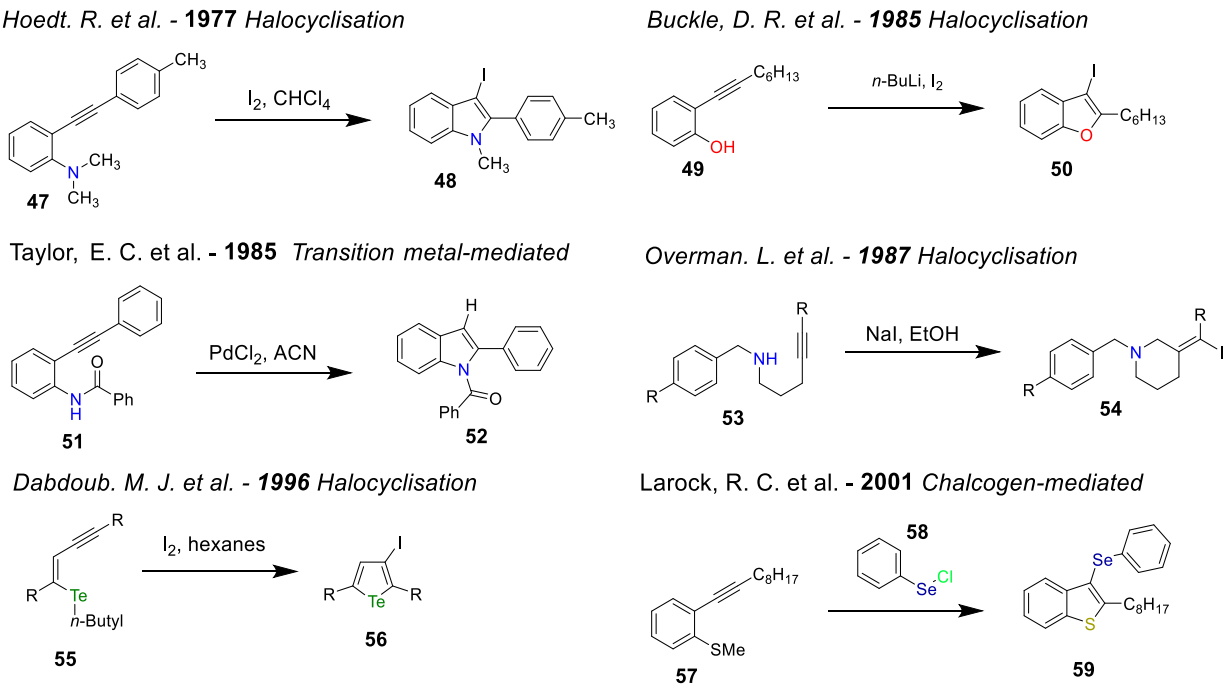
If diverse synthetic methods are not provided for organic electronic chemists, they do not have as greater ability to manipulate the functionality of their π-rich materials. This in turn, will limit the ability to create and enhance organic electronic devices and materials. This requires suitable synthetic research to be conducted that addresses the requirements of the application space, variation in heteroatom incorporation, ring size and organisation. If achieved, the π-rich materials space could experience accelerated research outcomes. One area of interest is an improved capacity to introduce heavier, more metallic elements (such as Se and Te) to enhance performance in specific applications.[79, 80] However, not all potential applications can be predicted. Accordingly, as with countless other synthetic methodology studies, the true potential applications of methodology innovations cannot be pre-emptively discerned. Consider the major contributions to synthetic chemistry that have been made: Palladium-catalysed cross coupling in organic synthesis (Richard F, Heck, Ei-ichi Negishi, Akira Suzuki, Nobel prize 2010), the development of chirally-catalysed oxidation reactions (K. Barry Sharpless, Nobel prize 2001) and the development of methodology for chemical synthesis on solid phases (Robert Bruce Merrifield, Nobel prize 1984).[81] Each of these revolutionary contributions to science, have paved the way application-based research to progress. Pd-coupling reduced the bottle-neck of carbon-carbon bond forming reactions in materials and medicinal application synthesis,[82] chirally-catalysed oxidation reactions have fuelled chiral catalysis and asymmetric natural product synthesis.[83] Finally Merrifield's solid-phase synthesis developments were paramount in the progression of peptide synthesis and the use of peptides in drug discovery.[84] These synthetic developments received notoriety not because they have

intricate mechanisms, but because they are useful and have led to new and enhanced practical outcomes.

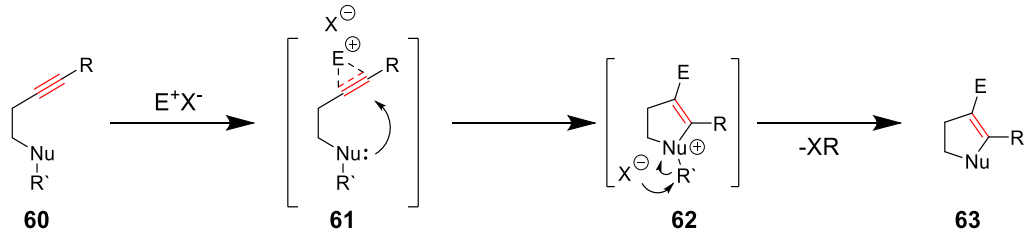
1.6 Electrophilic cyclisation (EC)

To help address the requirement for synthetic development in the π-rich space, we were first attracted to electrophilic cyclisation (EC). This reaction has for decades afforded small heteroacenes in a one step, efficient cyclisation reaction from alkynyl starting materials.[85]

The vast majority of electrophilic cyclisations in the 1960s-1990s focused on cyclisation of alkenes to give saturated heterocycles, likely due to the knowledge surrounding them being much better developed than alkynes. Alkyne synthesis was also not well developed at this time with Sonogashira coupling still evolving.[86] However in the late 1970s this began to change with emerging reports of electrophilic cyclisation of activated alkynes. Scheme 4 depicts notable contributions to the development of alkyne-activated electrophilic cyclisation from its invention.[87-91] The mechanism of alkyne-activated electrophilic cyclisation was also reasonably well defined early in the piece. One of the first descriptions of EC by Hoedt and co-workers (**47**→**48**) recognised that the proximity of the alkyne and nucleophilic dimethylamine are responsible for the electrophilic attack of iodine, noting that a cation intermediate was likely.[87] The atom economical mechanism of EC as it is known today is represented in Scheme 5. The presence of an electrophile (EX) initiates cyclisation and is in turn incorporated into a cation intermediate **62** that undergoes electrofugal loss of the R` group to give the cyclised product **63**.



Scheme 4: Notable examples of electrophilic cyclisation from invention to the year 2006.[87-92]



Scheme 5: Mechanism of electrophilic cyclisation.

Scheme 5 also shows the multiple sights of variation that exist in this reaction mechanism, the electrophile (E^+), nucleophile (Nu) and alkynyl terminal R group. The product is also shown as a non-aromatic five membered ring, but products of this cyclisation can be aromatic, non-aromatic, fused with other aryl rings and feature up to seven membered rings.

For the electrophile, iodocyclisation has dominated EC from invention due to the only requirement of reaction being the addition of simple iodine, which is cheap and readily available. The iodocyclisation product also features a newly incorporated iodo-group (**63**, E=I) that bears great utility for further functionalisation.[93] Other halocyclisations to incorporate a chloro- or bromo-group have also been well documented.[94, 95] Referring back to Scheme 4, the electrophile has also been varied from a halogen to include transition-metal (**51**→**52**)[91] and chalcogen mediated (**57**→**59**)[92] electrophilic cyclisation. These contributions significantly increased the potential diversity of electrophilic cyclisation and its capacity to afford diverse

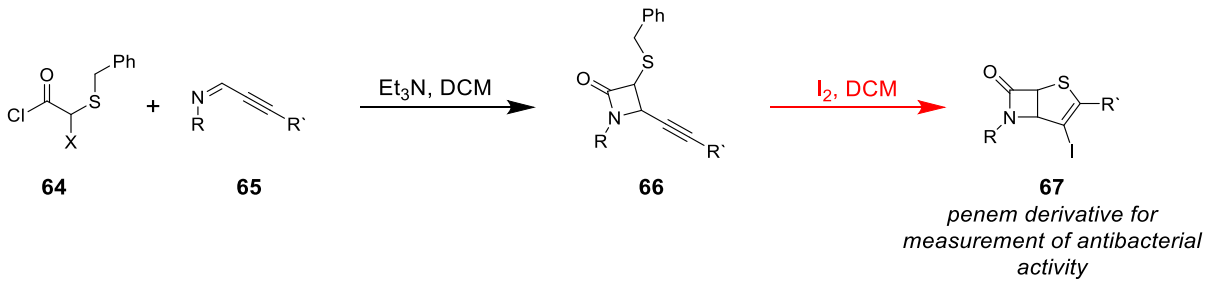
heteroacenes. Although it is worth noting that as Taylor's transition metal-mediated cyclisation was not described as an EC, there were little developments in the transition metal-mediated space until after 2000.[96]

Since the invention of EC, the reaction has been found to be very tolerant to variation of the nucleophile, largely presenting as sulfur[92], oxygen[97, 98] nitrogen[99, 100] or chalcogens such as selenium[101, 102] or tellurium[103]. The terminal R group as shown in Schemes 4 and 5 has also been varied to include aryl, alkyl and silyl examples. There appears to be a very large functional group tolerance in this R position.

Therefore, EC has been demonstrated to be an extremely efficient reaction that allows the incorporation of uncommon elements from across the period table to furnish novel heterocycles. It is also performed under mild conditions, complying with the requirements of green chemistry. Subsequently the applications of this reaction to the relevant organic chemistry fields will be explored to address how this particular synthetic innovation has directly or indirectly lead to practical application outcomes.

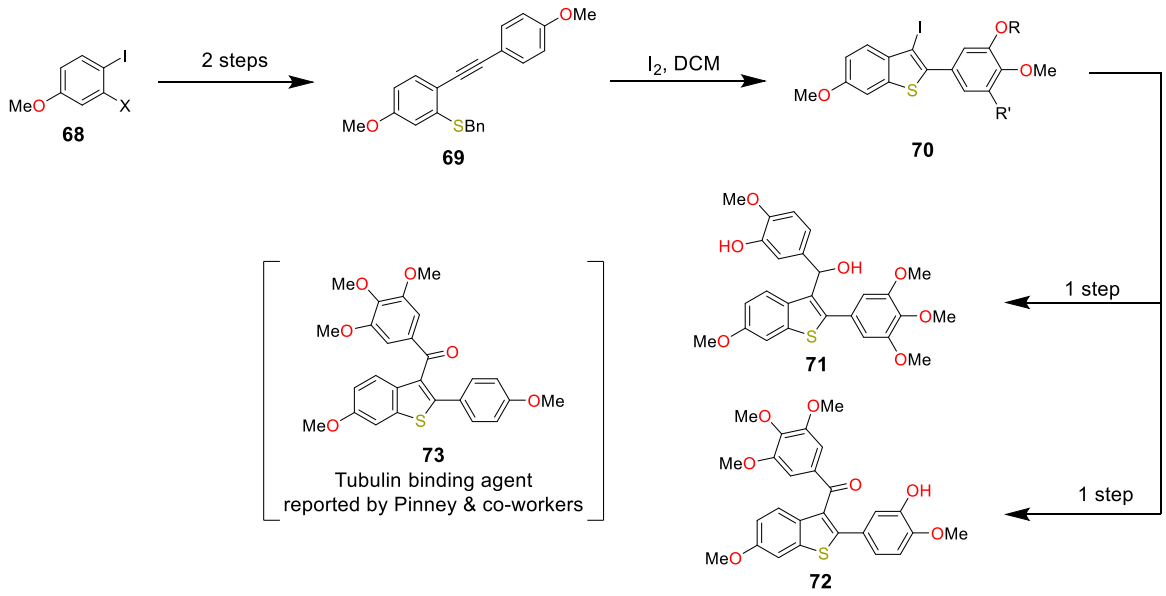
1.6.1 Applications of electrophilic cyclisation

The first reported application of the EC of an alkyne occurred in 1994 whereby derivatives of penicillin and penem-like ring systems were afforded, in an effort to improve upon the current antibiotic treatments (Scheme 6).[104] In this communication, alkyne containing compound **66** was afforded in one step (from **64** and **65**) before undergoing iodocyclisation to afford penem derivative **67**. In this publication the desired materials were furnished smoothly from their alkynyl precursors. Interestingly, despite this work there were few other publications at this time or in the following years that similarly employed EC for the synthesis of biologically relevant compounds.



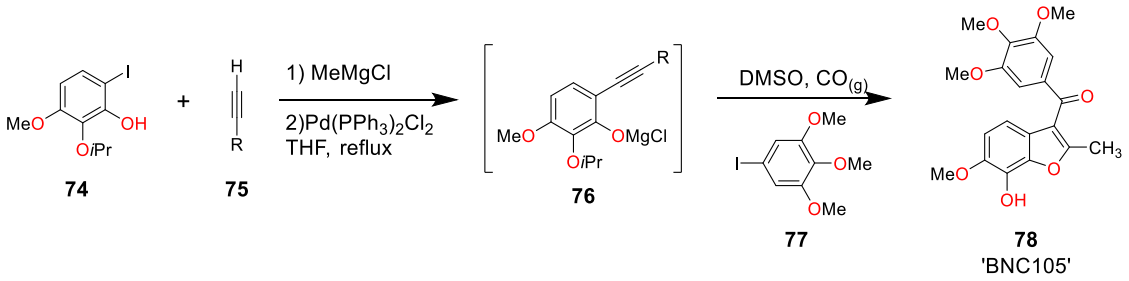
Scheme 6: One of the first reported utilisations of electrophilic cyclisation to afford a biologically relevant compound.

However in 2001 this trend changed when Flynn and co-workers took electrophilic cyclisation and greatly enhanced its perceived utility by affording biologically relevant anti-cancer agents (Scheme 7).[105, 106] At this time benzothiophenes were already shown to have exciting pharmaceutical applications such as anti-inflammatory agents, analgesics and anti-depressants.[107] This work demonstrated not only their more efficient synthesis but also measured their tubulin binding activity, resulting in a study of combretastatin A-4 (a naturally occurring anti-mitotic agent) derivatives that shed light on the SAR relationship between benzothiophenes and tubulin binding and polymerisation activity.



Scheme 7: Utilisation of iodocyclisation by Flynn and co-workers to afford benzothiophene tubulin binding analogues.

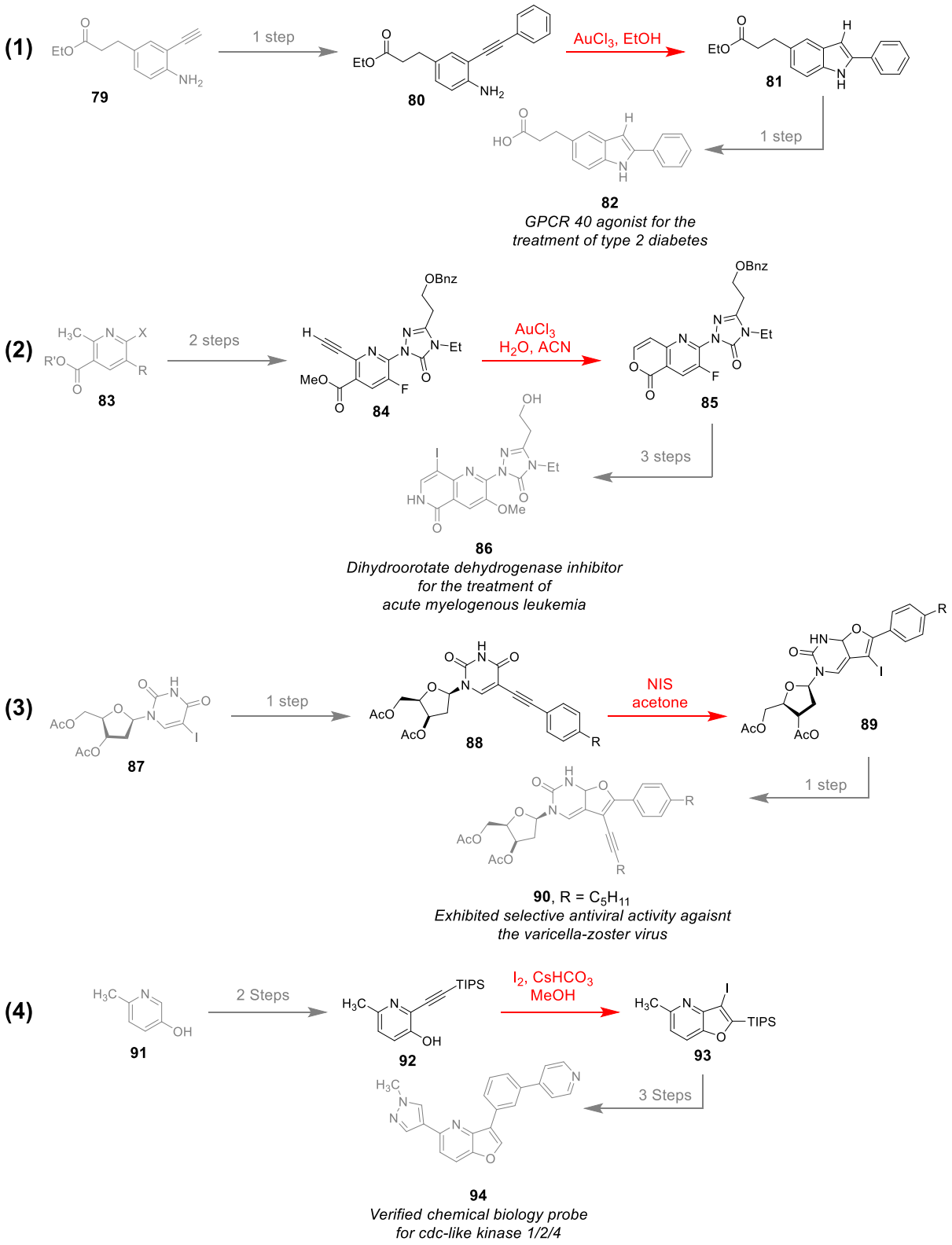
In conjunction with these efforts Flynn and Chaplin also developed a transition metal-mediated electrophilic cyclisation to afford benzofurans that was then utilised to afford anti-cancer agent 'BNC105' (**78**) (Scheme 8).[108] BNC105 is a commercially relevant drug that has been involved in clinical trials for the treatment of advanced stage cancers. Therefore, the synthesis of this compound has been exemplified on the kilogram scale, demonstrating the electrophilic cyclisations tolerability to pharmaceutically relevant large-scale synthesis.[108-111] After the original communication, BNC105 has been patented for treatment of both ovarian cancer and chronic lymphocytic leukemia.[112, 113] Since Flynn's work in 2001, electrophilic cyclisation has cemented its value in affording benzo-thiophenes[114-116] -furans[117-119] and -indoles[120-122] for applications in medicinal chemistry.



*Scheme 8: Application of a transition metal-mediated electrophilic cyclisation as developed by Flynn and Chaplan to the synthesis of commercially relevant anti-cancer agent BNC105 (**78**).*[108]

Over the past ~20 years since these seminal publications, drug discovery has embraced electrophilic cyclisation due to its efficient properties and commonly employed ability to install a halogen in the cyclised product, which is very commonly utilised for subsequent couplings.

A small summary of the most recent application-based utilisations of electrophilic cyclisation within (2020-2021) where biologically relevant compounds were furnished is described in Scheme 9. Reaction steps before and after the EC step are also represented to help contextualise the relevant cyclisation step and where it sits in the synthesis of biologically relevant compounds. Reaction pathway (4) shows the employment of electrophilic cyclisation to enhance the synthesis of a biologically relevant high-quality kinase biochemical probe. The new synthetic pathway featuring EC improved total yield from 23% to 36% and reduced the number of steps from nine to six.[123] It is also worth noting that when reviewing recent literature there is an increased presence of transition-metal mediated cyclisation as represented in Scheme 9.

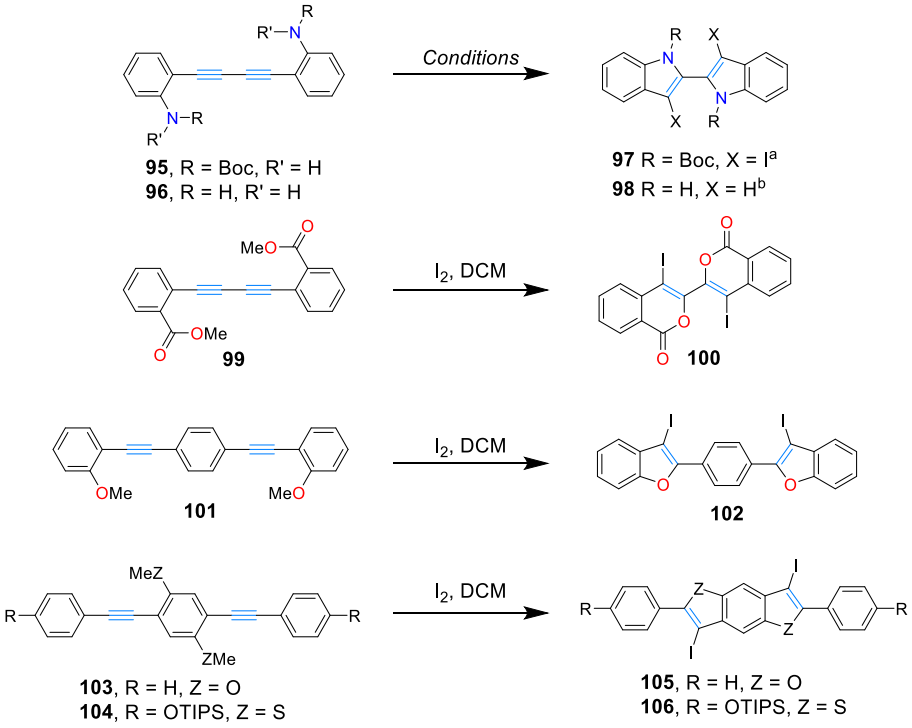


Scheme 9: Recent employments of electrophilic cyclisation in biological studies (1)[124], (2)[125], (3)[126] and (4)[123] with the relevant reaction arrow coloured red.

This simply demonstrates the utility of the ability to vary the electrophile for cyclisation to provide for chemists that don't want substitution in the 3-position of the newly formed ring. Considering these examples, it can be seen that electrophilic cyclisation has clearly been and will continue to be an important reaction in the formation of small heteroacenes for applications in medicinal chemistry.

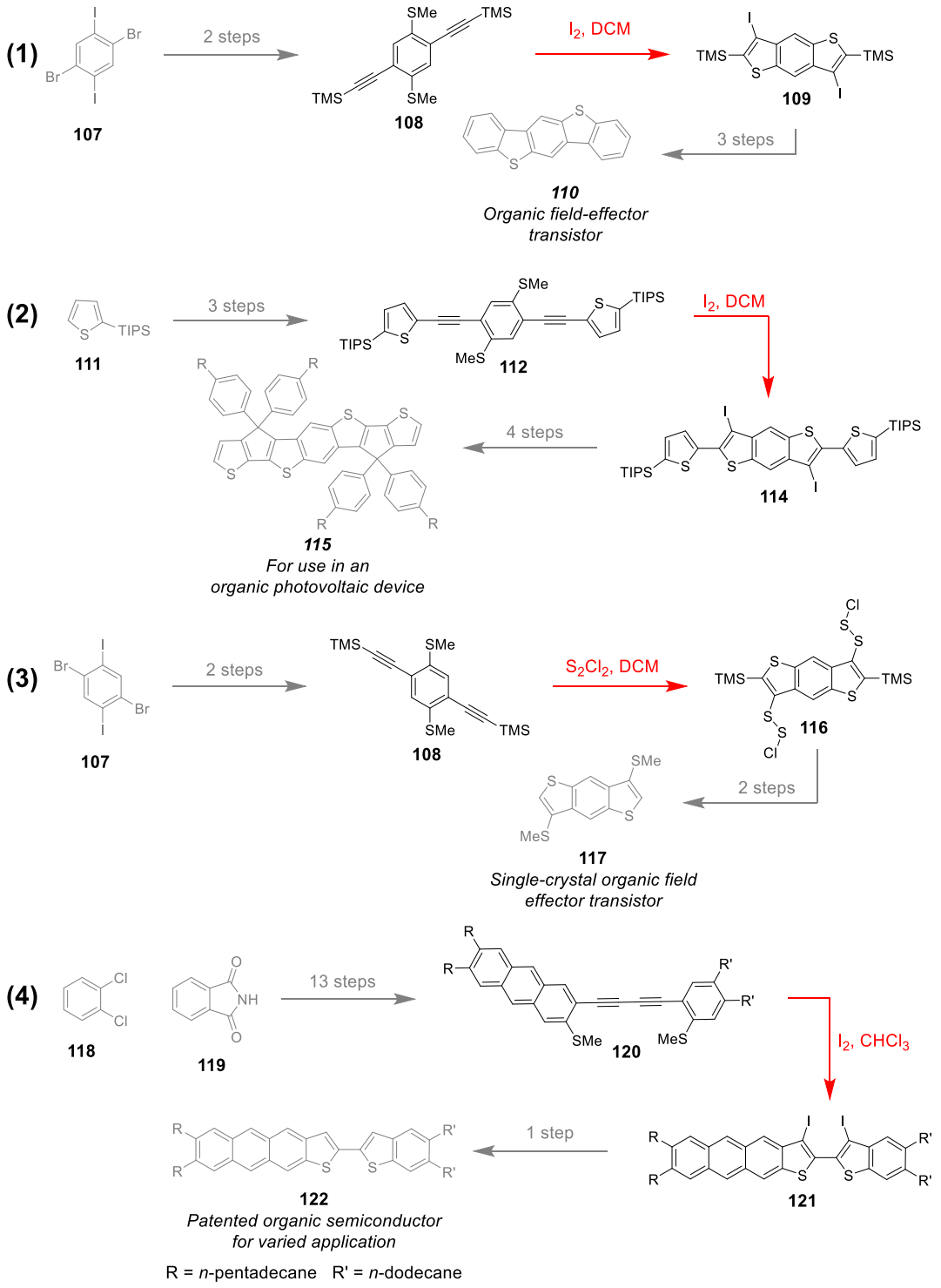
1.7 Poly-electrophilic cyclisation (PEC)

Due to the evidenced utility of traditional electrophilic cyclisation within drug discovery, there has been a keen interest in ensuring the full scope of the cyclisation reaction is realised. In the early 2000s various research groups began to report an evolution of EC whereby multiple instances of the cyclisation reaction occur within a single reaction step, this will be referred to as poly-electrophilic cyclisation (Scheme 10).[98, 99, 127-129] Here the broader capabilities of electrophilic cyclisation were revealed as larger heteroacenes were afforded by the same atom economical mechanism. This development of EC has afforded double-benzofurans[130], double-benzothiophenes[131] and unsymmetrical products where the concurrent cyclisation furnished both a benzofuran and benzothiophene.[132] As a result of these published works, electrophilic cyclisation was well positioned to not only service drug discovery, but also the larger poly-fused system needs of materials science. Due to the new focal point of these multi-cyclisations being materials science, this has encouraged the incorporation of more diverse heteroatoms, namely chalcogens (S, Se, Te).[133]



Scheme 10: Initial reported examples of one step PEC.
[a]IPy_2BF_4/HBF_4, DCE, [b]$NaAuCl_4{\cdot}2H_2O$, EtOH. [129, 127, 98, 99, 128]

Scheme 11 shows some select examples of PEC being employed for the synthesis of organic semiconducting materials for application in OFETs (**110**, **117**) and OPVs (**115**, **122**). Through these examples it can be seen how the utilisation of multiple instances of electrophilic cyclisation has afforded diverse ring-fusion patterns. Reactions before and after the relevant cyclisation step (shown in red) are again represented to demonstrate how PEC fits into synthetic materials science efforts.



Scheme 11: Applications of concurrent cyclisation of 'skipped' diynes for use as an organic field effector transistor (1)[134](3)[135], in an organic photovoltaic device (2)[136] and an organic semi-conductor (4) [137].

Although not shown, materials scientists have also utilised PEC for the synthesis of compounds for application as a p-type semiconductor film and electronic device[138], nano material

superfluid,[139] liquid crystal display[140] and optical chemosensor[141]. Further demonstrating the broad applications of EC.

Therefore, the reported extensions of traditional EC have provided a novel pathway to larger π-rich compounds that have been utilised in organic electronic and photonic devices. These works also demonstrated that EC has great potential as a unique reaction that can be manipulated to serve different purposes in various fields of organic chemistry (drug discovery and materials science).

1.8 Flynn lab contributions to PEC

Thus far, PEC has been described as novel method of affording slightly larger heteroacenes than traditional EC, with little variation of the reaction mechanism. However, in the last decade, the scope of PEC reactions has significantly expanded to afford an array of novel and diverse π-rich products. One research group that is responsible for several noteworthy contributions in this space, is the Flynn lab. Scheme 12 outlines a summary of both published and unpublished work from the group that evidences PEC in the synthesis of novel heteroacene products. Through these works Flynn and co-workers have sought to not only explore the reactions applications in organic synthesis but also enhance its utility to the materials science space. It is worth noting that of course other research groups have made important contributions to the PEC space. However, these contributions have been contemporaneous to the efforts within the Flynn lab and this thesis. Accordingly, these efforts will be suitably discussed and represented as they pertain to Chapters of work within this Thesis.

Reaction Scheme (1) within Scheme 12 illustrates the repeated use of iodocyclisation as an iterative approach to angularly fused poly-thiophene **128**.[142] Products of this nature are valued for their photonic and electronic properties that can be exploited for applications in materials science.[143, 144] This was one of the first reports of iodocyclisation being utilised for the synthesis of poly-fused aromatic systems.

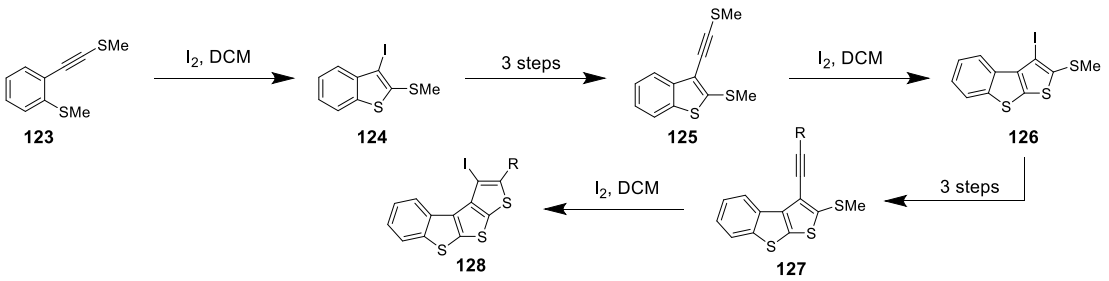
Reaction Scheme (2) describes the employment of iodocyclisation of phosphine oxide containing alkynes **130** and **132** to afford heteroacenes **131** and **133**.[145] Heteroacenes that contain phosphine oxide groups are particularly useful in the imaging field of work, often being employed as fluorescent dyes.[146-148] The use of iodocyclisation to afford these type of products not only enhanced synthetic access of π-rich P-heterocycles but also provided opportunity for post-cyclisation reaction to afford cyclic phosphonates such as **134** and **135**.

Reaction Scheme (3) reports the application of a dual electrophile (ECl_2) for the cyclisation of diyne **136** to afford linearly fused heterocycle **137**.[9] This was the first report of an electrophilic reagent that can participate in two instances of cyclisation (double-electrophilic cyclisation), enhancing the scope of EC. The other method of forming heteroacenes reported by Flynn and Gupta was of a double-electrophilic cyclisation followed by reductive elimination (DECRE). This reaction is transition metal-mediated and affords three new heterocycles with a helical ring fusion pattern (**139**).

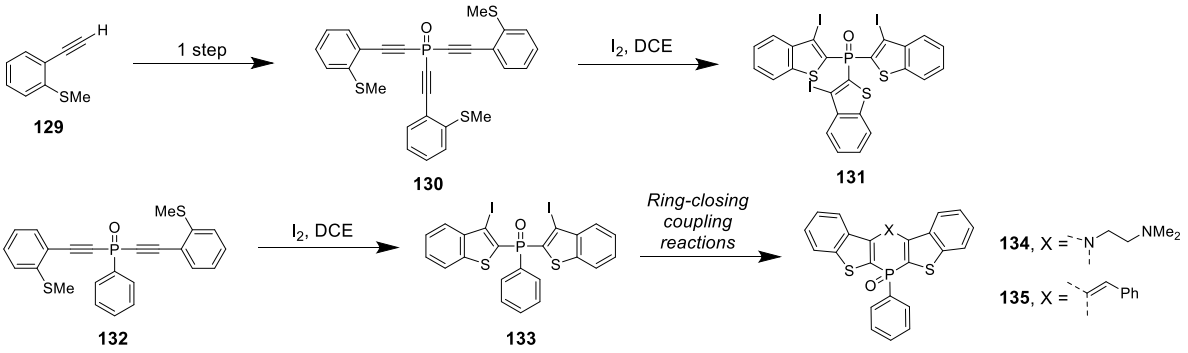
Finally, reaction Scheme (4) shows unpublished work that serves as an extension of the DECRE reaction shown in reaction Scheme (3). These efforts have focused on the transition-metal mediated double cyclisation and reductive elimination reaction reported by Akhil, expanding its utility to afford the large heteroacenes illustrated (**141**, **143**, **146** and **147**). Within this work Chew and Law afforded heteroacenes with varied heteroatom incorporation, aryl ring patterns and 3D shape. This work also explored the use of both Pd- and Au-mediated cyclisations to compare their ability to confer EC. The findings of this exploration were that addition of stochiometric portions of $AuCl_3$ to polyynes such as **140** and **144** led to complete cyclisation, affording **141** and **146**. However the utilisation of catalytic portions of Pd(TFA) (in conjunction with an oxidant, chloranil) achieved cyclisation in the more resistant polyynes (**140**, Y = N, **142** and **146**). Therefore, this work not only expanded the DECRE reaction to afford larger products with varied ring fusion patterns but also enhanced the methodology to include the use of cheaper Pd catalysts.

These efforts from the Flynn lab clearly demonstrate how EC can be enhanced and developed to afford novel π-rich products. Due to the nature of the reaction, there is also excellent opportunity to incorporate diversity with variation of the nucleophile, electrophile or alkynyl starting material. As discussed previously, these are exactly the types of reactions that go a long way to servicing to the requirements of materials science to manipulate π-functionality throughout structural manipulation.

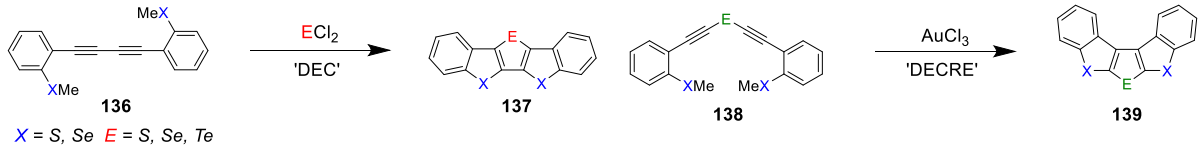
(1) Synthesis of fused thiophenes *via* reiterative iodocyclisation



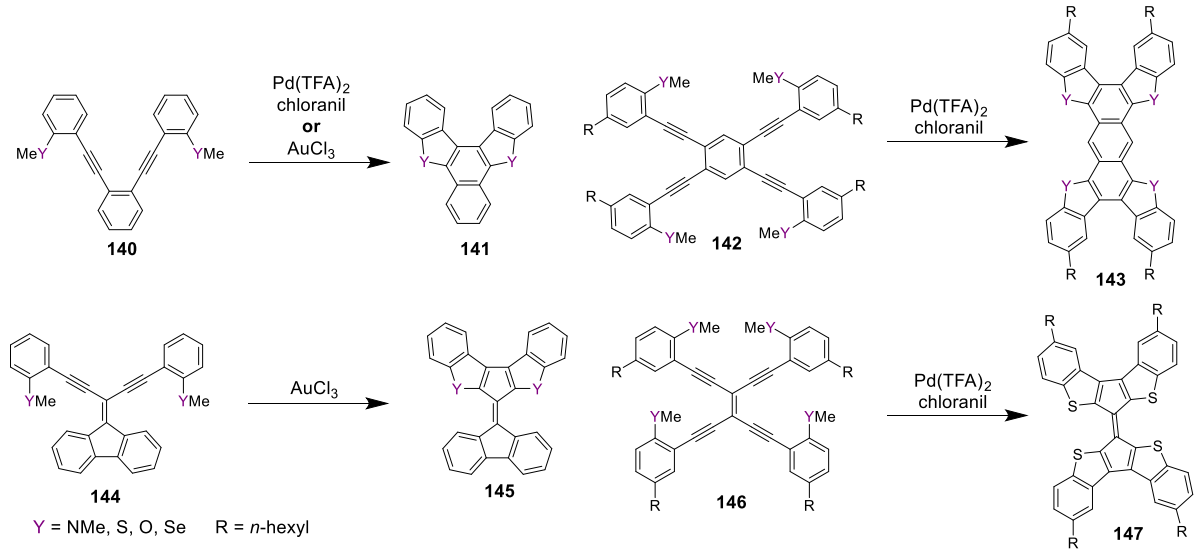
(2) Synthesis of P-substituted & P-centered heterocycles *via* iodocyclisation



(3) Synthesis of linear & angular heteroacenes *via* DEC & DECRE



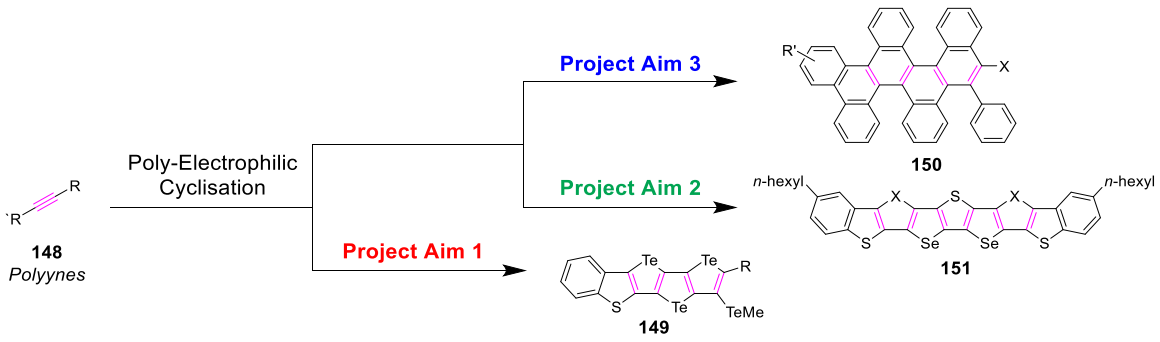
(4) Synthesis of novel angular heteroacenes *via* Pd & Au-mediated DECRE



Scheme 12: Summary of both published and unpublished works from Flynn and co-workers pertaining to poly-electrophilic cyclisation. [9,142,145] *(DEC = double electrophilic cyclisation, DECRE = DEC-reductive elimination).*

1.9 Generating novel bespoke methods of poly-electrophilic cyclisation

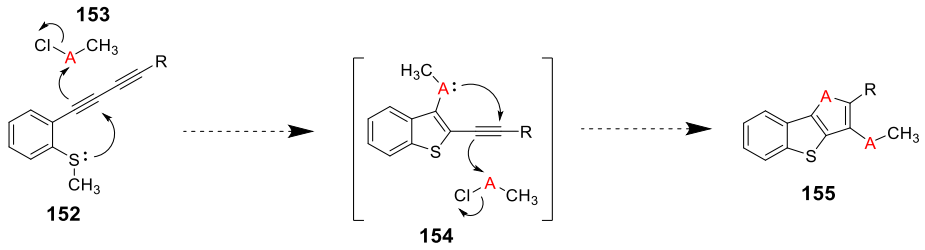
π-Rich molecules possess properties that make them uniquely positioned to be employed in varied applications of the materials science field. It can also be seen that in recent years electrophilic cyclisation has significantly evolved from a simple cyclisation that affords small heteroacenes to the synthesis of larger π-rich materials. This evolution being entirely attributed to innovative synthetic development works such as those reported from Flynn and co-workers. Despite these works, there remains a limitation of suitably bespoke methodologies that can afford diverse π-rich materials. Accordingly, it is the broad aim of this thesis to continue the work of the Flynn group by conducting a thorough investigation of the capacity of PEC to afford π-rich materials. This investigation must also ensure that methodologies enhance or developed must directly service the requirement of the materials science field. Scheme 13 gives a graphical representation of the three main areas of research that will be explored within this Thesis. Taking inspiration from works previously reported from the Flynn group, this work will explore the utilisation of cheap, readily available reagents to promote domino cascade reactions to convert polyyne **148** to polycycles **149**, **150** or **151**. Domino reactions as a class of chemical transformations hold particular use in the polycycle space as the synthesis of repeated fused units is well addressed by a reaction cascade. Accordingly, the successful employment of a domino PEC cascade would be an important contribution to the chemical methodologies available to materials scientists.



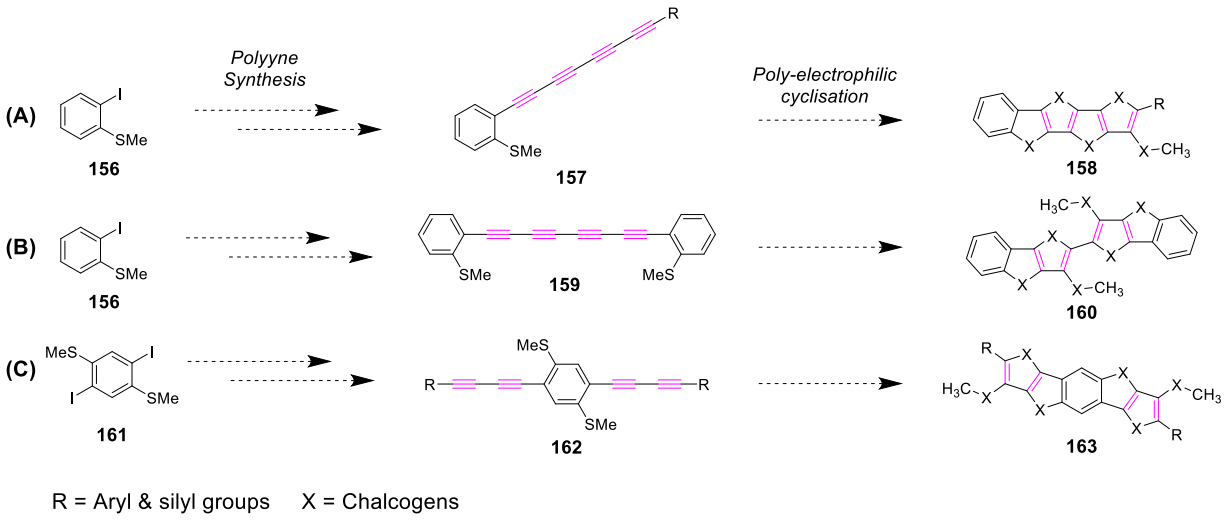
Scheme 13: Poly-cyclic products that will be achieved through poly-electrophilic cyclisation of polyynes.

1.9.1 Aim 1: Application of an ambiphilic chalcogen to form diverse poly-fused chalcogenophenes

The first aim of this thesis will explore the application of an ambiphilic reagent (performs as both a nucleophile and electrophile) to polyyne starting materials. It is proposed that such a reagent (**153**) could potentially propagate a cascade of cyclisations across a consecutive polyyne **152**, to form a poly-fused chalcogenophene product **155** (Scheme 14). The broad aims of this exploration of ambiphile initiated PEC are outlined in Scheme 15. From commercially available starting materials **156** and **161** the corresponding polyynes (**157**, **159** and **162**) will first be afforded to a high standard of reliability and efficiency. The remaining work will be focused on the attempted cyclisations, with variation of the ambiphilic chalcogen, X, one of the most important aspects of successful cyclisation. We expect this work if successful will provide a versatile and extremely efficient novel method by which materials scientists can afford π-rich materials that feature poly-fused chalcogenophenes.



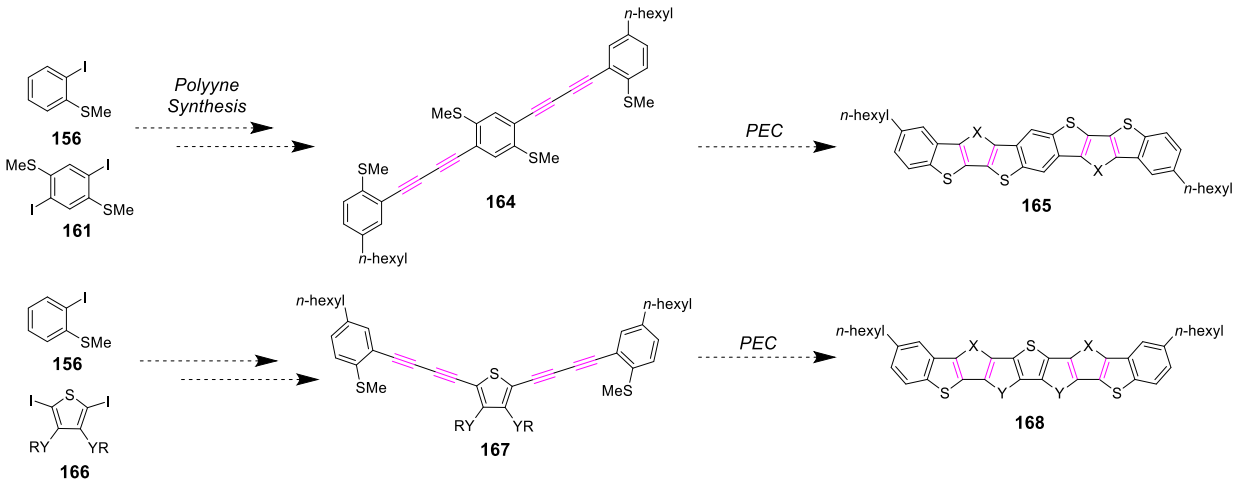
*Scheme 14: Proposed utilisation of ambiphilic reagent **153** to propagate a domino-cyclisation to afford **155**.*



Scheme 15: Proposed study that exposes consecutive polyynes to ambiphilic cyclising reagents to afford poly-fused chalcogenophenes.

1.9.2 Aim 2: Bi-directional exploration of double electrophilic cyclisation

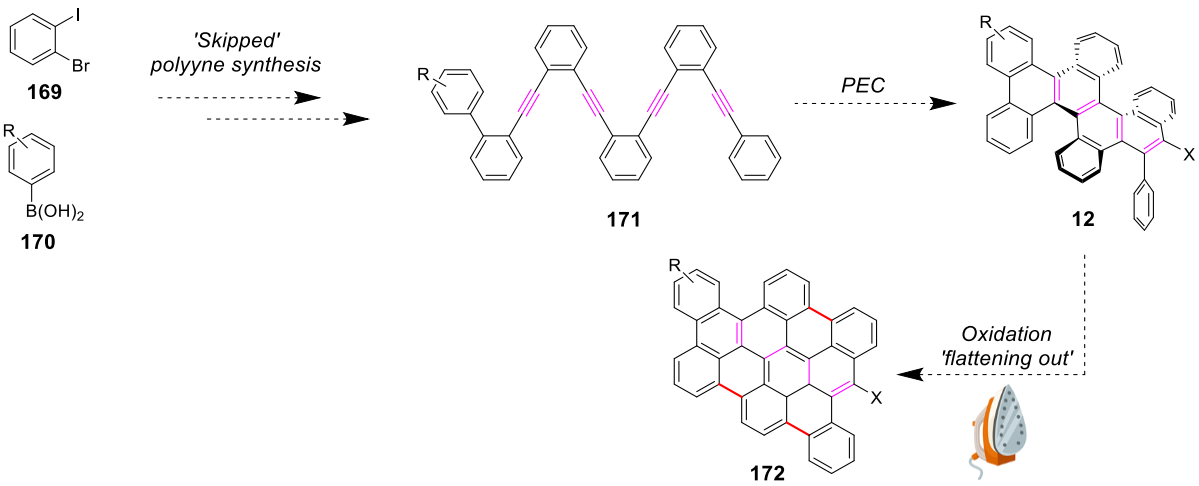
The second aim of this thesis will investigate the bi-directional application of double-electrophilic cyclisation (DEC) as reported by Gupta and Flynn.[9] This study will seek to further exemplify the utility of the DEC reaction mechanism and explore its limitations. Scheme 16 outlines the polyynes (**164** and **167**) that will be required within the study. Upon formation, the polyynes shown will be exposed to a variety of cyclising reagents with the aim to afford the poly-fused chalcogenophenes shown. If successful, this methodology will service the requirements of materials scientists in the furnishing of larger heteroacenes for applications in organic electronics.



Scheme 16: Proposed bi-directional application of cyclisations described by Flynn and Gupta.

1.9.3 Aim 3: PEC of skipped-polyynes to afford spiralacenes

The final aim of this thesis will seek to employ PEC for the formation of poly-fused acenes with a novel 3D conformation. Organic compound morphology can be an important structural property within organic electronics. Unfortunately, unique conformations are not well addressed by traditional chemical transformations and so synthetic development in this space would be well received. Scheme 17 outlines the general aims of this investigation where a sequence of 'skipped' polyynes of increasing length will be initially afforded in an efficient manner. Following this, these materials will be subject to PEC conditions to evidence domino cyclisation to afford spiralacene **12**. This twisted acene then has opportunity to undergo oxidation to effectively 'flatten out' the compound to the planar **172**. Therefore, this synthetic methodology would provide access to acenes with varied morphology, catering to the needs to materials scientists well. Exploration of the chiral nature of **12** and further post-cyclisation functionalisation will also be required within the study.



*Scheme 17: Proposed poly-iodocyclisation of skipped polyyne **171** to form oligoacene **12** and **172**.*

2.0 Results and discussion: Domino reactions forming polyfused chalcogenophenes

2.1 Introduction

Poly-fused chalcogenophenes are an extremely valuable class of compounds to the field of organic electronics. Their applications including incorporation within organic semiconductors, for use in OLEDs, OFETs, and OPVs.[149, 150] Their unique utility in the space comes from three major aspects of their structure, the presence of heavy, metallic chalcogens (S, Se, Te) which upon incorporation have been shown to induce change in optical and electronic properties.[79, 80, 151] Their coplanarity (or molecular packing) that translates to important changes in device performance[152] and finally the presence of aromatic conjugation that increases molecular stability and electron mobility. This increased mobility can be utilised by the inclusion of an electron-donating group (donor) and an electron-withdrawing group (acceptor) (Fig. 12).[153] The addition of donor/acceptor compounds is one of the techniques that can increase or decrease the energy that is released upon recombination (electrons moving from high energy state to low energy state). The released (converted) energy is what goes on to complete an electrical circuit (OFET), emit light (OLED) or produce electrical energy for use/storage (OPV). Therefore, the incorporation of poly-fused chalcogenophenes within organic semiconductors provides opportunity to vary the energetics of the material and its electronic/photonic performance. Accordingly, chalcogenophenes clearly have several inherent properties that are useful to materials science chemists. Complementary to that, these properties can also be modified (number of fused rings, pattern of chalcogen incorporation, variation of the donor and acceptor groups) and that permits materials scientists the ability to fine tune the π-functionality of their emerging organic semiconducting materials.

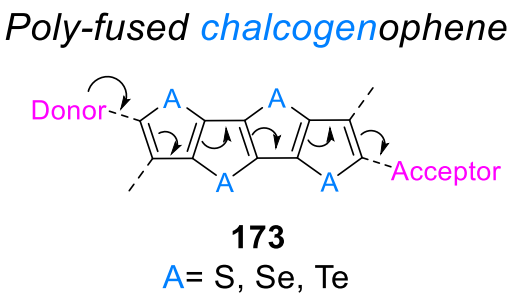
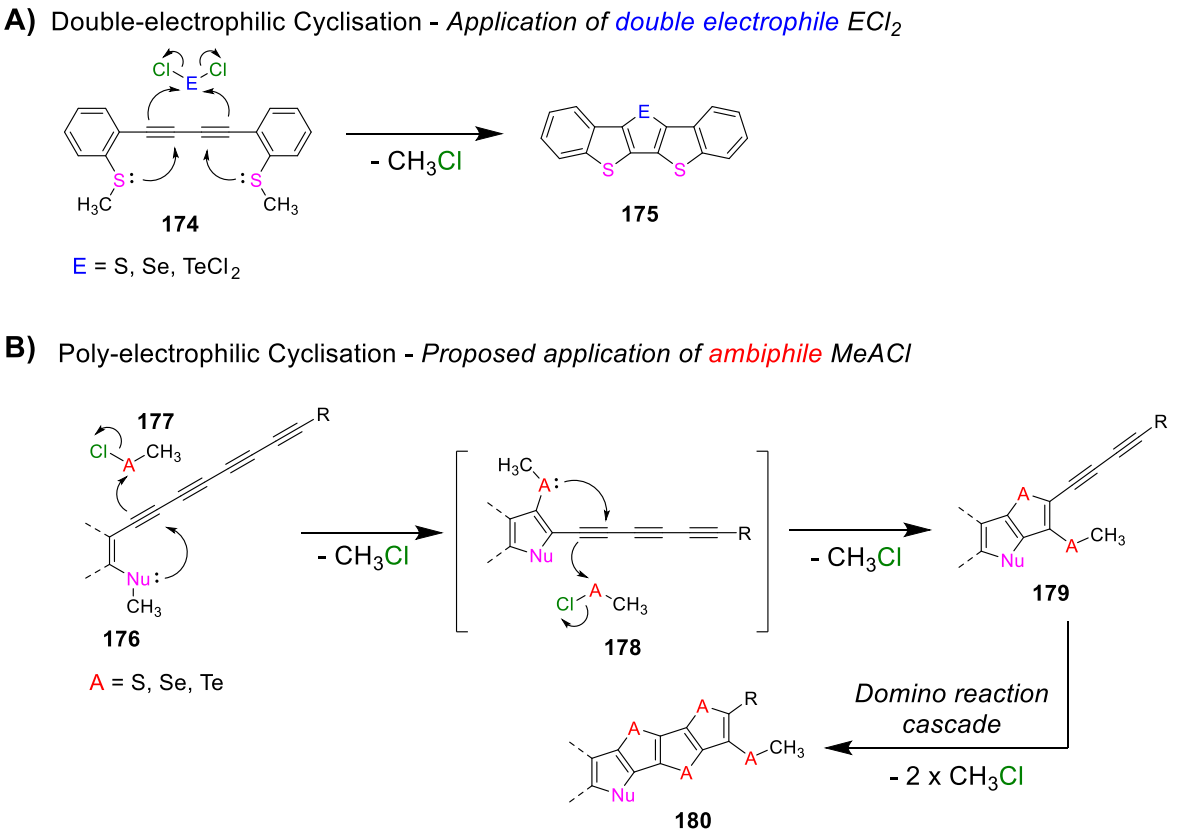


Figure 12: General poly-fused chalcogenophenes with arrows showing the movement of electrons across the molecule.

Unfortunately, the same structural features that make poly-fused chalcogenophenes so applicable to organic electronics (poly-fused nature and presence of chalcogens) also create difficulties in their synthesis. The polycyclic nature requires methodologies that afford multiple aryl rings, which often relies on uneconomical reactions. Synthetic reactions that afford selenophenes or tellurophenes are also severely limited. Consequently, a 'bottle-neck' of limited synthetic methods reduces the incorporation of these materials in organic electronic research and product development. Accordingly, innovation in this chemical space is clearly required to reduce this 'bottle-neck'.

As previously described, Flynn and Gupta reported the use of a 'double-electrophile' ECl_2 (E = chalcogens S, Se and Te) to afford three contiguously fused chalcogenophenes, through two consecutive instances of electrophilic cyclisation (Scheme 18, A).[9] ECl_2 possess unique character whereby each -Cl group provides an opportunity for the chalcogen 'E' to be attacked by an activated alkyne. This relates to chalcogens unique ability to act as either nucleophiles or electrophiles based on what chemical groups are bonded to them. Halogens are nucleofuges (leaving groups) that give chalcogens electrophilic (E) character. Conversely, alkyl groups are electrofuges (leaving groups that do not retain a lone pair of electrons), giving the chalcogen nucleophilic character. This is shown in cyclisation of **174** where sulfur (a chalcogen) with an attached $-CH_3$, is acting as a nucleophile as it attacks the tethered alkyne. Inspired by this unique ability of chalcogens, it is the proposal of this project that a chalcogen with both a -Cl and $-CH_3$ present (**177**) would have 'ambiphilic' character where 'A' can perform as both an electrophile and nucleophile within the same reaction step (Scheme 18, B). If successful, **177** could be applied to polyyne systems such as **176** to afford poly-fused chalcogenophene **180** in a single atom economical step.

The first proposed reaction step of polyyne **176** with ambiphile **177** would mimic the traditional cyclisation shown in Flynn's work, with the incorporation of 'A' that is here performing as an electrophile. In contrast with the DEC reaction (Scheme 18, A) once installed, 'A' now has only a $-CH_3$ present, conferring its ability to now perform as a nucleophile to afford **179**. With linear polyynes, these two steps could continue potentially repeat in a domino reaction cascade to afford **180** *via* poly-electrophilic cyclisation (PEC). We believe a reaction of this nature would service the materials science field well, as the requirement for large molecules with repeated units is well addressed by domino-type reactions.

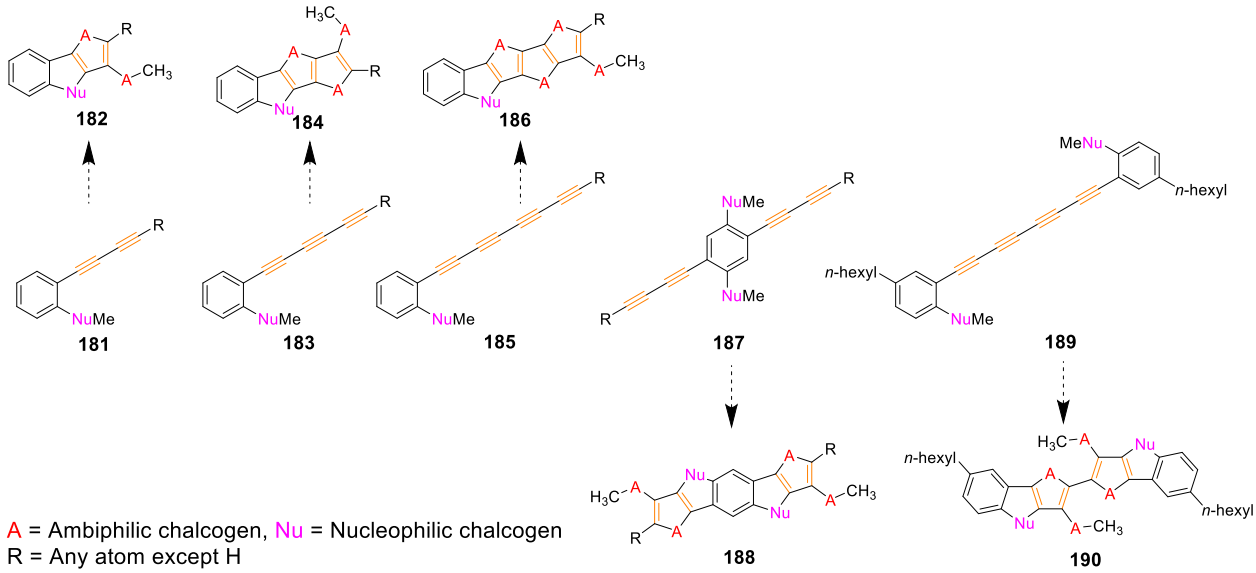


Scheme 18: A) Previously demonstrated DEC with the use of double electrophile ECl_2 and B) proposed PEC with the use of an ambiphile MeACl.

The polyynes that will be pursued for application of PEC within this Thesis work are shown in Scheme 19. The successful cyclisation of polyynes **181**, **183** and **185** would exemplify the reaction cascade to increasing degrees, uni-directionally. Cyclisation of polyynes **187** and **189** would demonstrate the bi-directional application of PEC. Of course, to achieve these aims, the polyyne starting materials shown will need to be synthetically afforded.

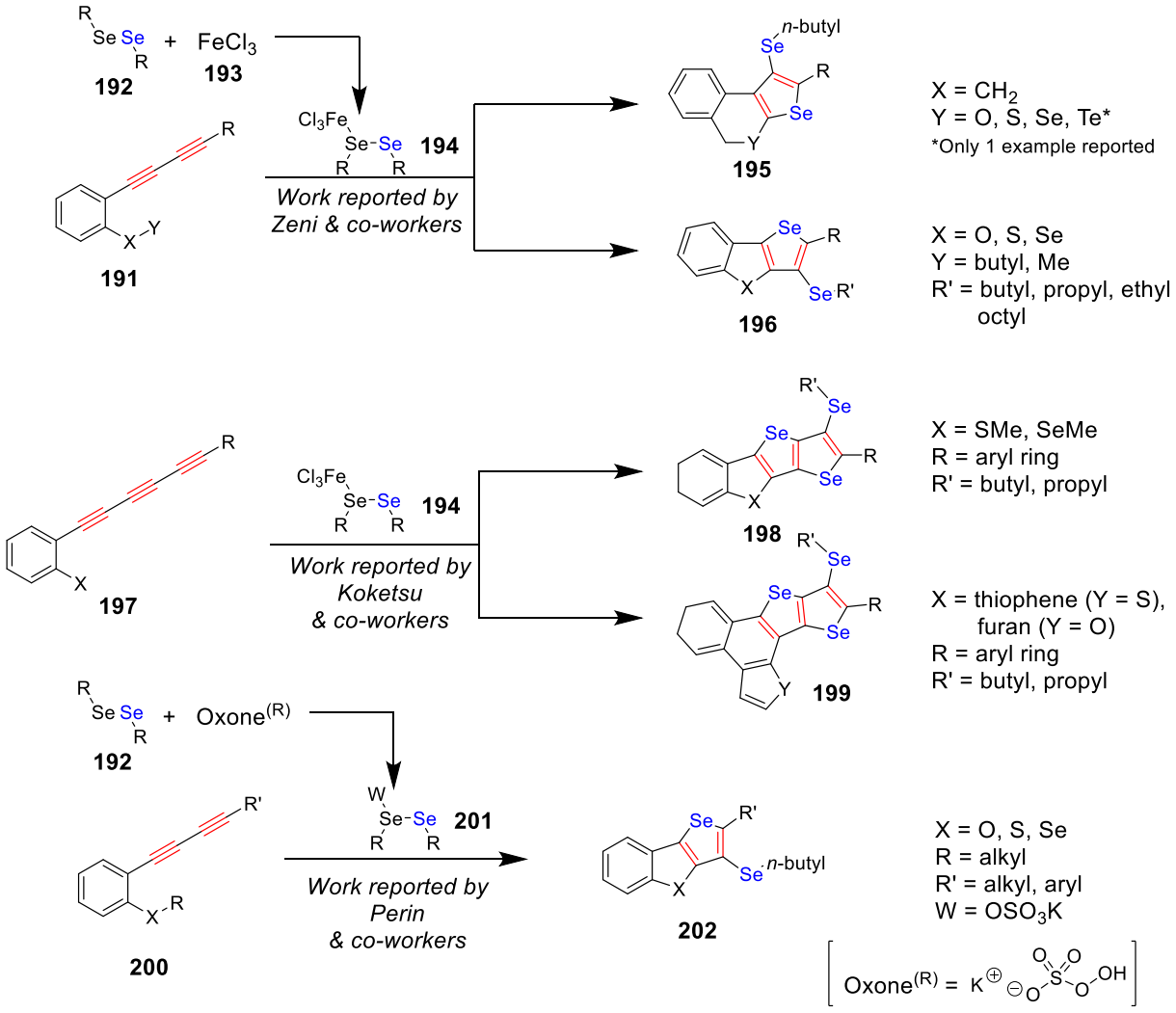
Historically, synthesis of molecules featuring multiple consecutive alkyne bonds can be quite difficult. This largely results from low stability of intermediates and at times the products themselves. Unprotected alkynes (if R = H in Scheme 19) present the largest instability risk, however, this can be managed through limited exposure to harsh conditions such as high reaction temperature, extreme pH or column chromatography. The nature of the chemical group that is present on the opposite end of the unprotected polyyne can also increase the stability of the molecule.[154] Accordingly, it is a subsequent aim of this project that routes of

polyyne synthesis are suitably optimised to be as reliable and efficient as possible, so as not to reduce the advantages of their subsequent cyclisations.



Scheme 19: Proposed polyynes for employment in PEC studies.

In parallel with our PEC efforts described in this chapter, Zeni[10-12], Koketsu[13] and Perin[155] have reported the PEC of polyynes featuring up to three alkynes (Scheme 20). The most notable difference between the works shown in Scheme 20 and the aims of this chapter is the use of an iron salt ($FeCl_3$) or oxidant (Oxone®) to confer ambiphilic ability in chalcogens. Works described in Scheme 20 add $FeCl_3$ or Oxone® to a di-alkyl diselenide **192** with the purpose of forming co-ordinated species **194** or **201**. Consider a hypothetical line being drawn vertically between the two bonded selenium atoms of **194** or **201**, the left-hand side of the molecule is now acting as a nucleofuge, the same way -Cl does, conferring electrophilic ability in the Se. The right-hand side features a remaining R group (R = akyl group). This R group is the electrofuge conferring the Se nucleophilic activity (as $-CH_3$ does). When the ambiphilic selenium reagent **194** or **201** is exposed to a polyyne, PEC is performed to afford diverse π-rich products (**195**, **196**, **198**, **199** and **202**). Both groups have exemplified important iterations of PEC, however within these works there is very limited incorporation of tellurium.



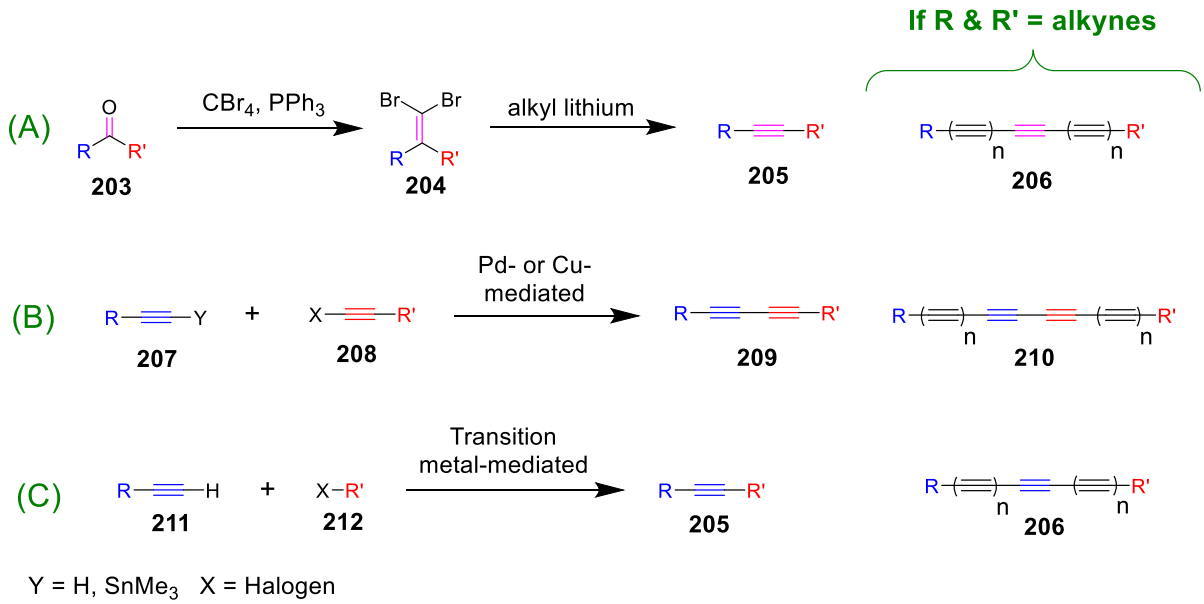
Scheme 20: Previous work in the chalcogenophenes forming poly-electrophilic cyclisation space. [10-13]

The remainder of this chapter will detail all efforts made to address the aims outlined in this introduction. Portions of the following work are published in the ACS journal *Organic Letters*[156]. Below is a fuller account of this work including not as yet published work relating in particular to optimisation of polyyne synthesis and attempted post-cyclisation modifications.

2.2 Accessing polyynes for application to uni-directional PEC

The planned PEC reaction is intrinsically atom economical and efficient, however the overall efficiency of this novel methodology, will be highly dependent on gaining ready access to the relevant polyynes. There is a variety of methodologies that afford consecutive polyynes, both symmetrical and unsymmetrical.[8] Scheme 21 gives a broad summary of the most commonly

employed reactions to afford alkynes.[86, 154, 157-161] Methods A, B and C illustrate reactions or reaction classes that afford alkyne containing products **205** or **209**. When comparing methods A, B and C, each reaction possesses different advantages that would benefit in the synthesis of various polyynes. Method A doesn't require the use of relatively unstable polyynes such as **211**; method B affords diynes with great efficiency and method C being a Sonogashira/Negishi type coupling translates to a reaction that has good tolerance to variation in R and R'. This is not always the case in methods A and B. Products **206** and **210** are shown to exemplify how the reactions shown can afford consecutive polyynes. Each of these methods of synthesis will be explored in some capacity to afford the polyynes relevant to this chapter.



Scheme 21: The four major reaction types utilised in the formation of unsymmetrical polyynes. (A) Fritsch-Buttenberg-Wiechell (FBW) rearrangement, (B) Cadiot-Chodkiewicz or Stille coupling, (C) Sonogashira or Negishi coupling.

The proposed polyynes for initial exploration of uni-directional PEC are detailed in Figure 13. Methyl sulfide (SMe) was selected as the tethered nucleophile due to it being the most exemplified chalcogen in this position. This gives the project the best starting position with room for subsequent variation studies. The end-capping group (R) will be varied to measure its effect on domino cyclisation outcomes, if any.

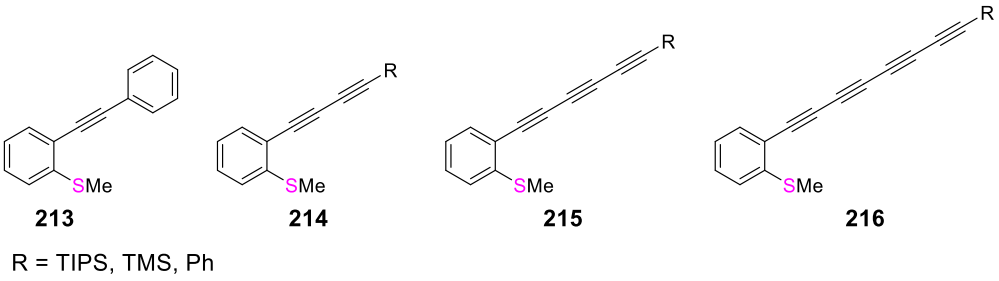
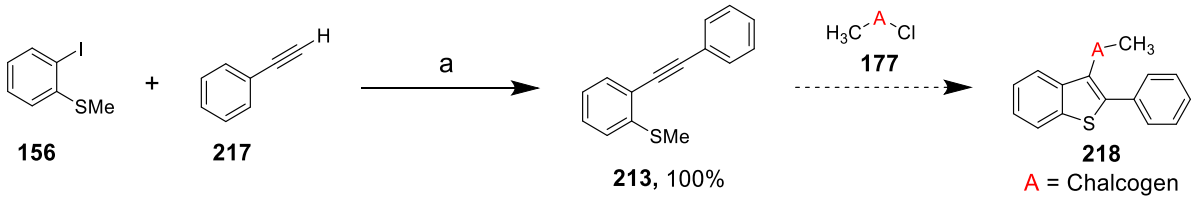


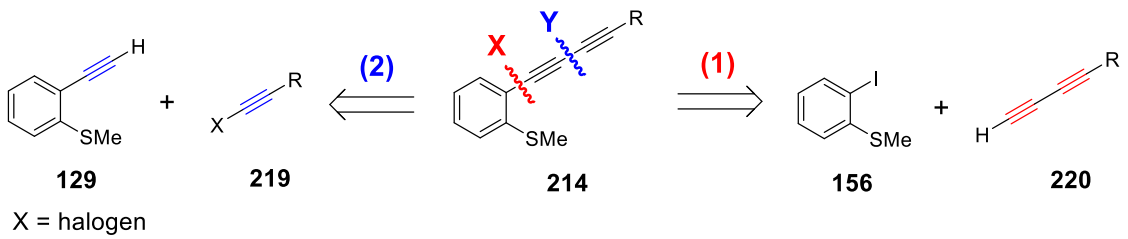
Figure 13: Polyynes required for the uni-directional exploration of PEC.

Monoalkyne **213** was smoothly produced in quantitative yield *via* Sonogashira coupling of phenyl acetylene **217** to iodothioanisole **156** (Scheme 22). This alkyne will serve as a 'starting point' to ensure **177** can perform as an electrophile in traditional electrophilic cyclisation before testing its ambiphilic ability on the extended polyynes. All cyclisation attempts with **213** will be discussed within Chapter 2.4 onwards.



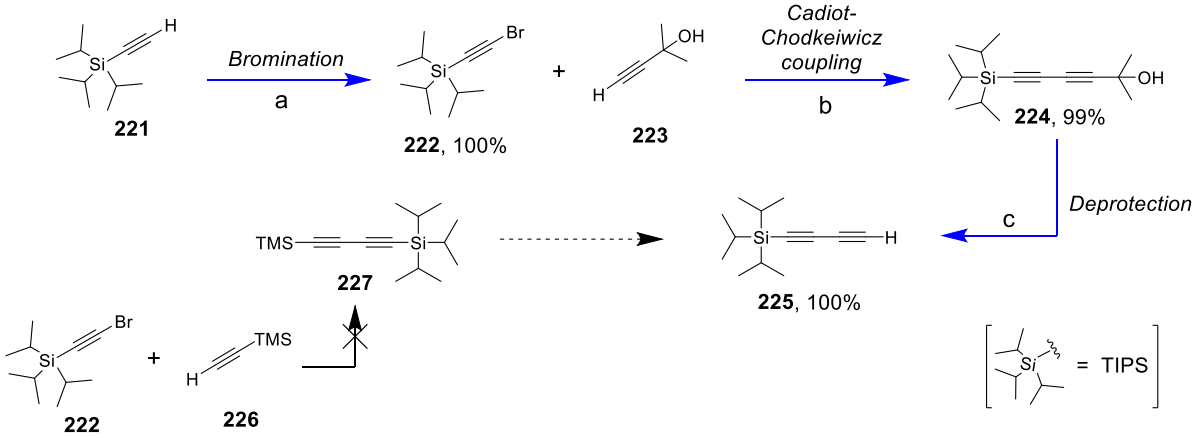
*Scheme 22: Synthesis of monoyne **213** and proposed subsequent cyclisation. a) CuI, $Pd(PPh_3)_2Cl_2$, Et_3N.*

The synthesis of diyne **214** can be attempted through multiple routes. Scheme 23 presents the retrosynthetic pathways that will be explored. The final bonds to be formed in their respective pathways are indicated with X (Route 1) and Y (Route 2). Route 1 aims to utilise Sonogashira coupling of diyne **220** to iodothioanisole **156**. Route 2 proposes a cross-coupling of alkynes **129** and **219** to afford diyne **214**. Route 1 was selected as the first retrosynthetic pathway to be explored.



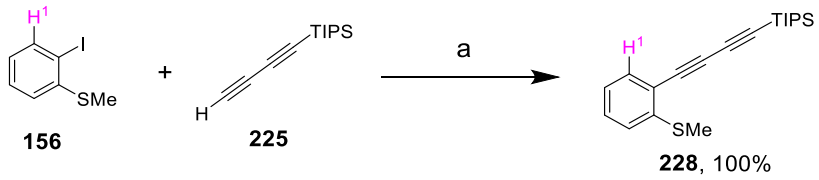
*Scheme 23: General retrosynthetic routes (1) and (2) to afford diyne **214**.*

The synthesis of TIPS capped diyne **225** is detailed in Scheme 24. The blue arrows show a bromination/cross-coupling/deprotection pathway that has been previously employed to afford **225**.[162, 163] This synthetic route was successfully applied within this chapter, although it required some procedural optimisation efforts. Bromination of TIPS acetylene **221** was successful up to a 20 g scale giving **222** in 100% yield with product presence verified by ^{1}H NMR analysis showing the loss of the singlet assigned to the acetylene CH (2.34 ppm). After some optimisation of reagent equivalence, cross coupling between **222** and **223** was achieved in 99% yield. Product presence was measured through ^{1}H NMR analysis by the appearance of singlets at 1.53 ppm and 1.08 ppm that integrated to 6 (2 × CH_3) and 21 (TIPS) protons respectively. The final deprotection step to afford **225** from **224** was attempted by addition of the base KOH in toluene, heating the reaction to reflux. KOH is only commercially available as pellets so must be crushed in a mortar and pestle prior to use to increase surface area and so reactivity. The crushing must also be performed in toluene as KOH is hygroscopic and will otherwise form an inactive paste with air moisture. Pleasingly, powdered KOH successfully furnished diyne **225** in quantitative yield. However as 50 eq. of KOH was required for 100% conversion, the pellet-crushing technique did not lend itself well to synthesis on multi-gram scale. Therefore, *t*-BuOK (available as a solid powder) was employed to replace KOH for large scale synthesis, giving identical yield. The presence of diyne **225** was confirmed by a singlet at 2.07 ppm assigned to the acetylene CH and he lack of a 2 × CH_3 singlet at 1.53 ppm associated with **224**. Scheme 24 also depicts another route of attempted access of diyne **225** from the coupling of brominated TIPS alkyne **222** and TMS acetylene **226**. This pathway was not viable and no conversion to product **227** was detected in ^{1}H NMR using Cadiot-Chodkiewicz conditions.



*Scheme 24: Optimisation of accessing deprotected TIPS diyne **225**. a) NBS, $AgNO_3$, acetone, b) CuCl, $HONH_2.HCl$, MeOH, n-butylamine, c) KOH or t-BuOK, toluene.*

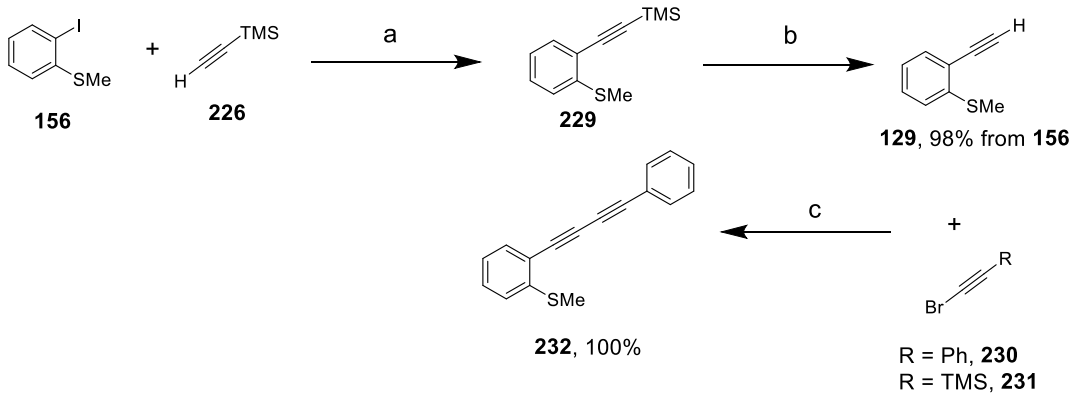
After successfully furnishing diyne **225** the alkynes was subject to Sonogashira coupling conditions with iodothioanisole **156** (Scheme 25). Fortunately, TIPS diyne **228** was afforded in quantitative yield with the only by-product being the homo-coupled product of excess diyne **225**, which was removed upon column chromatography. Conversion from **156** to **228** was evidenced in part by ^{1}H NMR analysis showing the upfield shift (7.81 → 7.47 ppm) of the resonance (*dd*) assigned to the CH ortho to the iodo-group (shown as H^1 in Scheme 25) in **156** and ortho to the alkyne in **228**. Halogens are desheilding due to their high electronegativity, therefore the upfield shift of neighbouring protons is characteristic of their replacement. ^{13}C NMR and LCMS also confirmed the presence of **228**.



*Scheme 25: Successful Sonogashira coupling of **156** and diyne **225** to afford **228**. a) CuI, $Pd(PPh_3)_4$, DIPA.*

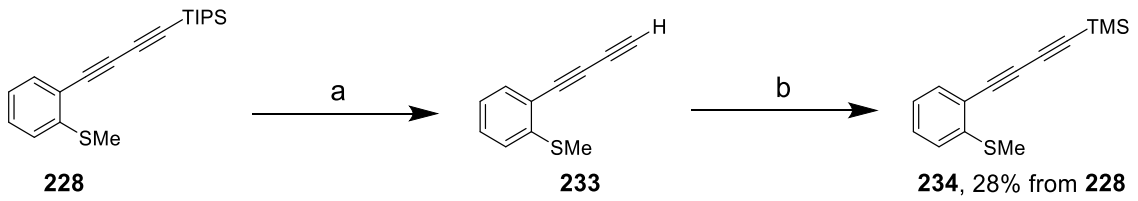
A depicted in Figure 13, diyne **214** is to feature a TIPS, TMS and phenyl (Ph) capping group in the R position, for comparison purposes. As TMS will serve as a less-bulky group, for size comparison with TIPS and Ph being chemically distinct from TIPS. It was proposed that the remaining required diynes be afforded through a synthetic pathway more akin to route 2 as

shown in Scheme 23. The successful application of this method to afford diyne **232** is shown in Scheme 26. Acetylene **129** was first produced according to previous literature with ^{1}H NMR spectra and LCMS data consistent with the literature precedent.[142] Acetylene **129** was then cross-coupled with bromo alkynes **230** (R=Ph) and **231** (R=TMS). Fortunately, phenyl capped diyne **232** was furnished in quantitative yield through employment of Cadiot-Chokeiwicz coupling conditions. The presence of Ph capped diyne **232** was verified by loss of the acetylene CH singlet from **129** (3.47 ppm), ^{13}C NMR spectra and HRMS data. Bromo alkyne **231** (R=TMS) did not successfully couple with acetylene **129** and so an alternate route to a TMS capped diyne was required.



*Scheme 26: Synthetic access of phenyl capped diyne **232**. a) CuI, Pd(PPh$_3$)$_2$Cl$_2$, DIPA, b) KF, MeOH, Et$_2$O, c) CuCl, HONH2.HCl, n-butylamine, MeOH.*

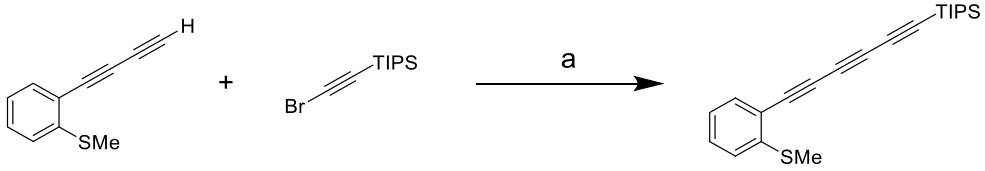
Scheme 27 presents an alternative approach to TMS diyne **234** that involves the initial deprotection of TIPS diyne **228** to afford acetylene **233**. The presence of diyne acetylene **233** was evidenced in ^{1}H NMR spectra by the lack of TIPS associated resonances at 1.12 ppm and the appearance of a CH acetylene singlet at 2.61 ppm. Conversion from acetylene **233** to TMS diyne **234** was subsequently achieved through *n*-BuLi mediated addition of trimethlysilane. Conversion to diyne **234** was confirmed by ^{1}H NMR analysis and LCMS data. The low yield of **234** was attributed to low stability of the lithiated intermediate of **233** and some degradation on exposure to silica for purification purposes.



228 **233** **234**, 28% from **228**

*Scheme 27: Synthetic access of diyne **234** from **228**. a) TBAF, THF, b) n-BuLi, TMS chloride, THF.*

After furnishing all required diynes (**228**, **232**, **234**), concurrent cyclisation studies gave indication that TIPS diyne **228** was out-performing phenyl diyne **232** and TMS diyne **234** in regard to cyclisation outcomes (See Chapter 2.5). Therefore, it was proposed that triyne **215** and tetrayne **216** (Fig. 13) be produced with TIPS capping groups (R=TIPS). Accordingly, Scheme 28 presents the successful cross-coupling of previously afforded acetylene **233** and bromo-alkyne **222** to afford triyne **235** in moderate yield of 65%. Analysis of reaction ^{1}H NMR spectra, showed the lack of an acetylene CH singlet (2.61 ppm) associated with **233** and the presence of a TIPS resonance at 1.09 ppm, indicating the formation of TMS capped diyne **235**. ^{13}C NMR spectra also showed 6 quaternary carbons within the alkynyl region (60-90 ppm) that were successfully assigned to product **235**.



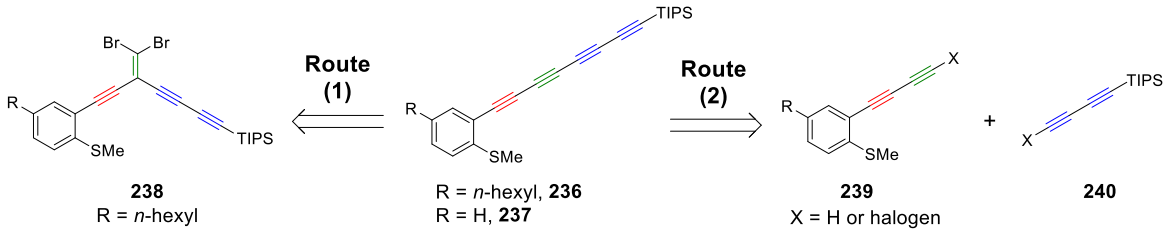
233 **222** **235**, 62%

*Scheme 28: Successful reaction of **233** and **222** to afford triyne **235**. a) CuCl, $HONH_2$.HCl, n-butylamine, MeOH.*

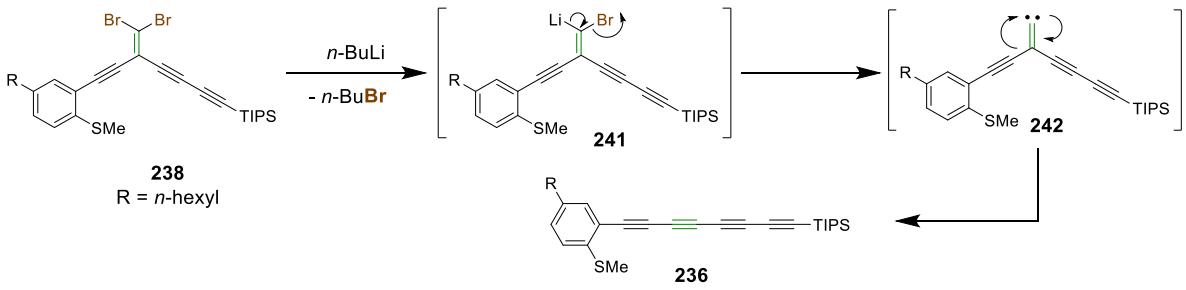
2.2.1 Synthetic access of TIPS-capped tetraynes

Following the smooth furnishing of diynes **228**, **232** and **234** and triyne **235**, attempts to afford tetraynes **236** and **237** were initiated (Scheme 29). Inclusion of both tetraynes **236** and **237** was proposed due to concerns of low predicted solubility of **237** and its corresponding cyclised material. Low solubility can affect reaction outcomes and so the synthesis of both tetraynes were explored, should **237** prove undesirable for PEC. Shown within Scheme 29 are two proposed retrosynthetic routes: route 1 utilises a Fritsch-Buttenberg-Wiechell (FBW)

rearrangement[164-166] to convert **238** to **236**. This reaction has a unique mechanism that is employed here to create internal alkynes (shown in green) from geminal dibromide starting materials through an alkyl lithium-mediated reaction (Scheme 30).[167] Route 2 aims to cross-couple diynes **239** and **240** to afford either **236** or **237**. Each of these routes were explored to identify the most optimal route to afford tetraynes **236** and **237**.



*Scheme 29: Retrosynthetic approaches to tetraynes **236** and **237**. Route (1): Fritsch-Buttenberg-Wiechell (FBW) rearrangement-based approach, route (2) Diyne cross-coupling-based approach.*

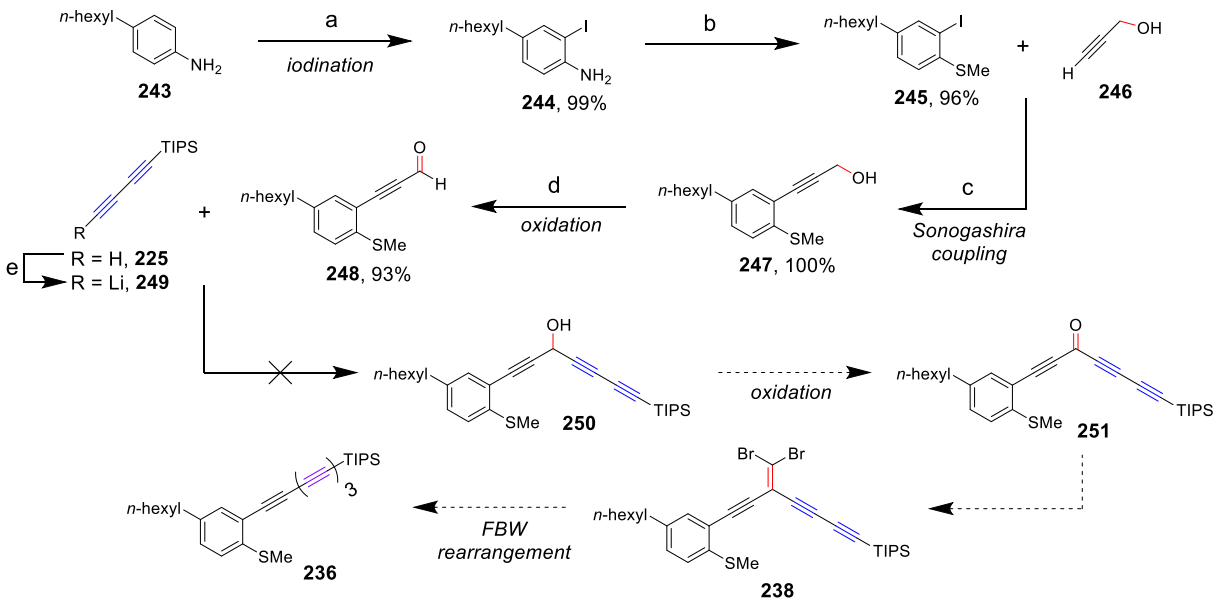


*Scheme 30: Mechanistic explanation of the conversion between **238** to **236** via Fritsch-Buttenberg-Wiechell (FBW) rearrangement.*

Route 1 to tetrayne **236** was investigated initially, with Schemes 31-33 illustrating all attempts made within this FBW rearrangement-based approach. As shown in Scheme 30 the FBW approach requires geminal dibromide species **238** for conversion to tetrayne product **236**. Therefore, the initial aim was to afford **238** *via* the route shown in Scheme 31.[165, 168, 169] This pathway commences with the successful iodination of commercially available *n*-hexylaniline **243** which afforded 2-iodoaniline **244** in excellent yield (99%). **244** was then converted to hexylated-iodothioanisole **245** in 96% yield. This material (**245**) was then prepared for Sonogashira coupling with propargyl alcohol **246** which smoothly produced alcohol **247** in quantitative yield. In each case, product presence was confirmed by ^{1}H and ^{13}C NMR analysis and LRMS data. The subsequent oxidation of alcohol **247** to afford aldehyde **248** was attempted

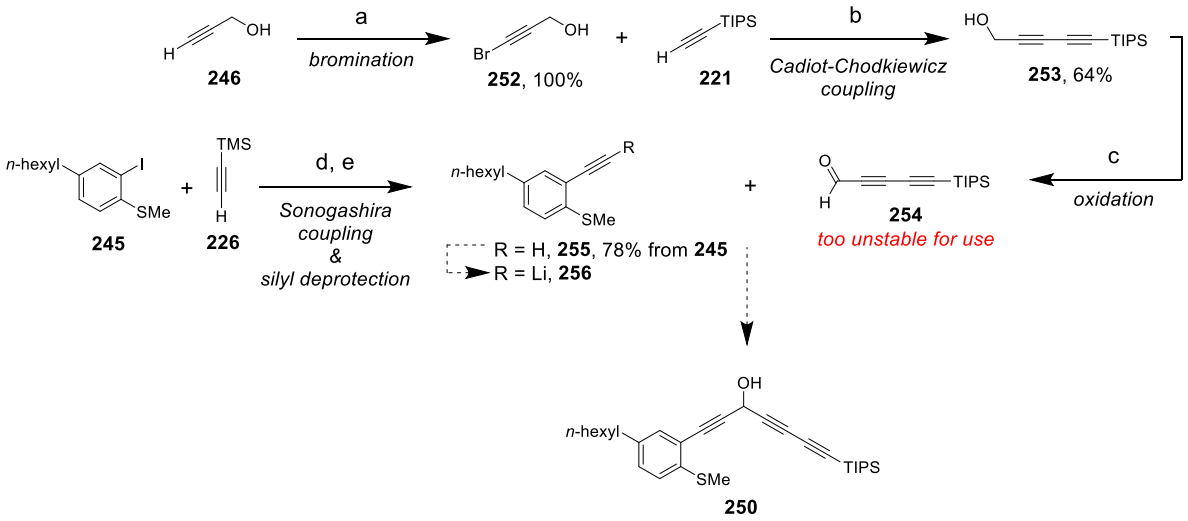
with Swern oxidation conditions[170] (oxalyl chloride, DMSO, DCM, Et_3N), DMP (Dess-martin periodinane) in DCM or MnO_2 in DCM. Each of these conditions furnished aldehyde **248** in good yield, however it was found that DMP gave consistently higher yield (93%) of the three conditions, even on multi-gram scale and did not require column chromatography.

Once aldehyde **248** was reliably produced, TIPS diyne **225** could then be treated with *n*-BuLi to furnish lithiated intermediate **249**. The reaction solution containing **249** was then added to a cooled solution of aldehyde **248** with the aim of producing secondary alcohol **250**. Unfortunately, the formation **250** was not observed in ^{1}H NMR analysis with a resultant complex spectrum indicating low stability of intermediate **249** or secondary alcohol **250**.



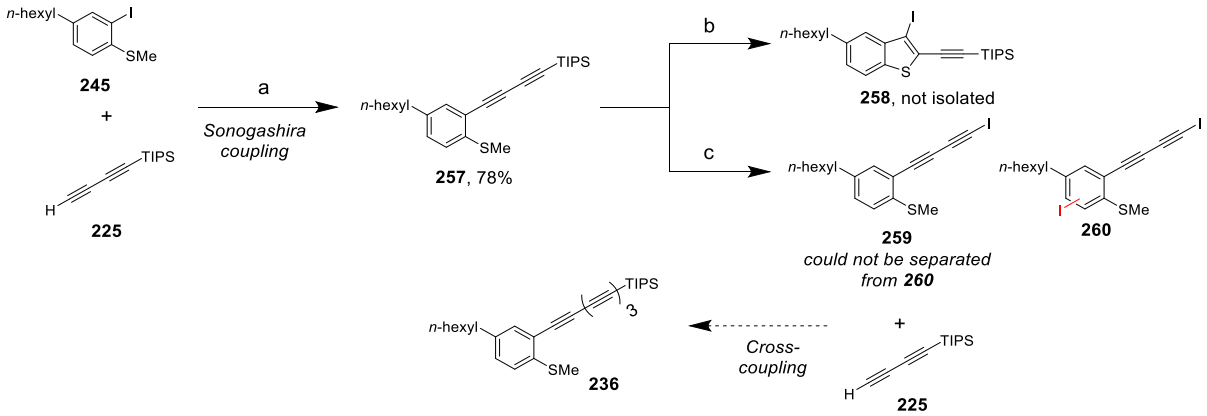
*Scheme 31: Attempted synthesis of tetrayne **236**. a) I_2, $NaHCO_3$, H_2O, DCM, b) S_2Me_2, isoamyl nitrite, c) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, d) DMP, DCM, e) n-BuLi, dry THF.*

An alternative pathway to secondary alcohol **250** was proposed in Scheme 32. This pathway utilises alkyne cross-coupling chemistry with the aim of affording aldehyde capped diyne **254** for the synthesis of **250**. Although alcohol/TIPS capped diyne **253** was smoothly afforded, subsequent oxidation attempts revealed that although aldehyde **254** could be produced in reaction mixture (verified by ^{1}H NMR), it proved too unstable for isolation.



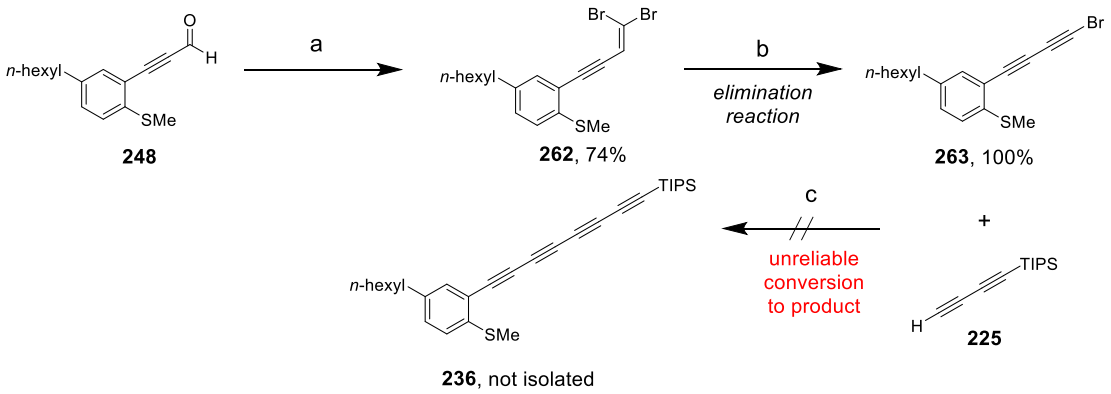
*Scheme 32: Attempted synthesis of secondary alcohol **250** for application to the synthesis of tetrayne **236**. a) NBS, $AgNO_3$, acetone, b) CuCl, $HONH_2.HCl$, n-butylamine, H_2O, c) DMP, DCM, d) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, e) TBAF, THF*

Due to the lack of success through the FBW rearrangement-based method, the cross-coupling method as it was broadly shown in route 2 of Scheme 19 was explored for its ability to afford tetraynes **236** and **237**. Scheme 33 presents a proposed synthetic route to afford tetrayne **236**. Pleasingly, initial Sonogashira coupling of hexyl-iodothioanisole **245** and diyne **225** smoothly produced TIPS capped alkyne **257** in 78% yield. This synthetic route then required the conversion of **257** to **259** *via* a silyl for halogen substitution reaction (substituting TIPS for I). This reaction was attempted under two sets of conditions: b) NIS (*N*-iodosuccinimide), TBAF, in ACN and c) NIS, $AgNO_3$ in acetone. Conditions b) afforded a single product. However, ^{1}H NMR analysis showed the presence of resonances associated with the TIPS group (1.12 ppm) and the lack of the 'SMe' singlet at 2.48 ppm. Consequently, it was proposed that NIS had iodocyclised diyne **257** to afford substituted benzothiophene **258**. Contrastingly, conditions c) furnished desired product **259** and over iodinated product **260** in equal ratio. Column chromatography was attempted to isolate the desired product **259**, however separation was not achieved to a satisfactory degree. Due to these undesired outcomes, an alternative pathway to tetrayne **236** was required.



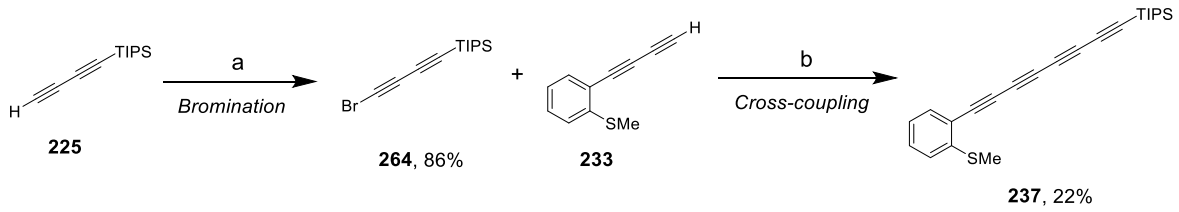
*Scheme 33: Attempted synthesis of tetrayne **236** via cross-coupling approach. a) CuI, $Pd(PPh_3)_4$, PPh_3, Et_3N, b) N-iodosuccinimide (NIS), TBAF, ACN, c) NIS, $AgNO_3$, acetone.*

Scheme 34 presents a synthetic pathway to hexyl-tetrayne **236** that utilises brominated diyne **263** for cross-coupling with TIPS diyne **225** to afford the relevant tetrayne. To commence, previously synthesised aldehyde **248** was first converted to the corresponding geminal dibromide **262** through Corey-Fuchs conditions (CBr_4 and PPh_3 in DCM) affording **262** in 74% yield. The subsequent elimination reaction then utilised 1 eq. of LiMHDS, successfully furnishing brominated diyne **263** in quantitative yield. Finally, cross-coupling between brominated diyne **263** and TIPS diyne **225** could be attempted. Initially this coupling was performed under Cadiot-Chodkiewicz conditions due to their success when coupling monoynes. However, no conversion to tetrayne product **236** was observed in ^1H NMR, with only unreacted diyne **263** and the homocoupled product of **225** detected in NMR spectra. The application of Sonogashira coupling conditions to tetrayne **236** improved conversion to product, however after multiple iterations, reaction outcomes were not consistent. This indicated there may be some stability issues associated with **263** or within the reaction mechanism as product **236** presence varied with each iteration.



*Scheme 34: Attempted synthesis of tetrayne **236**. a) CBr_4, PPh_3, DCM, b) LiMHDS, dry THF, c) CuI, $Pd(PPh_3)_2Cl_2$, DIPA.*

Following these results, an attempt was made to afford non-hexylated tetrayne **237** (Scheme 35). This pathway employs a cross coupling reaction between TIPS brominated diyne **264** and unprotected diyne **233** to potentially afford tetrayne **237**. Pleasingly, following the successful bromination of TIPS diyne **225** to afford **264**, subsequent cross-coupling with acetylene **233** yielded the desired tetrayne **237** in 22% yield. Product presence was evidenced by ^{1}H and ^{13}C NMR analysis and HRMS data. Although this yield is lower than desired, the work to afford linear tetraynes (**236** or **237**) has clearly evidenced the difficulties in synthesis of polyynes featuring less than three consecutive alkyne bonds. Accordingly, affording tetrayne **237** in a respectable yield was a gratifying outcome.



*Scheme 35: Synthesis of tetrayne **237**. a) NBS, $AgNO_3$, acetone, b) CuCl, $HNONH_2.HCl$, MeOH, Et_2O, n-butylamine.*

2.3 Accessing precursors for bi-directional studies

As described previously, the aim of this domino reaction study is to investigate both uni- and bi-directional cyclisation (Fig. 14). Tetraynes **265** and **266** are proposed as cyclisation precursors for the exploration of both divergent and convergent bi-directional cyclisation,

respectively. Polyyne **265** features end capping TIPS groups to maintain consistency with the uni-directional polyynes accessed. Tetrayne **266** features two *n*-hexyl groups to increase solubility of the tetrayne and any cyclisation products. Just like the synthesis of uni-directional polyynes, best efforts will be made to afford the relevant tetraynes in an efficient and reliable manner.

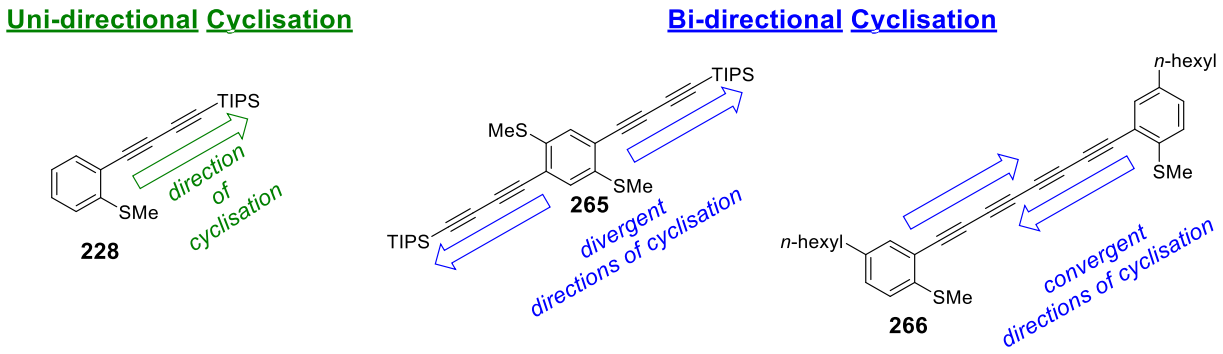
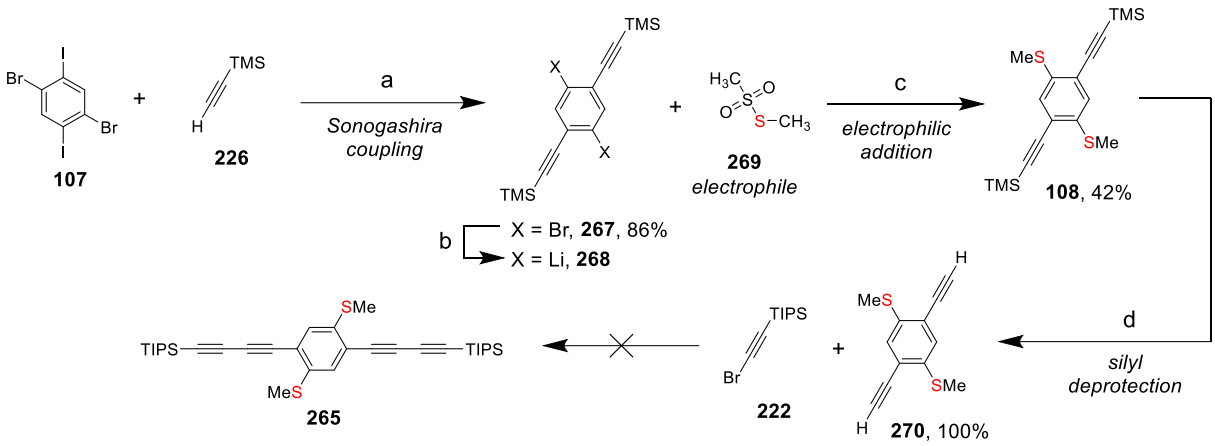


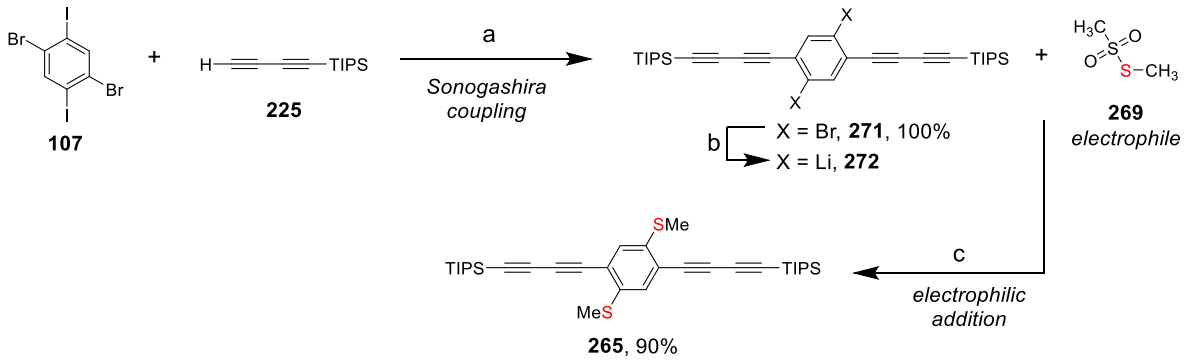
Figure 14: Demonstrating the difference between the proposed uni- and bi-directional electrophilic cyclisation. Within bi-directional cyclisation, divergent and convergent will be explored.

The proposed route of synthesis to afford polyyne **265** is shown in Scheme 36. This pathway commenced with the coupling of TMS acetylene **226** and tetra-halogenated benzene **107** to afford di-alkynyl **267** in 86% yield. Subsequent substitution of the bromo groups of **267** for the 'SMe' groups of **108**, was proposed through a tandem halogen for metal exchange reaction (C-Br → C-Li) to afford intermediate **268**, followed by the addition of electrophile **269**. The initial lithiation step to afford intermediate **268** performed well, measured by the appearance of an aryl CH singlet at 7.38 ppm in ^{1}H NMR. Pleasingly, addition of excess electrophile **269** to this reaction mixture afforded product **108** in 42% yield. The TMS groups of **108** were then removed to afford di-acetylene **270** in quantitative yield. Unfortunately, attempted cross-coupling of di-acetylene **270** and brominated TIPS alkyne **222** did not produce polyyne **265**. Preferential polymerisation of di-acetylene **270** was attributed to the lack of conversion to desired tetrayne **265**.



*Scheme 36: Attempted synthesis of polyyne **265**. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, b) n-BuLi, dry THF, c) dry THF, d) KF, MeOH, Et_2O.*

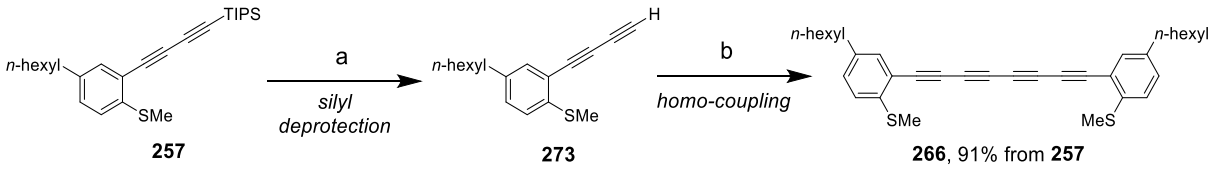
Following the unsuccessful cross-coupling to afford tetrayne **265**, an alternative approach to was required, Scheme 37 outlines the proposed alternate strategy. This pathway commenced with the Sonogashira coupling of tetra-halogenated benzene **107** and TIPS diyne **225**. This reaction performed very well giving tetrayne **271** in quantitative yield. Product presence was evidenced by the appearance of an aryl CH singlet at 7.71 ppm in ^{1}H NMR and no evidence of starting material **107** (8.02 ppm, CH singlet)[171]. Pleasingly, subsequent lithiation of tetrayne **271** to afford intermediate **272** followed by the addition of electrophile **269**, smoothly afforded tetrayne **265** in 90% yield.



*Scheme 37: Synthetic route to afford tetrayne **265**. a) CuI, $Pd(PPh_3)_4$, Et_3N, b) n-BuLi, dry THF, c) dry THF.*

The successful synthesis of symmetrical tetrayne **266** is outlined in Scheme 38. Product **266** was produced through tandem silyl deprotection of hexylated-TIPS diyne **257** and subsequent

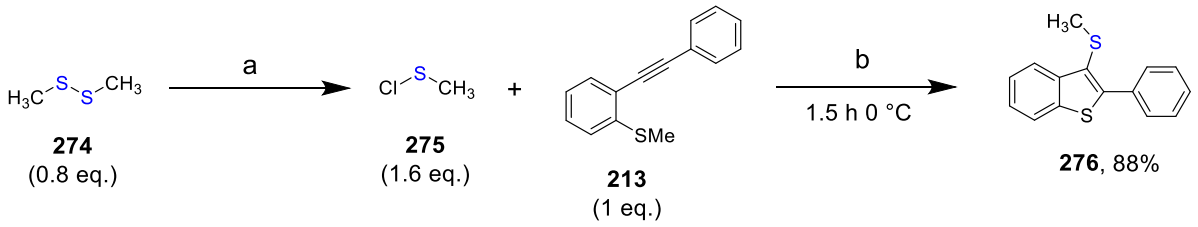
homo-coupling of acetylene **273**. Tetrayne **266** was furnished in excellent yield (91%) from hexylated-TIPS diyne **257**. Product formation was verified *via* ^{1}H and ^{13}C NMR analysis.



*Scheme 38: Synthetic access of tetrayne **266** from TIPS diyne **257**. a) TBAF, acetic acid, THF, b) CuOAc.H_2O, MeOH, pyridine.*

2.4 Affording the ambiphile

The overarching aim of this cyclisation study is to explore the application of an ambiphilic cyclising reactant, to afford poly-fused chalcogenophenes in an atom economical reaction cascade. To commence the exploration, ambiphile **275** was first afforded from the corresponding dimethyl disulfide **274** (Scheme 39). Ambiphile **275** has been previously accessed through exposure of dimethyl disulfide **274** to chlorine gas.[172] More recently, sulfuryl chloride has been successfully employed as the chlorinating agent.[173] Sulfuryl chloride is much each easier to handle safely as it is a liquid, and so it was utilised within this project to afford **275**.

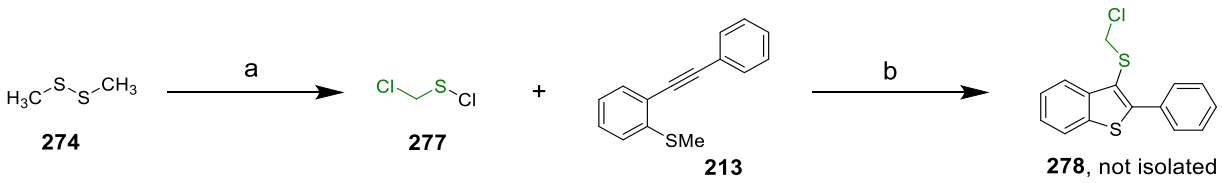


*Scheme 39: Simple monoyne cyclisation study to ensure cyclisation will occur with ambiphile **275** before application to more complex systems. a) SO_2Cl_2 (1 eq.), DCM, b) DCM.*

This chlorination reaction performed well with conversion measured through ^{1}H NMR analysis by the disappearance of the 2 × CH_3 singlet at 2.39 ppm (associated with dimethyl disulfide **274**) and appearance of a CH_3 singlet at 2.90 ppm (associated with ambiphile **275**). Pleasingly, addition of the reaction mixture containing ambiphile **275** to a solution of alkyne **213** in DCM

at 0 °C, furnished cyclised product **276** after 1.5 h. This result gave a strong indication that ambiphile **275**, at the very least, can perform as an electrophile, when participating in electrophilic cyclisation.

It was also noted that upon addition of SO_2Cl_2 to dimethyl disulfide **274** there was the occasional presence of another singlet at 5.12 ppm in ^{1}H NMR. It was suggested that this singlet was associated with the over chlorinated material **277** (Scheme 40). The structure of **277** was confirmed by addition of a reaction mixture containing the singlet at 5.12 ppm (in ^{1}H NMR) to a solution of alkyne **213** in DCM. Through subsequent ^{1}H NMR and ^{13}C NMR analysis, the presence of cyclised compound **278** was confirmed. Although the production of cyclised compound **278** is interesting, di-chlorinated material **277** is not predicted to exhibit the same ambiphilic nature as **275**. Accordingly, in all future efforts to afford ambiphile **275** sub-stochiometric portions of sulfuryl chloride were added to dimethyl disulfide **274** to avoid formation of **277**. Therefore, in each application of ambiphile **275** throughout this Chapter, ^{1}H NMR analysis was used to verify the presence desired ambiphile **275** and the lack of undesired over chlorinated material **277**.

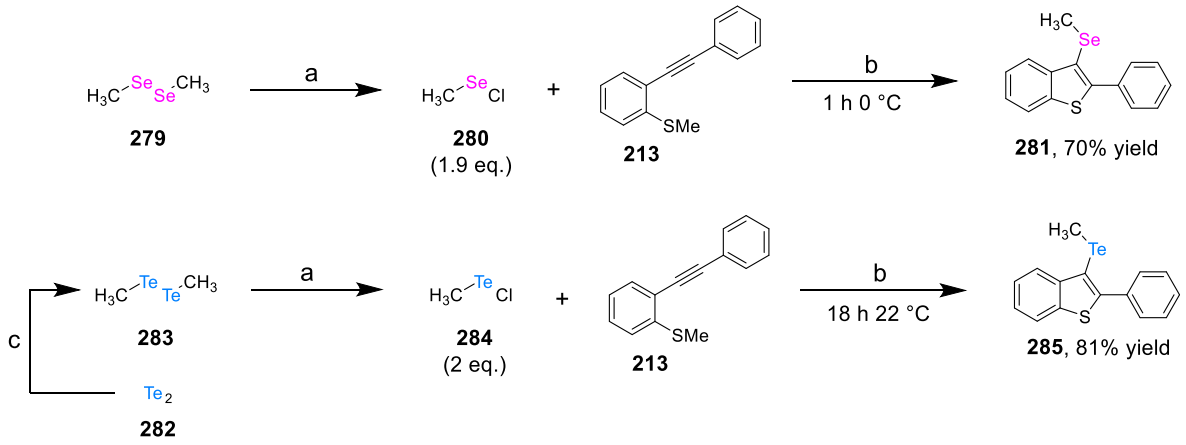


274 **277** **213** **278**, not isolated

*Scheme 40: Double chlorination of dimethyl disulfide **274** to afford **277** before addition to alkyne **213** to afford **278**. a) SO_2Cl_2 (2 eq.), DCM, b) DCM.*

The chlorination conditions applied to dimethyl disulfide **274**, were also successfully applied to dimethyl diselenide **279** and dimethyl ditelluride **283** (Scheme 41) with their presence confirmed *via* ^{1}H NMR analysis. As dimethyl ditelluride **283** is not commercially available it was produced from solid tellurium (**282**) through exposure to methyl lithium. The presence of dimethyl ditelluride **283** was confirmed by presence of a 2 × CH_3 singlet at 2.66 ppm in ^{1}H NMR spectra. Both ambiphiles **280** and **284** were added to respective solutions of alkyne **213** in DCM to afford the corresponding cyclisation products **281** and **285** in good yield. The smooth furnishing of mono-cyclised products **276** (S), **281** (Se) and **285** (Te) was an encouraging early result for the project as it evidenced the electrophilic ability of reagents **275**

(S), **280** (Se) and **284** (Te). Therefore, what remained was a thorough investigation as to their ambiphilic ability when applied to more extended polyynes systems.



*Scheme 41: Synthetic access of ambiphiles **280** and **284** for application to alkyne **213** to afford **281** and **285** respectively. a) SO_2Cl_2 (0.9 eq.) DCM, b) DCM, c) MeLi, dry THF.*

2.5 Domino poly-electrophilic cyclisation (PEC)

The ambiphilic reagents that have been afforded for use in this PEC study are show in in Figure 15. Also shown are all the polyyne cyclisation starting materials that these ambiphiles will be applied to. The aim of this study is to evidence an atom economical domino reaction version of electrophilic cyclisation. If successful, this reaction could potentially incorporate any chalcogen desired to furnish valuable poly-fused chalcogenophenes products in a single reaction cascade. With each attempt to exemplify PEC, success was measured by the presence of product in ^{1}H and ^{13}C NMR and HRMS analysis. Cyclised products were confirmed by the loss of alkynyl quaternary carbon resonances in ^{13}C NMR, correct mass detected in HRMS and all ^{1}H NMR resonances being assignable to the desired product.

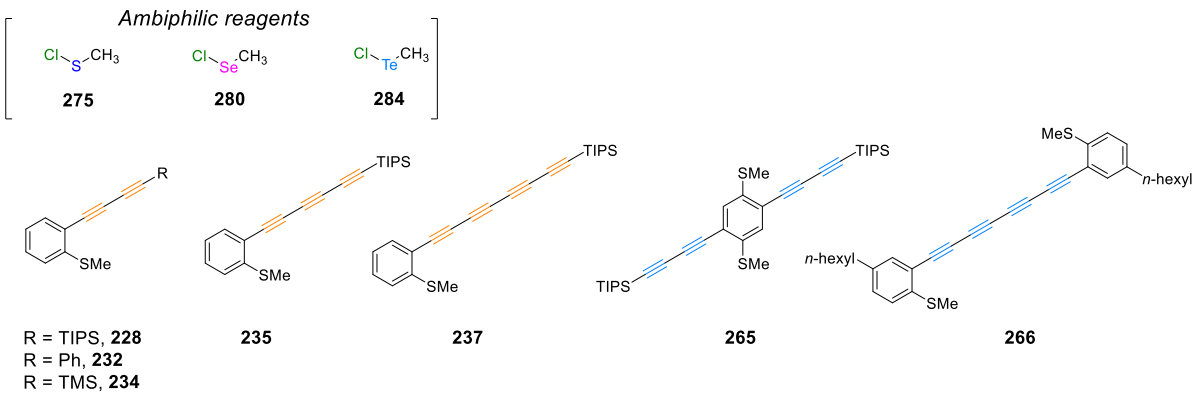
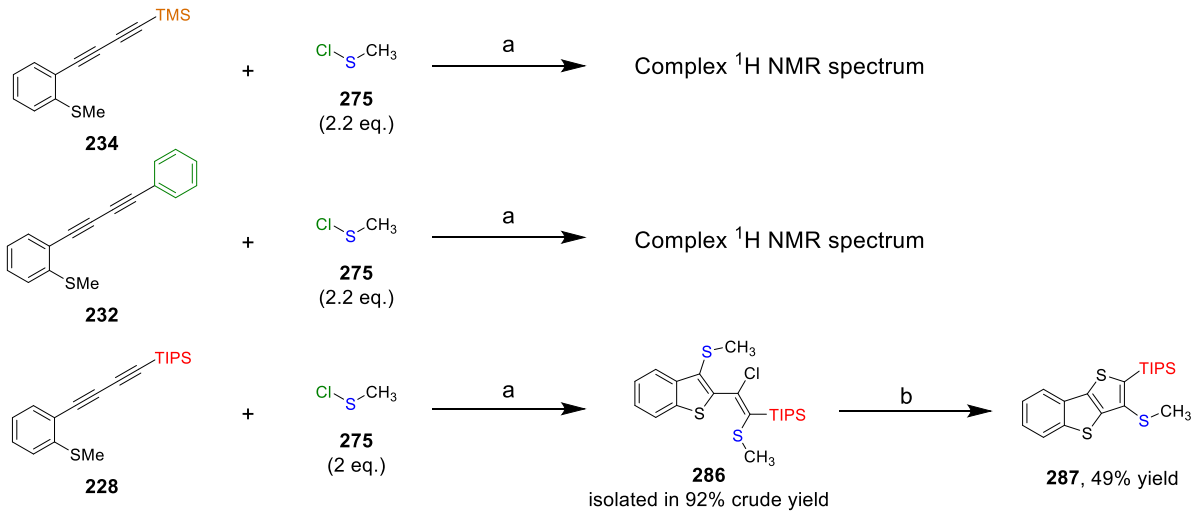


Figure 15: Polyyne precursors and ambiphilic reagents for PEC studies.

2.5.1 Uni-directional PEC

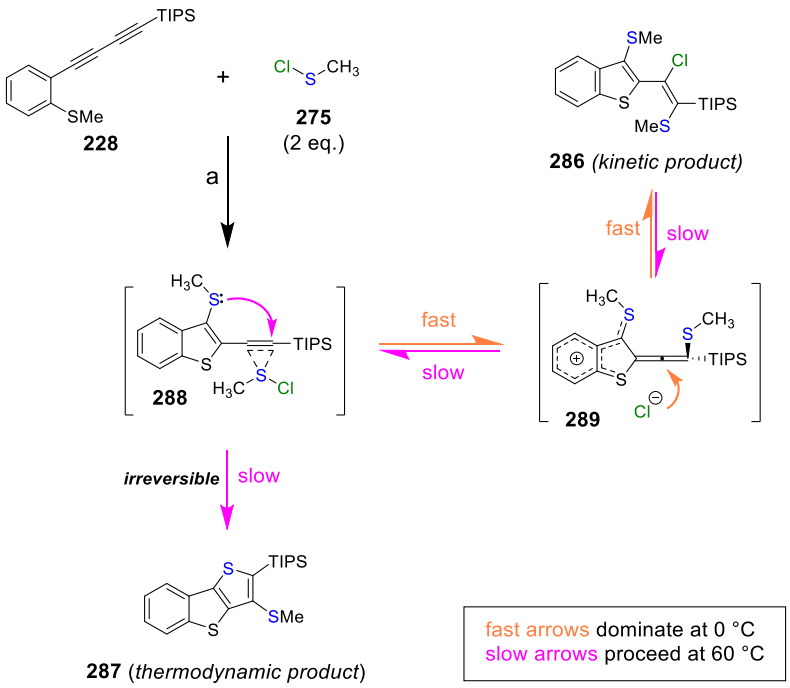
The outcomes of cyclisation with S ambiphile **275** and diynes **234** (TMS), **232** (Ph) and **228** (TIPS) are shown in Scheme 42. Unfortunately, attempted cyclisation of TMS diyne **234** and phenyl diyne **232** resulted in negligible product presence observed in ^{1}H NMR spectra. ^{1}H NMR did however show the lack of starting material resonances, indicating that cyclisation was occurring but perhaps intermediates were not suitably stable in reaction mixture.



*Scheme 42: Outcome of PEC of diynes **234**, **232** and **228** with sulfur based ambiphile **275**. a) DCM, 0 °C 1 h, b) reflux, 40 h.*

Contrastingly, reaction between S ambiphile **275** and TIPS diyne **228** smoothly produced one product after 1 h at 0 °C. However, ^{1}H and ^{13}C NMR analysis indicated the presence of two

CH_3 groups present within the compound, suggesting it was not the fully cyclised material **287**. ^{1}H NMR showed two singlets that integrated equally but with slightly different chemical shifts (2.57 and 2.38 ppm). Structure **286** was proposed as a product of tandem mono-cyclisation and addition reaction between TIPS diyne **228** and S ambiphile **275**. Following isolation of partially cyclised product **286**, it was then found that the reaction mixture could be heated to convert **286** to the fully cyclised material **287**. Accordingly, it was concluded that **286** may be the kinetic product of cyclisation and **287** the thermodynamic product. Scheme 43 presents a cyclisation reaction mechanism that rationalises these results.



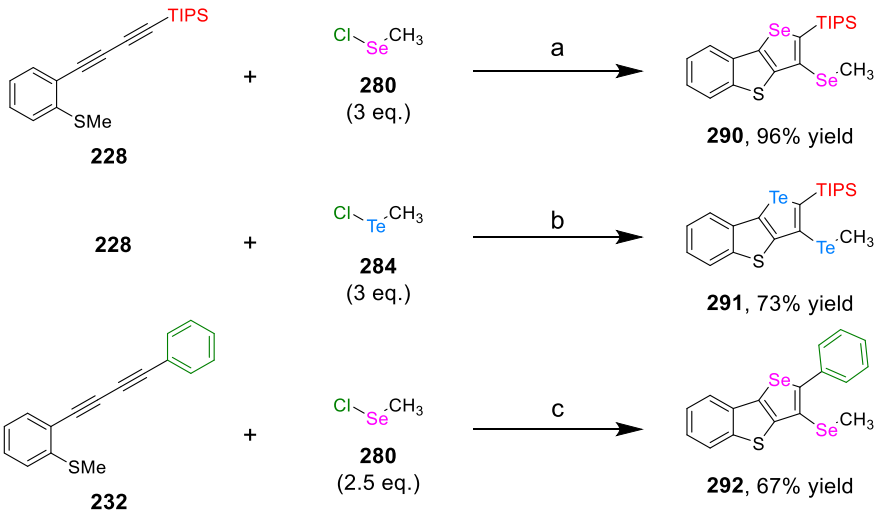
*Scheme 43: Proposed mechanism of the formation of kinetic product **286** and thermodynamic product **287** from reaction between TIPS diyne **228** and ambiphile **275**. a) DCM 0 °C 1h.*

To first afford the kinetic product **286**, mono-cyclisation of TIPS diyne **228** with S ambiphile **275** occurs to produce intermediate **288**. At this point, it was original theorised that the newly incorporated S-CH_3 would nucleophilically attack the alkyne in a second instance of electrophilic cyclisation (pink mechanism arrow). However, this did not occur when the reaction was performed at 0 °C. At this temperature as the second cyclisation is not occurring, the alkyne bond of **288** remains in a solution of S ambiphile **275** in DCM. Unsurprisingly, this leads to S ambiphile **275** eventually adding across the alkyne to afford intermediate **289**, this type of alkyne addition reaction has been evidenced previously under similar conditions.[174, 175]

The pathway from **288** to kinetic product **286** is also aided through delocalisation through the benzothiophene unit as shown in intermediate **289**. This stabilises the intermediate, better facilitating conversion to kinetic product **286**. However, this addition reaction is also reversible, when heat (60 °C) is supplied to the reaction mixture, the molecule of S ambiphile **275** that added to the alkyne of intermediate **289** can be expelled to return to intermediate **288**. Once intermediate **288** is present in the heated reaction mixture, suitable energy is present to slowly, and irreversibly, convert to thermodynamic product **287**.

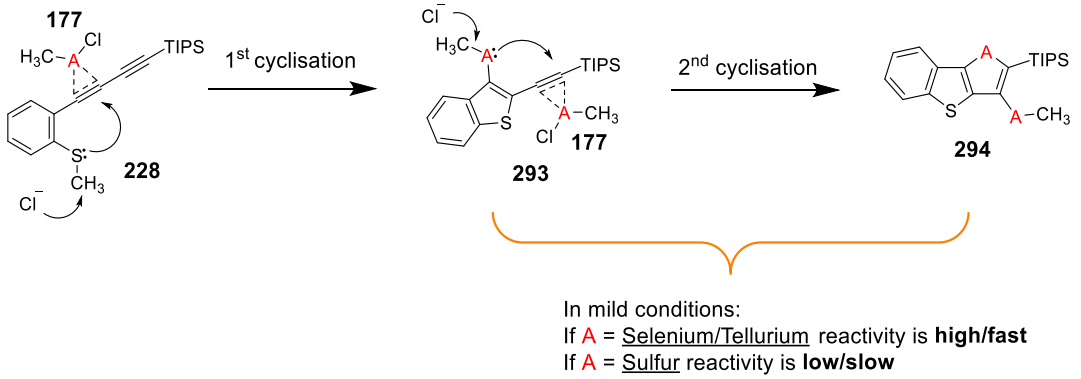
There are two important points to take from the cyclisation outcomes of Scheme 42, firstly TIPS diyne **228** outperforms TMS diyne **234** and phenyl diyne **232** in affording a clean product of cyclisation. This indicates the chemical and structural nature of TIPS is important to conferring effective cyclisation. Additionally, the nucleophilicity of sulfur is too low to promote domino cyclisations at low temperature (0 °C), however this can be overcome with increased reaction temperature (60 °C) and time (40 h). Se and Te are more nucleophilic elements than sulfur and so the employment of Se ambiphile **280** and Te ambiphile **284** allowed us to compare cyclisation outcomes following their addition to TIPS diyne **228**.

Scheme 44 presents the PEC outcomes of TIPS diyne **228** and phenyl diyne **232** upon exposure to Se and Te ambiphiles **280** and **284**, respectively. To our great satisfaction, TIPS diyne **228** was successfully cyclised upon exposure to both Se containing ambiphile **280** and Te containing **284** to afford chalcogenophenes **290** and **291** in high yield. Utilising ^{1}H and ^{13}C NMR and HRMS data to confirm product presence, these materials were produced under mild conditions (-20-22 °C).



*Scheme 44: Successful cyclisation of diynes **228** and **232** to afford chalcogenophenes products **290**, **291** and **292**. a) DCE, 0 °C 1 h, b) DCM, 22 °C, 18 h, c) DCE, -20 °C, 1 h.*

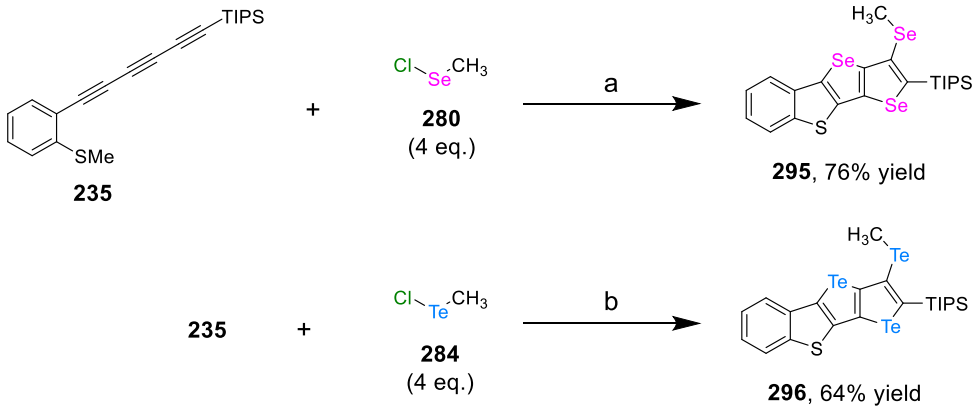
The results of Scheme 44 are in direct contrast to the reaction outcome of TIPS diyne **228** and S containing ambiphile **275** shown in Scheme 42. So why does S require a higher temperature to cyclise than Se and Te? A reconciliation of these contrasting results is shown in Scheme 45. All chalcogens (S, Se and Te) perform equally as electrophiles in the first cyclisation to afford intermediate **293**. However, when it comes to the second cyclisation, the chalcogen (denoted with A) within **293** is required to perform as a nucleophile. Se and Te are more nucleophilic elements than S, therefore when A = Se or Te, this second cyclisation is fast and will afford **294** at low temperature. When A = S, the weaker nucleophile is a lot slower to cyclise, therefore requiring increased time and temperature to afford the fully cyclised **294**.



Scheme 45: Mechanistic explanation of different results upon use of sulfur rather than selenium or tellurium ambiphiles.

It is also noteworthy that phenyl diyne **232** was successfully cyclised with Se containing ambiphile **280** to afford chalcogenophene **292**. This is in direct contrast to the lack of success with S ambiphile **275**. This is further exemplification of the improved cyclisation outcomes upon use of a Se containing ambiphile in comparison to sulfur. In this case, it is likely that the faster cyclisation that results from the use of Se ambiphile **280** avoids unstable reaction intermediates of phenyl diyne **232** being present in the reaction mixture for too long.

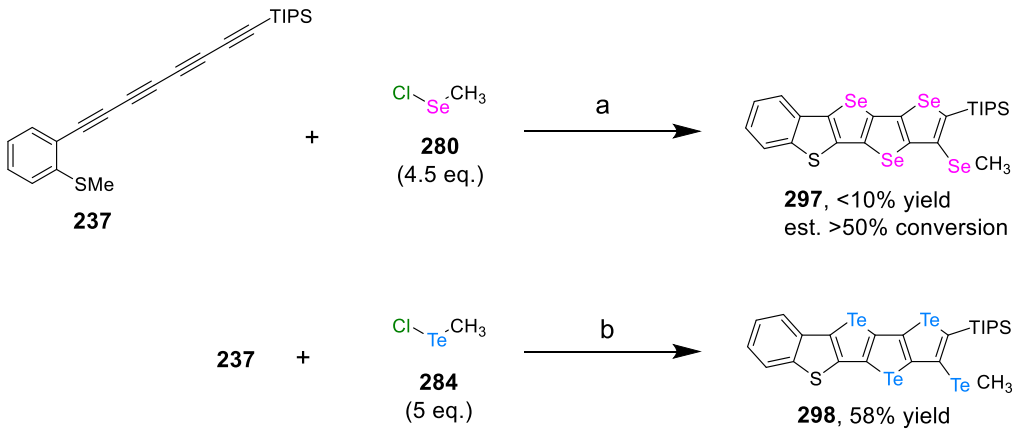
Gratifyingly, triyne **235** smoothly afforded fully cyclised chalcogenophenes **295** and **296** in good yield and under mild conditions (reaction temperature 0 °C and 22 °C, respectively) (Scheme 46). This demonstrated that PEC could afford three contiguously fused chalcogenophenes in a single reaction cascade. The results of both Scheme 44 and 46 also demonstrate the versatility of the evidenced PEC to incorporate either Se or Te. Both elements are underrepresented in the synthetic methods to afford heteroacenes therefore this outcome represents an important advancement for the study.



*Scheme 46: Successful cyclisation of triyne **235** to afford poly-fused chalcogenophenes **295** and **296**. a) DCE, 0 °C, 1 h, b) DCM, 22 °C, 18 h.*

The outcomes of cyclisation of tetrayne **237** with both Se containing ambiphile **280** and Te containing **284** are outlined in Scheme 47. In an outstanding result for the project, the tetrayne starting material **237** was successfully cyclised to afford the corresponding poly-fused tellurophene **298** in good yield. The efficient formation of this material marks the first ever reported synthetically afforded compound that features three fused tellurophenes. Contrastingly, addition of Se ambiphile **280** to tetrayne **237** gave a complex ^{1}H NMR spectrum of reaction intermediates. It was later found that heating the reaction mixture to 60-80 °C,

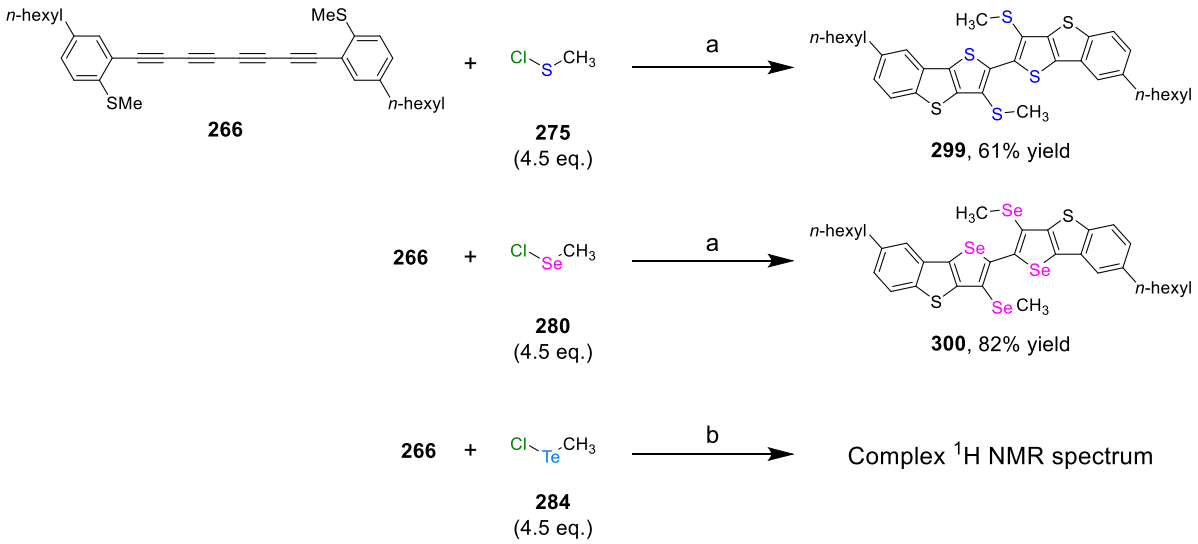
reduced the presence of these intermediates that were proposed to be similar to the kinetic products shown in Scheme 43. Although reaction intermediate presence could be reduced up to a point, the remaining presence complicated purification attempts, resulting in the low yield of <10%. Although this yield was disappointing, the product **297** was still isolated and characterised, demonstrating the ability of Se ambiphile **280** to participate in a reaction cascade across up to four consecutive alkynes.



*Scheme 47: Successful cyclisation of tetrayne **237** to afford poly-fused chalcogenophenes **297** and **298**. a) DCE, 60 °C 2 d, 80 °C 2 d., b) DCM, 22 °C, 18 h.*

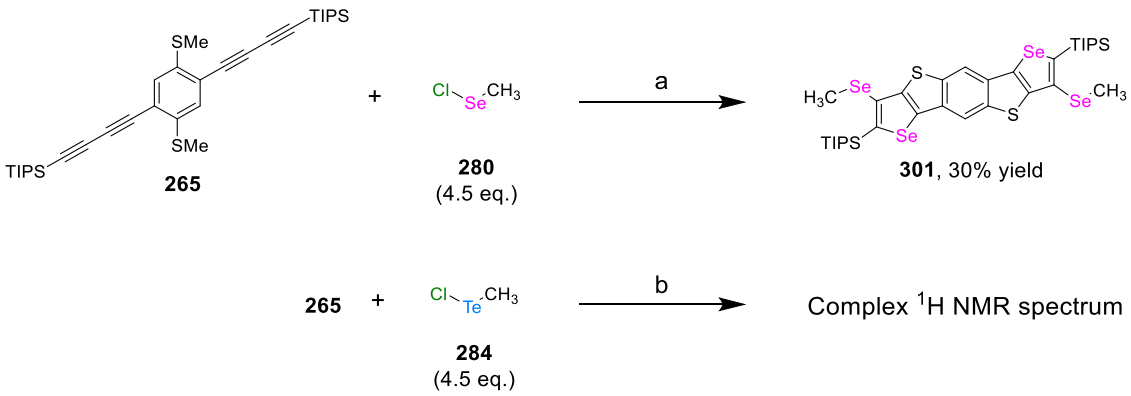
2.5.2 Bi-directional PEC

Following the great success of uni-directional PEC, the bi-directional equivalent was explored. Scheme 48 describes the reaction outcomes upon treatment of tetrayne **266** with the sulfur, selenium and tellurium ambiphiles **275**, **280** and **284**, respectively. Pleasingly, convergent bi-directional cyclisation of tetrayne **266** was successfully evidenced, affording both **299** and **300** in moderate-high yield. It is interesting that in this context, S ambiphile **275** conferred smooth cyclisation, as opposed to the cyclisation outcomes described in Scheme 42. Surprisingly, when Te containing ambiphile **284** was applied to tetrayne **266**, a complex ^{1}H NMR resulted. This was attributed to the lower solubility of Te species as compared to S and Se, affecting reaction outcome.



*Scheme 48: Cyclisation outcomes of polyyne **266** with ambiphiles **275**, **280** and **284**. a) DCM, 0 °C, 1 h, b) DCM, 0-22 °C.*

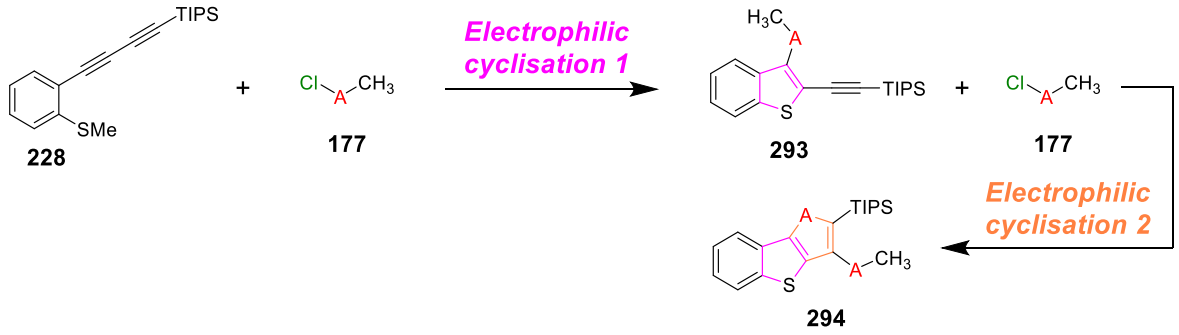
Bi-directional cyclisation was also evidenced divergently with tetrayne **265** successfully cyclising with Se ambiphile **280** to afford chalcogenophene **301** (Scheme 49). The low yield of **301** was attributed to poor solubility affecting isolation and purification attempts. The poor solubility also made ^{13}C NMR analysis difficult as quaternary carbons could not be detected. 2D NMR experiments (HMBC and HSQC) were employed to detect quaternary carbon resonances of **301** through their correlations with more easily detected protons. Cyclisation of tetrayne **265** with Te ambiphile **284** was also attempted, however a complex ^{1}H NMR spectrum was observed. This outcome was attributed to the low solubility of tellurophenes combined with their corresponding products proving incompatible with cyclisation.



*Scheme 49: Successful cyclisation of tetrayne **265** to afford chalcogenophene **301**. a) DCM, 0 °C, 1 h, b) DCM 0-22 °C.*

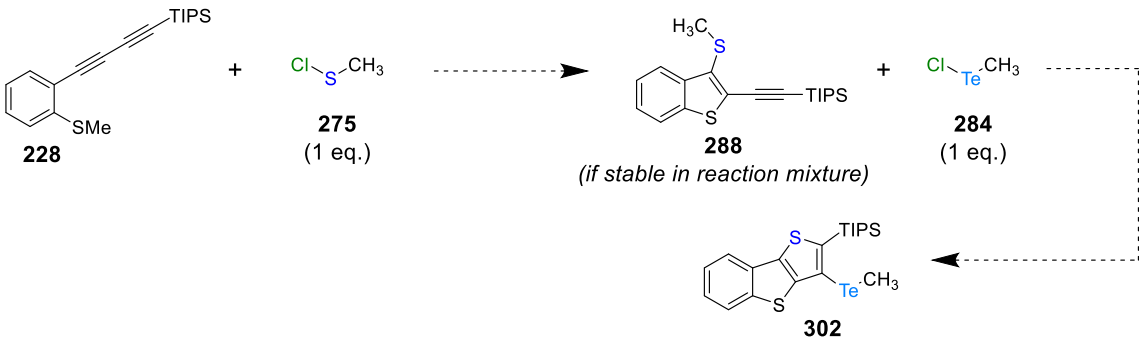
2.5.3 Limiting PEC of polyyne starting materials

The outstanding results of the PEC study with ambiphiles **275**, **280** and **284** clearly demonstrated that a domino-cascade of repeating electrophilic cyclisations is possible when these ambiphiles are exposed to suitable polyynes. The reaction mechanism has also been described as likely occurring through a series of iterative cyclisations as shown in Scheme 50. Regarding this domino reaction pathway, one question that remains is whether a partially cyclised material such as **293** could be isolated?



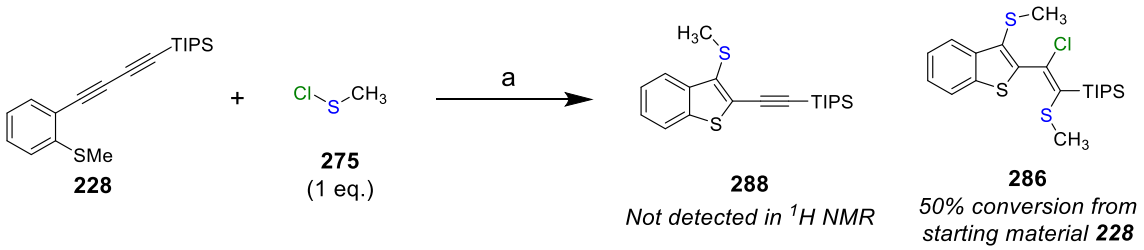
*Scheme 50: General scheme showing previously exemplified diyne **228** cyclisation.*

Scheme 51 outlines a potential application of partially cyclised polyynes. The proposed scheme shows the addition of 1 eq. of S ambiphile **275** to TIPS diyne **228** to first afford partially cyclised intermediate **288**. Subsequently, Te ambiphile **284** would be added with the aim of affording chalcogenophene **302**. The proposed pathway would provide opportunity to incorporate alternating chalcogens, increasing the scope of PEC and enhancing its utility to afford varied poly-fused chalcogenophenes. Before the pathway shown below was attempted, we first verified whether **288** could be isolated or observed in reaction mixture by NMR analysis.

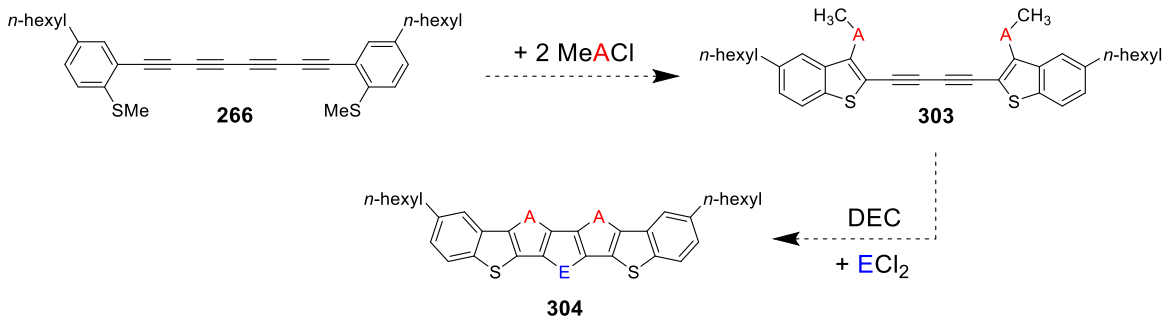


*Scheme 51: Proposed method of controlling poly-cyclisation through addition of stochiometric portions of **275** and **284** to incorporate alternating chalcogens.*

Scheme 52 outlines attempts to afford a mono-cyclised **288** from diyne **228**. S ambiphile **275** was selected due to its second cyclisation being slower than that of Se or Te, with the potential to provide better opportunity for isolation before the second cyclisation occurs. Unfortunately, with each attempt addition of 1 eq. of S ambiphile **275** to diyne **228** resulted in a ^{1}H NMR spectrum that showed the presence of both starting material diyne **228** and kinetic cyclisation product **286**. This indicated that partially cyclised material **288** was not present in reaction mixture in sufficient time required for NMR monitoring, as conversion to **286** occurred too promptly. Following this, it was proposed that bi-directional symmetrical tetrayne **266** be explored in this context of partial cyclisation. Scheme 53 outlines this exploration and the proposed DEC based application of a partially cyclised product **303**.

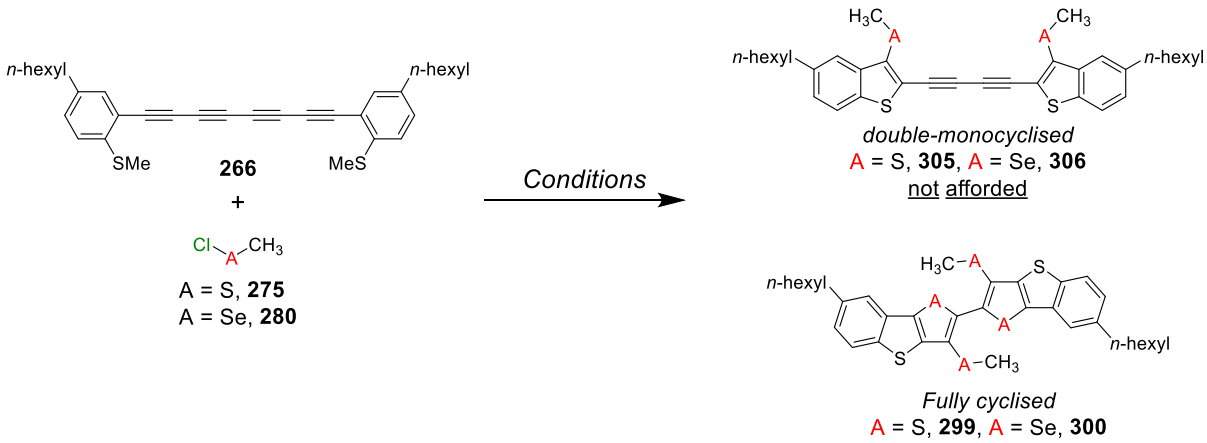


*Scheme 52: Attempts to furnish monocyclised material **288** from diyne **228**. a) DCM, 0 °C, 1 h.*



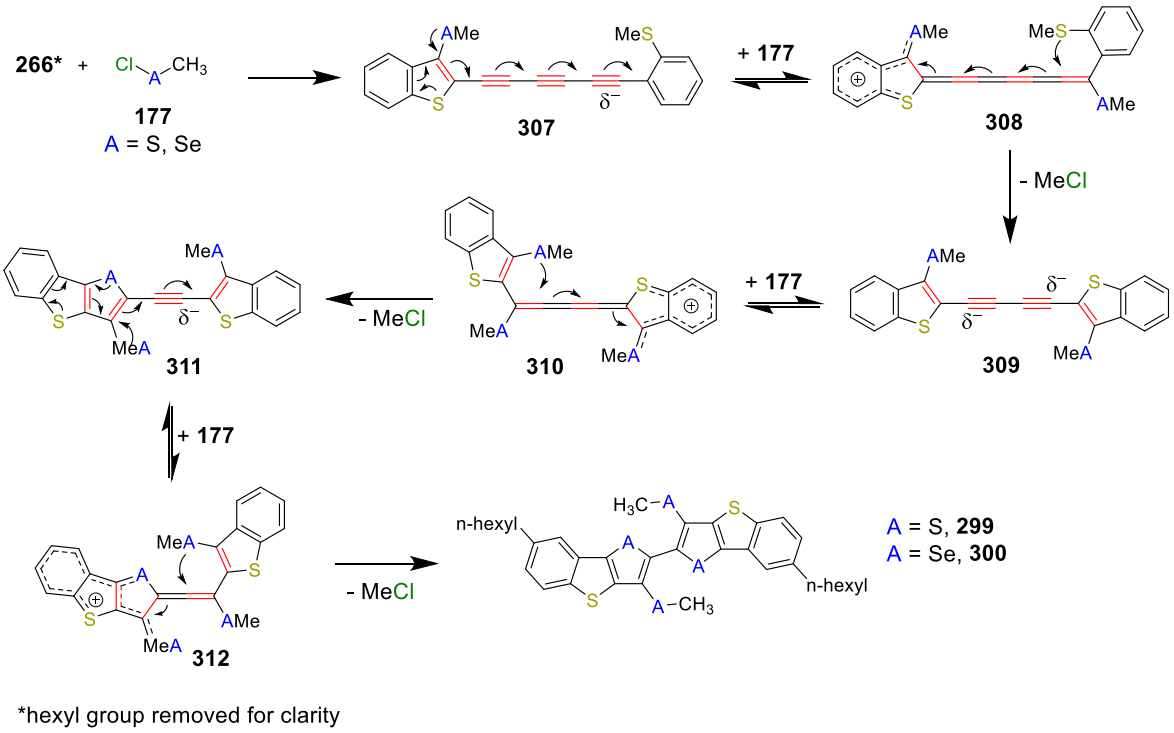
*Scheme 53: Proposed DEC application of partially cyclised **303** to afford **304***

Iterative attempts to afford double-monocyclised products **305** or **306** from reaction between tetrayne **266** and ambiphiles **275** and **280** are shown in Scheme 54. Entries 1 and 2 detail the first reaction attempts at -78 °C, before heating to 0 °C as no reaction was observed in ^{1}H NMR at -78 °C. After the reaction had stirred at 0 °C for 1 h, ^{1}H NMR analysis confirmed the presence of only uncyclised starting material **266** and the fully cyclised material **299** or **300**. The reaction was then performed at -20 °C (Entry 3) to reach a 'middle ground' between the outcome of reaction at -78 °C (no reaction) and 0 °C (fully cyclised). This temperature proved too cold for reaction to occur as only starting material tetrayne **266** was present in ^{1}H NMR analysis. The final attempt (Entry 4) detailed in the table was monitored by ^{1}H NMR after each addition of 0.5 eq. of S ambiphile **275** at 0°C. It was hypothesised that irrespective of its stability, some partially cyclised material **305** could be observed with slow addition of **275**. Unfortunately, this did not occur and only tetrayne **266** was observed in early spectra analysis. Heating the reaction to 22 °C gave a complex ^{1}H NMR spectrum. It was then concluded that clearly PEC of tetrayne **266** does not allow for isolation of partially cyclised materials. Scheme 55 outlines the proposed mechanistic reasoning for this outcome.



Entry	Reaction Conditions	Outcome
1	1.9 eq. of **275**, DCM, 1 h -78 °C, 1 h 0 °C	Starting material **266** + fully cyclised material **299**
2	2 eq. of **280**, DCM, 1 h -78 °C, 1 h 0 °C	Starting material **266** + fully cyclised material **300**
3	0.9 eq. of **275**, DCM, 1 h -20 °C	Starting material **266**
4	0.5-2 eq.* of **275**, DCM, 1 h 0 °C, 1 h 22°C * Reaction monitored by ^{1}H NMR after each addition of 0.5 eq. of **275**	Complex spectrum

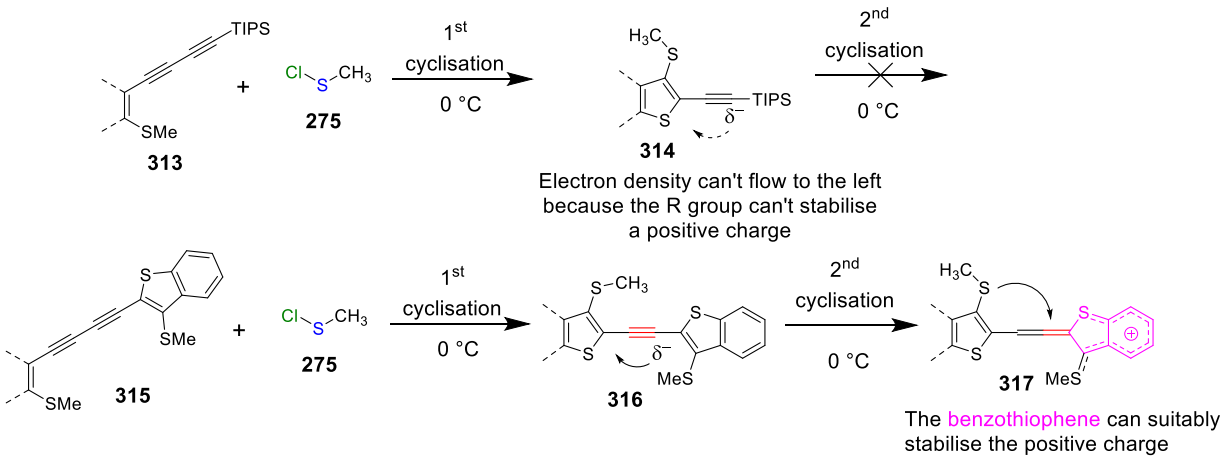
*Scheme 54: Iterative attempts to partially cyclise tetrayne **266** to afford monocyclised or double-monocyclised materials.*



Scheme 55: Proposed mechanism of convergent bi-directional cyclisation that does not allow for partial cyclisation. Scheme modified from published manuscript[156].

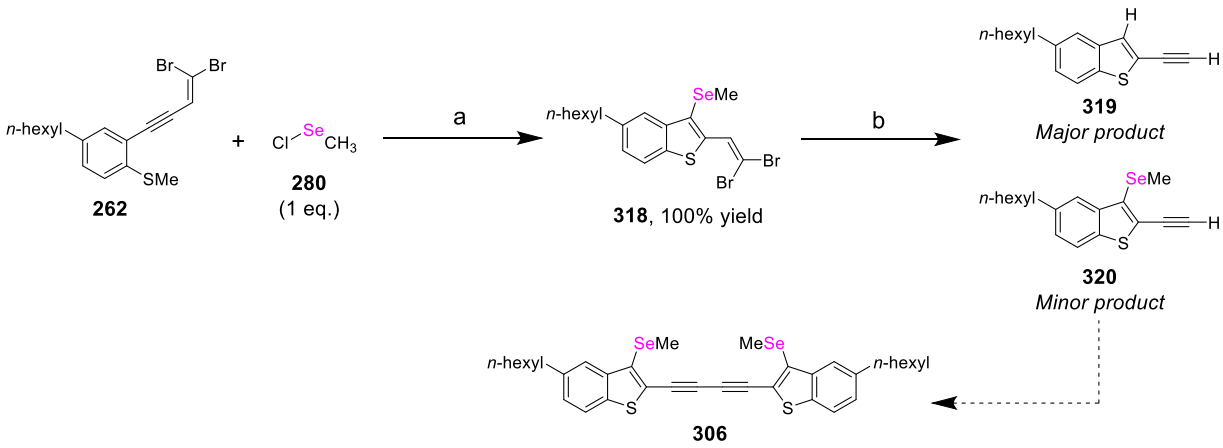
Within Scheme 55 we propose that cyclisation of **266** occurs *via* a 'see-saw' mechanism where alternating shifts in electron density move from one end of the polyyne to the other with each cyclisation. As this electron density shifts, it allows cyclisations to occur with increasing momentum. Therefore, once PEC is initiated to afford intermediate **307**, the subsequent domino reaction cascade to fully cyclised **299** or **300** gains 'pace' with each cyclisation. Accordingly, partially cyclised intermediates will never be isolated as they do not exist long enough in reaction mixture to be observed by NMR or LCMS analysis techniques. This 'see-sawing' flow of electron density is a result of three structural features of intermediate **307**: i) the presence of the chalcogen 'A' (A=S or Se) having a lone-pain of electrons to donate, ii) linear alkynes that can facilitate the transfer of electron density and; iii) the presence of a benzothiophene ring system. This ring system sufficiently stabilises the positive charge that results from the lack of electron density as shown in **308**. Each of these structural features helps to facilitate the elegant mechanism of PEC shown. Although the inability to isolate partially cyclised intermediates does limit the ability to incorporate alternating chalcogens, it does confirm the propensity of the polyynes reported to undergo the entire domino cascade of PEC.

This mechanism also reconciles the contrasting performance of S ambiphile **275** when applied to symmetrical tetrayne **266** (smooth cyclisation) and TIPS diyne **228** (required 40 h at 60 °C to cyclise). Scheme 56 (of which takes exerts from Scheme 55) illustrates the reason for this discrepancy. Although intermediate **314** features sulfur, an electron dense chalcogen that can donate a lone pair and the alkyne to transfer electron density, it does not feature symmetrical benzothiophene ring systems (as **316** does). Without this last structural feature, the electron density that results from first cyclisation cannot 'flow' back to the thiophene of **314**, because the TIPS group cannot stabilise a positive charge. Accordingly, the domino reaction is halted, with intermediate **314**, whereas in the case of **316**, this continues through to the second cyclisation.



*Scheme 56: Mechanistic explanation for better performance of **275** in convergent bi-directional cyclisation than uni-directional cyclisation.*

As partially cyclised polyynes cannot be produced through careful addition of limited eq. of ambiphiles, an alternative approach was proposed (Scheme 57). In this method, geminal dibromide **262** is cyclised with Se ambiphile **280** to give benzothiophene **318** in quantitative yield. The aim was that the cyclised geminal dibromide **318** could be treated with *n*-BuLi to undergo a Corey-Fuchs reaction, affording alkyne **320**. However, upon exposure of **318** to 2 eq. of *n*-BuLi at -78 °C, ^{1}H NMR analysis showed the major product as the protonated material **319**. The desired product **320** was also present but in negligible yield, demonstrating that this approach was not viable due to the high propensity for the SeMe group of **318** to be lithiated by *n*-BuLi.



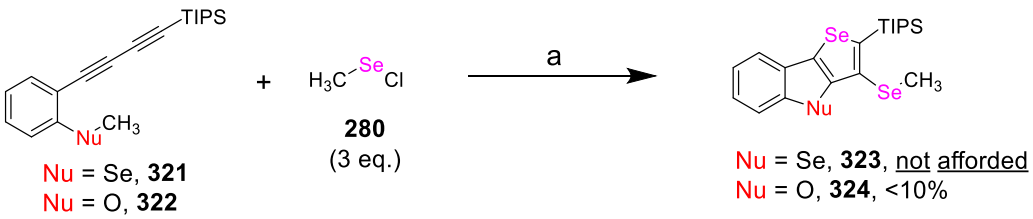
Scheme 57: Proposed synthetic route to exert control over number for cyclised rings in polyyne starting materials. a) DCM, 0 °C, 1 h, b) n-BuLi, dry THF.

2.6 PEC scope investigations

Following the success of both uni- and bi-directional PEC, it was proposed that some further investigation of the scope of this reaction be explored. These minor investigations did not greatly enhance the scope of the PEC reaction but instead revealed some limitations of the reaction that may warrant further exploration. These efforts are summarised below.

2.6.1 Variation of the tethered nucleophile

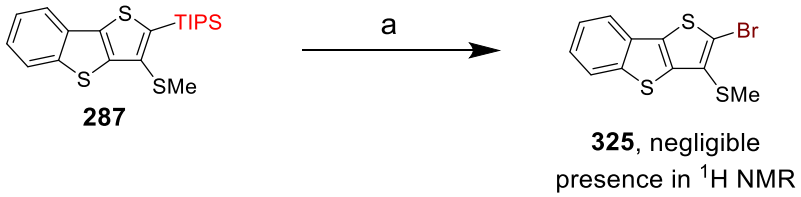
Both diynes **321** and **322** were smoothly afforded from commercially available starting materials (Scheme 58). The procedures for their synthesis are described in the experimental, Chapter 5.2. These diynes were then exposed to Se ambiphile **280** to exemplify PEC. The oxygen containing diyne **322** successfully cyclised to afford chalcogenophene **324**, although in low yield. The reaction between Se ambiphile **280** and **321** led to a complex ^{1}H NMR spectrum that did not contain any discernible product (**323**). These results demonstrated the superior character of sulfur that confers more efficient electrophilic cyclisation.



*Scheme 58: Cyclisation outcomes of TIPS diynes **321** and **322**. a) DCM, 0-22 °C.*

2.6.2 Post cyclisation TIPS for bromo exchange

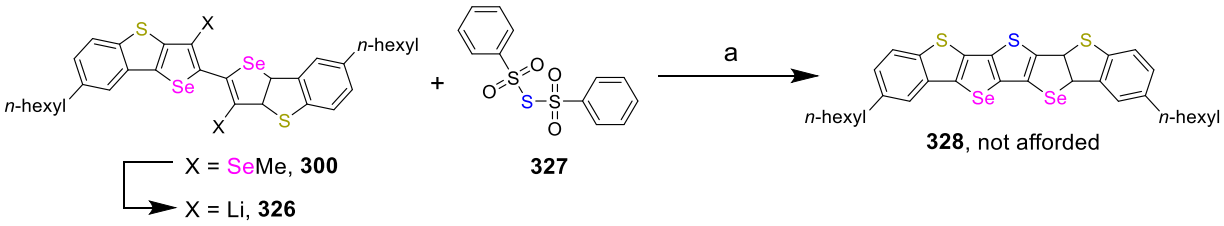
The presence of a halogen group in organic compounds provides as an incredibly useful position to perform coupling reactions for further functionalisation. Exchanging silyl groups such as TMS and TIPS for halogens were previously exemplified.[176-178] As many of the products of PEC feature a TIPS group, it was proposed that an attempt be made to convert **287** to **325** (Scheme 59). Multiple attempts were made to furnish **325**, utilising Br_2 or NBS as brominating agents, however negligible product was observed in NMR analysis.



*Scheme 59: Attempted TIPS for bromo exchange reaction to afford **325**. a) Attempted conditions are detailed in the Appendix, Chapter 7.3.*

2.6.3 Ring-closing electrophilic addition

Following the great success of bi-directional poly-electrophilic cyclisation, it was noted that the convergently cyclised **300** possessed two functional groups (SeMe) that could undergo further reaction afford another fused aryl ring (Scheme 60). Attempts to afford **328** confirmed the presence of lithiated intermediate **326**, however, either the low stability of **326** or resistance to electrophilic addition resulted in no conversion to product **328**.



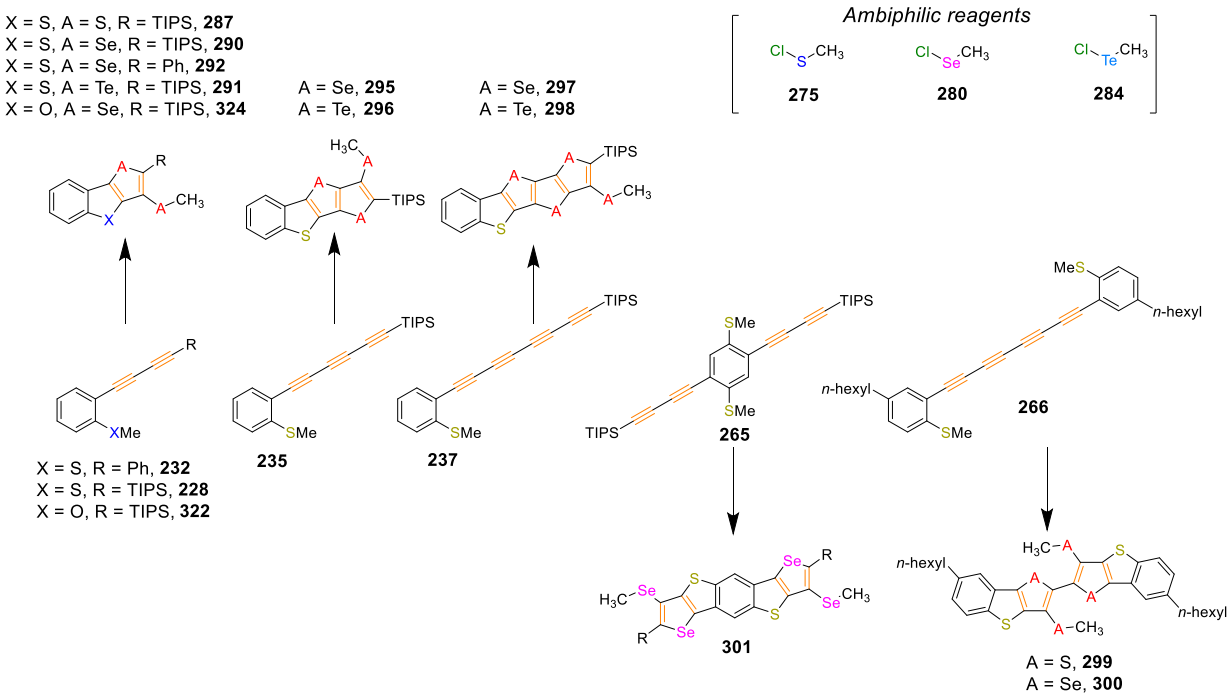
*Scheme 60: Attempted double-electrophilic addition reaction to afford poly-fused material **328**. a) Attempted conditions are detailed in the Appendix, Chapter 7.3.*

2.7 Conclusions and future work

This chapter of work has presented a novel and atom economical method of affording poly-fused chalcogenophenes from polyyne starting materials. Scheme 61 presents a summary of the achievements of this study that utilised S, Se and Te containing ambiphiles (**275**, **280** and **284**, respectively) to afford the varied chalcogenophene products shown. This methodology was demonstrated to afford poly-fused thiophenes, selenophenes and tellurophenes, both symmetrical and unsymmetrical of varied size and ring-fusion pattern. Of particular note is also the formation of poly-fused tellurophene **298** that is the first reported synthetically afforded compound to feature three fused tellurophenes. This PEC reaction therefore bears great utility to the field of organic electronics as a bespoke method that can afford diverse poly-fused chalcogenophenes in a single reaction cascade.

Within this chapter, the PEC reaction was shown to perform best when the more nucleophilic ambiphiles **280** (Se) and **284** (Te) were employed. However, the limitations of sulfur promoted cyclisation (by use of **275**) were overcome with increased time/temperature or upon application to a better equipped polyyne such as tetrayne **266**. Attempts to isolate partially cyclised intermediates only exemplified the efficient mechanism by which these products are afforded. This mechanism presented how when suitable ambiphiles are employed the domino reaction cascade proceeds too quickly to observe intermediates. This likely contributes to the remarkably clean conversion to the chalcogenophene product.

Future work that remains is the further functionalisation of products of cyclisation. Continual efforts to ring-close **299** and **300** would greatly enhance the perceived utility of these materials. Reactions that evidence the utility of the TIPS group incorporation would also be beneficial. Efforts will also be made to complete density functional calculations to confirm reaction mechanisms presented in this work.



*Scheme 61: Summary of evidenced domino PEC of polyynes shown with ambiphiles **275**, **280** and **284**.*

3.0 Results and discussion: Bi-directional application of double-electrophilic cyclisation

3.1 Introduction

Fused aromatic ring systems are employed within organic electronics because of their unique ability to delocalise π-electrons across the entire molecule. These ring systems can be made up of acenes and heteroacenes (Fig. 16). Both have been previously explored in organic electronic applications.[2]

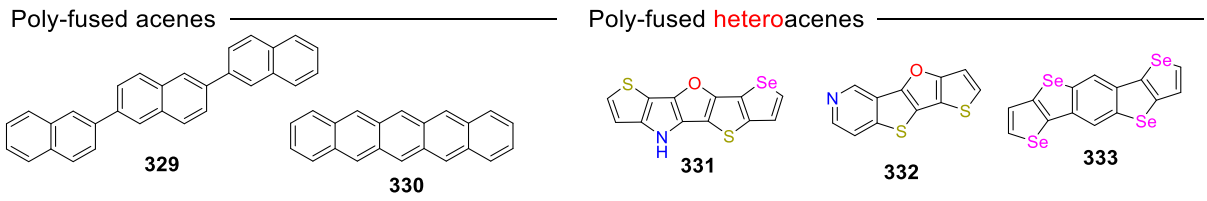


Figure 16: General representation of poly-fused acenes and heteroacenes.

Acenes have demonstrated an enhanced ability to perform as semiconductors with pentacene (five fused benzene rings) receiving a lot of attention for its performance as an OFET.[179-181] Heteroacenes are equally noteworthy, demonstrating improved molecular stability from acenes and comparable performance (Fig. 17). From Figure 16, it can also be seen that heteroacenes have a far greater opportunity for diversification, such as the number of heteroatoms, the elements employed and their pattern of incorporation. Each of these points of variation can correspond to changes in electronic properties.[182-185] Accordingly, poly-fused heteroacenes, are particularly valuable to the materials science field.

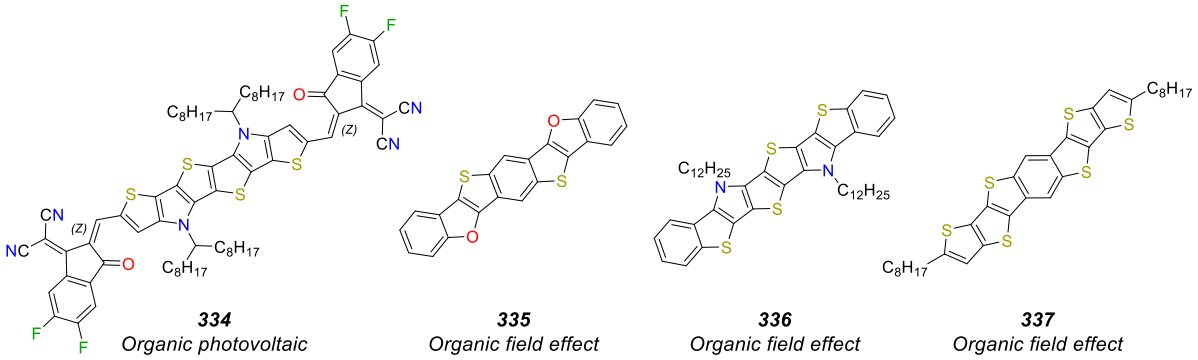
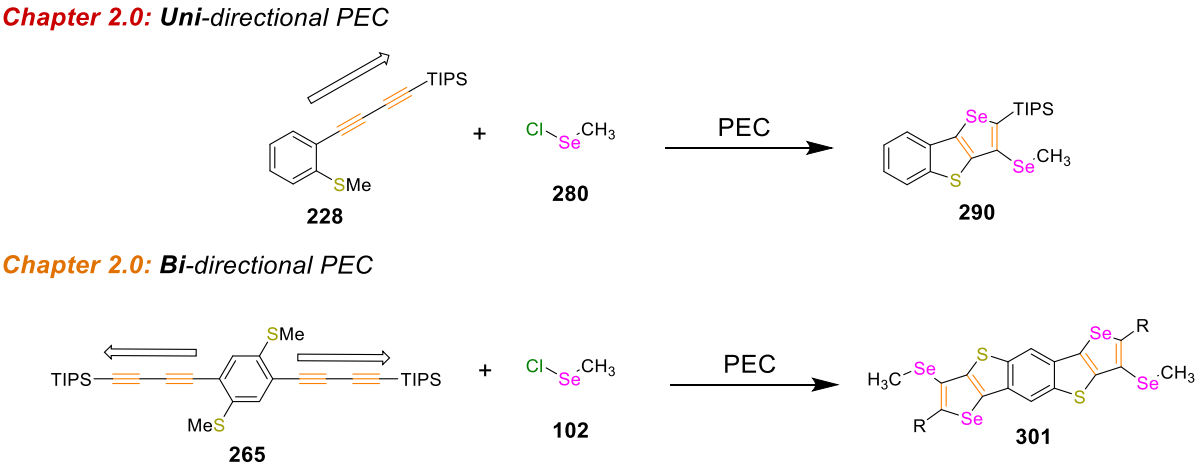


*Figure 17: Poly-fused heteroacenes for application in organic electronics. (**334**[186], **335**[48], **336**[187], **337**[188])*

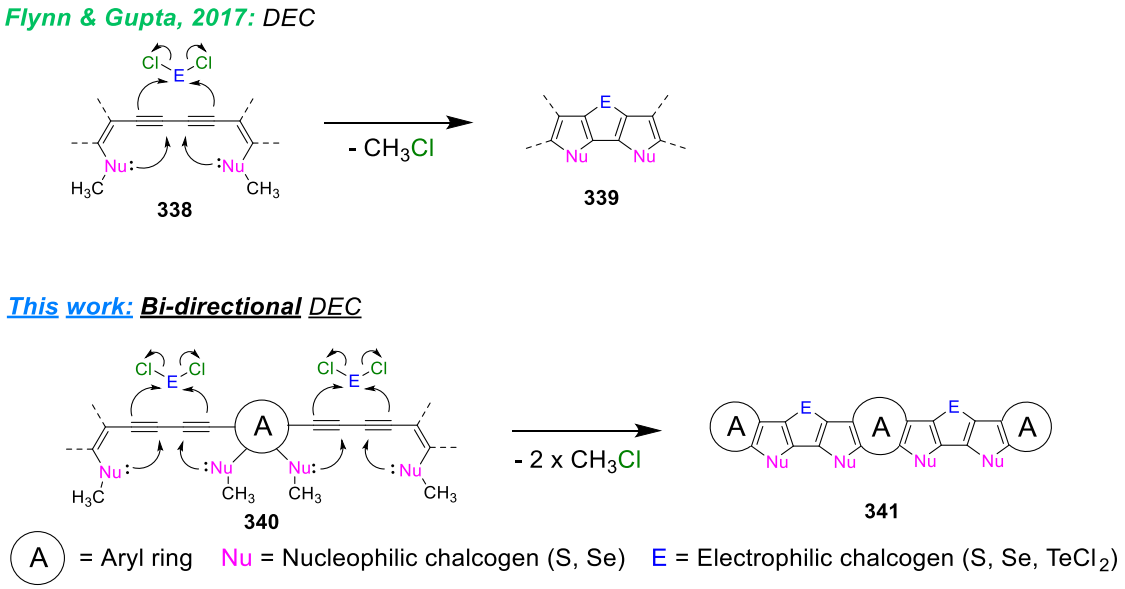
Although their utility is evident, large poly-fused heterocycles are not well afforded by current synthetic methodologies. The synthesis of small heteroacenes is well developed, however pathways that afford poly-fused systems are generally lengthy, inefficient, and not atom economical.[189] The commonly employed solution to this problem, is to utilise commercially available heterocycles and utilise transition metal-mediate coupling chemistry (Sonogashira, Negishi, Suzuki etc.) to afford a poly-fused systems, as shown in Scheme 1 (within Chapter 1.1).[190] Employment of this method of synthesis limits diversity and device performance. Synthetic innovation in the poly-fused heteroacene space is clearly required, with particular focus on the ability to afford larger poly-fused systems.

Chapter 2.0 presented a form of poly-electrophilic cyclisation (PEC) that produced chalcogenophenes featuring two-five fused aryl rings using an ambiphilic reagent (Scheme 62). Pleasingly, PEC was evidenced not only uni-directionally, but also bi-directionally. This increased the scope of the reaction and furnished larger, symmetrical products (such as **301**). These results prompted the question, what other cyclisation reactions could be applied bi-directionally to afford large poly-fused heteroacene products?



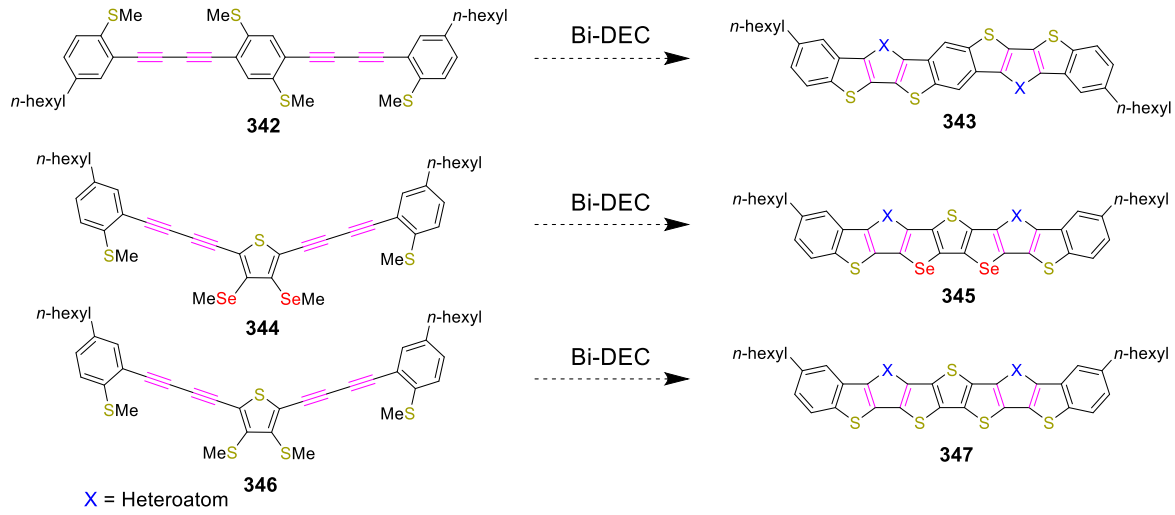
Scheme 62: Uni- and bi-directional poly-electrophilic cyclisation as shown in Chapter 2.0.

The work presented in Chapter 2.0 was originally inspired by cyclisations reported by Flynn and Gupta that furnished small heteroacenes through double-electrophilic cyclisation (DEC) as shown in Scheme 63.[9] The previously described work utilised a double electrophile (ECl_2, E = electrophilic chalcogen) to promote two instances of electrophilic cyclisation within a single atom economical step. However, aside from inspiring subsequent bodies of work (Chapter 2.0 of this Thesis), the reaction itself has not been further explored since the original communication. It was therefore the aim of this work that DEC be explored bi-directionally. If successful, this would afford large poly-fused heteroacenes potentially featuring up to nine fused aryl rings.



Scheme 63: Previously demonstrated DEC (top) and the proposed bi-directional application (bottom).

The proposed tetraynes **342**, **344** and **346** for application to the proposed bi-directional DEC (bi-DEC) reaction are shown in Scheme 64. These tetraynes were designed with the goal of demonstrating the ability of bi-DEC to afford diverse poly-fused heteroacene products. This variation of hetero elements utilised, their pattern of incorporation and ring fusion pattern (five or six membered rings) are all included within this Scheme. Of course, each polyyne will need to be efficiently afforded so as not to limit the potential applications of bi-DEC. Accordingly, polyyne optimisation studies were performed to ensure all avenues of synthesis are explored to achieve the best result for the study.



Scheme 64: Proposed polyynes for application to bi-directional double-electrophilic cyclisation.

3.2 Tetrayne synthesis

As described, tetraynes **342**, **344** and **346** were required in sufficient quantities to pursue the aims of this Chapter (Fig. 18). Affording these tetraynes efficiently was an important goal of the study so as not to limit the utility of subsequent cyclisation methodologies. There are clearly important variations incorporated in these materials, such as the aryl core ring including benzene and thiophene. This core variation will alter the 2D shape upon cyclisation and provide diversity in terms of heteroatom incorporation and ring fusion pattern. As previously described, variation of each of these structural features are important to materials scientist's ability to modify π-functionality, therefore if successful this new methodology will serve the field well. For the purposes of this tetrayne synthesis section **342** and **344** were selected as the two initial

targets of synthesis as it was assumed that chemistry developed to access **344** would translate well to **346**.

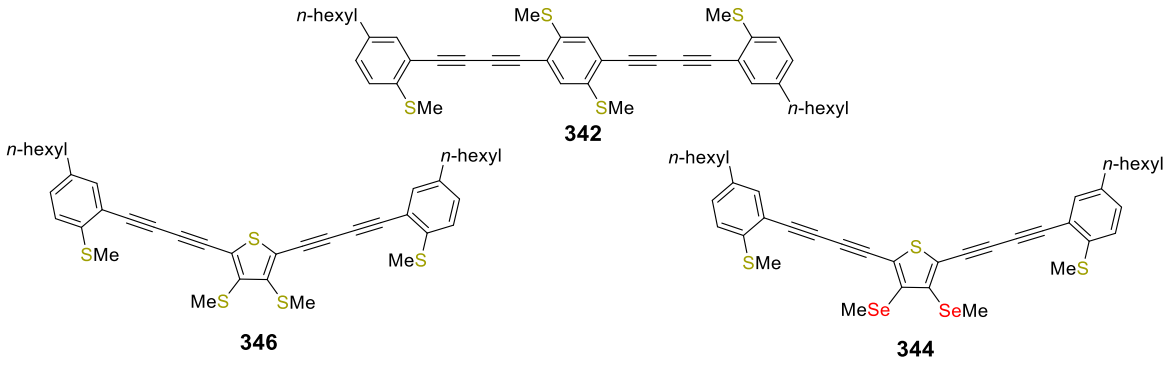
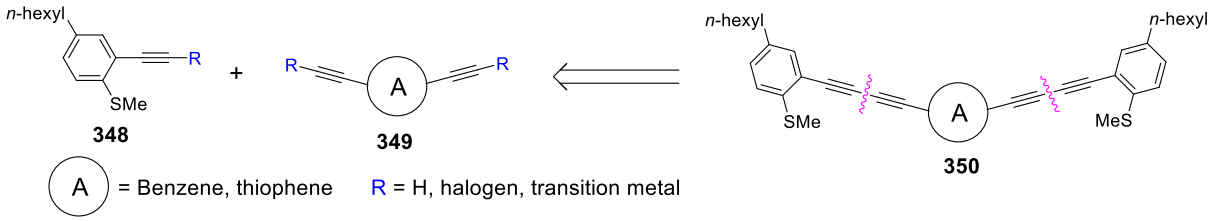


Figure 18: Polyynes to be afforded for bi-directional double electrophilic cyclisation.

3.2.1 Alkyne cross-coupling approach

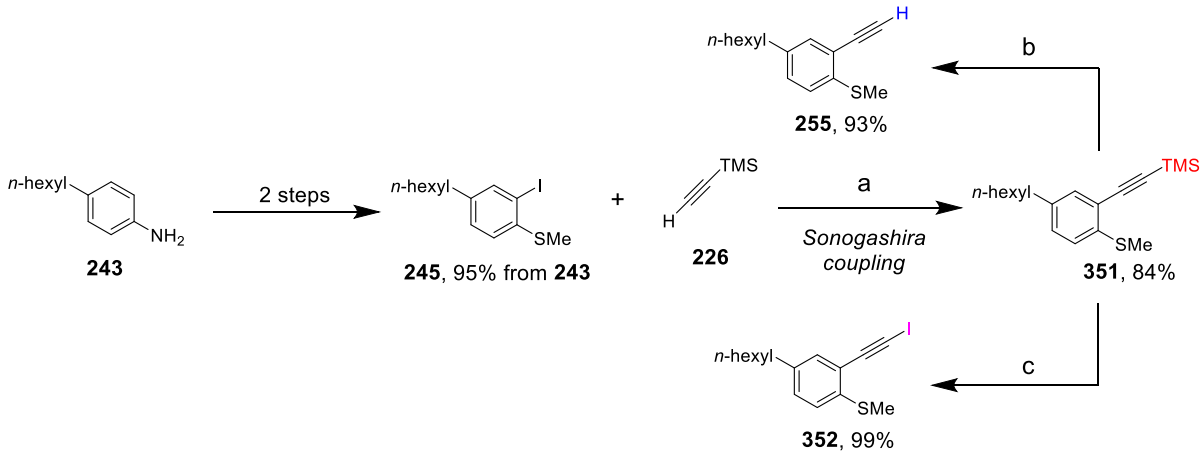
Due to the successful utilisation of alkyne cross coupling reactions (Cadiot-Chodkiewicz and Sonogashira) between acetylenes (≡C-H) and halogenated alkynes (≡C-I/Br) in Chapter 2.0, it was proposed that this technique be again employed to furnish tetrayne **350** (Scheme 65). This approach has the large advantage of avoiding handling unprotected diynes, as unprotected monoynes are notably more stable. Work was commenced to first afford alkyne **348** with varying functional groups (R = H or I), so that either could be utilised in cross-coupling reaction attempts.



*Scheme 65: Proposed retrosynthesis of general tetrayne **350** through alkyne cross coupling.*

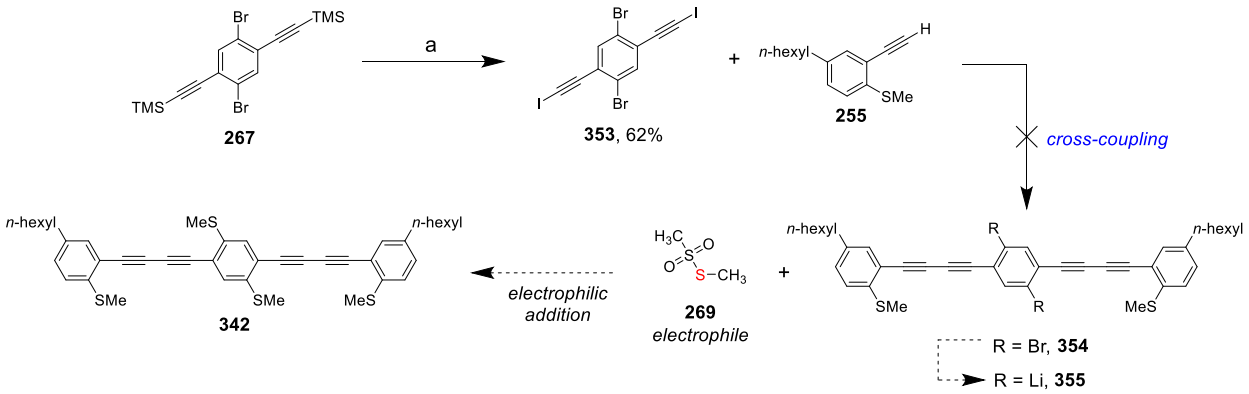
The successful synthesis of both acetylene **255** and iodo-alkyne **352** are shown in Scheme 66. Hexylated-iodothioanisole **245** has been previously produced within this Thesis (refer to Chapter 2.2). TMS alkyne **351** was smoothly afforded *via* Sonogashira coupling of hexylated-

iodothioanisole **245** with TMS acetylene **226**. Acetylene **255** was then furnished from silyl deprotection of TMS alkyne **351**, with product presence confirmed by the appearance of an alkyne CH singlet at 3.43 ppm in ^{1}H NMR. Halogenated alkyne **352** was accessed through a NIS mediated silyl for halogen exchange reaction, with product formation verified by the disappearance of the TMS singlet in ^{1}H NMR spectra. It was also found that the benzene ring of **352** is somewhat susceptible to iodination by NIS, however this was effectively controlled by using 0.98 eq. of NIS, maintaining the reaction temperature at 0 °C and limiting reaction time to one hour.



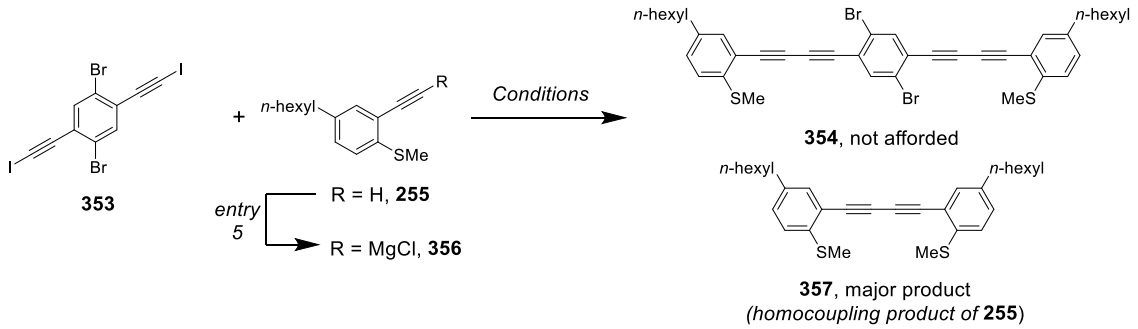
*Scheme 66: Synthesis of **255** and **352** for use in cross-coupling synthetic pathways. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, b) TBAF, THF, c) N-iodosuccinimide, KOH, MeOH.*

Following the successful synthesis of acetylene **255** and iodo-alkyne **352**, these alkynes could then be applied to the attempted synthesis of tetraynes **342** and **344**. Scheme 67 outlines an attempted synthesis of tetrayne **342**. In the pathway shown, di-TMS alkyne **267** (afforded previously from 1,2-diiodo-3,4-dibromobenzene)[191] was converted to di-iodo-alkyne **353** *via* a one-step silyl for halogen exchange reaction. NMR analysis was used to measure for product presence, noting the disappearance of the TMS singlet at 0.27 ppm in ^{1}H NMR spectra and the presence of a halogenated quaternary carbon resonance (C-I, 91.3 ppm) in ^{13}C NMR. Following the formation of di-iodo-alkyne **353**, attempts were made to cross-couple with acetylene **255**.



*Scheme 67: Attempted synthesis of tetrayne **342**. a) N-iodosuccinimide, KOH, MeOH.*

Scheme 68 details a summary of attempts made to cross couple di-iodo-alkyne **353** and acetylene **255**. Entries 1 and 2 employed Cadiot-Chodkiewicz conditions and entries 3 and 4, Sonogashira conditions. In each case, the only major products observed in ^{1}H NMR analysis were the unreacted starting materials (**353** and **255**) and homocoupled product **357**. Homocoupling of unprotected alkynes such as **255** can be mediated by the presence of copper salts (such as CuI or CuCl). Best efforts were made to limit homocoupling, however, the presence of unreacted starting materials despite heating the reaction indicates that cross-coupling was not occurring under these conditions, regardless of homocoupling. Entry 5 details the attempted utilisation of *i*-PrMgCl to facilitate cross-coupling, by first converting acetylene **255** to intermediate **356**. Unfortunately, the addition of **356** to di-iodoalkyne **353**, resulted in a complex ^{1}H NMR spectrum.

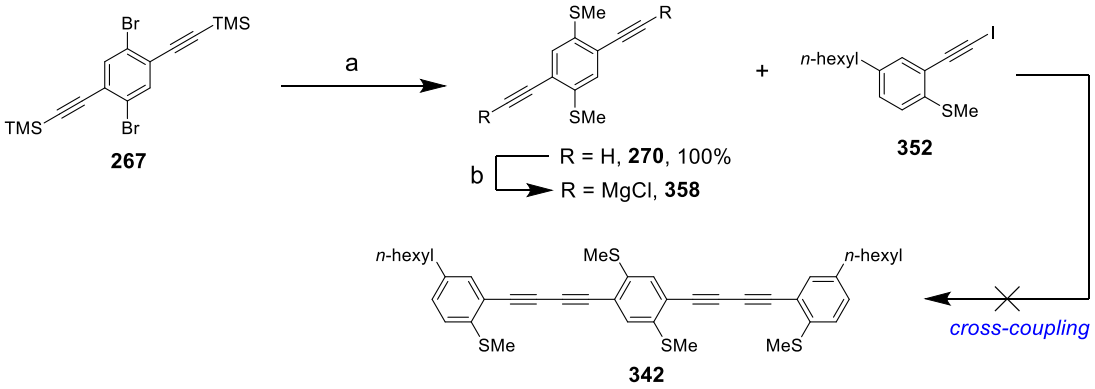


Entry	Reaction Conditions	Outcome
1	CuCl, *n*-butylamine, $HONH_2 \cdot HCl$, MeOH, 22 °C	Unreacted **353** + homocoupled product **357**
2	CuCl, *n*-butylamine, $HONH_2 \cdot HCl$, MeOH, 22 °C (acetylene added as Et_2O solution)	Unreacted **353** + homocoupled product **357**
3	CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF, 22 °C (slow addition of acetylene over 2 hours)	Unreacted **353** and **255** + some homocoupled product **357**
4	CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF, 65 °C (slow addition of acetylene over 2 hours)	Unreacted **353** and **255** + some homocoupled product **357**
5	*Iso*-propyl MgCl (2.2eq), dry THF, 0-22 °C	Complex ^{1}H NMR spectra

*Scheme 68: Iterations of attempted cross-coupling of **255** and **353** to afford **354**.*

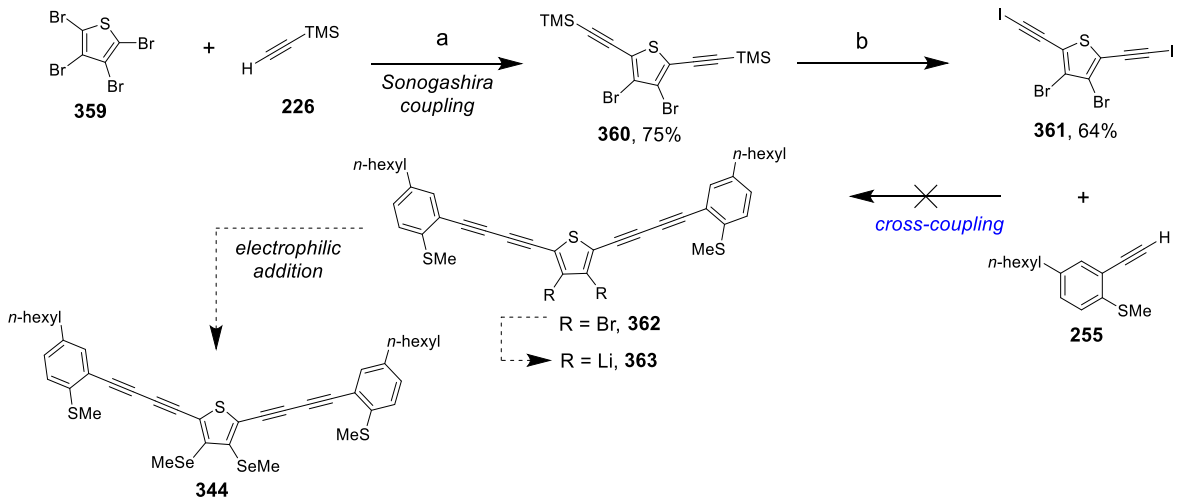
Scheme 69 outlines an alternative pathway to afford tetrayne **342** that employs attempted cross-coupling between di-acetylene **270** and iodo-alkyne **352**. Within this pathway, di-TMS alkyne **267** was first converted to di-acetylene **270** through addition of KF in MeOH. The di-acetylene was produced in quantitative yield. Subsequent coupling between di-acetylene **270** and iodo-alkyne **352** was first attempted *via i*-PrMgCl mediated coupling with intermediate **358**. Unfortunately, upon addition of intermediate **358** to a solution of iodo-alkyne **352** there was negligible presence of resonances that could be attributed to tetrayne **342** in ^{1}H NMR analysis. There was also the presence of a black insoluble material in the reaction mixture. It was proposed that this material could be the polymerised-homocoupled product of **270** or **358**. This

could not be confirmed due to very low solubility in NMR solvents. The coupling of di-acetylene **270** and iodo-alkyne **352** was then attempted under Sonogashira conditions, however only unreacted **352** was observed in NMR analysis. The reaction mixture again contained an insoluble material that was proposed to be the polymerised product of acetylene **270**.



*Scheme 69: Attempted synthesis of tetrayne **342**. a) KF, MeOH, Et_2O, b) i-PrMgCl, dry THF.*

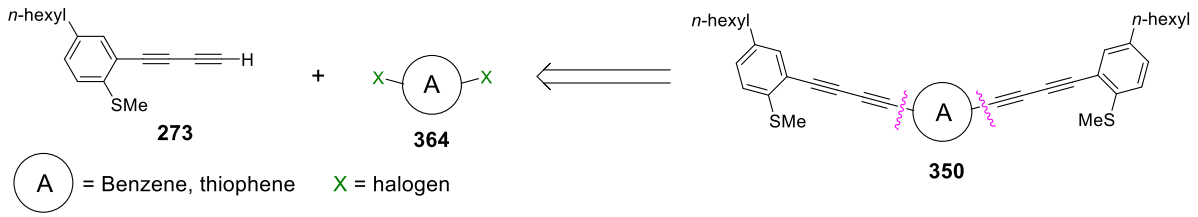
Concurrently, exploration of the cross-coupling method to afford tetrayne **344** was performed, to ensure a thorough investigation of the method (Scheme 70). The pathway commenced with the double coupling of TMS acetylene **226** with tetrabrominated thiophene **359** to afford thiophene **360**. The presence of dibrominated thiophene **360** was measured by ^{13}C NMR analysis with all quaternary resonances successfully assigned to the symmetrical product. This material was then subject to silyl for halogen exchange conditions to afford di-iodoalkyne thiophene **361** in 64% yield. Product formation was again confirmed *via* ^{13}C NMR analysis as no protons were present in the material. Following this, cross-coupling between di-iodoalkyne thiophene **361** and acetylene **255** was attempted. Unfortunately, with each attempt, negligible presence of tetrayne product **362** was observed in NMR spectra. The unsuccessful furnishing of polyynes **342** and **344** through the cross-coupling synthetic routes described prompted the investigation of alternative approaches to these tetraynes



*Scheme 70: Attempted synthesis of tetrayne **344**. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF, b) N-iodosuccinimide, KOH, MeOH.*

3.2.2 Sonogashira diyne coupling approach to polyynes

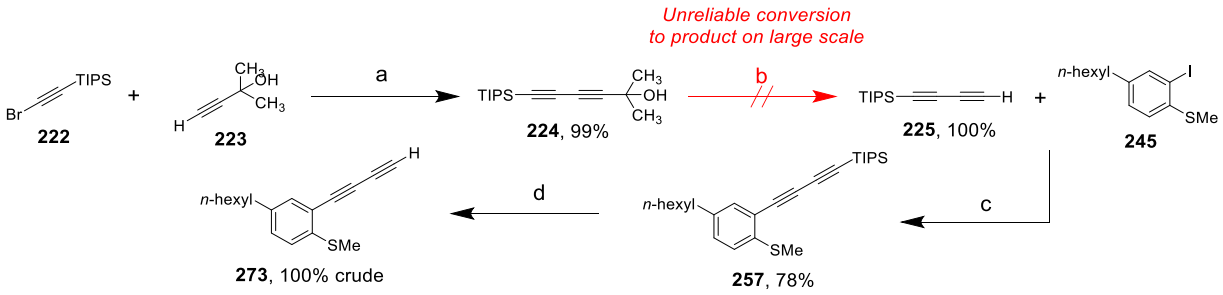
Following the unsuccessful utilisation of alkyne cross-coupling to afford the relevant tetraynes, an alternative approach was required for investigation. Scheme 71 shows a general approach to general tetrayne **350** that would employ Sonogashira coupling conditions to couple unprotected diyne **273** to the halogenated aromatic ring **364**. Unprotected diyne **273** has been previously accessed (within Chapter 2.3), thus, exploring this approach to tetrayne **350** will be suitably efficient.



*Scheme 71: Modified retrosynthetic approach to tetrayne **350**.*

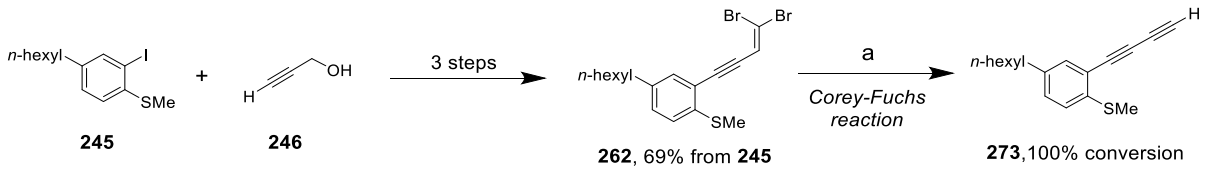
Diyne **273** was previously afforded on small scale, however this retrosynthetic approach to **350** would require the synthesis of **273** to a large scale. Accordingly, there will be some optimisation efforts to ensure the pathway to afford unprotected diyne **273** can tolerate large scale synthesis. Scheme 72 shows the synthetic route that was employed previously to afford diyne **273**. Unfortunately, the deprotection reaction between TIPS/alcohol capped diyne **224**

and acetylene diyne **225** was found to be capricious due to the employed base, *t*-BuOK. Conversion to product **225** was heavily dependent on the source of *t*-BuOK, resulting in varied degrees of product conversion from 0 to 100%. This outcome was proposed to be a function of the hygroscopic nature of *t*-BuOK whereby even if best efforts are made to avoid H_2O contamination, the material can display decreased reactivity.



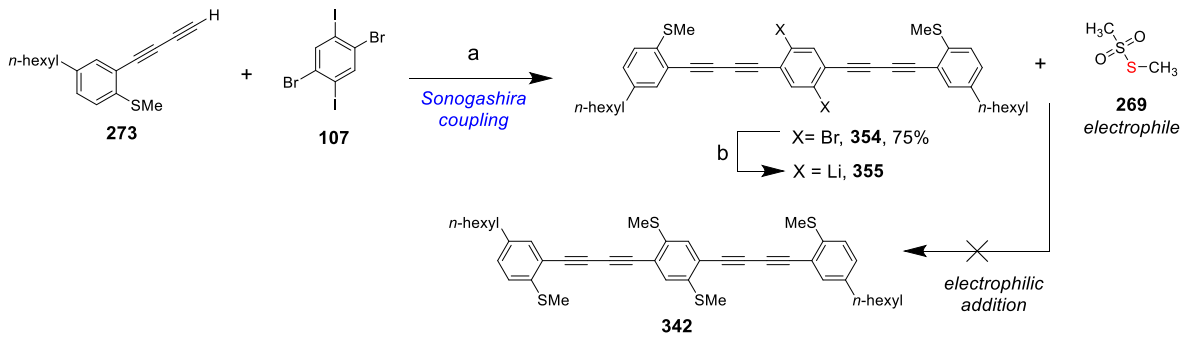
*Scheme 72: Previously utilised synthetic pathway to afford unprotected diyne **273**. a) CuCl, $HONH_2{\cdot}HCl$, n-butylamine, MeOH, b) t-BuOK, toluene, c) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF, d) TBAF, acetic acid, THF.*

Due to the unsatisfactory scale-up of the pathway shown in Scheme 72, an alternative approach to unprotected diyne **273** was proposed (Scheme 73). This synthesis utilises previously produced geminal dibromide **262** (refer to Chapter 2.2) to afford unprotected diyne **273** *via* a Corey-Fuchs reaction. Geminal dibromide **262** was afforded from hexylated-iodothioanisole **245** through Sonogashira coupling of propargyl alcohol **246** and subsequent oxidation and geminal-dibromide conversion. Pleasingly, following the addition of *n*-BuLi to a solution of geminal dibromide **262**, the Corey-Fuchs reaction produced 100% conversion to product **273**. Unprotected diyne **273** presented some low-level instability thereby requiring the material to be stored and used as a crude solution. Thus the isolated yield was not determined. Fortunately, conversion to diyne **273** from geminal di-bromide **262** reliably presented 100% conversion to product with minimal presence of contamination materials in ^{1}H NMR. Therefore, purification was not required, and the material was suitably stable in solution when stored at 4 °C for approximately one month. Accordingly, Scheme 73 presents an efficient and reliable pathway to diyne **273** that can be performed on a multi-gram scale.



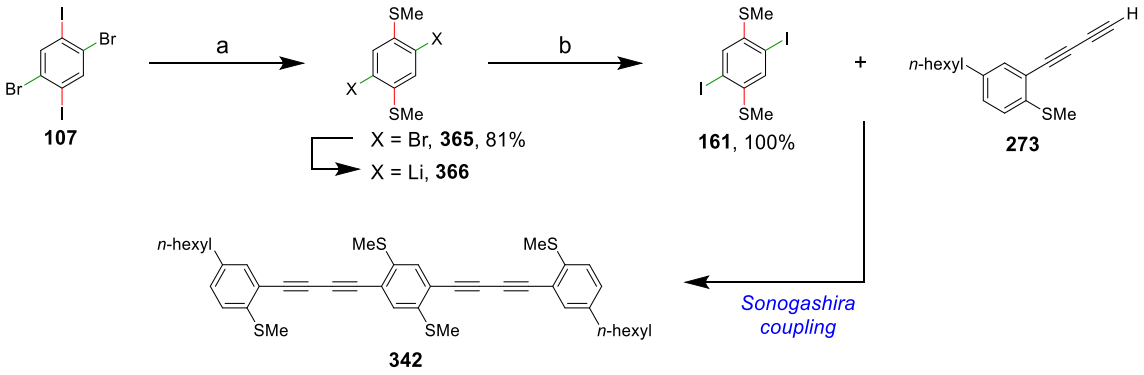
*Scheme 73: Synthesis of diyne **273** from geminal dibromide **262**. a) n-BuLi, dry THF.*

Following the successful large-scale synthesis of unprotected diyne **273**, attempts to utilise this material to afford tetraynes **342**, **344** and **346** commenced. Scheme 74 outlines the attempted synthesis of tetrayne **342** from diyne **273** and tetra-halogenated benzene **107**. The initial Sonogashira coupling between diyne **273** and **107** performed smoothly, affording di-brominated tetrayne **354** in 75% yield. Product presence was confirmed by ^{1}H NMR analysis showing the shift of the **107** assigned aryl CH singlet from 8.05 ppm to 7.75 ppm and loss of the acetylene CH singlet of diyne **273** at 2.59 ppm. Conversion from di-brominated tetrayne **354** to desired tetrayne **342** was then attempted *via* addition of *n*-BuLi to afford intermediate **355**, followed by the addition of electrophile **269**. Unfortunately, despite multiple attempts, the resulting ^{1}H NMR spectra was complex and only contained negligible presence of desired product **342**. ^{1}H NMR analysis verified that conversion from di-brominated tetrayne **354** to intermediate **355** occurred, however the addition of electrophile **269** consistently resulted in a complex ^{1}H NMR spectrum. This was attributed to the low stability of lithiated intermediate **355**, such that allowing the reaction to warm to 0-22 °C for electrophilic addition to occur led to decomposition. Electrophilic addition at sub-zero temperatures proved to be unsuccessful in our attempts, thus, an alternative approach to tetrayne **342** was required.



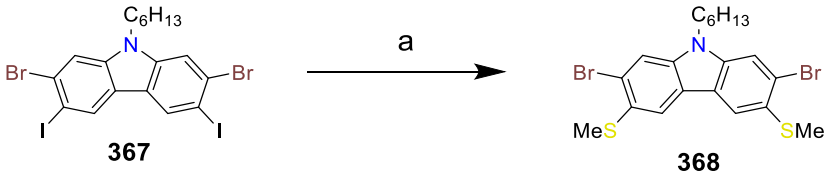
*Scheme 74: Attempted synthesis of tetrayne **342**. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF, b) n-BuLi, dry THF.*

Scheme 75 outlines, a synthetic route to tetrayne **342** that first converts tetra-halogenated benzene **107** to di-sulfide benzene **365**, which was then iodinated to form **161**, before Sonogashira coupling is attempted with diyne **273**. Addition of SMe groups to the iodo-positions of benzene **107** was first attempted through Li-mediated electrophilic addition similar to that attempted in Scheme 74 (**354** → **342**). However, tetra-halogenated benzene **107** and di-brominated benzene **365** are only sparingly soluble in DCM at 22 °C and the lithiation reaction must be performed below 0 °C to avoid decomposition of lithiated intermediates. Therefore, efficient conversion to **365** would be difficult through this method. Previous literature was surveyed for alternative reaction conditions to afford **365** from tetra-halogenated benzene **107**. As the starting material **107** possess both iodo- and bromo- groups, it is important that reaction procedure employed displays halogen selectivity so that only the iodo-groups are converted to SMe groups.



*Scheme 75: Successful synthesis of tetrayne **342**. a) S_2Me_2, Cu, K_2CO_3, $Pd(PPh_3)_4$, DMF, b) n-BuLi, 1,2-diiodoethane, dry Et_2O.*

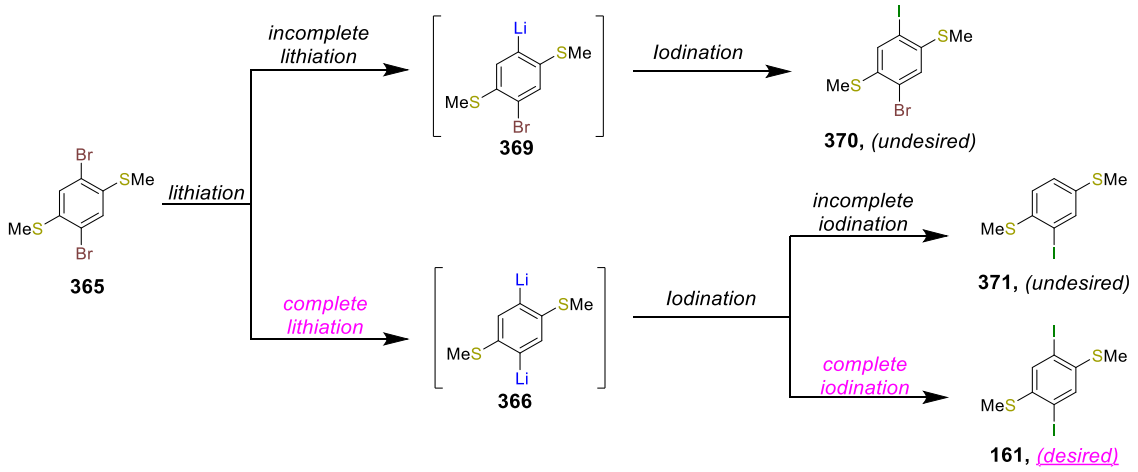
Work reported by Masuya and co-workers showed the effective conversion of two iodo-groups to the corresponding methyl sulfanes with unaffected bromo groups present in the ortho position (Scheme 76).[192] Conditions reported described the addition of copper, K_2CO_3 and dimethyl disulfide to a DMSO solution of **367**. The reaction mixture was then heated to 110 °C for 24 h to successfully afford **368**. Due to the tetra-halogenated benzene **107** bearing important similarities to **367** and a high reaction temperature being utilised, which will increase solubilisation, this procedure was employed for the conversion of **107** to **365**.



*Scheme 76: Reaction reported by Masuya and co-workers that exemplifies the conversion of the iodo groups in **367** to the 'SMe' groups of **368**. a) S_2Me_2 (2eq.), Cu (2eq.), K_2CO_3 (2eq.), DMSO, 110 °C, 24 h.*[192]

Initial attempts to furnish di-bromide-di-sulfide benzene **365** from **107** through employment of Masuya conditions, resulted in low conversion to product **365**. ^{1}H NMR analysis showed the presence of singlets at 7.26 ppm (CH) and 2.47 ppm (CH_3) that were assigned to **365**. Several attempts were made to improve the yield by increasing the equivalence of reagents to promote conversion to product **365**, however, this resulted in negligible improvements. It was then proposed that $Pd(PPh_3)_4$ be added to the reaction mixture to better facilitate the coupling of dimethyl disulfide (S_2Me_2). The addition of the Pd catalyst significantly increased conversion to **365** from **107**. $Pd(PPh_3)_4$ was then added in 1.1 eq. in conjunction with the portion-wise addition of 20 eq. of dimethyl disulfide to afford **365** in 81% yield (Scheme 75).

Conversion from tetra-halogenated benzene **107** to di-brominated benzene **365** improved solubility significantly and so lithiation reactions with **365** were not predicted to have the same solubility and/or stability issues as were described for **107**. Accordingly, attempts were made to first convert di-brominated benzene **365** to lithiated intermediate **366**, followed by the addition of an iodo-source (I_2, NIS, 1,2-diiodoethane) allowing conversion to di-iodo-di-sulfide benzene **161**. There are two stages within this reaction: lithiation and iodination. As there are two positions at which these stages will occur, there are multiple by-products that may be observed in ^{1}H NMR. Scheme 77 displays the intermediates and products that can result from the attempted conversion from starting material **365** to the final desired product **161**. Within these attempts, care was taken to identify reaction products and intermediates that were present in reaction mixture. This allowed us to ascertain which reaction stage, if any, were not performing to completion.



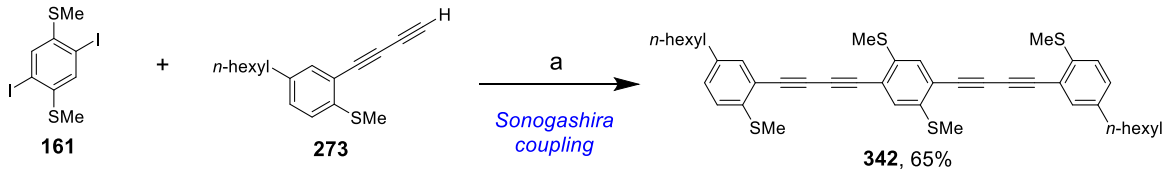
*Scheme 77: Conversion from **365** to products **370** (undesired), **371** (undesired) or **161** (desired) through the lithiated intermediates shown.*

The first attempt to convert di-brominated benzene **365** to di-iodo-di-sulfide benzene **161** utilised *n*-BuLi (2.2 eq.) in dry THF, allowing conversion from **365** to double-lithiated intermediate **366** to take place over 20 mins at -78 °C. Iodinating agent 1,2-diidoethane was then added in 2.2 eq. and the reaction was allowed to warm to 22 °C to encourage electrophilic addition. Resultant ^{1}H NMR spectra showed starting material **365** and multiple reaction products of which included the desired **161**. An aryl CH singlet at 7.44 ppm was assigned to **161**, however conversion to the desired product was <25%, thus optimisation was required.

The first modification to the reaction conditions was to change the solvent from THF to Et_2O to ensure that the reaction was not limited by solubility. Equivalence of 1,2-diiodoethane and *n*-BuLi were also increased slightly and the temperature of lithiation was increased to 0 °C to ensure consumption of starting material **365**. Gratifyingly, NMR spectra of the reaction with the modified conditions indicated no presence of the singlet associated with starting material **365** (7.26 ppm) and the increased presence of the singlet assigned to desired product **161** (7.44 ppm). Double-lithiated intermediate **366** was also observed in NMR analysis (CH singlet at 7.19 ppm)[193], indicating iodination was not performing to completion. Accordingly, equivalence of 1,2-diiodoethane was increased significantly which led to the complete conversion to **161** in quantitative yield.

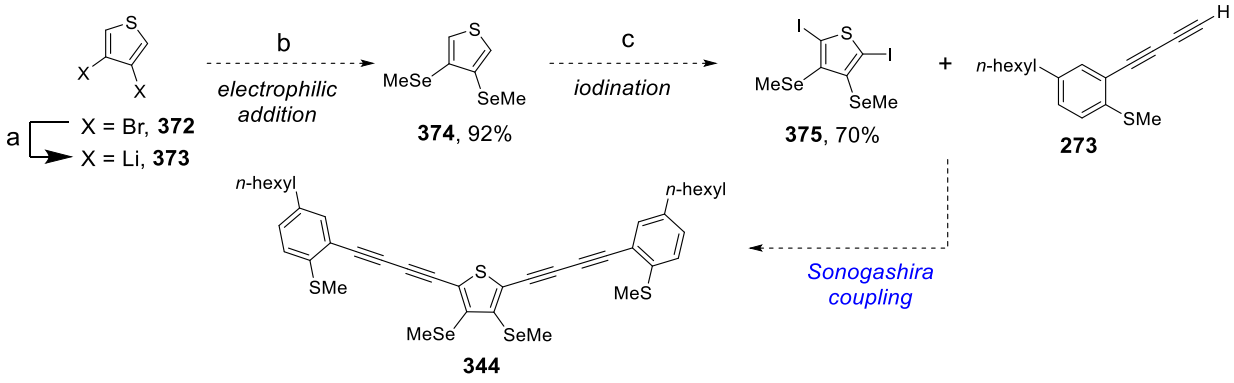
Following the successful furnishing of tetra-substituted benzene **161**, coupling with diyne **273** was attempted (Scheme 78). The reaction was performed under Sonogashira coupling conditions with the reaction heated to 60 °C to aid with solubility and reaction progress. Pleasingly the reaction performed very well, furnishing tetrayne **342** in good yield of 65%. Due

to the low solubility of tetrayne **342** in Et_2O, filtering the reaction mixture over Celite® and washing with Et_2O, separated **342** from all other organic material. Therefore. after subsequent washing with H_2O, pure **342** was furnished.

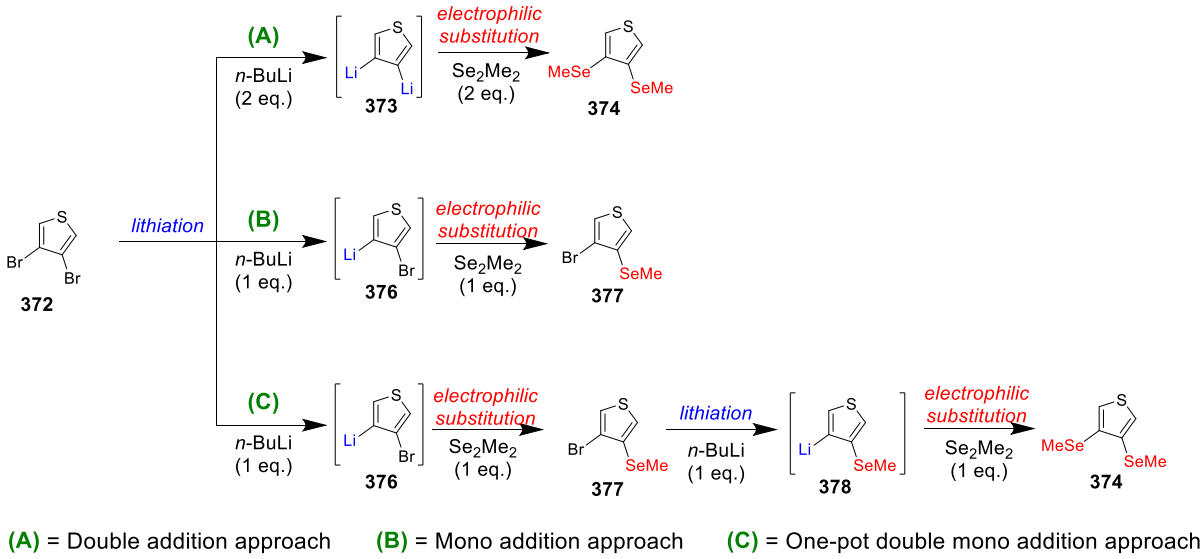


*Scheme 78: Sonogashira coupling of diyne **273** and disulfide aryl **161** to afford tetrayne **342**. a) CuI, $Pd(PPh_3)_4$, DIPA.*

The successful approach to furnish **342** was subsequently applied to the thiophene tetrayne scaffold **344** after some considerable development (Scheme 79). In the first reaction in this pathway, we attempted to lithiate 3,4-dibromothiophene **372** to afford intermediate **373**, which was followed by electrophilic addition of dimethyl diselenide to afford di-substituted thiophene **374**. This reaction can be performed through the three different approaches as shown in Scheme 80.



*Scheme 79: Successful synthesis of tetrayne **344**. a) n-BuLi, dry Et_2O, b) Se_2Me_2, dry Et_2O, c) n-BuLi, DIPA, 1,2-diiodoethane, dry Et_2O, d) CuI, $Pd(PPh_3)_4$, DIPA.*



*Scheme 80: General synthetic approaches applied to afford disubstituted thiophene **374** from **372**.*

Double addition (A) is an attractive approach, although achieving complete lithiation and electrophilic addition can be difficult. Mono addition (B) is a more conservative approach that seeks to react with only one bromo group at a time. After unsymmetrical thiophene **377** is furnished, this material is isolated and again subjected to the same reaction conditions to convert the remaining bromo-group. Although more likely to succeed than (A), approach (B) requires two isolation and purification steps, which is undesirable. Approach (C) affords thiophene **377** in a similar fashion to approach (B) however, within (C), thiophene **377** is not isolated but instead immediately re-cooled and re-subjected to lithiation and electrophilic addition conditions. This approach requires multiple reaction stages, but can result in good conversion to the desired product. Each approach was explored in a contemporaneous study that sought to determine the best method. With each attempt, ^{1}H NMR analysis was utilised to identify the reaction outcome.

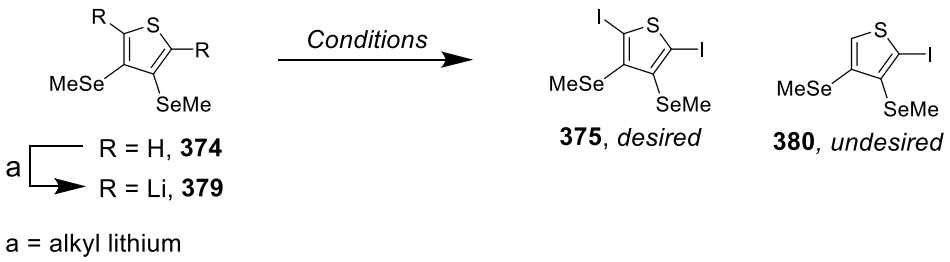
Employment of approach (A) to afford desired product **374** resulted in the complete consumption of starting material **372** (2 × CH singlet at 7.29 ppm), the presence of desired thiophene **374** as the minor product (CH singlet at 7.15 ppm) and mono-addition thiophene **377** as the major product (doublets at 7.32 and 7.08 ppm with 3.3 Hz *J* coupling). The presence of mono addition product **377** indicating the lithiation step did not go to completion.

Approach (B) resulted in the presence of desired product **377** and mono-lithiated intermediate **376** (associated singlets occur at 7.31 ppm, 7.41 ppm). The lack of starting material **372** from approach (B) indicates lithiation went to completion. However, subsequent electrophilic

addition proved to be unsuccessful as the lithiated intermediate **376** remained present in the reaction mixture.

Pleasingly approach (C) exclusively produced double-addition product **374** with no intermediates present in ^{1}H NMR analysis. Accordingly, the one-pot double mono addition approach (C) was employed to furnish **374** on large scale, affording the 3,4-substituted thiophene in 92% yield.

Following the successful synthesis of di-substituted thiophene **374**, double iodination attempts to afford **375** were then explored (Scheme 81). Scheme 81 details all attempts made to evidence double iodination of 3,4-substituted thiophene **374**. The desired product **375** has no aromatic protons to be observed in ^{1}H NMR spectra so product presence was measured by the presence of a CH_3 singlet that has no associated aryl resonances as this differentiates the double-iodinated thiophene **375** from mono-iodinated thiophene **380** and starting material **374**.



Entry	Reaction Conditions	Outcome
1	NIS (2.2 eq.), *p*-triflouroacetic acid (0.1 eq.), EtOH, 3 h, 22 °C	No reaction
2	NIS (2.2 eq.), acetic acid (0.1 M), THF, 18 h, reflux, dark	Starting material **374** + desired product **375** + complex spectrum/degradation
3	NIS (2.2 eq.), acetic acid (0.1M), THF (0.1M), 5 h, reflux, dark	Starting material **374** + undesired product **380**
4	NIS (10 eq.), acetic acid (0.1M), THF (0.1M), 2 h, reflux, dark	Complex spectrum

5	Iodine (2 eq.), $AgSO_3CF_3$ (2 eq.), DCM, 18 h, 0-22 °C	No reaction
6	*n*-BuLi (2.2eq.), dry THF, iodine (2.2 eq.), 18h, 0-22 °C	Complex spectrum
7	Lithium diisopropylamide (2.2 eq.), iodine (2.2 eq.), dry Et_2O, 18 h, 0-22 °C	Major products: **374** + **380** (exact ratio, 2:1:3, **374**:**375**:**380**)
8	Lithium diisopropylamide (3.2 eq.), iodine (3.2 eq.), dry Et_2O, 18 h, 0-22 °C	Major product: **375** (exact ratio, 1:7:1, **374**:**375**:**380**)
9	Lithium diisopropylamide (5 eq.), iodine (8 eq.), dry Et_2O, 18 h, 0-22 °C	Major product: **375** (exact ratio, 1:7:1, **374**:**375**:**380**)
10	Lithium diisopropylamide (3.2 eq.), NIS (4 eq.), dry Et_2O, 18 h, 0-22 °C	Major product: **374** (exact ratio, 3:1:1, **374**:**375**:**380**)
11	Lithium diisopropylamide (3.2 eq.), 1,2-diiodoethane (4 eq.), dry Et_2O, 1 h, 0-22 °C	>85% conversion to desired product **375**
12	Lithium diisopropylamide (3.2 eq.), 1,2-diiodoethane (6 eq.), dry Et_2O, 1 h, 0-22 °C	>95% conversion to desired product **375**

*Scheme 81: Iterations of double iodination of thiophene **374** to furnish **375**.*

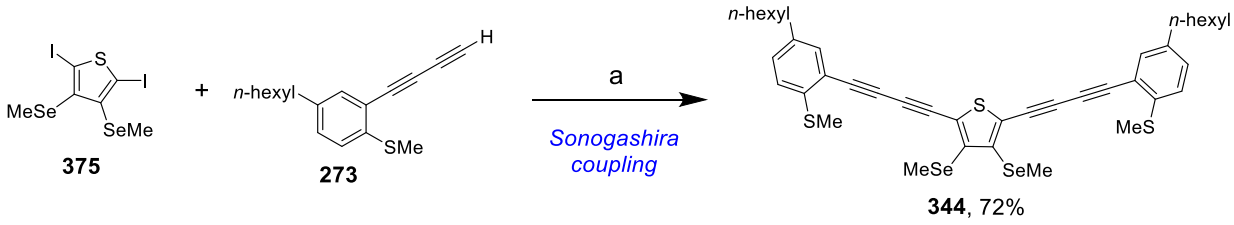
Entries 1-5 explored acid-promoted iodination reaction to afford double-iodinated thiophene **375**. These iterations demonstrated the temperature sensitivity of the reaction, when conducted at 22 °C, this prompted no conversion, but heating for more than 5 h at 60 °C resulted in a complex ^{1}H NMR spectrum. When the iodination was attempted within 5 h at 60 °C, mono-iodinated **380** was the only product observed. Increase in NIS equivalence also led to a complex ^{1}H NMR spectrum.

The remaining entries (entries 6-12) describe the conversion of starting material **374** to lithiated intermediate **379** before addition of an electrophilic iodide source. Initially *n*-BuLi was employed to afford intermediate **379** in dry THF. However, when iodine was added to this

reaction mixture, a complex NMR spectrum resulted. Following this, LDA was utilised to convert starting material **374** to intermediate **379** before iodo-addition. The stronger base significantly improved reaction outcome as NMR spectra was free of degradation products and contained only starting material **374**, desired product **375** and undesired product **380**. To increase conversion to double-iodinated thiophene **375**, the equivalence of LDA and iodine was increased (entries 8 and 9). This led to formation of **375** as the major product of reaction, however, starting material **374** and mono-iodinated thiophene **380** were still present as minor products.

It was then proposed that screening of different iodine sources should be conducted for improvement in reaction outcome. Entries 9, 10 and 11 were performed concurrently, to compare the employment of iodine, NIS and 1,2-diiodoethane. Fortunately, 1,2-diiodoethane outperformed NIS and iodine, conferring >85% conversion to desired product double-iodinated thiophene **375**. Increasing the equivalence of 1,2-diiodoethane further (from 4 eq. to 6 eq.) was the final reaction optimisation required, furnishing the desired product **375** in 70% yield after purification.

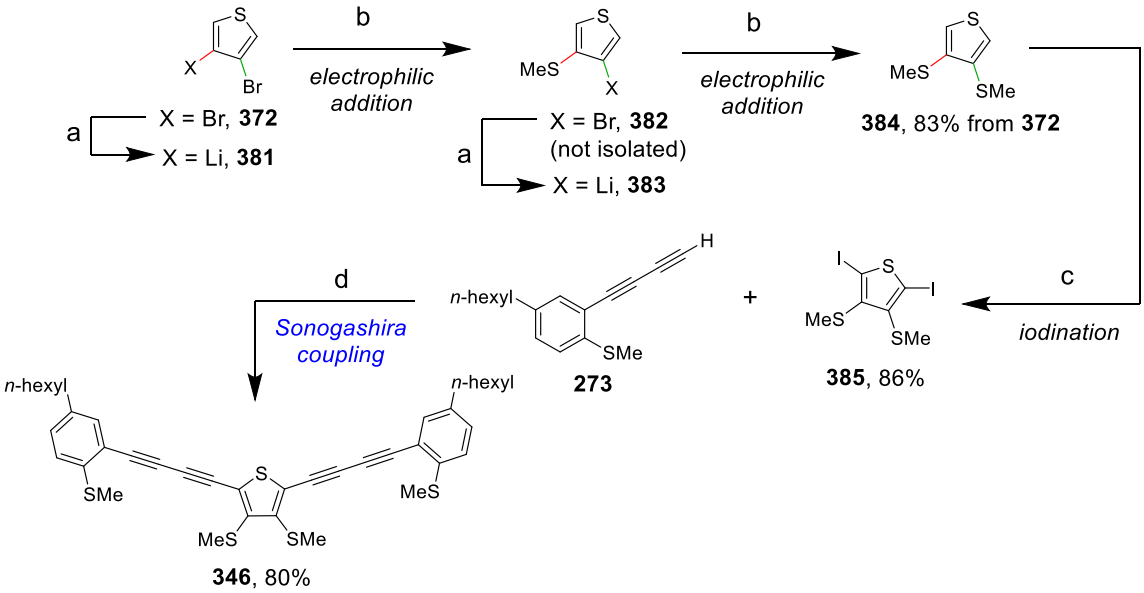
Finally, Sonogashira coupling between thiophene **375** and diyne **273** was attempted (Scheme 82). Coupling was performed at 60 °C, adding diyne acetylene **273** in two portions of 2 eq. each. Pleasingly, tetrayne **344** was afforded in good yield of 72%.



*Scheme 82: Sonogashira coupling of diyne **273** and tetra-substituted thiophene **375** to afford tetrayne **344**. a) CuI, Pd(PPh$_3$)$_4$, DIPA.*

The application of the 'Sonogashira diyne coupling' approach to the synthesis of tetrayne **346** is shown in Scheme 83. Tetrayne **346** was synthetically accessed by a colleague within the Flynn lab (Dorothy Ko) as a part of her Honours degree under the co-supervision of the author this thesis. Commercially available 3,4-dibromo thiophene **372** was converted to mono-addition product **382** through mono-lithiated intermediate **381**. This electrophilic addition was

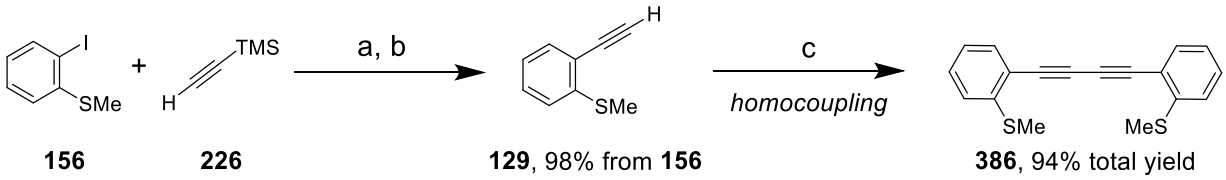
repeated to afford 3,4-disubstituted thiophene **384**. Subsequent double iodination utilised *p*-toluenesulfonic acid and NIS in EtOH to furnish the desired tetra-substituted thiophene **385** in 86% yield. The following Sonogashira coupling of thiophene **385** and diyne **273** performed smoothly, affording tetrayne **346** in high yield (80%).



*Scheme 83: Successful synthesis of tetrayne **346**. a) LDA, Et_2O, b) S_2Me_2, Et_2O c) NIS, p-toluenesulfonic acid, EtOH, d) CuI, $Pd(PPh_3)_4$, DIPA.*

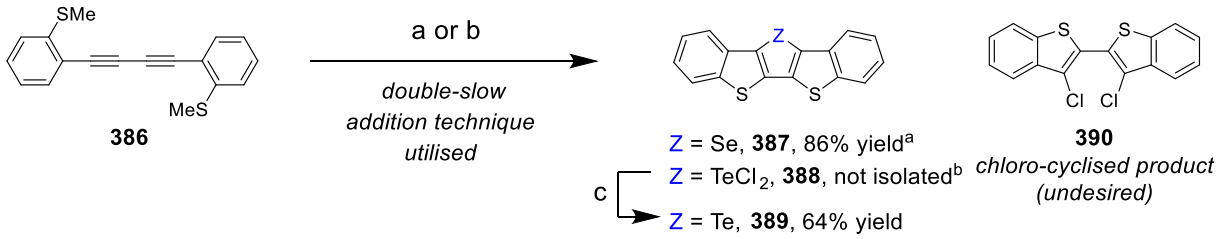
3.3 Bi-directional double-electrophilic cyclisation

Following the efficient furnishing of the tetraynes required (**342**, **344** and **346**), cyclisation attempts commenced. As this study is an extension of previous work from Flynn and Gupta, it was proposed that all cyclisation conditions applied to the bi-directional tetraynes are first trialled on simple diyne **386**. Accordingly, diyne **386** was furnished according to procedures described by Flynn and Gupta as depicted in Scheme 84.



*Scheme 84: Diyne **386** afforded according to previously described methods. a) CuI, $Pd(PPh_3)_2Cl_2$, Et_3N, b) KF, Et_2O, MeOH, c) $Cu(OAc)_2 \cdot H_2O$, MeOH, pyridine.*

Scheme 85 shows the successful DEC of simple diyne **386** to afford Se cyclised **387** and Te cyclised **389** (after reductive work-up from **388**). The conditions employed were identical to those described in the DEC manuscript and gave consistent characterisation data and comparable yield.



*Scheme 85: Demonstration of previously reported DEC of **386** to afford **387** and **389**. a) $SeCl_2$ (1 eq.), DCE 80 °C, b) $TeCl_4$ (1 eq.), DCE 80 °C, c) $Na_2S_2O_3$ work-up.*

Within previous DEC studies, varied techniques of addition were explored: double-slow addition, single-slow addition of the electrophile and single-slow addition of the alkyne (Fig. 19). The double-slow addition technique proved most successful as it allowed the alkyne and electrophile to be always equally present in the reaction mixture, reducing the chances for polymerisation of starting materials. Accordingly, this technique was employed to furnish Se cyclised **387** and Te cyclised **388** and **389**. Within bi-DEC studies, it was important to keep these addition techniques in mind so that the optimal cyclisation procedure is reported.

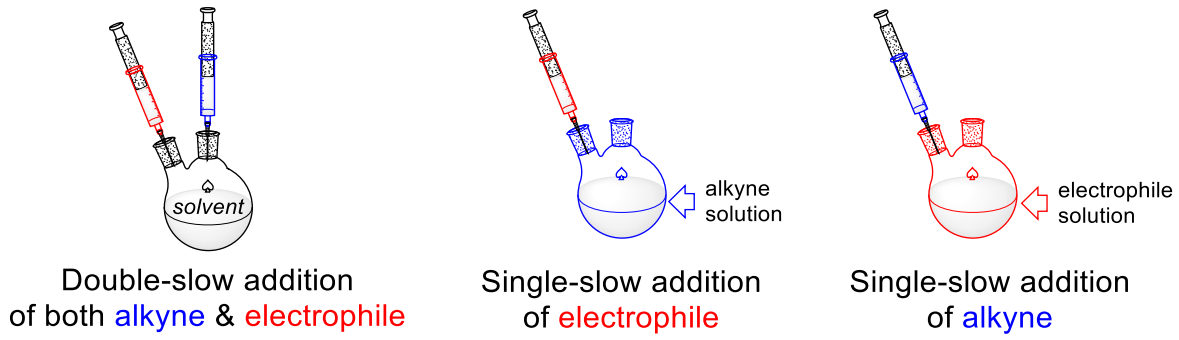
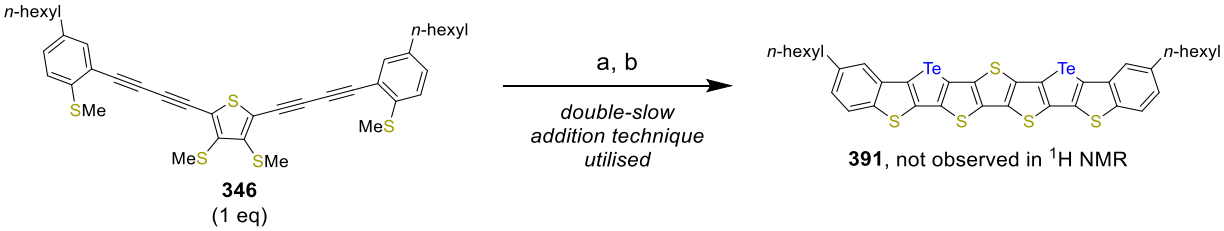


Figure 19: Graphical representation of DEC reaction techniques: double slow addition and single slow addition of either the electrophile or the alkyne starting material.

$SeCl_2$ that was employed to furnish **387** is not commercially available and so is afforded by the chlorination of selenium powder ($Se_2 + 2SO_2Cl_2 \rightarrow 2\mathbf{SeCl_2} + 2SO_2$). However, if not performed carefully, excess chlorinating agent (SO_2Cl_2) can be present in the $SeCl_2$ solution that is added to diyne **386**. This SO_2Cl_2 presence will result in the presence of chloro-cyclised product **390** (Scheme 85). The commercially available reagent $SeCl_4$ was explored as a substitute of $SeCl_2$, however its employment gave chloro-cyclised **390** as the major product. Therefore, although effective in the formation of **387**, commercially available $TeCl_4$ is a more suitable reagent than $SeCl_2$ to be employed in bi-DEC studies.

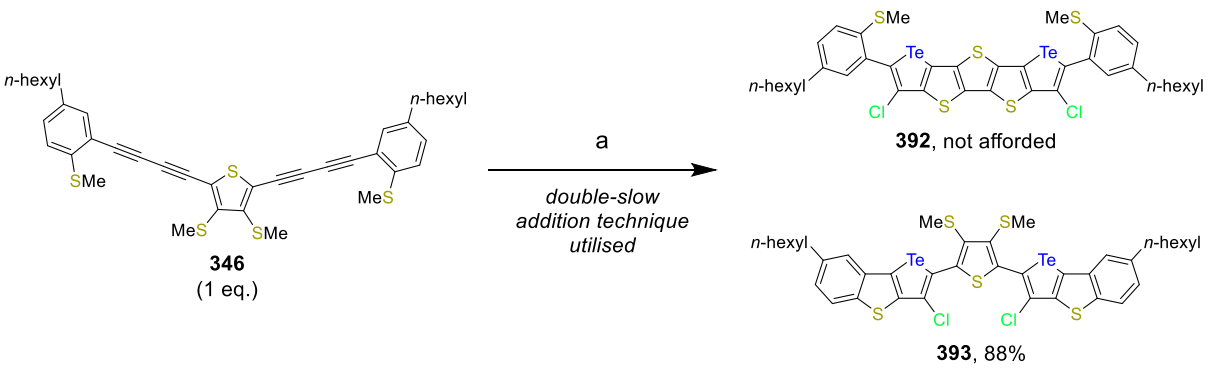
3.3.1 Bi-directional DEC with tellurium

Tetrayne **346** was selected to commence bi-DEC studies, with $TeCl_4$ employed as the double electrophile (Scheme 86). The initial attempt also utilised the double-slow addition technique due to its success with the simple diyne **386** to afford Te cyclised **389**. Upon reaction of tetrayne **346** and $TeCl_4$, NMR analysis indicated the lack of any resonances associated with starting material **346** and the presence of one product.



*Scheme 86: Attempted bi-DEC of tetrayne **346** to afford **391**. a) $TeCl_4$ (2eq.), DCE:dioxane, 80 °C, b) $Na_2S_2O_3$ reductive work-up.*

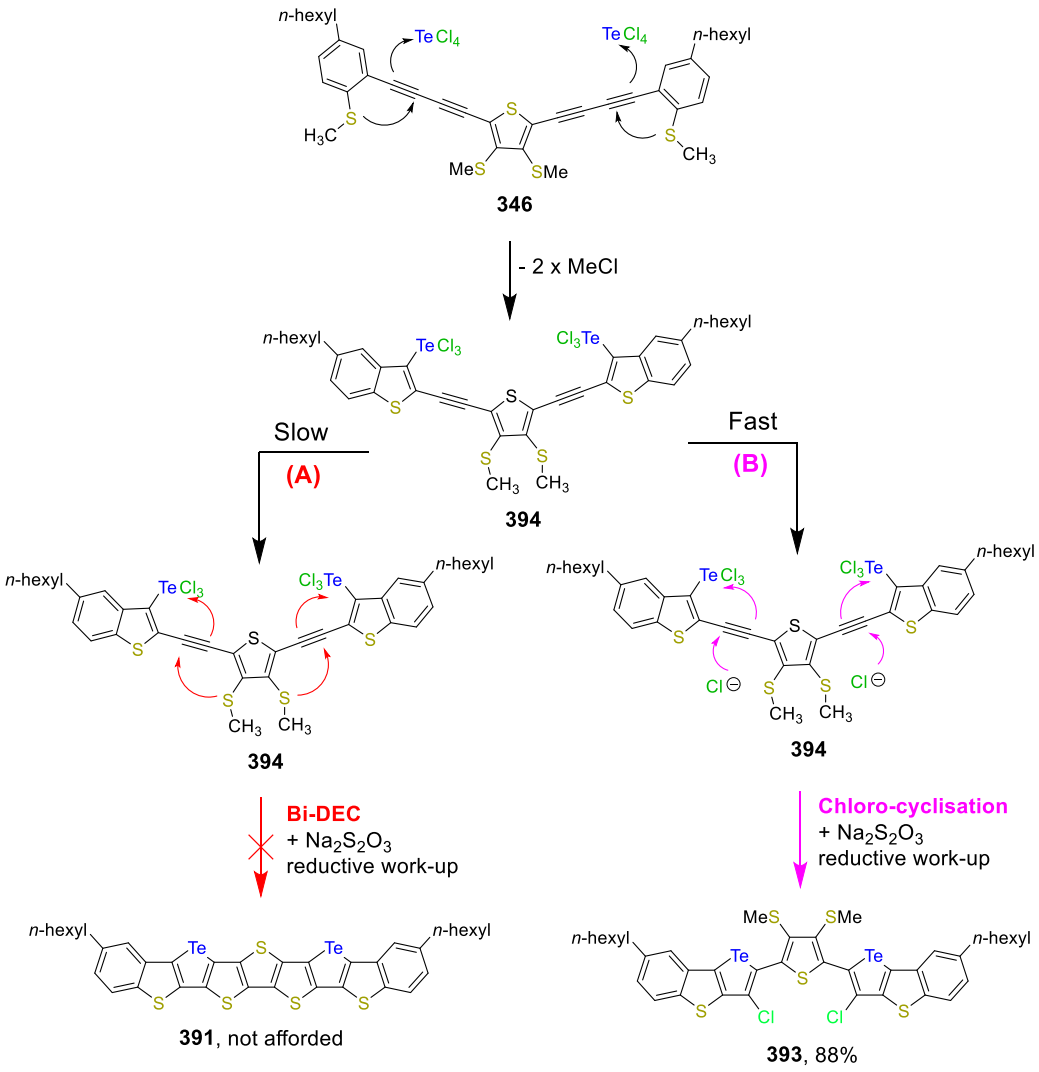
^{1}H NMR analysis showed that all aromatic resonances associated with **346** had shifted upon reaction, indicating chemical change in the benzene ring system, which would occur with cyclisation to afford **391**. However, spectra also showed the presence of a CH_3 singlet at 2.57 ppm that was associated with the observed product of cyclisation. This chemical shift is consistent with a SMe group with spectra integration indicating the product had two symmetrical SMe groups present. Following observation of this CH_3 singlet, it was concluded that **391** was not the observed product of cyclisation. Scheme 87 present two possible products (**392** and **393**) of cyclisation could align with the NMR spectra described. Each of these compounds appears to exhibit some evidence of chloro-cyclisation. This can be reconciled as $TeCl_4$ can act as a source of Cl-, of which can induce chloro-cyclisation of alkynes. Each of these potential products are not easily discernible from each other using only NMR or mass spectral data, thus, crystallographic data was obtained (See appendices Chapter 7.3 for crystallography images). This data confirmed **393** as the product of cyclisation between tetrayne **346** and $TeCl_4$. It was also found that when $TeCl_4$, is employed as the limiting reagent (0.5 eq.) **393** was isolated in 88% yield.



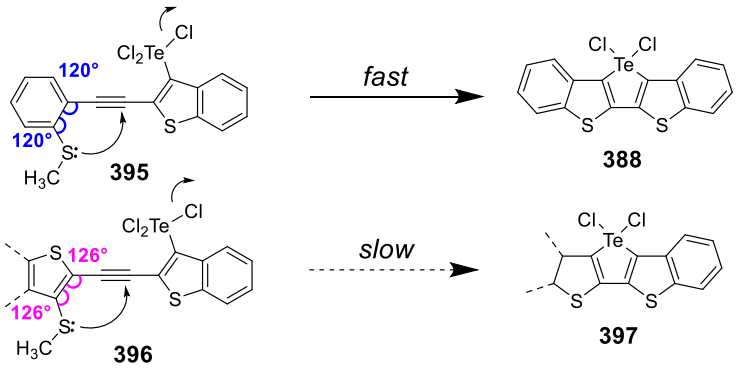
*Scheme 87: Possible products of the attempted bi-DEC of tetrayne **346**. a) $TeCl_4$, DCE:dioxane, 80 °C*

Although partially cyclised **393** was an unintended product, it was important to reconcile its formation to help ascertain why the intended bi-DEC to **391** had not occurred. Accordingly, Scheme 88 presents the proposed mechanism for the formation of the unintended product **393**, and how this contrasts with the predicted mechanism of bi-DEC that was intended to afford **391**. It was suggested that upon addition of $TeCl_4$ to **346**, two mono-cyclisations occur to afford **394**. This intermediate then has two potential paths of subsequent reaction: (A) the intended bi-DEC and (B) chloro-cyclisation. As **393** was the observed product of cyclisation, pathway (B) is clearly favoured over bi-DEC pathway (A). Therefore, it must be concluded that conversion from **394** to **391** is energetically unfavoured. This prompts the question: which structural features of **394** are not conducive to subsequent electrophilic cyclisation with $TeCl_3$?

Scheme 89 presents a possible answer by showing the difference in bond angles between a cyclising benzene (**395**) and thiophene (**396**) ring system. In a benzene ring system, the alkyne and nucleophile (SMe) are physically closer than they are in a thiophene ring system. Therefore, there will be more energy required to electrophilically cyclise **396** than **395**. When this is combined with sulfur being one of the weaker chalcogen nucleophiles (compared to Se and Te), it can be understood that significant energy is required for a material such as **396** or indeed **394** to undergo DEC.



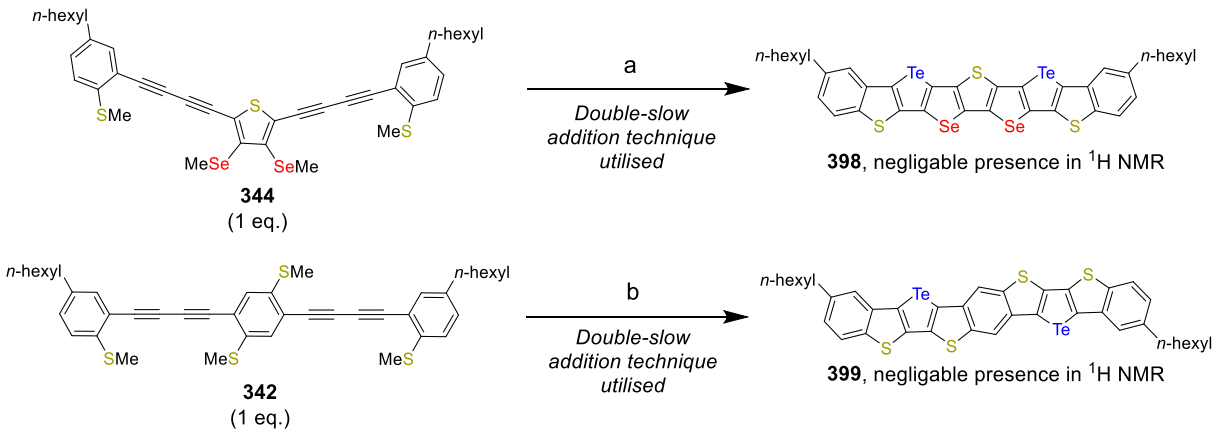
*Scheme 88: Proposed mechanism for the formation of **393**.*



Scheme 89: General scheme showing the difference between bond angles within electrophilic cyclisation of benzene and thiophene rings.

Potentially, the other tetraynes furnished for application to bi-DEC can address these shortcomings (Scheme 90). Tetrayne **344**, replaces the SMe substituents on the thiophene ring of **346** with the larger and more nucleophilic SeMe groups. Tetrayne **342** features a benzene core that will better replicate the bond angles of DEC of diyne **386**. Accordingly, it was hypothesised that these polyynes (**342** and **344**) will better evidence bi-DEC to afford **398** and **399**.

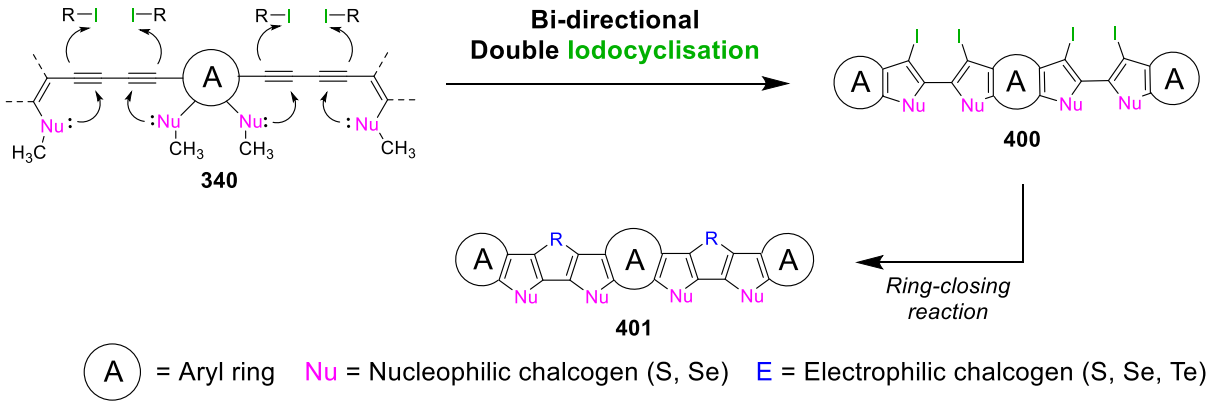
Unfortunately, attempted bi-DEC of tetrayne **344** with $TeCl_4$ consistently gave spectra that showed the presence of multiple products in a complex spectrum. Although this outcome is different from that of 'SMe' containing **346**, it was still undesired as the cyclised product **398** was only negligibly present. Following this, tetrayne **342** was subject to bi-DEC conditions with $TeCl_4$. A similar cyclisation result persisted, NMR spectra with each attempt evidenced the presence of multiple cyclisation products within a complex spectrum. Variation of the addition technique was explored, however employment of single-slow addition consistently resulted in polymerisation to an insoluble material. It was therefore concluded that bi-DEC with $TeCl_4$ was not furnishing the desired results and thus, was abandoned as a method of evidencing bi-DEC.



*Scheme 90: Proposed bi-directional DEC of tetraynes **342** and **344** to afford **398** and **399**. a) $TeCl_4$ (2.5 eq.), 80 °C, DCE:dioxane, b) $TeCl_4$ (1-4 eq.), 80 °C, DCE:dioxane.*

3.4 Bi-directional double iodocyclisation (Bi-DI)

Following the unsuccessful employment of $TeCl_4$ to evidence bi-DEC of tetraynes (**342**, **344** and **346**) it was proposed that an alternative approach to the demonstration of bi-DEC be explored. Scheme 91 outlines the employment of an electrophilic iodide source (I_2, NIS etc.) to promote bi-directional double iodocyclisation (bi-DI) to afford general structure **400**. This cyclisation can then be followed by any manner of ring-closing reaction to afford poly-fused heteroacene **401**. The iodo-groups within **400** provide excellent opportunity for coupling reactions such as Buchwald-Hartwig or Heck reactions, to afford diverse set of products. Accordingly, both reaction steps shown (bi-DI and ring-closing) will be thoroughly investigated, commencing with the bi-DI.

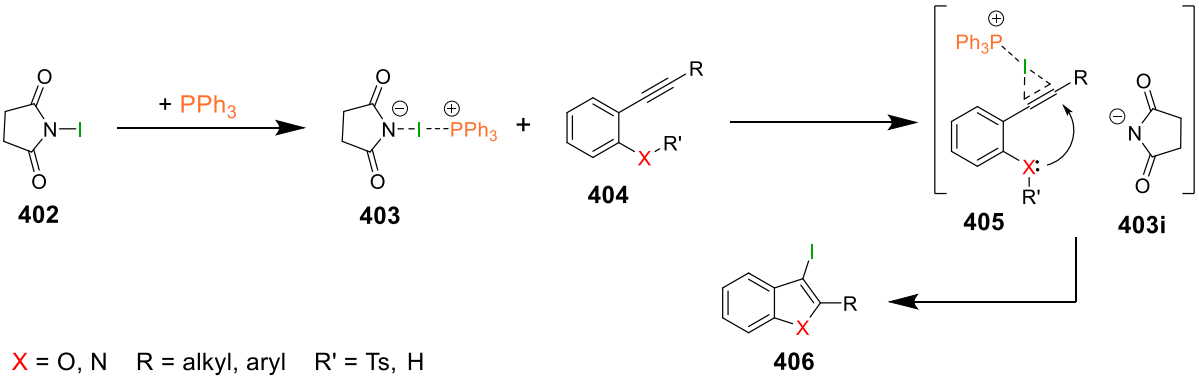


*Scheme 91: Proposed bi-directional double iodocyclisation and ring closing reaction to afford poly-fused heteroacene **401**.*

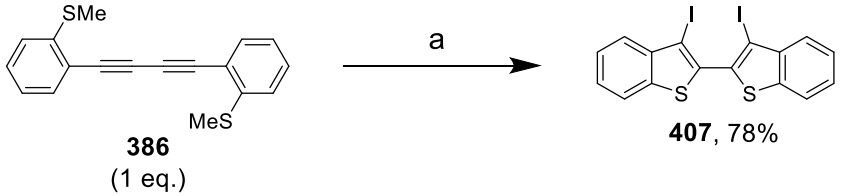
To initiate this study, it was proposed that double iodocyclisation be first evidenced in the simple diyne **386** before application to the large tetraynes (**342**, **344**, and **346**). Double iodocyclisation of diyne **386** has been demonstrated previously *via* addition of iodine (I_2) to a DCE solution of **386**.[9] Although successful in affording the iodocyclised material in high yield (85%) one drawback of this approach is possible iodine/iodide (I^-) contamination of the cyclised product, which can complicate subsequent reaction steps.[194]

Recently, Li and co-workers reported the use of NIS and PPh_3 for the preparation of iodocyclised benzo-furans and -indoles (Scheme 92).[195] As shown in the reaction mechanism, the only by-products of reaction are PPh_3 and succinimide **403i**. Both are easily removed upon column chromatography and their presence can be easily observed *via* NMR analysis.

Pleasingly, these conditions were applied to diyne **386** to afford iodocyclised **407** in 78% yield (Scheme 93). Resin bound PPh_3 was employed for easier purification, details of this reagent can be found in Experimental Chapter 5.1.

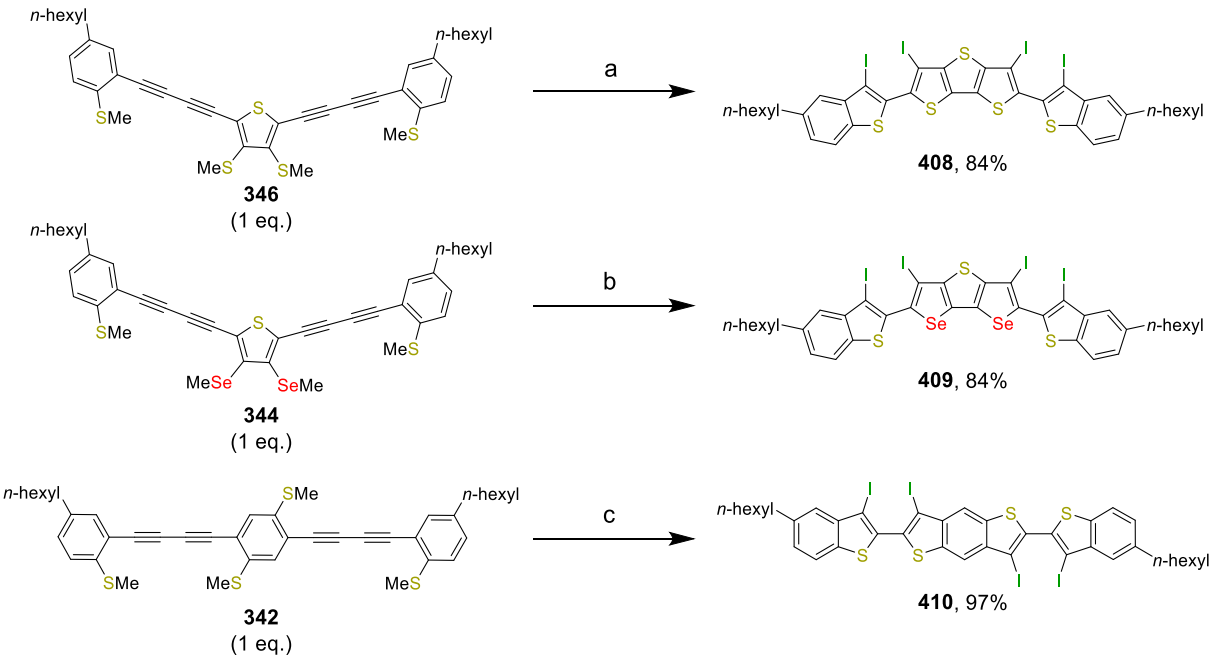


Scheme 92: Mechanism of NIS/PPh_3 mediated iodocyclisation as reported by Li and co-workers.[195]



*Scheme 93: double iodocyclisation of diyne **386** to afford **407**. a) NIS (4.4 eq.), PPh_3 resin (0.2 eq.), DCE, 60 °C, 18 h.*

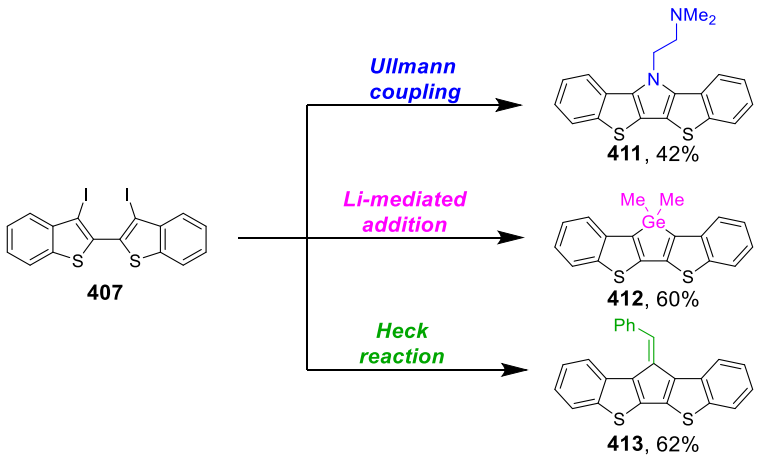
Following the successful double iodocyclisation of diyne **386**, the same conditions were applied to tetraynes **346**, **344** and **342** to evidence bi-DI (Scheme 94). Delightfully, all tetrayne starting materials were successfully iodocyclised to afford heteroacenes **408-410** in high yield. In each case product presence was verified by ^{1}H and ^{13}C NMR analysis. Tetraynes **346** and **344** were successfully cyclised with the conditions described by Li and co-workers. However, tetrayne **342** displayed cleaner conversion to product **410** through addition of iodine instead of the NIS/PPh_3 method. Due to the low solubility of iodocyclised **410**, removal of by-products was more effective and so the issue of I_2/I^- contamination of **410** was not perceived to be an issue. Following these demonstrations of bi-DI, each cyclised heteroacene was subject to subsequent ring-closing reaction exploration.



*Scheme 94: Bi-directional double iodocyclisation of tetraynes **346**, **344** and **342** to afford **408**-**410**. a) NIS (8 eq.), PPh_3 resin (0.5 eq.), DCE, 70 °C, 18 h, b) NIS (8 eq.), PPh_3 resin (0.5 eq.), DCE, 60 °C, 18 h, c) I_2 (9 eq.), DCE, 80 °C, 18 h.*

3.5 Ring-closing reactions

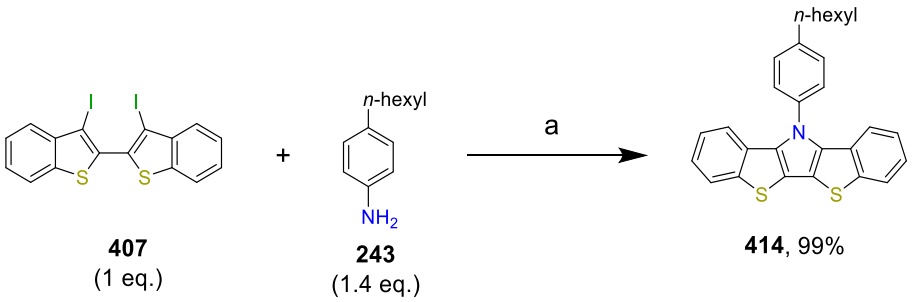
Following the successful demonstration of bi-DI, exploration could commence on the subsequent ring-closing reaction. Three reaction classes will be explored as a part of this work: Buchwald-Hartwig coupling[196-198], Li-mediated electrophilic addition and the Heck reaction[199, 200]. Some of these reactions have been explored with simple di-iodide **407** in Gupta and Flynn's previous work, demonstrating their validity as ring-closing reactions (Scheme 95).



Scheme 95: Previously reported ring-closing reactions by Flynn and Gupta.

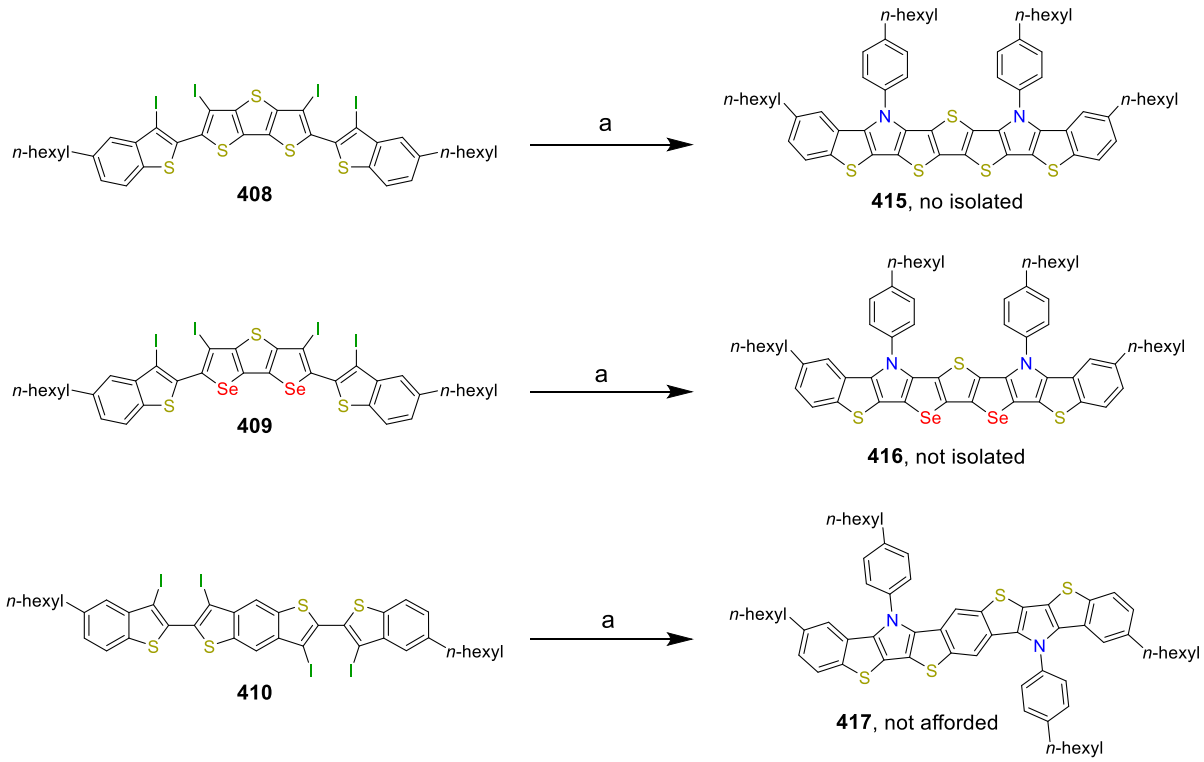
3.5.1 Buchwald-Hartwig coupling

The Buchwald-Hartwig (B-H) reaction is an extremely useful Pd-mediated method of forming C-N bonds. It has been well exemplified in drug discovery, natural product synthesis and materials science.[196] Traditionally the reaction was shown to couple one halogenated carbon with a corresponding primary or secondary amine to form the single new C-N bond. However, the reaction has also been expanded to demonstrate 'double' couplings between a primary amine and a di-halogenated systems to form new pyrrole rings.[201] This form of double B-H coupling was attempted with iodocyclised diyne **407** as shown in Scheme 96. Pleasingly, after some optimisation efforts, 4-hexylaniline **243** successfully coupled with di-iodo heterocycle **407** to afford **414** in excellent yield (99%). Aniline **243** was selected for coupling as the long hexyl chain would likely provide increased solubility when applied to the larger heterocycles.



*Scheme 96: Buchwald-Hartwig coupling of di-halogenated **407** with 4-hexylaniline **243** to afford **414**. a) Cs_2CO_3 (4 eq.), Xantphos (0.4 eq.), $Pd_2(dba)_3$ (0.2 eq.), toluene, reflux, 40 h.*

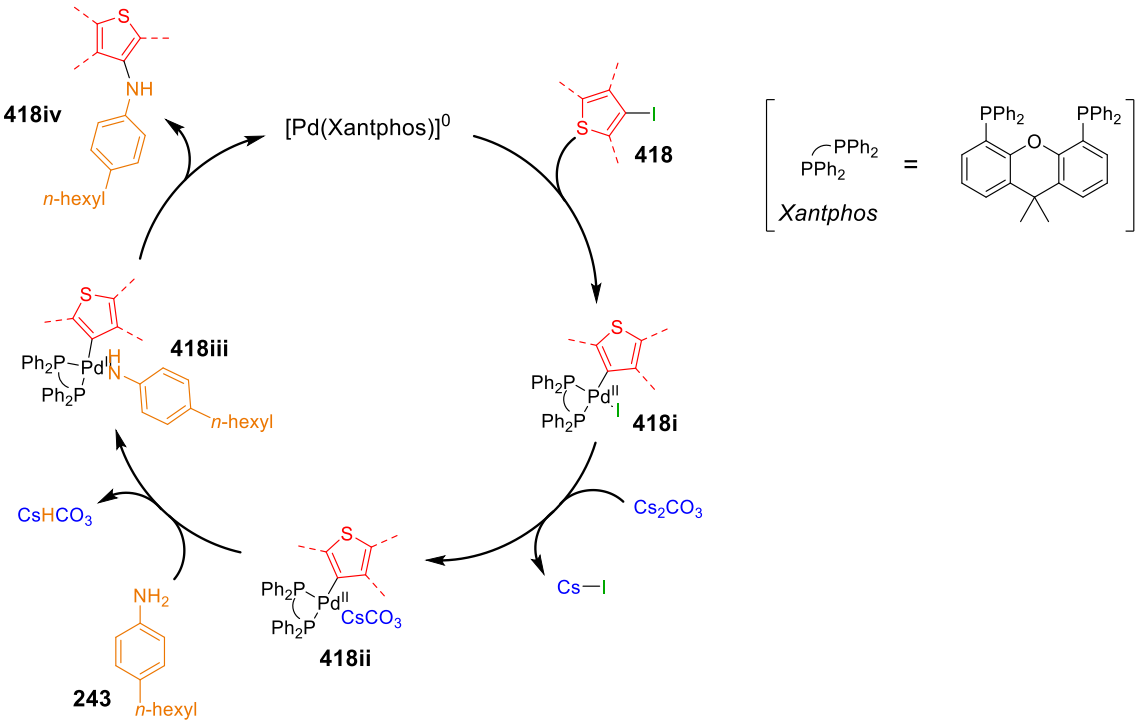
Due to the successful ring-closing of di-iodo **407** to afford **414**, B-H coupling was applied to the larger heteroacenes systems **408**, **409** and **410** (Scheme 97). In each attempt, reaction progress and isolation attempts were monitored by ^{1}H and ^{13}C NMR analysis. Early iterations that applied the aforementioned B-H conditions, to **408** and **409** appeared promising with the presence of small resonances in ^{1}H NMR spectra that were assignable to products **415** and **416**, respectively. Although no starting material was observed in NMR analysis, multiple aromatic resonances were also present that were assigned to reaction intermediates. Unfortunately, attempts to increase the presence of these resonances by further addition of catalyst or reagent, increasing temperature or reaction time all resulted in a complex NMR spectrum. It was then inferred that not only is this reaction is relatively slow, the B-H coupling is also sensitive to changes in reaction conditions. Variation in coupling conditions was also explored with the Pd catalyst varied between $Pd_2(dba)_3$, $Pd(OAc)_2$ and the ligand bound *t*-BuBrettPhos Pd G3. The ligand was varied between Xantphos, Xphos, DPPF and *t*-BuBrettPhos and the base between Cs_2CO_3 and *t*-BuONa. The solvent system was also varied between dry toluene, dry dioxane and mixtures of the two. Unfortunately, careful NMR reaction monitoring throughout these variations concluded that the originally employed conditions ($Pd_2(dba)_3$, Cs_2CO_3, Xantphos in toluene) still proved the most successful despite the small presence of the desired products **415** and **416**. Accordingly, attempts were made to isolate the B-H products from these conditions for further characterisation despite the predicted low yield. Unfortunately, the reaction mixture was not stable upon isolation.



*Scheme 97: Attempted ring-closing B-H coupling to afford poly-fused heterocycles **415-417**. a) $Pd_2(dba)_3$, Cs_2CO_3, Xantphos in toluene or toluene:dioxane*

It was concluded that reaction intermediates and products **415** and **416** may not be stable to harsh reaction conditions or purification efforts involving silica gel. The Buchwald-Hartwig reaction proceeds through a catalytic cycle and there are four instances of C-N bond formation required with multiple possible reaction intermediates (Scheme 98). The incorporation of the aniline ring within **415** and/or **416** may also destabilise the heteroacene, complicating synthesis.

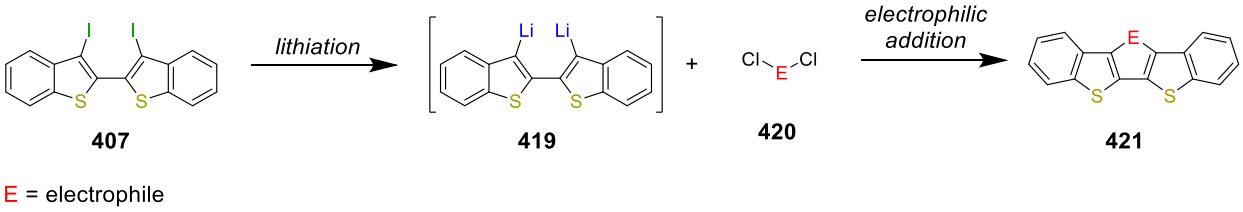
Ring closing B-H coupling was also attempted with heterocycle **410** utilising $Pd_2(dba)_3$, Cs_2CO_3 and Xantphos in toluene (Scheme 97). Regrettably, negligible presence of product **417** was observed in NMR analysis. Starting material **410** and many aryl resonances were observed in spectra, indicating very low conversion to product **417**. It was concluded that the complex nature of a double Buchwald-Hartwig reaction mechanism combined with a complex heterocyclic starting material (**408-410**) proved too capricious for the reliable formation of product (**415-417**).



Scheme 98: General mechanism of Buchwald-Hartwig coupling reaction.

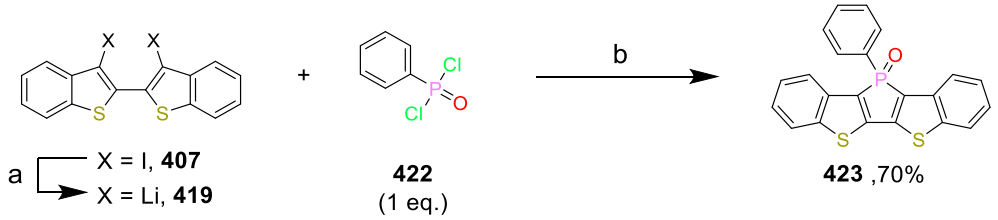
3.5.2 Lithium-mediated electrophilic addition

Li-mediated electrophilic addition can be an extremely useful reaction to install heteroatoms at halogenated carbons. Scheme 99 outlines the proposed use of this ring-closing reaction to afford poly-fused system **421**. As shown, there are two stages within the reaction, iodo for Li exchange to afford intermediate **419** and subsequent addition of a suitable electrophile (ECl_2, **420**). The presence of intermediate **419** can be verified through ^{1}H NMR analysis, following aqueous work-up, prior to the addition of electrophile **420**. Pleasingly, exposure of **407** to 2 eq. of *n*-BuLi resulted in 100% conversion to lithiated intermediate **419**, which was confirmed by ^{1}H NMR analysis. A CH singlet at 7.52 ppm was assigned to the lithiated positions of **419**.



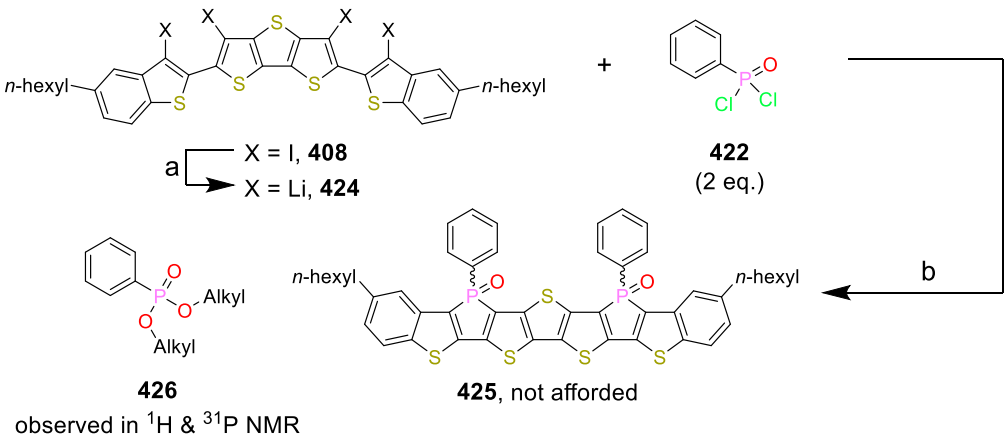
*Scheme 99: General scheme of Li-mediated electrophilic addition of **420** to afford **421**.*

Following confirmation of the lithiation step, three suitable electrophiles were trialled in concurrent small-scale reactions for the sole purpose of NMR reaction monitoring. Thionyl chloride, dimethylgermanium dichloride and phenylphosphonic dichloride **422** were utilised within this study (Scheme 100). Incorporation of any of these groups would increase the applications of the bi-DI methodology as P=O, S=O and Ge containing heterocycles are commonly employed in materials science.[202-204] Phosphonic electrophile **422** displayed the highest conversion to product, affording **423** in 70% yield.



*Scheme 100: Electrophilic addition of phenylphosphonic dichloride **422** to afford **423**. a) n-BuLi, dry Et_2O, 0 °C 1 h, b) dry Et_2O, 22 °C 18 h.*

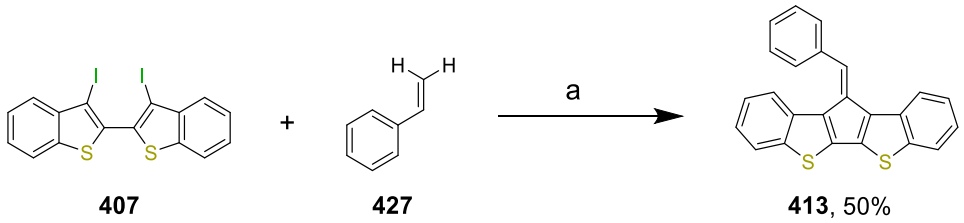
Following the successful electrophilic addition of phosphonic electrophile **422** to di-lithiated intermediate **419**, these conditions were applied to the larger heterocycle **408** (Scheme 101). Pleasingly, the presence of intermediate **424** was confirmed the presence of two CH singlets at 7.47 and 7.40 ppm in ^{1}H NMR that were assigned to the lithiated carbons of **424**. Unfortunately, addition of phosphonic electrophile **422** to tetra-lithiated intermediate **424** was not observed in NMR analysis. Purification of resultant reaction mixture identified starting material **424** and by-product **426** as the major reaction products. It was concluded that phosphonic electrophile **422** had reacted with some alcohols present in the *n*-butyl lithium source. An alternative source of *n*-BuLi was employed, however this resulted in only unreacted phosphonic electrophile **422** and intermediate **424**. Therefore, it was concluded that although tetra-lithiated intermediate **424** can be produced in reaction mixture, clearly electrophilic addition was not occurring.



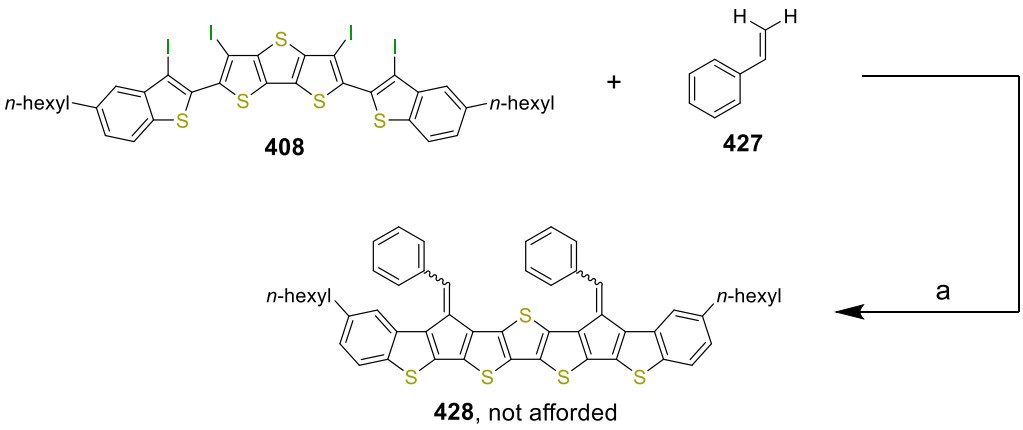
*Scheme 101: Attempted synthesis of **425** through electrophilic addition of **422** to lithiated intermediate **424**. a) n-BuLi (4.1 eq.), dry Et_2O, -78 °C 1.5 h, b) dry Et_2O, 22 °C 18 h.*

3.5.3 Heck reaction

The heck reaction forms new C-C bonds through a Pd-mediated reaction mechanism. As previously shown, Gupta and Flynn afforded heterocycle **413** from di-iodo **407** (Scheme 102).[9] The displayed reaction was successfully performed within this study in 50% yield, utilising conditions consistent with those reported. Initial attempts were made to apply the double Heck reaction to heterocycle **408** (Scheme 103). Unfortunately, ^{1}H NMR reaction monitoring only indicated the presence of unreacted **408** and styrene **427**. Due to time constraints, optimisation of Heck reaction conditions was not performed.



*Scheme 102: Successful furnishing of **413** through a double Heck reaction between **407** and styrene **427**. a) $Pd(OAc)_2$, PPh_3, KOAc, DMF, 80 °C, 18 h.*



*Scheme 103: Attempted double Heck reaction between **408** and styrene **427** to afford **428**. a) $Pd(OAc)_2$, PPh_3, KOAc, DMF, 80 °C, 18 h.*

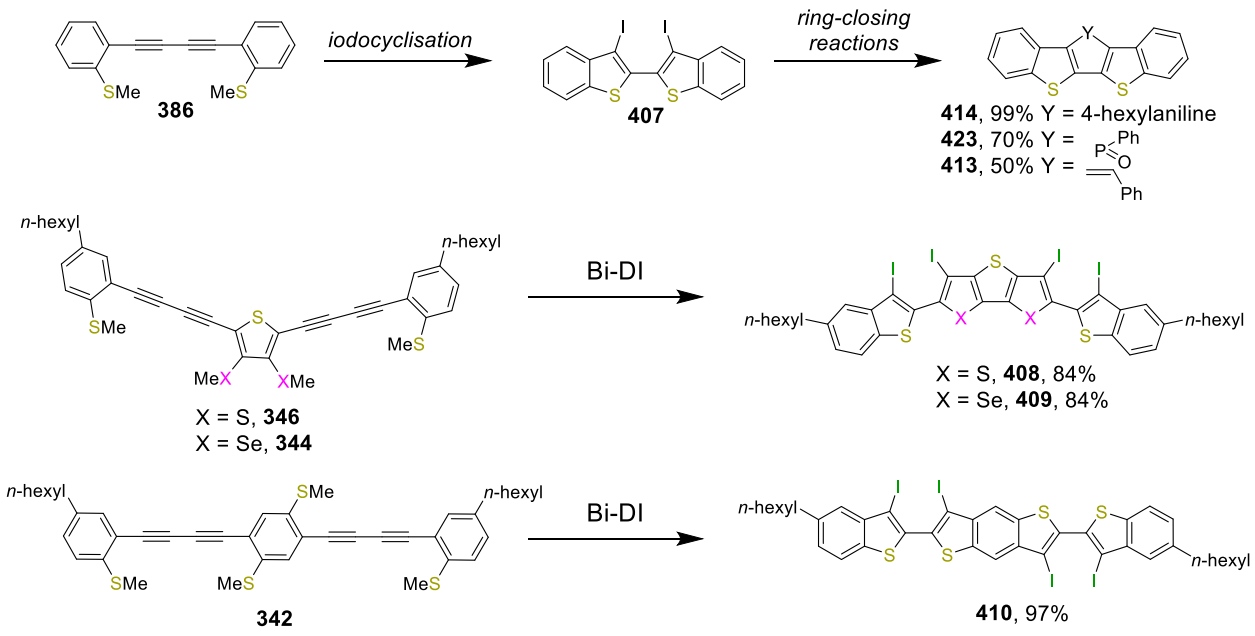
3.6 Conclusions and future work

This chapter has presented a thorough investigation of the bi-directional application of double-electrophilic cyclisation. Three tetraynes, **342**, **344** and **346** were accessed through optimised synthetic pathways for employment in this bi-DEC study. Unfortunately, DEC with $TeCl_4$ did not translate to the more complex tetrayne systems with $TeCl_4$ promoted chloro-cyclisation preferentially proceeding. Following this, bi-directional double iodocyclisation (bi-DI) was explored as an alternative form of the bi-DEC methodology. Pleasingly, all tetraynes were efficiently cyclised under bi-DI conditions in high yield (Scheme 104). Subsequent ring-closing reactions were explored to enhance the utility of bi-DI. Limited studies were performed to investigate Buchwald-Hartwig coupling, Li-mediated electrophilic addition and the Heck reaction as a means of forming a poly-fused heteroacene. These ring-closing reactions were well evidenced in the simple di-iodo **407** system affording products **413**, **414** and **423** in moderate-excellent yield. Unfortunately, these ring-closing reactions did not translate to the more complex tetrayne systems **408**-**410**. The lack of conversion to product likely due to instability of the products or reaction intermediates, further evidencing the complexity of the reaction mechanism.

Further study regarding the ring-closing reaction would be warranted to include the exploration of alternative incorporating groups. This may increase reaction intermediate and product stability if the electronics of the compounds are suitably considered. In conjunction with these efforts, Heck coupling conditions could be further optimised with variation of the catalyst, base or ligand that could not be exemplified in this thesis due to time constraints. Bi-directional

halocyclisation could also be expanded to include bromo- and chloro- cyclisation to measure the effect on ring-closing reaction outcome. Within the Li-mediated addition approach, other electrophiles could also be explored to ascertain whether the stability of the lithiated intermediate of **408** could successfully ring-close.

Although the larger poly-fused systems could not be produced through the described ring-closing reactions, this chapter has made significant contributions to the understanding of the DEC reaction. Bi-DI has also afforded diverse heteroacenes that feature varied ring fusion patterns, heteroatom incorporation and 2D conformations. Therefore, we believe this work has further elucidated the scope and limitations of PEC reactions whilst affording heteroacenes that that pose great utility to the materials science field.



Scheme 104: Summary of heteroacenes afforded within this Chapter.

4.0 Results and discussion: Poly-electrophilic cyclisation for the formation of spiralacenes

4.1 Introduction

Poly-fused acenes have highly conjugated, extended frameworks that confer a wide-range of electronic and photonic properties.[205, 206] Their structural features have made them extremely amenable to the transport of excited states and acting as charge carriers.[207] Their favourable electronic properties can also be enhanced with increasing oligomer length (number of fused acene rings). Accordingly, these materials are often thought of as easily 'tuneable' structures for application to organic semiconductor devices. However, when oligomer length is increased, accompanied with the enhanced electronic properties are decreasing stability and insolubility, complicating their production.[208] This is best exemplified with the price of tetracene (four fused phenyl rings) being 100 times that of anthracene (three fused phenyl rings) as a function of the increased difficulty of synthesis. Therefore, the promising properties that planar acenes can exhibit are extremely limited by the difficulty surrounding their synthesis and handling. Non-planar acenes present an exciting alternative that share the favourable electronic properties of planar acenes but demonstrate enhanced stability and solubility (Fig. 20). Non-planar acenes (NPAs) owing to their unique morphology also exhibit unique performance within organic electronic devices.[209] Within this class of compounds there is also opportunity to introduce chirality (Fig. 20, **430** if R ≠ R'). This provides another opportunity for investigation of the structure-property-relationship (SPR) within materials research through use of varied pure enantiomers or mixtures.

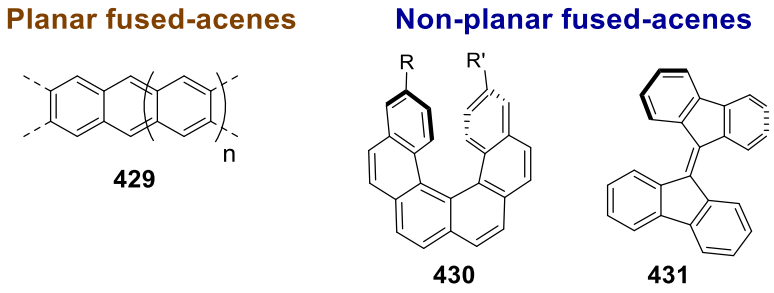
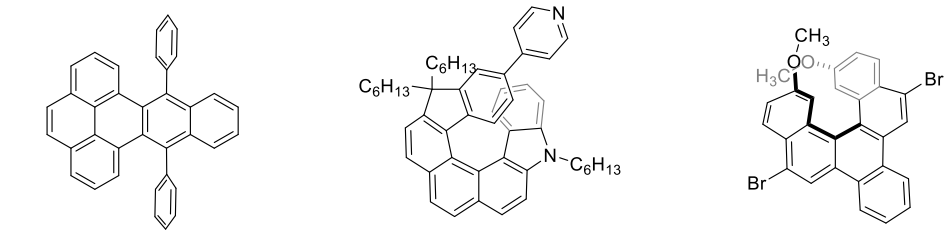


Figure 20: Planar and non-planar poly-fused acenes.

A compound class that makes up a very large portion of NPAs is the helicenes. Helicenes are directional non-planar poly-fused acenes systems that display a helical 3D conformation. Their

unique conformation and chemical characteristics have led to a plethora of applications, including materials science.[68] Figure 21 illustrates some select examples of NPAs employed within materials science with compounds **433** and **434** being examples of helicenes.[210-212] Helicene **433** is an example of a chiral helicene, of which was patented for use as an enantiomeric mixture. As NPAs have been employed in organic electronics, it has become abundantly clear that organic molecule morphology has a direct correlation with multiple electronic and photonic properties.[213, 214] Therefore, there is a keen interest in the discovery and exploration of new and varied 3D poly-fused acene conformations.



432
For application in an OLED

433
For application in an OLED

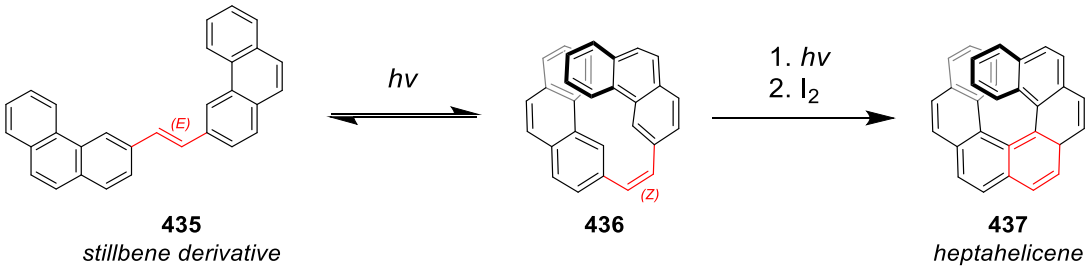
434
Exhibits cyan flourescence

*Figure 21: Examples of non-planar poly-fused acenes employed in materials science (**432**[211], **433**[210], **434**[212]).*

The synthesis of NPAs has received significant interest due to their utility.[215-218] Traditional chemical transformations do not adequately address the formation of such novel structures. Therefore, there has been a concerted effort to develop bespoke methodologies for the formation of NPAs. Scheme 105 illustrates a general method of helicene formation that relies on the light catalysed isomerisation between the E and Z isomers of stilbene derivative **435**. The Z-isomer (**436**) positions the left- and right-hand sides of the molecule in close proximity to each other so that subsequent photochemical reaction and oxidation can afford helicene **437**. Although this conversion was first reported in the 1960s, photochemical electrocyclisation still remains as the dominant method utilised for the synthesis of helicenes, as they effectively form the 'hinging' benzene ring that affords the helical skeleton.[219, 220]

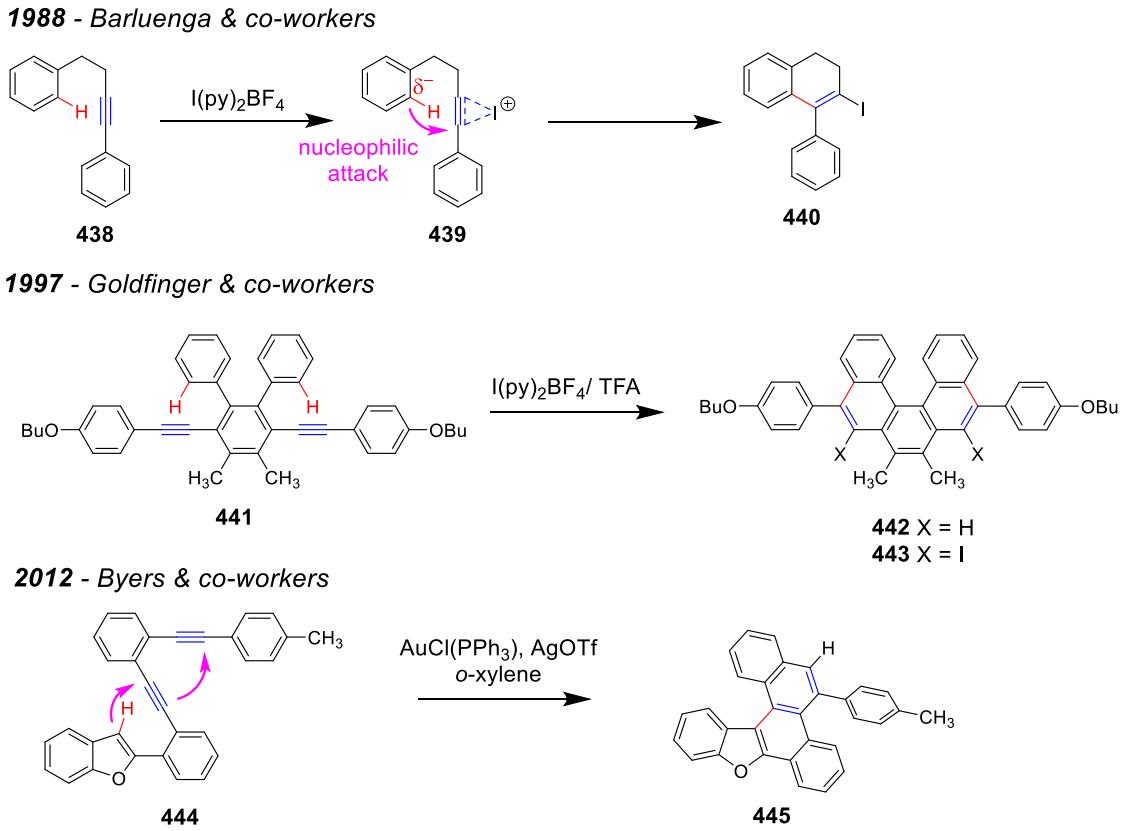
Although this chemistry is important, it is limited to the formation of one 3D conformation. Aside from traditional helicenes, there are limited methodologies that efficiently afford acenes with novel 3D conformations. Whilst compound morphology is one of the most important structural characteristics that determines device performance, current synthetic methodologies

do not suitably address variation in 3D space. It was therefore the aim of this work that a novel synthetic methodology be demonstrated that affords acenes with a novel 3D conformation, to assist the materials science exploration of these interesting structures.



*Scheme 105: Generally employed synthesis of heptahelicene **437**.*[216]

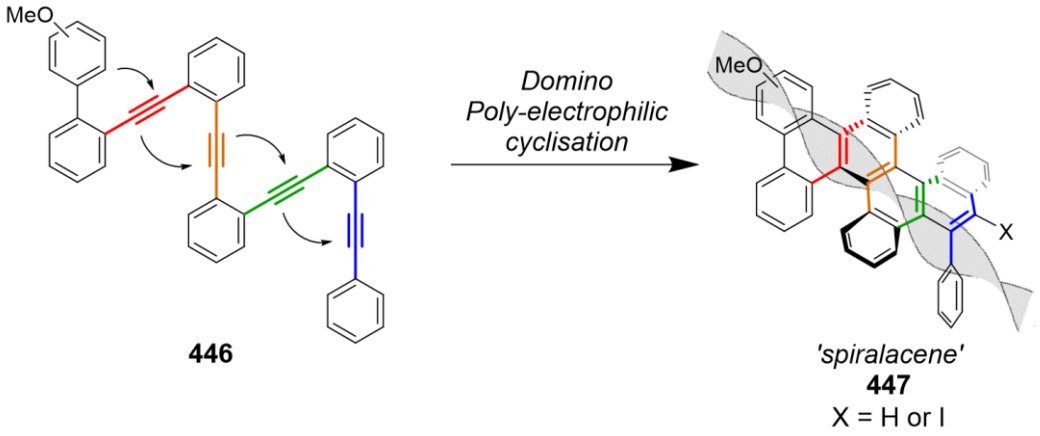
Domino cyclisation reactions are an efficient and effective method of forming polycyclic systems. As electrophilic cyclisation is such an atom economical and versatile reaction, it was proposed that a poly-electrophilic cyclisation reaction to afford poly-acenes be explored. Within this thesis and the overwhelming portion of literature reports, electrophilic cyclisation (EC) has been described as a reaction to afford heteroacenes. However, examples of EC to afford acenes date back to the 1980s (Scheme 106). In these reports, a suitably activated C-H (coloured red) acts as the nucleophile that attacks the tethered alkynyl bond in **439**. This type of EC has been exemplified as both a protocyclisation (**442** and **445**) and iodocyclisation (**440** and **443**). Following the original report by Barluenga[221], Goldfinger[222] significantly enhanced the scope of this acene forming reaction by demonstrating it bi-directionally. The more contemporary work by Byers[223] reports a PEC to afford the polycyclic system **445**. Therefore, EC has been clearly shown to afford poly-fused acenes in the same atom economical method by which heteroacenes are. It is therefore the proposal of this work that poly-electrophilic cyclisation to afford NPAs be explored.



Scheme 106: Literature examples of electrophilic cyclisation for the formation of fused acene systems.[221-223]

After careful research and consideration, Scheme 107 presents the major hypothesis of this exploration of PEC to afford NPAs with novel 3D conformations. Skipped polyyne **446** (methoxy substitution to be determined) was subjected to PEC, similar to works described in Scheme 106. However, in contrast from those previous works, the product **447** will exhibit a twisted spiral-shaped conformation and could therefore be referred to as a 'spiralacene'. The incorporation of methoxy groups serves two purposes with the EDGs activating the ring system towards cyclisation but also acting as 'donors' (influence electronic and photonic activity) within **447**. A similar acene ring-fusion pattern has been reported concurrently to this work, confirming the predicted twisted 3D conformation (Fig. 22).[224, 225] This figure also describes the dihedral angles between the planes within twisted acenes **448** and **449**. Although the graphical representation of dihedral angles shows perfectly flat planes A and B, this is not always the case, the planes can be 'bent' resulting in two dihedral angles that are not equal, as is the case in **449**. Another communication that was published contemporaneous to this work reported the synthesis of a similar structure to spiralacene **447** (contained fewer rings) using forcing conditions with low yields (190 °C on alumina, 5% yield).[226] The 3D morphology of

the compound was not discussed in the publication, however, this communication demonstrates the significant interest in these novel structures.



*Scheme 107: Proposed domino poly-electrophilic cyclisation to afford spiralacene **447**.*

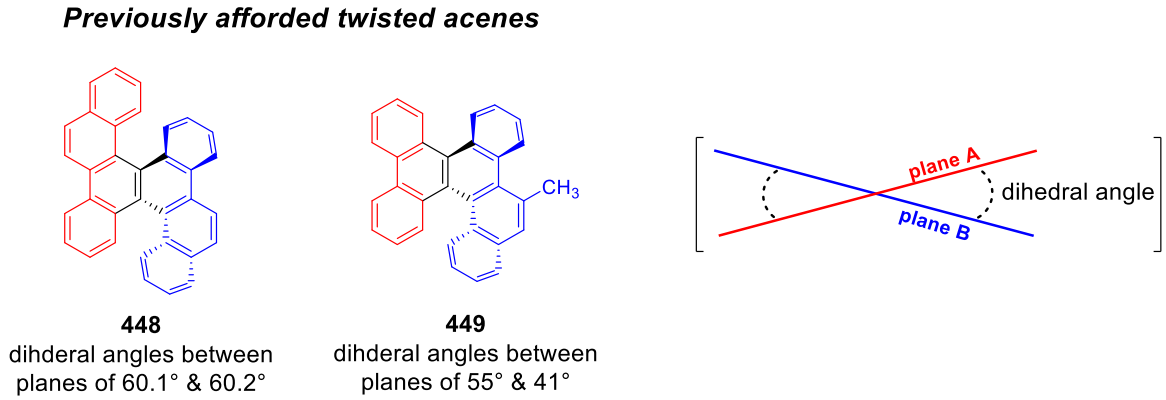
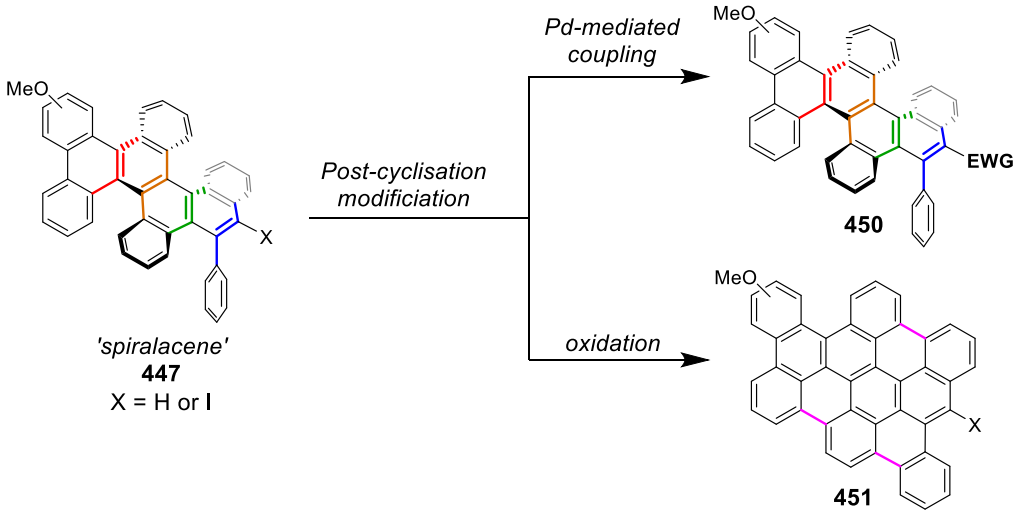


*Figure 22: NPAs afforded previously featuring similar 3D conformations to the proposed spiralacene **447**.* [224, 225] *Also shown is a graphical representation of how the dihedral angles are measured between the different planes within **448** and **449**.*

It was also proposed that following the formation of spiralacene **447** some post-cyclisation functionalisation reactions be explored (Scheme 108). Should X = I in **447**, Pd-mediated coupling could be utilised to install an electron-withdrawing group (**450**) to alter the HOMO-LUMO gap of the compound. Oxidation of spiralacene **447** can also be explored to effectively 'flatten out' the spiralacene to afford poly-acene ribbon **451**. Polyacene ribbons have demonstrated unique electronic properties and so the ability to easily covert from a twisted-spiral (**447**) to a planar polyacene (**451**) would increase the scope of the study. The PEC to

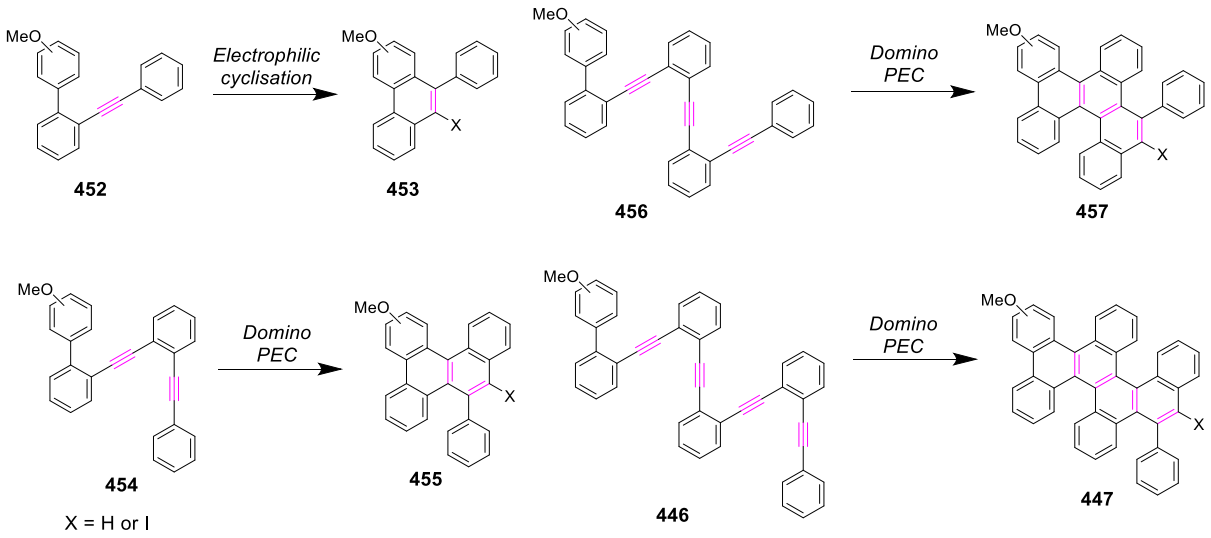
afford spiralacene **447** from polyyne **446** could also be modified to incorporate a chiral catalyst for chiral induction studies. These investigations will serve as a secondary set of goals for the spiralacene project. The focus of this chapter will be the proof-of-concept study of a PEC reaction to afford spiralacene **447**.



*Scheme 108: Proposed post-cyclisation modifications to afford functionalised materials **450** and **451**.*

To suitably investigate the domino PEC to afford spiralacene **447**, an iterative approach will be taken (Scheme 109). Commencing with mono-yne **452**, cyclisation will be demonstrated across 1-4 alkyne bonds, utilising diyne **454**, triyne **456** and finally tetrayne **446**. This approach allows for optimisation of reaction conditions to occur on the simpler and more easily accessed alkynes (**452** and **454**) before application to tetrayne **446**. The details of cyclisation that were determined in early work with alkyne **452** included the methoxy substitution pattern and both proto- (X = H) or iodo-cyclisation (X = I) procedures.

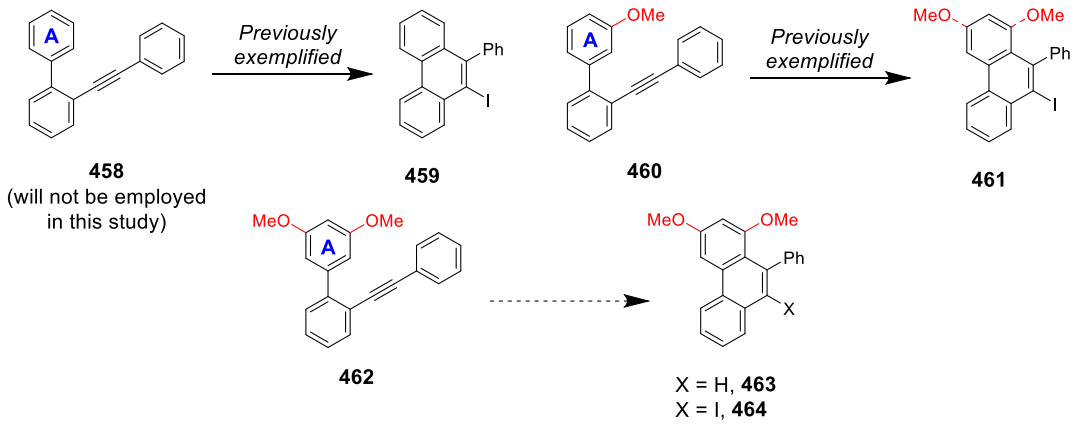
As with all explorations of a polyyne to polycycle conversion, efficient synthetic access to the polyyne starting materials is important. Fortunately, ‘skipped’ polyynes (polyynes featuring non-consecutive alkyne bonds) as shown in Scheme 109, generally experience smoother synthesis than consecutive 1,3-polyynes. Therefore, synthesis of described polyynes was not expected to possess any hurdles and relied heavily on Sonogashira coupling conditions to afford alkyne intermediates and products.



Scheme 109: Proposed alkynes for cyclisation to afford the poly-fused spiralacenes shown.

4.2 Investigation of methoxy substitution pattern

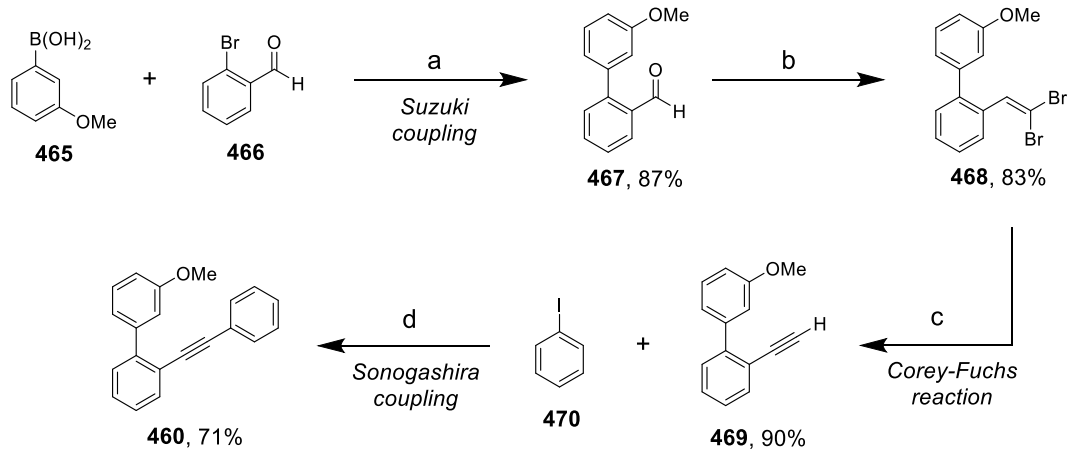
Methoxy groups are a source of electron density that when donated into ring systems will increase electronegativity and therefore, better activate that aryl ring towards reaction. Therefore, it was proposed that some methoxy substitution be included in the aryl ring (A) of alkynes to best promote electrophilic cyclisation (Scheme 110). This scheme shows three mono-alkynes, the non-substituted (**458**), mono-methoxy (**460**) and di-methoxy (**462**). Successful electrophilic cyclisation of both non-substituted **458** and mono-methoxy alkyne **460** have been shown previously, noting that **460** can be cyclised to afford two different regioisomers.[227] It was hypothesised that alkyne **462** should present the most activated aryl ring system due to the presence of two activating methoxy groups. Although simple alkyne **458** has been cyclised previously, the lack of any activating methoxy groups was predicted to bear a negative effect on cyclisation in more complex triyne or tetrayne systems. It is therefore proposed that only mono-methoxy alkyne **460** and di-methoxy alkyne **462** be utilised in subsequent cyclisation studies.



*Scheme 110: Proposed alkynes **460** and **462** for exploration of methoxy substitution pattern.*[227]

4.2.1 Synthesis of alkyne starting materials

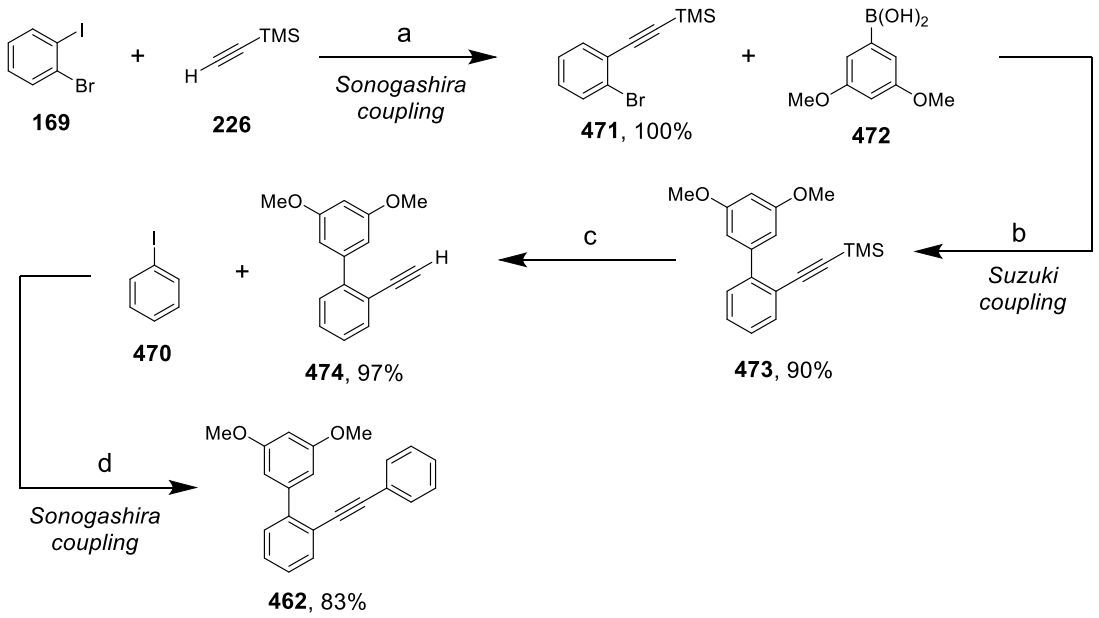
The successful synthesis of mono-methoxy alkyne **460** is outlined in Scheme 111. The aldehyde **467**, geminal dibromide **468** and acetylene **469** have been previously accessed, thus, identical reaction conditions were employed.[228, 229] Pleasingly, Sonogashira coupling between acetylene **469** and iodobenzene **470** smoothly afforded mono-methoxy alkyne **460** in 71% yield.



*Scheme 111: Synthesis of alkyne **460**. a) $Pd(PPh_3)_4$, Na_2CO_3, DME, EtOH, H_2O, b) CBr_4, PPh_3, DCM, c) n-BuLi, dry THF, d) CuI, $Pd(PPh_3)_4$, DIPA.*

Scheme 112 illustrates the successful synthesis of di-methoxy alkyne **462**. This pathway commenced with Sonogashira coupling of TMS acetylene **226** and 1-bromo-2-iodo benzene **169**. This coupling proceeded smoothly, affording **471** in quantitative yield. Subsequent Suzuki

coupling between **471** and boronic acid **472** then furnished TMS alkyne **473** in excellent yield (90%). TMS alkyne **473** later underwent silyl deprotection to afford acetylene **474** for Sonogashira coupling with iodobenzene **470**. Pleasingly, di-methoxy alkyne **462** was produced in 83% yield with NMR and HRMS confirming product formation.



*Scheme 112: Synthesis of alkyne **462**. a) CuI, $Pd(PPh_3)_2Cl_2$, Et_3N, THF, b) $Pd(PPh_3)_4$, Cs_2CO_3, EtOH, toluene, H_2O, c) K_2CO_3, MeOH, THF, d) CuI, $Pd(PPh_3)_2Cl_2$, DIPA.*

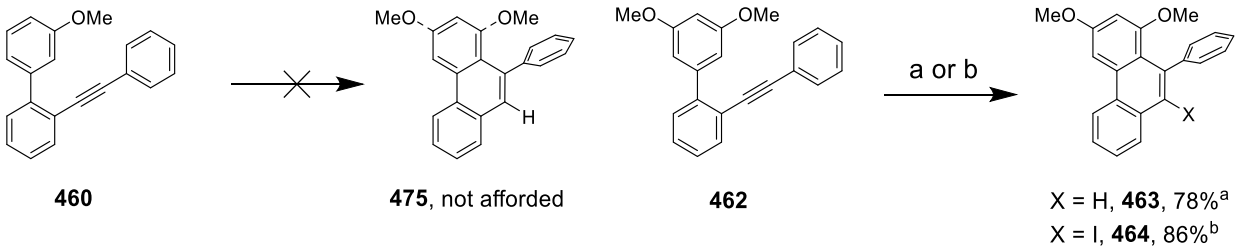
4.2.2 Mono-electrophilic cyclisation

Cyclisation studies of mono-methoxy alkyne **460** and di-methoxy alkyne **462** were conducted contemporaneously to facilitate comparison of cyclisation outcomes (Scheme 113). The purpose of this mono-cyclisation study is to ascertain the ideal cyclisation conditions and methoxy substitution pattern (**460** or **462**) to carry forward within this study. All cyclisation attempts were monitored by NMR and LCMS analysis.

Cyclisation attempts commenced by utilising Lewis acids and transition metals to promote protocyclisation to afford acenes **475** and **463**. Transitions metals $PtCl_2$[230] or Pd(TFA) were first employed however no reaction was elicited with either alkyne starting material (**460** or **462**). Following this, Lewis acids $FeCl_3$, $InCl_3$[231] or $Cu(OTf)_2$[232] were explored for their ability to confer electrophilic cyclisation. The respective addition of either of these Lewis acids to mono-methoxy alkyne **460** resulted in unreacted starting material observed in NMR analysis.

However, when trialling Lewis acids with di-methoxy alkyne **462**, the addition $Cu(OTf)_2$ to **462** resulted in complete conversion to protocyclised product **463**. Due to the resistance towards cyclisation observed in mono-methoxy alkyne **460**, it was concluded that di-methoxy alkyne **462** was significantly more activated towards electrophilic cyclisation. It was then proposed that all future polyynes accessed in this work feature the same di-methoxy substitution pattern as **462**.

Utilising conditions described by Li and co-workers[195], di-methoxy alkyne **462** was also successfully iodocyclised to afford **464** in 86% yield. Accordingly, both successful proto- and iodo-cyclisation conditions were explored for their application to the larger polyyne systems.



*Scheme 113: Attempted cyclisations of alkynes **460** and **462** to afford **475**, **463** and **464**. a) $Cu(OTf)_2$ (0.1 eq.), dry toluene, 80 °C 4 h. b) NIS (1.9 eq.), PPh_3 resin (0.1 eq.), dry DCE, reflux 2 h.*

4.3 Synthesis of di-methoxy skipped polyynes

As described above, di-methoxy substitution of the alkyne starting material best activated the ring system towards electrophilic cyclisation. Therefore, polyynes **476**, **477** and **478** (Fig. 23) were proposed for application to the PEC study of this chapter. Accordingly, each of these 'skipped' polyynes were synthetically afforded through efficient synthetic pathways. The details of these pathways are discussed below.

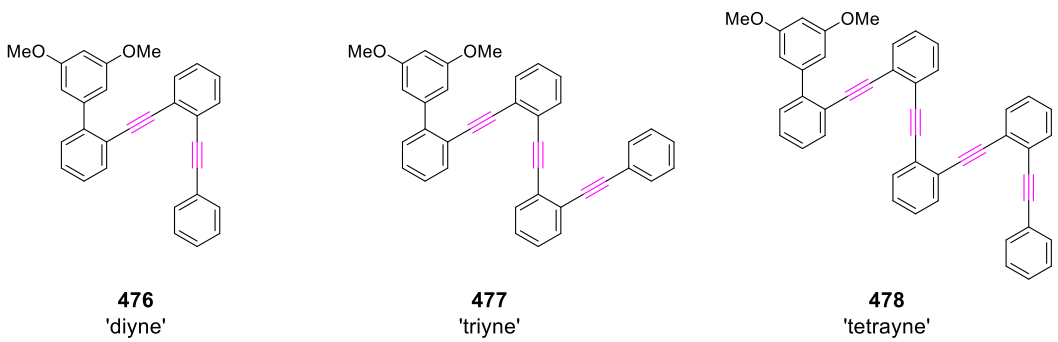
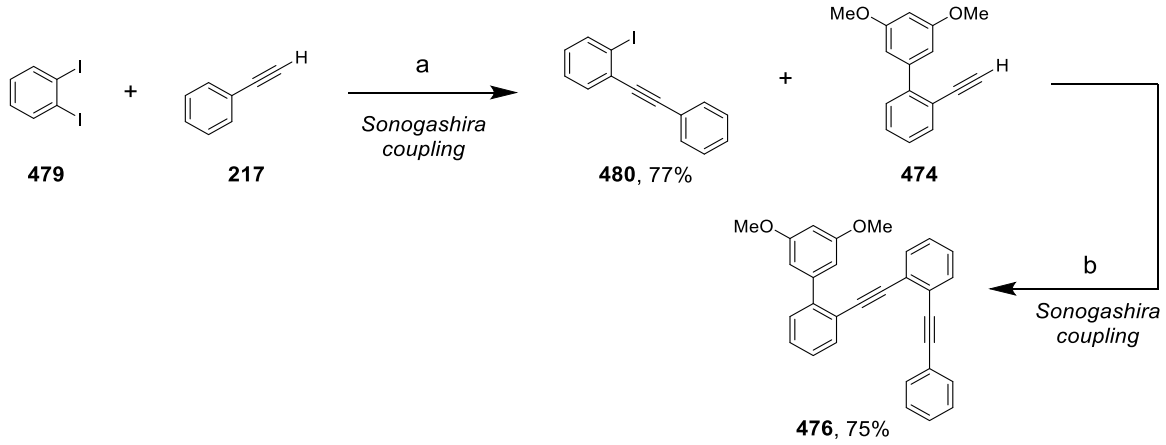


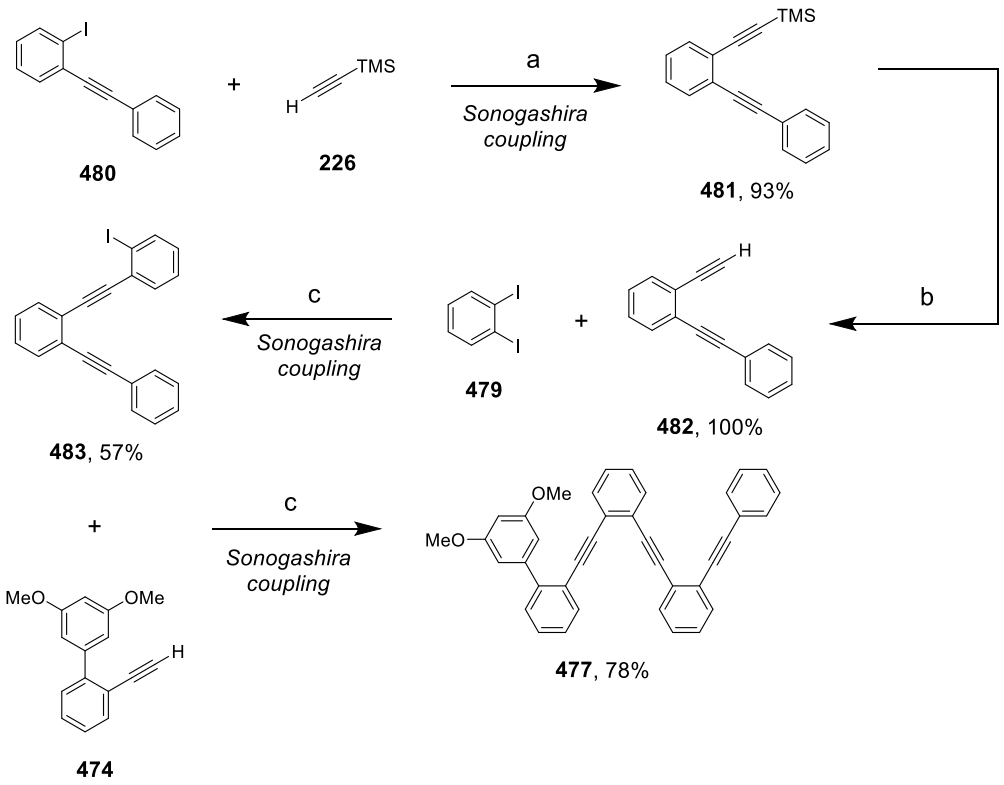
Figure 23: Proposed di-methoxy substituted polyynes for PEC exploration.

The successful synthesis of di-methoxy diyne **476** is outlined within Scheme 114. Synthesis started with the successful Sonogashira coupling of phenylacetylene **217** and diiodobenzene **479** to afford **480** in 77% yield. Sonogashira coupling conditions were then again employed to couple **474** with previously accessed acetylene **474** to furnish desired diyne **476** in 75% yield.



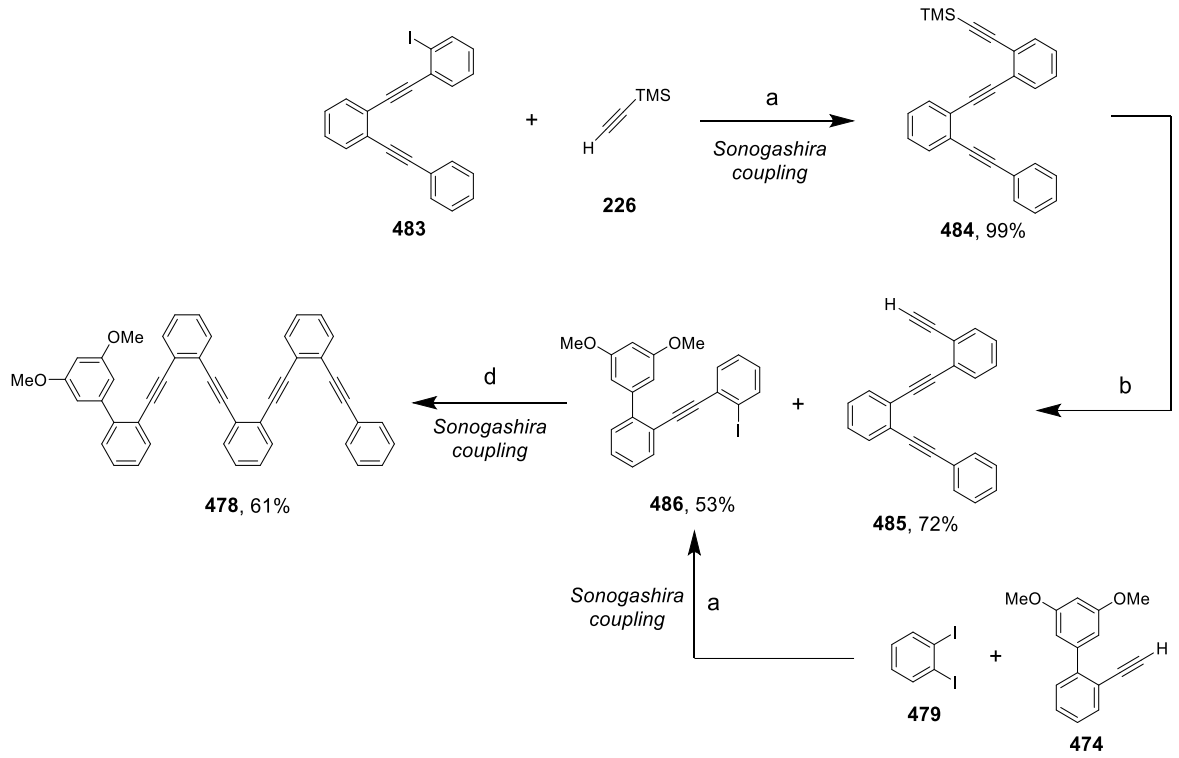
*Scheme 114: Synthesis of diyne **476**. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, toluene, b) CuI, $Pd(PPh_3)_4$, DIPA.*

Scheme 115 describes the successful synthesis of di-methoxy triyne **477**. TMS acetylene **226** was first coupled to previously afforded alkyne **480** to afford TMS diyne **481** in excellent yield of 93%. TMS diyne **226** was then subject to K_2CO_3 in MeOH to remove the TMS group, producing acetylene **482** in quantitative yield. Acetylene **482** was then selectively Sonogashira coupled with 0.5 eq. of diiodobenzene **479** to afford diyne **483**. Finally, diyne **483** and acetylene **474** were coupled *via* Sonogashira conditions to afford the desired triyne **477** in 78% yield.



*Scheme 115: Synthesis of triyne **477**. a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, THF b) K_2CO_3, MeOH, c) CuI, $Pd(PPh_3)_4$, DIPA.*

Finally, Scheme 116 outlines the successful synthesis of di-methoxy tetrayne **478**. Synthesis commenced with previously afforded diyne **483** coupled with TMS acetylene **226** to afford TMS protected triyne **484**. TMS triyne **484** then underwent silyl deprotection to afford unprotected triyne **485** in 72% yield. Previously produced acetylene **474** was then coupled with diiodobenzene **479** to afford alkyne **486**. Lastly, unprotected triyne **485** and alkyne **486** were coupled to afford desired tetrayne **478** in 61% yield. It was extremely pleasing that all 'skipped' polyynes (**476**, **477** and **478**) required within this chapter were furnished smoothly through generally efficient and high yielding synthetic pathways.

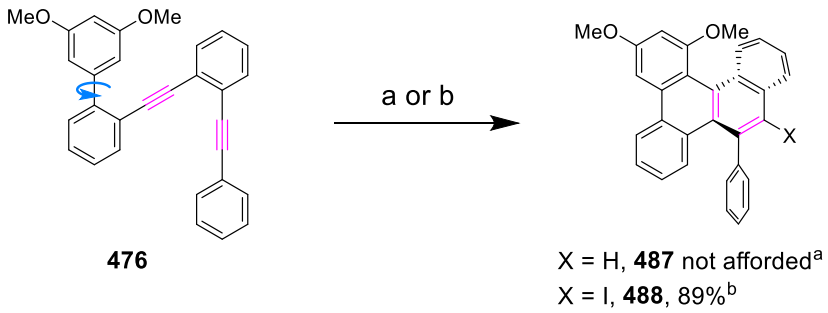


*Scheme 116: Synthesis of tetrayne **478** a) CuI, $Pd(PPh_3)_2Cl_2$, DIPA, b) K_2CO_3, MeOH, Et_2O, c) CuI, $Pd(PPh_3)_2Cl_2$, DIPA:toluene.*

4.4 Poly-iodocyclisation of skipped polyynes

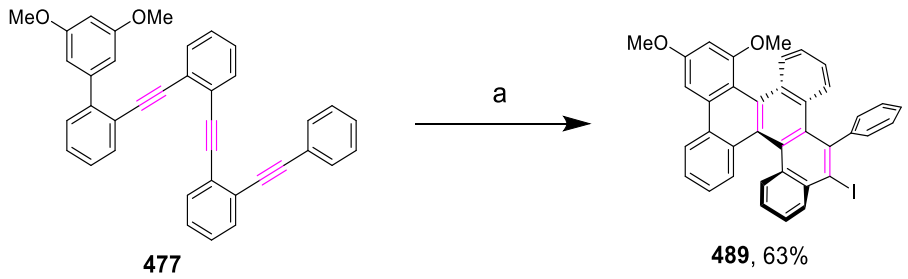
Following the smooth synthesis of 'skipped' polyynes **476**, **477** and **478**, we commenced the PEC cyclisation studies of these polyynes. Scheme 117 depicts the attempted cyclisation of di-methoxy diyne **476** to afford either protocyclised **487** or iodocyclised **488**. Unfortunately, addition of $Cu(OTf)_2$ (20 mol%) to a heated solution of diyne **476** resulted in no conversion to product with only starting material observed in ^{1}H NMR. Further addition of $Cu(OTf)_2$ before allowing the reaction to stir for 2 days at 110 °C did not improve reaction outcome. In parallel to these efforts, iodocyclisation of diyne **476** was also attempted. Addition of NIS and catalytic PPh_3 resin to a solution of diyne **476** in DCE gave complete conversion to poly-iodocyclised product **488** after 18 h at 22 °C. A major indicator of product **488** presence was the 'splitting' of the methoxy peak in ^{1}H NMR, which appeared as a singlet in the ^{1}H NMR of the diyne starting material **476**. Diyne **476** has free rotation about the single bond that connects the methoxy substituted benzene ring to the rest of the compound (blue arrow in Scheme 117). Therefore, as the two methoxy groups of **476** are symmetrical their NMR resonances appear as one singlet (3.71 ppm, 2 × CH_3). However, upon cyclisation each methoxy group is in a different chemical environment and substitution pattern, resulting in the presence of two

separate methoxy singlets at 4.09 and 3.77 ppm. In conjunction with this characteristic change in the methoxy region of ^{1}H NMR, ^{13}C NMR and HRMS data further confirmed the presence of **488**. Column chromatography was utilised to remove any excess NIS or succinimide to afford iodocyclised **488** in 89% yield.



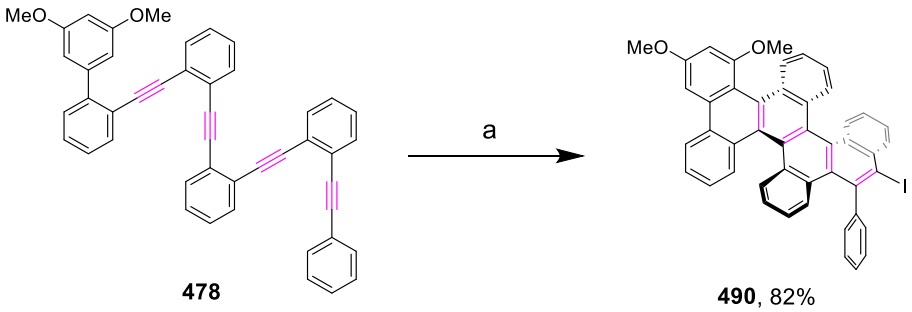
*Scheme 117: Poly-iodocyclisation of diyne **476** to afford **488**. a) Protocyclisatio: Cu(OTf)$_2$ (0.2 eq.), dry toluene, 80 °C, b) Iodocyclisation: NIS (2.2 eq.), PPh$_3$ resin (0.2 eq.) DCE, 18 h 22 °C.*

Following the successful iodocyclisation of di-methoxy diyne **476**, these cyclisation conditions were applied to di-methoxy triyne **477** and tetrayne **478** (Schemes 118 and 119, respectively). Pleasingly, both polyynes successfully poly-iodocyclised to afford products **489** and **490** in 63% and 82% yield, respectively. The presence of **489** and **490** was again confirmed by NMR analysis showing the aforementioned 'splitting' of the methoxy singlet, along with changes in the aromatic region of ^{1}H NMR. This was further confirmed through HRMS and ^{13}C NMR analysis. During attempts to optimise the yield of both **489** and **490**, ^{1}H NMR reaction monitoring indicated the methoxy substituted ring of the cyclised products were sensitive to iodination. Fortunately, by-products of this nature were avoided by careful limitation of both NIS and PPh$_3$ resin equivalence.



477 **489**, 63%

*Scheme 118: Poly-iodocyclisation of triyne **477** to afford **489**. a) NIS (3.2 eq.), PPh_3 resin (0.5 eq.), DCE, 22 °C 20h.*



478 **490**, 82%

*Scheme 119: Poly-iodocyclisation of tetrayne **478** to afford **490**. a) NIS (6 eq.), PPh_3 resin (0.2 eq.), DCE, 22 °C, 20 h.*

4.4.1 Crystal structure of spiralacene product

To confirm the 3D conformation of the spiralacenes furnished in this work, X-ray crystallography was performed by Prof. Jonathan White with poly-iodocyclised product **489** (Fig. 24). Aside from some disorder about one of the methoxy groups (appears as though the oxygen has three CH_3 attached) this crystal structure clearly demonstrates the twisted spiral conformation of spiralacene **489**. The dihedral angles between each plane were measured to be 48.2° and 51.9°, as shown in Figure 24. This is relatively consistent with twisted polyacene **449** (41° and 55°) previously described by Mohamed et al.[225] The inclusion of the methoxy groups likely repel the second plane further back than if all aryl rings were unsubstituted.

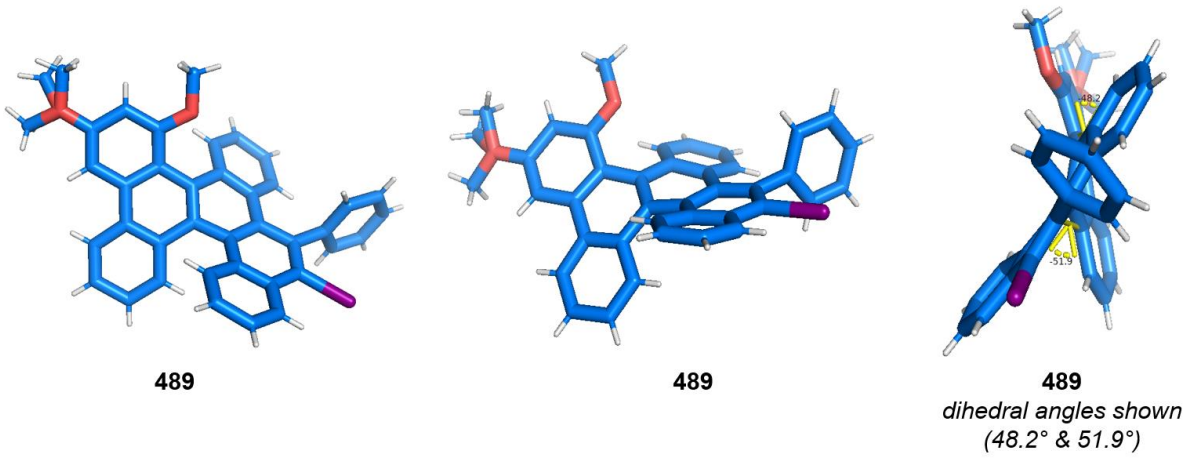


*Figure 24: Crystal structure of poly-iodocyclised product **489**.*

4.5 Conclusions and future work

The concise efforts in this chapter of work have presented further utilisation of PEC to afford poly-fused aryl systems for application to materials science. Materials science chemists need to be able to constantly vary the structure and morphology of molecules utilised to ensure the optimal structure property relationship is achieved. This work has presented an atom-economical domino reaction by which twisted-spiral shaped poly-fused acenes can be afforded from 'skipped' polyynes starting materials (Fig. 25). Di-methoxy substitution patterns were found to confer best cyclisation outcomes with di-methoxy monoyne **462** participating in both proto- and iodo-cyclisation to afford **463** and **464**, respectively. Following the unsuccessful protocyclisation of diyne **476**, iodocyclisation conditions were successfully applied to polyynes **476**, **477** and **478**. X-ray crystallography then confirmed the suspected 3D twisted-spiral shape of spiralacene **489**.

Future work in this space is ongoing within the Flynn lab. These efforts are focused around three main aspects of the work that are remaining. The first focuses on determining the chirality of spiralacenes **489** and **490**, specifically, verifying that they are stable to racemisation (have a high inversion barrier). Following this, chiral phosphines will also be explored for their application with the aim of inducing a particular enantiomer. The second aspect pertains to Pd-mediated coupling with spiralacene **490** to install an EWG such as 4-nitrophenyl boronic acid (Scheme 120). Upon coupling, **492** possess both an acceptor and donor. The presence of both groups can have important implications to electronic and photonic activity. Finally, DDQ-mediated oxidation of spiralacene **490** or **492** will be explored to exemplify the utility of

spiralacenes as they can be employed in their twisted form or ‘flattened’ out to afford polyacene ribbon **493** or **494**.

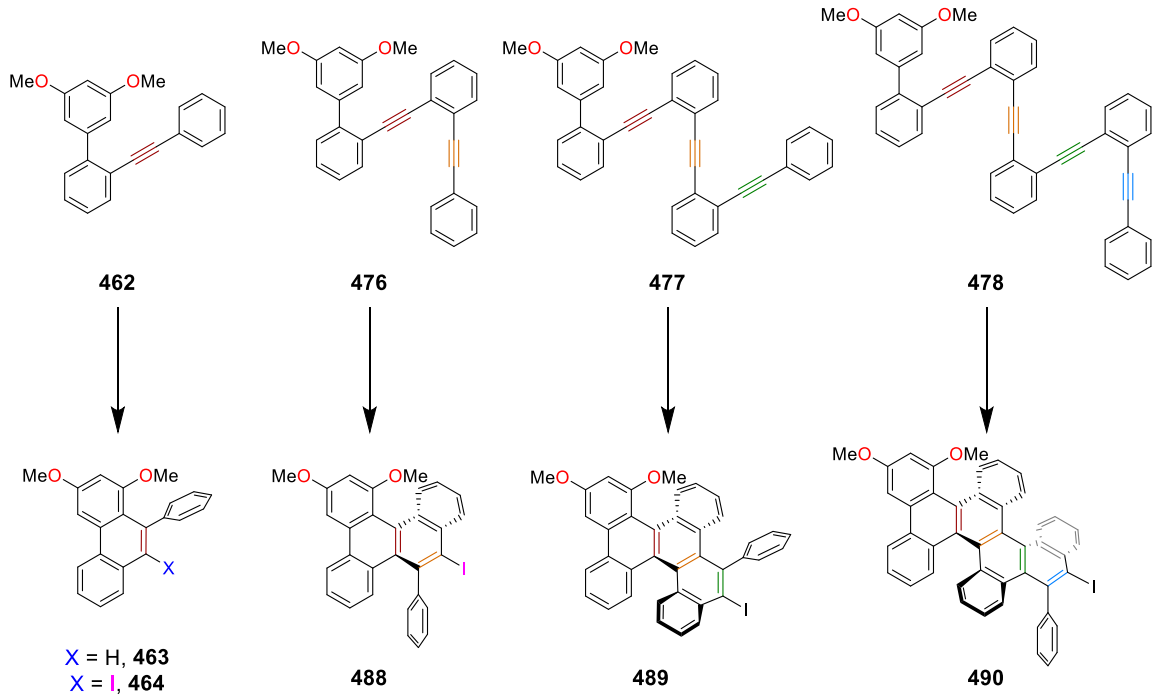
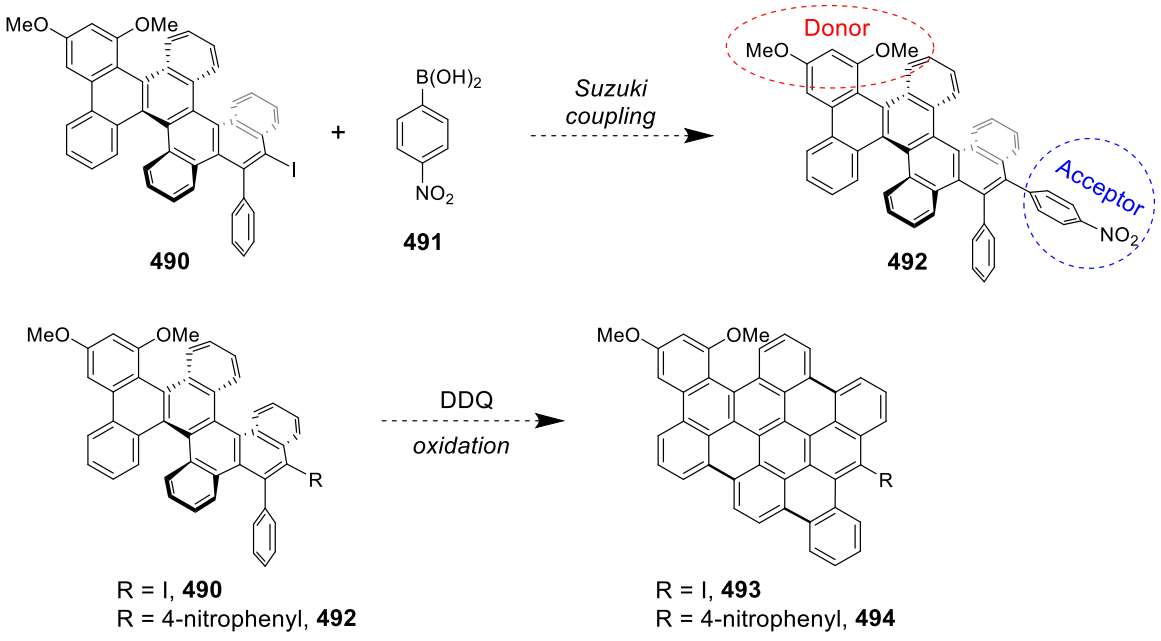


Figure: 25: Non-planar poly-fused acenes afforded through domino poly-iodocyclisation of ‘skipped’ polyynes.



Scheme 120: Future work proposed within the spiralacene project.

5.0 Experimental

5.1 General experimental

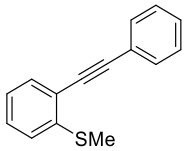
All reactions were performed under an inert atmosphere of anhydrous $N_{2(g)}$ and all glassware was dried by heating under vacuum before use. All reactions heated above 22 °C were performed by placing the reaction RBF in a heated sand bath. DCE and THF were purchased in an anhydrous form and stored under $N_{2(g)}$. All column chromatography was performed on silica gel (40−63 μm or 20-45 μm). Analytical TLC was performed using aluminium backed 0.2 mm thick silica gel 60 GF254 plates. TLC plates were analysed using a 254 nm UV lamp and/or stained using a solution of phosphomolybdic acid (5% w/v ethanol) followed by heating. ^{1}H NMR spectra were obtained at 400 MHz, ^{77}Se NMR spectra at 76 MHz and ^{13}C DEPT-Q NMR spectra at 100 MHz, the number of attached hydrogens to each carbon atom was determined using Distortionless Enhancement by Polarization Transfer with detection of quaternary carbons (DEPTQ-135), as indicated. High-resolution mass spectra were recorded on both a time-of-flight mass spectrometer fitted with either an electrospray (ESI) ion or atmospheric pressure chemical ionization (APCI) source, the capillary voltage was 4000 V or on an exactive mass spectrometer fitted with an ASAP ion source. The nitrogen nebulizing/desolvation gas used for vaporization was heated to 550 °C in these experiments. The sheath gas flow rate was set to 10, the auxiliary gas flow rate to 0 and the sweep gas flow rate to 2 (all arbitrary units). The discharge current was 4 mA and the capillary temperature was 320 °C. Liquid chromatography−Mass spectrometry (LC−MS) was performed using either APCI or ESI LC−MS. Each method used 254 nm detector and a reverse phase C8(2) 5 μ 50 × 4.6 mm 100A column. The column temperature was 30 °C and the injection volume was 5 μL. The eluent system used was H_2O containing 0.1% formic acid (solvent A) and ACN containing 0.1% formic acid (solvent B). The gradient for ESI LC-MS was 5 to 100% B over A in 4 min then 100% B for 6 min. The gradient for APCI LC-MS was 5 to 100% B over A in 2 min then 100% B for 2 min. Triphenylphosphine resin: (diphenylphosphineopolystyrene, 0.9±0.06 mmol/g).

The following materials were prepared according to literature procedures: (bromoethynyl)trimethylsilane (**231**),[233] 3-bromoprop-2-yn-1-ol (**252**),[234] 5-(triisopropylsilyl)penta-2,4-diyn-1-ol (**253**),[235] ((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (**267**),[191] 1-ethynyl-2-methoxybenzene,[142] ((3,4-dibromothiophene-2,5-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (**360**),[236] 1,4-bis(2-(methylthio)phenyl)buta-

1,3-diyne (**386**) and **413**,[9] 3'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (**467**),[229] 2-(2,2-dibromovinyl)-3'-methoxy-1,1'-biphenyl (**468**) and 2-ethynyl-3'-methoxy-1,1'-biphenyl (**469**),[228] ((2-bromophenyl)ethynyl)trimethylsilane (**471**),[237] 1-iodo-2-(phenylethynyl)benzene (**480**),[238] trimethyl((2-(phenylethynyl)phenyl)ethynyl)silane (**481**) and 1-ethynyl-2-(phenylethynyl)benzene (**482**).[239]

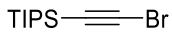
5.2 Chapter 2 Experimental

Methyl(2-(phenylethynyl)phenyl)sulfane (213):



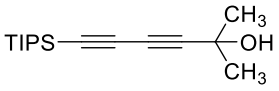
To a RBF under $N_{2(g)}$ was added 2-iodothioanisole (1.0 g, 3.9 mmol), $Pd(PPh_3)_2Cl_2$ (56.12 mg, 0.0799 mmol), CuI (7.61 mg, 0.039 mmol) and Et_3N (16 mL). The solution was allowed to stir for 5 min at 22 °C before phenylacetylene (0.53 mL, 4.7 mmol, as a 1 M solution in Et_3N) was added dropwise over 10 min. The reaction was then degassed with $N_{2(g)}$ × 2 before being allowed to stir for 2 h at 22 °C. The reaction was then dilute with EtOAc and filtered through a pad of Celite® before being washed with brine (2 × 10 mL). The organic solution was then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude orange oil was then furnished with no purification (875 mg, 100% mass-balance for a material of 97% purity by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.32 – 7.28 (m, 1H), 7.20 – 7.17 (m, 1H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 2.52 (s, 3H). LCMS: t_R = 7.7 min, *m/z*: 225.0 [M+H$^+$]. These data are consistent with that previously reported for this compound.[240]

(Bromoethynyl)triisopropylsilane (222):



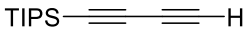
To a RBF under $N_{2(g)}$ was added (triisopropylsilyl)acetylene (6.15 mL, 27.4 mmol), NBS (5.61 g, 31.5 mmol), $AgNO_3$ (4.65 g, 27.4 mmol) and acetone (100 mL). The reaction was allowed to stir at 22 °C for 2 h. The reaction was then quenched through addition of H_2O (30 mL) and diluted with hexanes (10 mL). After separation, the aqueous layer was extracted with additional hexanes (3 × 25 mL) and washed with brine (2 × 20 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a clear oil (7.29 g, 102% mass-balance for a material of 98% purity by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (d, *J* = 1.2 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.6 (C), 61.8 (C), 18.6 (6 × CH_3), 11.4 (3 × CH). These data are consistent with that previously reported for this compound.[241]

2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (224):



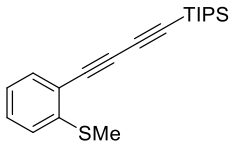
To a RBF under $N_{2(g)}$ was added 2-methylbut-3-yn-2-ol (10.7 mL, 109 mmol), *n*-butylamine (16.3 mL, 164 mmol), CuCl (162.8 mg, 1.644 mmol), $HONH_2.HCl$ (1.14 g, 16.4 mmol), MeOH (160 mL) and H_2O (80 mL). The reaction was then degassed with $N_{2(g)}$ × 3 before **222** (14.33 g, 54.85 mmol, as 0.55 M MeOH solution) was added slowly. The reaction was then allowed to stir for 24 h at 22 °C. After this time the reaction was quenched through addition of H_2O (15 mL) and diluted with Et_2O (10 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 20 mL) and washed with 10% citric acid solution (3 × 10 mL) and brine (2 × 20mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a cream solid (14.3 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 6H), 1.08 (s, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 89.0 (C), 84.8 (C), 80.8 (C), 67.8 (C), 65.6 (C), 31.1 (CH_3), 18.6 (6 × CH_3), 11.3 (3 × CH). These data are consistent with that previously reported for this compound.[163]

Buta-1,3-diyn-1-yltriisopropylsilane (225):



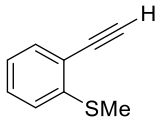
To a RBF under $N_{2(g)}$ was added **224** (500 mg, 1.89 mmol), potassium *tert*-butoxide (1.27 g, 11.3 mmol) and toluene (10 mL). The reaction was then heated at reflux for 2 h. After this time the reaction was cooled to 22 °C before being quenched through addition of H_2O (10mL) and diluted with hexanes (5 mL). After separation, the aqueous layer was extracted with additional hexanes (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a brown oil (400 mg, 103% mass-balance for a material of 98% purity by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 1H), 1.09 (s, 21H); LCMS (APCI hydrophobic): t_R = 1.9 min *m/z*: 207.0 [$M+H^+$]. These data are consistent with that previously reported for this compound.[242]

Triisopropyl((2-(methylthio)phenyl)buta-1,3-diyn-1-yl)silane (228):



To a RBF under $N_{2(g)}$ was added 2-iodothioanisole (0.08 mL, 0.59 mmol), PPh_3 (15.7 mg, 0.059 mmol), $Pd(PPh_3)_4$ (34.6 mg, 0.029 mmol) and Et_3N (3 mL). The reaction was degassed with $N_{2(g)}$ × 3 before CuI (17.1 mg, 0.089 mmol) was added and the reaction degassed again. The reaction was then heated to 50 °C. A degassed solution of **225** (264.5 mg, 1.281 mmol) in Et_3N (6.4 mL) was then added slowly to the reaction mixture and the reaction was allowed to stir for 2.5 h at 50 °C. After this time the reaction was quenched through gradual addition of a sat. aq. NH_4Cl solution (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) and washed with a sat. aq. NH_4Cl solution (2 × 10 mL) and brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then purified by flash column chromatography (silica gel, 100% hexanes) to give the title compound as a yellow oil (200 mg, 103% mass-balance for a material of 98% purity by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.07 (td, *J* = 7.7, 1.2 Hz, 1H), 2.50 (s, 3H), 1.12 (d, *J* = 1.3 Hz, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 143.4 (C), 133.9 (CH), 129.6 (CH), 124.4 (CH), 119.7 (C), 89.8 (C), 89.4 (C), 80.8 (C), 72.8 (C), 18.6 (6 × CH_3), 15.2 (CH_3), 11.4 (3 × CH); LCMS: t_R = 9.5 min *m/z*: 329.2 [M+H$^+$]; HRMS (APCI) *m/z* [M+H]$^+$ Calcd. for $C_{20}H_{29}SSi$ 329.1754, Found 329.1754.

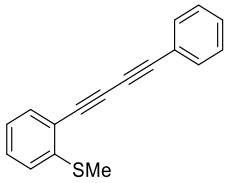
(2-Ethynylphenyl)(methyl)sulfane (129):



To a RBF under $N_{2(g)}$ was added 2-iodothioanisole (4.5 mL, 30 mmol), CuI (457 mg, 2.40 mmol), $Pd(PPh_3)_2Cl_2$ (632 mg, 0.90 mmol) and Et_3N (100 mL). The reaction was then degassed with $N_{2(g)}$ × 3 before trimethylsilylacetylene (5.0 mL, 36 mmol) was added dropwise. The reaction was allowed to stir at 22 °C for 18 h. The reaction mixture was then concentrated under reduced pressure before being taken up into Et_2O and filtered over a pad of Celite®, washing with Et_2O. The organic solution was then washed with H_2O (2 × 15 mL) and brine (2

× 15 mL). The organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then filtered through a pad of silica, washing with Et_2O. This gave the **229** as a yellow oil (6.7 g) and a portion of this material was directly used in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H), 7.31 – 7.25 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06 (td, *J* = 7.5, 1.2 Hz, 1H), 2.48 (s, 3H), 0.28 (s, 9H); LCMS: t_R = 6.1 min *m/z*: 221.0 [M+H$^+$]. To a RBF under $N_{2(g)}$ was added **229** (6.3 g, 28 mmol), KF (2.61 g, 44.9 mmol), Et_2O (20 mL) and MeOH (100 mL). The reaction was allowed to stir for 18 h at 22 °C. The reaction mixture was then concentrated under reduced pressure, taken up into Et_2O and wash with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a dark oil (4.4 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.19 – 7.15 (m, 1H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 3.47 (s, 1H), 2.50 (s, 3H); LCMS: t_R = 3.8 min *m/z*: 142.2 [M+H$^+$]. These data are consistent with that previously reported for this compound.[243]

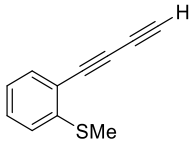
Methyl(2-(phenylbuta-1,3-diyn-1-yl)phenyl)sulfane (232):



To a RBF under $N_{2(g)}$ was added **129** (643 mg, 4.34 mmol), *n*-butylamine (1.13 mL, 11.4 mmol), CuCl (11.3 mg, 0.114 mmol), $HONH_2$.HCl (79.78 mg, 1.148 mmol) and MeOH (18 mL). (Bromoethynyl)benzene (1.0 g, 3.8 mmol) was then slowly added before the reaction was degassed with $N_{2(g)}$. The solution was allowed to stir for 18 h at 22 °C. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with Et_2O (10 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 15 mL) and washed with a 10% citric acid solution (2 × 10 mL) and brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 5% DCM in hexanes) to give the title compound as a pale yellow solid (975 mg, 103% mass-balance for a material of 97% purity by ^{1}H NMR). mp. 41-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.49 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.34 (dddd, *J* = 9.0, 7.7, 4.0, 1.1 Hz, 4H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.10 (td, *J* = 7.7, 1.1

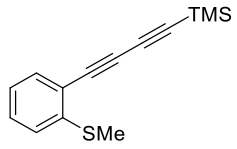
Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 143.3 (C), 133.6 (CH), 132.5 (CH), 129.6 (CH), 129.3 (CH), 128.5 (CH), 124.5 (CH), 124.4 (CH), 121.8 (C), 120.0 (C), 83.5 (C), 80.0 (C), 78.9 (C), 73.9 (C), 15.3 (CH_3); LCMS: t_R = 7.4 min *m/z*: 249.1 [M+H$^+$]; HRMS (APCI) *m/z* [M+H]$^+$ Calcd. for $C_{17}H_{13}S$ 249.0732, Found 249.0724.

(2-(Buta-1,3-diyn-1-yl)phenyl)(methyl)sulfane (233):



To an RBF under $N_{2(g)}$ was added **228** (850 mg, 2.58 mmol) and THF (7.5 mL). The solution was then cooled to 0 °C before TBAF (6 mL of a 1 M solution in THF) and acetic acid (0.35 mL) were added. The reaction was allowed to warm to 22 °C and stir at this temperature for 4 h. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with Et_2O (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) before being washed with sat. aq. NH_4Cl solution (1 × 10 mL) and brine (2 × 10 mL), MeOH was then added to aid layer separation (5 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was used in further reactions as a semi-pure oil (contains EtOAc and MeOTIPS). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.33 (td, *J* = 8.0, 1.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08 (m, 1H), 2.61 (s, 1H), 2.50 (s, 3H). These data are consistent with that previously reported for this compound.[9]

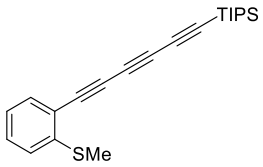
Trimethyl((2-(methylthio)phenyl)buta-1,3-diyn-1-yl)silane (234):



To a RBF under $N_{2(g)}$ was added **233** (101.6 mg, 0.589 mmol) and anhydrous THF (5 mL). The reaction was then cooled to -78 °C before *n*-BuLi (0.25 mL of a 2.46 M solution in pentane) was added dropwise. The reaction was then allowed to stir at this temperature for 1 h before trimethylsilyl chloride (0.08 mL, 0.63 mmol) was added. The reaction was allowed to warm to 22 °C and stir at this temperature for 24 h. The reaction was quenched through addition of H_2O

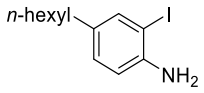
(5 mL) and diluted with Et_2O (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 5 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then purified by flash column chromatography (silica gel, 25% DCM in hexanes), to give the title compound as a brown oil (41 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 2.49 (s, 3H), 0.23 (s, 9H). LCMS: t_R = 7.6 min *m/z*: 244.1 [M^+]. These data are consistent with that previously reported for this compound.[244]

Triisopropyl((2-(methylthio)phenyl)hexa-1,3,5-triyn-1-yl)silane (235):



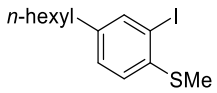
To an RBF under $N_{2(g)}$ was added **233** (1.57 g, 9.12 mmol), *n*-butylamine (2.25 mL, 22.8 mmol), CuCl (22.5 mg, 0.228 mmol), $HONH_2$.HCl (158.6 mg, 2.282 mmol) and MeOH (20 mL). **222** (1.98 g, as a 0.76 M solution in MeOH) was then slowly added and the reaction was allowed to stir for 18 h at 22 °C. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with Et_2O (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) before being washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then purified by flash column chromatography (silica gel, 10% DCM in hexanes) to give the title compound as a yellow-brown solid (1.6 g, 62%). mp 32-39 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.33 (ddd, *J* = 8.0, 7.5, 1.1 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1H), 2.49 (s, 3H), 1.09 (d, *J* = 2.1 Hz, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 144.4 (C), 134.2 (CH), 130.1 (CH), 124.6 (CH), 124.5 (CH), 119.2 (C), 89.9 (C), 87.7 (C), 80.4 (C), 73.9 (C), 69.3 (C), 60.4 (C), 18.6 (6 × CH_3), 15.3 (3 × CH_3), 11.4 (CH); LCMS: t_R = 9.6 min *m/z*: 353.2 [M+H^+], 354.2 [M+2H^+]; HRMS (APCI) *m/z* [M+H]$^+$ Calcd. for $C_{22}H_{29}SSi$ 353.1754, Found 353.1762.

4-Hexyl-2-iodoaniline (244):



To a RBF under $N_{2(g)}$ in the dark was added 4-hexylaniline (6.5 mL, 33.84 mmol), iodine (8.58 g, 33.8 mmol), $NaHCO_3$ (3.41 g, 40.6 mmol) in H_2O (40 mL) and DCM (17 mL). The reaction was then allowed to stir for 18 h at 22 °C. After this time the reaction was dilute with H_2O (10 mL) and sat. solution of $Na_2S_2O_3$ (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil (10.1 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.8 Hz, 1H), 6.95 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.38 (s, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.60 – 1.47 (m, 2H), 1.35 – 1.18 (m, 6H), 0.88 (dd, *J* = 9.2, 4.4 Hz, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 144.5 (C), 138.5 (CH), 134.9 (C), 129.5 (CH), 114.8 (CH), 84.5 (C), 34.6 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 14.2 (CH_3); LCMS: t_R = 7.5 min *m/z* : 304.1 [M+H$^+$]; HRMS (APCI) *m/z* [M]$^+$ Calcd. for $C_{12}H_{18}IN$ 303.0478, Found 303.0475.

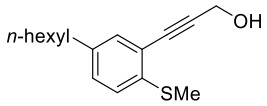
(4-Hexyl-2-iodophenyl)(methyl)sulfane (245):



To a RBF under $N_{2(g)}$ was added dimethyl disulfide (47.5 mL, 527 mmol) and isopentyl nitrite (10.6 mL, 79.1 mmol). **244** (8.0 g, 26 mmol) was then slowly added and the reaction was allowed to reflux at 70-80 °C for 2 h. After this time the reaction was concentrated under reduced pressure before being diluted with H_2O (15 mL) and Et_2O (15 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 20 mL) and washed with H_2O (15 mL) and brine (2 × 15 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then purified with a silica plug, eluting with hexanes to give the title compound as a deep red oil (8.1 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.8 Hz, 1H), 7.15 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 1.61 – 1.51 (m, 2H), 1.34 – 1.27 (m, 6H), 0.95 – 0.85 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 141.6 (C), 139.7 (C), 139.4 (CH), 129.1

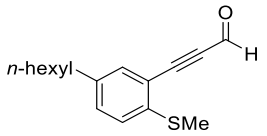
(CH), 125.5 (CH), 98.1 (C), 34.9 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 17.4 (CH_3), 14.2 (CH_3); HRMS (APCI) *m/z* $[M]^+$ Calcd. for $C_{13}H_{19}IS$ 334.0247, Found 334.0238.

3-(5-Hexyl-2-(methylthio)phenyl)prop-2-yn-1-ol (247):



To a RBF under $N_{2(g)}$ was added **245** (1.0 g, 2.9 mmol), CuI (56.97 mg, 0.2991 mmol), $Pd(PPh_3)_2Cl_2$ (104.9 mg, 0.1495 mmol) and Et_3N (10 mL). The reaction was then degassed with $N_{2(g)}$ × 3 before adding propargyl alcohol (0.26 mL, 4.4 mmol) and allowing the solution to stir for 18 h at 22 °C. After this time the reaction mixture was dilute with Et_2O before being filtered over a Celite® pad. The organic solution was then washed with H_2O (1 × 20 mL) and brine (2 × 20 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The dark oil was then subject to flash column chromatography (silica gel, 20% EtOAc in hexanes) to give the title compound as a dark orange oil (785 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.13 – 7.06 (m, 2H), 4.56 (s, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 2H), 1.57 (p, J = 7.3 Hz, 1H), 1.34 – 1.25 (m, 6H), 0.90 – 0.85 (m, 2H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.4 (C), 137.8 (C), 132.6 (CH), 129.3 (CH), 124.8 (CH), 120.9 (C), 93.3 (C), 83.2 (C), 51.5 (CH_2), 35.0 (CH_2), 31.6 (CH_2), 31.2 (CH_2), 28.8 (CH_2), 22.6 (CH_2), 15.4 (CH_3), 14.1 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{16}H_{23}OS$ 263.1464, Found 263.1459.

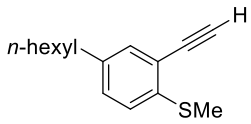
3-(5-Hexyl-2-(methylthio)phenyl)propiolaldehyde (248):



To a RBF under $N_{2(g)}$ was added **247** (3.0 g, 11 mol) and dichloromethane (120 mL). The reaction was then cooled to 0 °C before Dess-Martin periodinane (7.26 g, 17.11 mmol) was slowly added. The reaction mixture was warmed to 22 °C and allowed to stir at this temperature for 20 min. After this time the reaction was quenched through addition of EtOH (5 mL) and Et_2O (100 mL) and filtered through a Celite® pad. The organic solution was then washed with

1 M NaOH (3 × 20 mL), a saturated solution of $Na_2S_2O_3$ (3 × 20 mL) and brine (2 × 20 mL). The organic solution was then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as an orange oil (2.7 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.41 – 7.36 (m, 1H), 7.28 – 7.21 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.51 (s, 3H), 1.62 – 1.53 (m, 2H), 1.29 (dt, *J* = 5.9, 3.3 Hz, 6H), 0.91 – 0.85 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 176.5 (CH), 141.3 (C), 139.7 (C), 134.5 (CH), 132.2 (CH), 125.2 (CH), 117.6 (C), 93.7 (C), 92.9 (C), 34.9 (CH_2), 31.7 (CH_2), 31.1 (CH_2), 28.8 (CH_2), 22.6 (CH_2), 15.4 (CH_3), 14.1 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{16}H_{21}OS$ 261.1308, Found 261.1307.

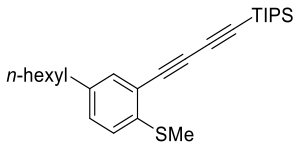
(2-Ethynyl-4-hexylphenyl)(methyl)sulfane (255):



To a RBF under $N_{2(g)}$ was added **245** (3.0 g, 8.9 mmol), CuI (17.09 mg, 0.0897 mmol), $Pd(PPh_3)_2Cl_2$ (125.9 mg, 0.1795 mmol) and Et_3N (30 mL). The reaction was then degassed with $N_{2(g)}$ × 3 before trimethylsilylacetylene (1.5 mL, 10.77 mmol) was added dropwise. The reaction was allowed to stir at 22 °C for 18 h. The reaction mixture was then concentrated under reduced pressure before being taken up into Et_2O and filtered over a pad of Celite®, washing with Et_2O. The organic solution was washed with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then subject to flash column chromatography (silica gel, 100% hexanes) to give **((5-hexyl-2-(methylthio)phenyl)ethynyl)trimethylsilane** as an orange oil (2.3 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.11 – 7.04 (m, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 1.57 (s, 2H), 1.28 (m, 6H), 0.88 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.3 (C), 138.6 (C), 132.8 (CH), 129.5 (CH), 124.7 (CH), 121.4 (C), 102.7 (C), 100.7 (C), 35.2 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 15.4 (CH_3), 14.2 (CH_3), 0.1 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{18}H_{29}SSi$ 305.1662, Found 305.1675. To a RBF under $N_{2(g)}$ was added **((5-hexyl-2-(methylthio)phenyl)ethynyl)trimethylsilane** (2.3 g, 7.5 mmol), TBAF (15 mL of a 1.0 M solution in THF) and THF (38 mL). he reaction was allowed to stir at 22 °C for 30 min. After this time, the reaction was quenched with H_2O (25 mL). After separation, the aqueous layer

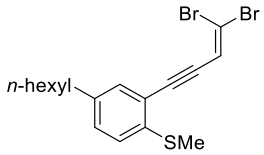
was extracted with additional Et_2O (3 × 20 mL) and washed with sat. NH_4Cl (aq.) (15 mL) and brine (2 × 15 mL). The combined organics were dried with $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil (1.63 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.5 Hz, 1H), 7.16 – 7.07 (m, 2H), 3.43 (s, 1H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.49 (s, 3H), 1.55 (s, 2H), 1.28 (s, 6H), 0.88 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.7 (C), 138.5 (C), 133.4 (CH), 129.8 (CH), 125.2 (CH), 83.0 (C), 35.2 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 15.7 (CH_3), 14.2 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{15}H_{21}S$ 233.1355, Found 233.1358.

((5-Hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)triisopropylsilane (257):



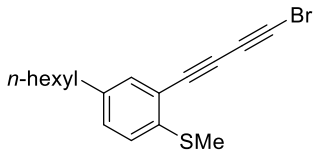
To a RBF under $N_{2(g)}$ was added **245** (1.53 g, 4.59 mmol), PPh_3 (120.5 mg, 0.4595 mmol), $Pd(PPh_3)_4$ (265 mg, 0.229 mmol), CuI (131.2 mg, 0.6892 mmol) and Et_3N (23 mL). The reaction flask was then degassed with $N_{2(g)}$ before **225** (8.13 mL of a 1.13 M solution in Et_3N) was added dropwise. The reaction was allowed to stir for 1 h at 50 °C. The reaction mixture was then concentrated under reduced pressure before being taken up into Et_2O and filtered over a pad of Celite®, washing with Et_2O. The organic solution was then washed with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified with flash column chromatography (silica gel, 100% hexanes) to give the title compound as a yellow oil (1.4 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 1.6 Hz, 1H), 7.11 (dt, *J* = 16.1, 5.0 Hz, 2H), 2.57 – 2.49 (t, *J* = 7.7 Hz, 2H), 2.48 (s, 3H), 1.60 – 1.49 (m, 2H), 1.30 (d, *J* = 6.7 Hz, 6H), 1.12 (s, 21H), 0.89 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.9 (C), 139.6 (C), 134.0 (CH), 130.1 (CH), 125.2 (CH), 120.0 (C), 89.5 (2 × C), 80.2 (C), 73.3 (C), 35.1 (CH_2), 31.8 (CH_2), 31.2 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 18.7 (6 × CH_3), 15.7 (CH_3), 14.2 (CH_3), 11.4 (3 × CH); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{26}H_{41}SSi$ 413.2693, Found 413.2703.

(2-(4,4-Dibromobut-3-en-1-yn-1-yl)-4-hexylphenyl)(methyl)sulfane (262):



Toa RBF under $N_{2(g)}$ was added **248** (173.6 mg, 0.666 mmol), CBr_4 (329 mg, 0.992 mmol) and dichloromethane (4.7 mL). The solution was then cooled to 0 °C before PPh_3 (520.5 mg, 1.984 mmol) was added and allowed to stir at the temperature for 15 mins. The reaction was diluted with Et_2O (20 mL) and filtered over a Celite® pad. The organic solution was then washed with brine (2 × 15 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to column chromatography (silica gel, 25% Et_2O in hexanes) to give the title compound as a dark-orange oil (203 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.16 – 7.06 (m, 2H), 6.85 (s, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.48 (s, 3H), 1.58 (d, *J* = 8.7 Hz, 2H), 1.34 – 1.27 (m, 6H), 0.91 – 0.85 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.5 (C), 138.6 (C), 132.7 (CH), 130.0 (CH), 125.1 (C), 120.8 (CH), 101.9 (C), 95.0 (C), 91.6 (C), 35.1 (CH_2), 31.7 (CH_2), 31.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.6 (CH_3), 14.2 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{17}H_{21}Br_2S$ 416.9705, Found 416.9692.

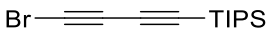
(2-(Bromobuta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (263):



To a RBF under $N_{2(g)}$ was added **262** (412 mg, 0.989 mmol) and anhydrous THF (5 mL). The solution was cooled to -78 °C followed by the drop-wise addition of LiHMDS (0.99 mL of a 1 M solution in THF). The reaction mixture was allowed to stir at -78 °C for 30 min before being warmed to 0 °C and stirring at this temperature for 1 h. After this time the reaction was quenched through addition of a saturated solution of $Na_2S_2O_3$ (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 20 mL) and washed with brine (2 × 15 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil (331 mg, 100%). ^{1}H NMR (400 MHz, , $CDCl_3$) δ 7.29 (dd, J = 1.9, 0.6 Hz, 1H), 7.17 – 7.06 (m, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.48 (s, 3H), 1.61 – 1.50 (m, 2H), 1.33 – 1.23 (m, 6H), 0.91 – 0.85 (m, 3H); ^{13}C NMR (DEPT-

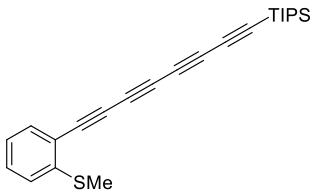
Q, 100 MHz, $CDCl_3$) δ 140.3 (C), 139.7 (C), 133.9 (CH), 130.4 (CH), 125.3 (CH), 119.5 (C), 79.8 (C), 71.9 (C), 65.5 (C), 46.3 (C), 35.1 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.7 (CH_3), 14.2 (CH_2). HRMS (ESI) *m/z* $[M+H]^+$ Calcd. for $C_{17}H_{20}BrS$ 335.0464, Found 335.0449.

(Bromobuta-1,3-diyn-1-yl)triisopropylsilane (264):



To a RBF under $N_{2(g)}$ was added **225** (400 mg, 1.93 mmol), NBS (413.9 mg, 2.325 mmol), $AgNO_3$ (32.9 mg, 0.193 mmol) and acetone (9.6 mL). The reaction was allowed to stir at 22 °C for 6 h before being diluted with H_2O (10 mL) and hexanes (5 mL). After separation, the aqueous layer was extracted with additional hexanes (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was afforded as a brown oil (476 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 21H). These data are consistent with that previously reported for this compound.[162]

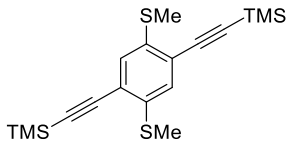
Triisopropyl((2-(methylthio)phenyl)octa-1,3,5,7-tetrayn-1-yl)silane (237):



To a RBF under $N_{2(g)}$ was added **233** (834 mg, 4.844 mmol), CuCl (14.3 mg, 0.145 mmol), $HONH_2$.HCl (101 mg, 1.45 mmol), *n*-butylamine (1.5 mL, 15 mmol) and Et_2O (12 mL). The reaction flask was degassed with $N_{2(g)}$ × 3 before **264** (1.2 g, 4.2 mmol) was added. The reaction was then allowed to stir for 18 h at 22 °C. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with Et_2O (10 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 15 mL) and washed with a 10% citric acid solution (2 × 10 mL) and brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 100% hexanes) to give the title compound as an orange oil (348 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.08 (td, *J* = 7.8, 1.2 Hz, 1H), 2.50 (s, 3H), 1.09 (d, *J* = 2.5 H, 21H);

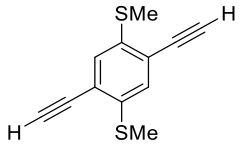
^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 144.7 (C), 134.5 (CH), 130.4 (CH), 124.7 (CH), 124.6 (CH), 118.8 (C), 89.7 (C), 87.2 (C), 80.4 (C), 74.0 (C), 69.4 (C), 65.4 (C), 61.3 (C), 61.2 (C), 18.6 (6 × CH_3), 15.3 (CH_3), 11.4 (3 × CH); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{24}H_{29}SSi$ 377.1754, Found 377.1744.

((2,5-Bis(methylthio)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (108):



To a RBF under $N_{2(g)}$ was added **267** (1.0 g, 2.3 mmol) and anhydrous THF (12 mL). The solution was cooled to -78 °C followed by the drop-wise addition of *n*-BuLi (2.9 mL of a 2.02 M solution in THF). The reaction mixture was allowed to stir at this temperature for 1 h before adding S-methyl methanesulfonothioate (0.55 mL, 5.8 mmol). The reaction was warmed to 22 °C and allowed to stir at this temperature for 1 h. After this time the reaction was quenched through slow addition of NH_4Cl sat. solution (100 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 50 mL) and washed with brine (2 × 50 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 10% DCM in hexanes) to give the title compound as a yellow solid (356 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 2.47 (s, 6H), 0.28 (s, 18H). This data is consistent with that previously reported for this compound.[133]

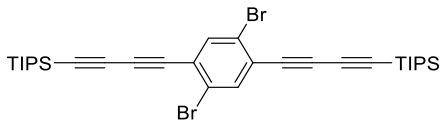
(2,5-Diethynyl-1,4-phenylene)bis(methylsulfane) (270):



To a RBF under $N_{2(g)}$ was added **108**(48.1 mg, 0.132 mmol), KF (23.11 mg, 0.3978 mmol), Et_2O (0.5 mL) and MeOH (2.5 mL). The reaction was allowed to stir for 18 h at 22 °C. The reaction mixture was then concentrated under reduced pressure, taken up into Et_2O and wash with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a white solid (28 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 2H), 3.55 (s, 2H), 2.49 (s, 6H); ^{13}C NMR

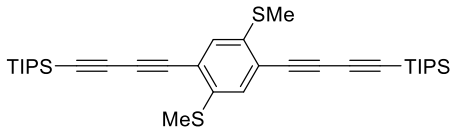
(DEPT-Q, 100 MHz, $CDCl_3$) δ 138.1 (C), 129.2 (CH), 121.7 (C), 85.3 (C), 15.6 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

((2,5-Dibromo-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(triisopropylsilane) (271):



To a RBF under $N_{2(g)}$ was added 1,4-diiodo-2,5-dibromobenzene (1.0 g, 2.0 mmol), PPh_3 (53.7 mg, 0.205 mmol), $Pd(PPh_3)_4$ (118.3 mg, 0.1024 mmol), CuI (58.57 mg, 0.3075 mmol) and Et_3N (10 mL). A solution of **225** (0.9 mL of a 4.53 M solution in Et_3N) was added and the reaction was allowed to stir at 22 °C for 1.5 h. The process of adding **225** (0.9 mL of a 4.53 M solution in Et_3N) and stirring (1.5 h) was repeated two more times. Finally the 4th portion of **225** (0.9 mL of a 4.53 M solution in Et_3N) was added and the stirring continued for 17 h. The reaction mixture was then concentrated under reduced pressure before being taken up into Et_2O and filtered over a pad of Celite®, washing with Et_2O. The organic solution was washed with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a cream solid (1.3 g, 101% mass-balance for a material of 98% purity by ^{1}H NMR). mp 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 1.11 (app. d, *J* = 2.8 Hz, 42H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 137.6 (CH), 126.1 (C), 124.3 (C), 92.7 (C), 88.8 (C), 82.1 (C), 72.0 (C), 18.7 (6 × CH_3), 11.4 (3 × CH); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{32}H_{45}Br_2Si_2$ 645.1404, Found 645.1385.

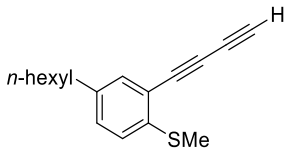
((2,5-Bis(methylthio)-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(triisopropylsilane) (265):



To a RBF under $N_{2(g)}$ was added **271** (532.1 mg, 0.8253 mmol) and anhydrous THF (4.12 mL) before the solution was cooled to -78 °C. *n*-BuLi (1.54 mL of a 2.14 M solution in pentane) was then slowly added and the reaction was allowed to stir at -78 °C for 1 h. After this time S-methyl methanethiosulfonate (0.31 mL, 3.3 mmol) was added and the reaction was allowed to

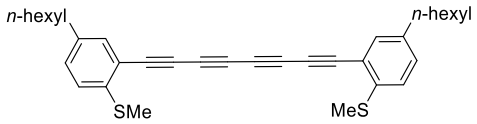
warm to 22 °C and stir at this temp for 1 h. After this time the reaction was quenched through gradual addition of a sat. aq. NH_4Cl solution (5 mL) and diluted with Et_2O (10 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 5 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow-brown waxy solid (477 mg, approximately 90% yield based on ^1H NMR, not further purified due to instability). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 2.47 (s, 6H), 1.11 (app. d, *J* = 2.0 Hz, 42H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.4 (C), 129.7 (CH), 121.4 (C), 92.0 (C), 89.1 (C), 82.9 (C), 72.3 (C), 18.7 (6 × CH_3), 15.6 (CH_3), 11.4 (3 × CH); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{34}H_{51}S_2Si_2$ 579.2965, Found 579.2966.

(2-(Buta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (273):



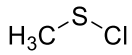
To an RBF under $N_{2(g)}$ was added **257** (1.13 g, 2.75 mmol) and THF (14 mL). The solution was then cooled to 0 °C before TBAF (11 mL of a 1.0 M solution in THF) and acetic acid (0.63 mL) were added. The reaction was allowed to warm to 22 °C and stir at this temperature for 4 h. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with Et_2O (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) before being washed with sat. aq. NH_4Cl solution (1 × 10 mL) and brine (2 × 10 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was used in further reactions as an Et_2O/THF solution. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.6 Hz, 1H), 7.13 (dt, *J* = 19.2, 5.0 Hz, 2H), 2.59 (s, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.48 (s, 3H), 1.61 – 1.51 (m, 2H), 1.51 – 1.37 (m, 2H), 1.31 – 1.24 (m, 4H), 0.88 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.2 (C), 139.5 (C), 133.8 (CH), 130.3 (CH), 125.2 (CH), 119.4 (C), 78.9 (C), 72.9 (C), 67.9 (C), 35.0 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 28.8 (CH_2), 22.6 (CH_2), 15.5 (CH_3), 14.0 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{17}H_{21}S$ 257.1358, Found 257.1356.

1,8-Bis(5-hexyl-2-(methylthio)phenyl)octa-1,3,5,7-tetrayne (266):



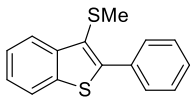
To an RBF under $N_{2(g)}$ was added $CuOAc.H_2O$ (326.6 mg, 1.636 mmol) MeOH (10 mL) and pyridine (10 mL). A MeOH (5 mL) solution of **273** (209.7 mg, 0.8181 mmol) was added. The reaction was then allowed to reflux for 4 h. After this time the reaction was cooled to 0 °C before being quenched through slow addition of 1N HCl solution (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) and washed with brine (2 × 10 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained as a brown thick oil (190 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 1.7 Hz, 2H), 7.14 (dt, *J* = 23.6, 5.0 Hz, 4H), 2.55 (t, *J* = 7.7 Hz, 4H), 2.49 (s, 6H), 1.60 – 1.51 (m, 4H), 1.29 (d, *J* = 1.9 Hz, 8H), 0.88 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 141.2 (C), 139.8 (C), 134.3 (CH), 130.9 (CH), 125.4 (CH), 119.0 (C), 79.9 (C), 75.9 (C), 69.0 (C), 64.4 (C), 35.1 (CH_2), 31.7 (CH_2), 31.2 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.7 (CH_3), 14.2 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{34}H_{39}S_2$ 511.2488, Found 511.2489.

Methyl hypochlorothioite (275):



To a RBF under $N_{2(g)}$ was added dimethyl disulfide (0.22 mL, 2.4 mmol) and CH_2Cl (5 mL) before the solution was cooled to -20 °C. Sulfuryl chloride (0.15 mL, 1.8 mmol) was then added to the reaction before being allowed to warm to 0 °C and stir at this temperature for 1 h. After this time the solution was used directly in further reactions. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 3H).

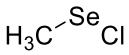
3-(Methylthio)-2-phenylbenzo[*b*]thiophene (276):



To a RBF under $N_{2(g)}$ was added **213** (100 mg, 0.445 mmol) and DCM (1 mL). The solution was cooled to 0 °C before **275** (1 mL of 0.74 M solution in DCM) was slowly added. The

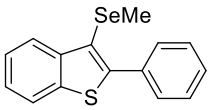
reaction was then allowed to stir for 1.5 h at 0 °C. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) before being washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 5% EtOAc in toluene) to give the title compound as a yellow oil (100 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, J = 8.1, 1.2, 0.7 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.79 – 7.76 (m, 2H), 7.51 – 7.36 (m, 5H), 2.26 (s, 3H); LCMS: t_R = 7.5 min *m/z*: 256.1 [M+H$^+$]. These data are consistent with that previously reported for this compound.[245]

Methyl hypochloroselenoite (280):



To a RBF under $N_{2(g)}$ was added DCM (2 mL) before being cooled to 0 °C. Dimethyl diselenide (0.14 mL, 1.4 mmol) and sulfuryl chloride (0.09 mL, 1.1 mmol) were then added and the reaction was allowed to stir for 1 h at 0 °C. After this time the solution was used directly in further reactions. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (s, 3H).

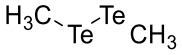
3-(Methylselanyl)-2-phenylbenzo[*b*]thiophene (281):



To a RBF under $N_{2(g)}$ was added **213** (100 mg, 0.445 mmol) and DCM (2 mL) before being cooled to 0 °C. A DCM solution of **280** (0.8 mL, 1.1 M) was then added before the reaction was allowed to stir for 1 h at 0 °C. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) before being washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 10% DCM in hexanes) to give the title compound as a red solid (94.9 mg, 70%). mp 99-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, J = 8.1, 1.1, 0.7 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.76 – 7.70 (m, 2H), 7.53 – 7.37 (m, 5H), 2.11 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 146.0 (C), 142.2 (C), 139.1 (C),

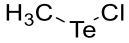
134.6 (C), 130.2 (CH), 128.7 (CH), 128.4 (CH), 125.0 (CH), 124.9 (CH), 124.9 (CH), 122.2 (CH), 117.7 (C), 8.9 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 60.2; LCMS: t_R = 7.6 min *m/z*: 304.0 [M+H$^+$]; HRMS (ESI) *m/z* [M+H]$^+$ Calcd. for $C_{15}H_{13}SSe$ 304.9897, Found 304.9884.

1,2-Dimethylditellane (283):



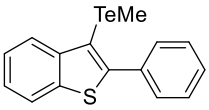
To a RBF under $N_{2(g)}$ was added tellurium (1.5 g, 12 mmol) and anhydrous THF (60 mL) before being cooled to 0 °C. MeLi (11.2 ml, 13.9 mmol) was then slowly added and the reaction then allowed to warm to 22 °C and stir at this temperature for 15 min. A sat. aq. NH_4Cl solution (50 mL) was then very slowly added to the reaction and it was allowed to stir in air for 1 h. After this time the organic layer was extracted with Et_2O (3 × 20 mL) and washed with brine (2 × 15 mL). The combined organics were dried over $MgSO_4$ and a heaped spatula tip of activated charcoal was added before being filtered and concentrated under reduced pressure to give the title compound as a deep red oil (1.5 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 6H).

Methyl hypochlorotelluroite (284):



To a RBF under $N_{2(g)}$ was added DCM (2 mL) and **283** (1.37g, 4.83 mmol) before being cooled to 0 °C. Sulfuryl chloride (0.20 mL, 2.4 mmol) was then added and the reaction was allowed to stir for 1 h at 0 °C. After this time the solution was used directly in further reactions. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (s, 3H).

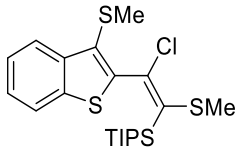
3-(Methyltellanyl)-2-phenylbenzo[b]thiophene (285):



To a RBF under $N_{2(g)}$ was added **213** (144.7 mg, 0.6450 mmol) and DCM (3 mL). A DCM solution of **284** (3.6 mL, 0.36 M) was slowly added. The reaction was then allowed to stir for 18 h at 22 °C. After this time heaped spatula tips of zinc dust were added to the reaction mixture

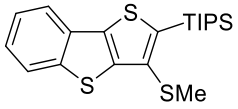
to remove excess MeTeCl. The reaction was diluted with H_2O (5 mL) and DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow solid (184 mg, 81%). mp 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (ddd, J = 8.1, 1.3, 0.7 Hz, 1H), 7.85 (ddd, J = 8.1, 1.3, 0.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.51 – 7.35 (m, 5H), 1.90 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 148.8 (C), 144.7 (C), 140.1 (C), 136.0 (C), 130.5 (CH), 128.7 (CH), 128.3 (CH), 127.4 (CH), 125.1 (CH), 125.0 (CH), 122.1 (CH), 101.8 (C), -15.8 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{15}H_{13}STe$ 354.9793, Found 354.9795.

(*Z*)-(2-Chloro-1-(methylthio)-2-(3-(methylthio)benzo[b]thiophen-2-yl)vinyl)triisopropylsilane (286):



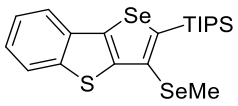
To a RBF under $N_{2(g)}$ was added **228** (100 mg, 0.304 mmol) and DCM (5 mL). The solution was then cooled to 0 °C before **275** (0.25 mL of a 2.4 M solution in DCM) was slowly added. The reaction was allowed to stir for 1 h at 0 °C. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with a sat. solution of sodium metabisulfite (1 × 10 mL) and brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was characterised and used without further purification as unwanted reactions occurred upon its subjection to silica chromatography (124 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 4.7, 1.4, 0.6 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.51 – 7.40 (m, 2H), 2.57 (s, 3H), 2.38 (s, 3H), 1.01 (m, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 143.6 (C), 142.3 (C), 139.1 (C), 138.9 (C), 137.3 (C), 128.9 (C), 126.0 (CH), 125.2 (CH), 123.7 (CH), 122.8 (CH), 19.4 (6 × CH_3), 19.0 (CH_3), 18.7 (CH_3), 12.6 (3 × CH); LCMS: t_R = 7.2 min *m/z*: 443.3 $[M+H^+]$; HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{21}H_{32}ClS_3Si$ 443.1118, Found 443.1120.

Benzo[*b*]thieno[2,3-d]thiophen-2-yltriisopropylsilane (287):



To a RBF under $N_{2(g)}$ was added **228** (1.0 g, 3.0 mmol) and DCM (5 mL). The solution was then cooled to 0 °C before **275** (2.5 mL of a 2.4 M solution in DCM) was slowly added. The reaction was then allowed to stir for 1 h at 0 °C. The reaction was subsequently heated to reflux for 20 h. Further **275** (1.2 mL of a 2.43 M solution in DCM) was then added and the reaction allowed to reflux for a further 20 h. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with DCM (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 15 mL) and washed with a sat. solution of sodium metabisulfite (1 × 10 mL) and brine (2 × 15 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 100% hexanes) to give the title compound as an orange solid (1.2 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.38 (m, 2H), 2.52 (d, *J* = 3.2 Hz, 3H), 1.69 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.21 – 1.15 (m, 18H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 143.0 (C), 140.3 (C), 139.1 (C), 132.9 (C), 132.0 (C), 124.8 (CH), 124.8 (CH), 124.1 (CH), 121.2 (CH), 19.0 (6 × CH_3), 17.9 (CH_3), 12.7 (3 × CH); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{20}H_{29}S_3Si$ 393.1195, Found 393.1198.

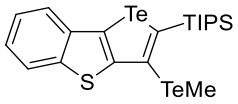
Triisopropyl(3-(methylselanyl)benzo[*b*]selenopheno[2,3-d]thiophen-2-yl)silane (290):



To a RBF under $N_{2(g)}$ was added **228** (104.9 mg, 0.334 mmol) and DCE (2 mL). The solution was then cooled to 0 °C before **280** (1.67 mL of a 0.6 M solution in DCM) was added. The reaction was stirred for 1 h at 0 °C before being dilute with H_2O (5 mL) and DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow solid (163 mg, 96%). mp 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 1H), 7.82 – 7.78 (m, 1H), 7.43 – 7.33 (m, 2H), 2.39 (s, 3H), 1.71 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.22 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 148.8 (C), 147.9 (C), 142.3 (C), 138.6 (C), 136.1 (C),

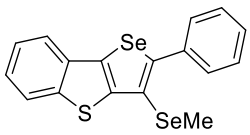
124.8 (CH), 124.7 (C), 123.9 (CH), 122.2 (CH), 19.2 (6 × CH_3), 13.3 (3 × CH), 8.7 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 656.2, 153.5; HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{20}H_{29}SSe_2Si$ 489.0086, Found 489.0084.

Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2,3-d]thiophen-2-yl)silane (291):



To a RBF under $N_{2(g)}$ was added **228** (105.7 mg, 0.3216 mmol) and DCM (2 mL). A DCM solution of **284** (2.7 mL, 0.36 M) was slowly added. The reaction was allowed to stir for 18 h at 22 °C. After this time heaped spatula tips of zinc dust were added to the reaction mixture to remove excess **284**. The reaction was then dilute with H_2O (5 mL) and DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow-brown waxy solid (136.8 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.75 – 7.70 (m, 1H), 7.43 – 7.31 (m, 2H), 2.15 (s, 3H), 1.18 (m, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 143.3 (C), 139.9 (C), 130.1 (CH), 127.3 (CH), 126.0 (CH), 125.2 (CH), 122.0 (CH), 110.2 (C), 101.8 (C), 100.9 (C), 18.8 (6 × CH_3), 11.5 (3 × CH), -16.0 (CH_3); HRMS (APCI) *m/z* $[M-MeTe]^+$ Calcd. for $C_{19}H_{25}SSiTe$ 443.0500, Found 443.0535.

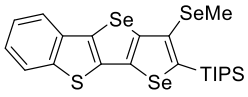
3-(Methylselanyl)-2-phenylbenzo[*b*]selenopheno[2,3-*d*]thiophene (292):



To a RBF under $N_{2(g)}$ was added **232** (102.8 mg, 0.413 mmol) and DCM (2 mL). The solution was cooled to -20 °C before **280** (1.72 mL of a 0.6 M solution in DCM) was added. The reaction was allowed to stir for 1 h at -20 °C before being quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a red solid (112 mg, 67%). mp 139-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.2,

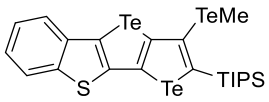
0.8 Hz, 1H), 7.79 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.49 – 7.34 (m, 5H), 2.24 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 151.3 (C), 146.8 (C), 140.5 (C), 136.4 (C), 136.1 (C), 132.3 (C), 129.7 (CH), 128.5 (CH), 124.9 (CH), 124.6 (CH), 123.8 (CH), 122.0 (CH), 115.0 (C), 8.8 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 5925.5, 121.0; LCMS: t_R = 7.9 min *m/z*: 407.9 [M+H$^+$]; HRMS (APCI) *m/z* [M+H]$^+$ Calcd. for $C_{17}H_{13}SSe_2$ 408.9065, Found 408.9063.

Triisopropyl(3-(methylselanyl)benzo[*b*]selenopheno[2',3':4,5]selenopheno[2,3-*d*]thiophen-2-yl)silane (295):



To a RBF under $N_{2(g)}$ was added **235** (100 mg, 0.283 mmol) and DCE (2 mL). The reaction was cooled to 0 °C before **280** (2.3 mL of a 0.49 M solution in DCM) was slowly added. The reaction was allowed to stir at this temperature for 1 h. The reaction was then quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was then isolated through trituration with hexanes from EtOAc. The filtrate was concentrated under reduced pressure to give the title compound as an orange solid (126 mg, 76%). mp 117 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 1H), 7.83 – 7.77 (m, 1H), 7.46 – 7.33 (m, 2H), 2.41 (s, 3H), 1.77 – 1.63 (m, 3H), 1.22 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 152.7 (C), 147.3 (C), 141.2 (C), 136.4 (C), 136.2 (C), 135.6 (C), 134.6 (C), 127.4 (C), 125.1 (CH), 124.7 (CH), 123.8 (CH), 121.7 (CH), 19.2 (6 × CH_3), 13.3 (3 × CH), 9.3 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 688.7, 508.6, 162.9; HRMS (ESI) *m/z* [M+H]$^+$ Calcd. for $C_{22}H_{29}SSe_3Si$ 590.9265, Found 590.9219.

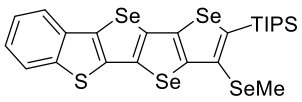
Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2',3':4,5]telluropheno[2,3-d]thiophen-2-yl)silane (296):



To a RBF under $N_{2(g)}$ was added **235** (107.1 mg, 0.3037 mmol) and DCM (3 mL). A DCM solution of **284** (4.6 mL, 0.26 M) was slowly added. The reaction was then allowed to stir for

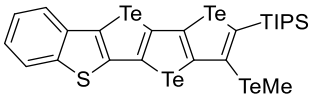
18 h at 22 °C. After this time heaped spatula tips of zinc dust were added to the reaction mixture to remove excess **284**. The reaction was dilute with H_2O (5 mL) and DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow solid (142.8 mg, 64%). mp 269-277 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.66 – 7.62 (m, 1H), 7.40 – 7.36 (m, 2H), 2.33 (s, 3H), 1.17 (d, *J* = 3.3 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (C), 141.3 (C), 141.1 (C), 126.2 (C), 125.9 (C), 125.1 (CH), 125.0 (CH), 123.8 (CH), 123.5 (CH), 111.1 (C), 106.8 (C), 105.6 (C), 18.9 (6 × CH_3), 11.6 (3 × CH), -14.9 (CH_3); HRMS (APCI) *m/z* $[M\text{-MeTe}]^+$ Calcd. for $C_{21}H_{25}SSiTe_2$ 592.9534, Found 592.9589.

Triisopropyl(3-(methylselanyl)benzo[b]selenopheno[2'',3'':4',5']selenopheno[2',3':4,5]selenopheno[2,3-d]thiophen-2-yl)silane (297):



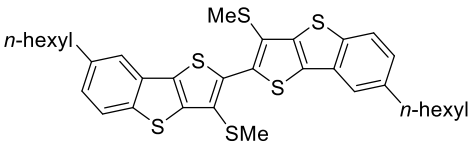
To a RBF under $N_{2(g)}$ was added **237** (55.5 mg, 0.1473 mmol), **280** (1.31 mL of a 0.5 M solution in DCM) and DCE (4 mL). The reaction was then heated to 60 °C for 2 days before heating to reflux for a further 2 days. The reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was then isolated through recrystallization from MeOH with $CHCl_3$ to give a red crystalline solid (42 mg, 10%). mp 190-196 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.77 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.46 – 7.33 (m, 2H), 2.39 (s, 3H), 1.68 (p, *J* = 7.5 Hz, 3H), 1.20 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (C), 146.8 (C), 141.2 (C), 138.9 (C), 136.1 (C), 135.9 (C), 135.1 (C), 134.8 (C), 133.4 (C), 127.2 (C), 125.3 (CH), 124.7 (CH), 124.0 (CH), 121.5 (CH), 19.2 (6 × CH_3), 13.4 (3 × CH), 9.3 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 689.1, 538.9, 512.8, 165.8; HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{24}H_{29}SSe_4Si$ 694.8433, Found 694.8421.

Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2'',3'':4',5']telluropheno[2',3':4,5]telluropheno[2,3-d]thiophen-2-yl)silane (298):



To a RBF under $N_{2(g)}$ was added **237** (93.6 mg, 0.248 mmol) and DCM (3 mL). A DCM solution of **284** (2.6 mL, 0.47 M) was slowly added. The reaction was then allowed to stir for 18 h at 22 °C. After this time heaped spatula tips of zinc dust were added to the reaction mixture to remove excess **284**. The reaction was diluted with H_2O (5 mL) and DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a yellow solid (127 mg, 58%). mp 237-246 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 1H), 7.71 – 7.66 (m, 1H), 7.43 – 7.33 (m, 2H), 2.36 (s, 3H), 1.16 (d, *J* = 3.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 (C), 146.7 (C), 141.1 (C), 139.8 (C), 128.9 (C), 127.4 (C), 127.4 (C), 125.3 (CH), 125.0 (CH), 123.4 (CH x2), 120.7 (C), 106.9 (C), 105.1 (C), 18.9 (6 × CH_3), 11.6 (3 × CH), -13.7 (CH_3); HRMS (APCI) *m/z* $[M\text{-}MeTe_2]^+$ Calcd. for $C_{23}H_{25}SSiTe_2$ 616.9535, Found 616.9532.

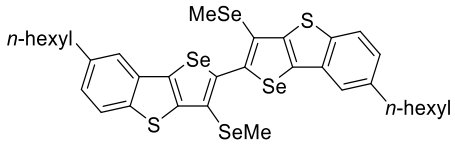
7,7'-Dihexyl-3,3'-bis(methylthio)-2,2'-bibenzo[b]thieno[2,3-d]thiophene (299):



To a RBF under $N_{2(g)}$ was added **266** (86.6 mg, 0.4244 mmol) and DCM (3 mL). The solution was then cooled to 0 °C before **275** (3.4 mL of a 0.56 M solution in DCM) was slowly added. The reaction was then allowed to stir for 1 h at 0 °C. After this time the reaction was dilute with H_2O (5 mL) and DCM (5 mL). The After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The brown oil title compound was then characterised as the crude material (estimated yield 61%) due to degradation on silica. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 1.0 Hz, 2H), 7.24 (dd, *J* = 8.4, 1.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 4H), 2.50 (s, 6H), 1.72 – 1.66 (m,

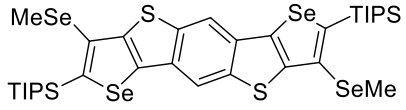
4H), 1.58 (s, 4H), 1.39 – 1.30 (m, 8H), 0.89 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 142.6 (C), 140.2 (C), 139.2 (C), 136.6 (C), 133.6 (C), 133.2 (C), 126.2 (CH), 125.6 (C), 123.6 (CH), 120.7 (CH), 36.0 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 18.3 (CH_3), 14.2 (CH_3); LCMS: t_R = 5.2 min *m/z*: 638.3 [M^+], 639.3 [$M+H^+$]; HRMS (APCI) *m/z* [$M-C_{12}H_{24}+H]^+$ Calcd. for $C_{22}H_{15}S_6$ 470.9493, Found 470.9493.

7,7'-Dihexyl-3,3'-bis(methylselanyl)-2,2'-bibenzo[b]selenopheno[2,3-d]thiophene (300):



To a RBF under $N_{2(g)}$ was added **266 (**936.6 mg, 1.833 mmol) and DCM (10 mL). The solution was then cooled to 0 °C before **280** (17.6 mL of a 0.47 M solution in DCM) was slowly added. The reaction was then allowed to stir for 1 h at 0 °C. After this time the reaction was dilute with H_2O (10 mL) and DCM (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 15 mL) and washed with brine (2 × 15 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown solid (1.2 g, 82%). mp 115-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.60 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.80 – 2.69 (m, 4H), 2.36 (s, 6H), 1.69 (dd, *J* = 14.5, 7.1 Hz, 4H), 1.35 (d, *J* = 14.9 Hz, 12H), 0.90 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 146.7 (C), 143.8 (C), 140.1 (C), 138.6 (C), 136.2 (C), 134.4 (C), 126.1 (CH), 123.4 (CH), 121.7 (CH), 119.0 (C), 36.0 (CH_2), 31.8 (2 × CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 9.8 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 618.1, 131.3; HRMS (APCI) *m/z* [$M+H]^+$ Calcd. for $C_{34}H_{39}S_2Se_4$ 828.9170, Found 828.9155.

(301):



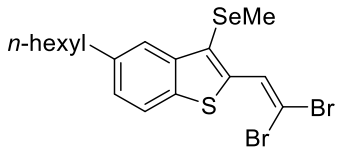
To a RBF under $N_{2(g)}$ was added **265** (271.5 mg, 0.4688 mmol) and DCM (5 mL). The solution was then cooled to 0 °C before **280** (4.0 mL of a 0.53 M solution in DCM) was slowly added. The reaction was then allowed to stir for 1 h at 0 °C. After this time hexanes (5 mL) was added to the reaction mixture and the precipitate filtered and washed with additional hexanes. The

title compound was then furnished as a cream solid (127 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 2.40 (s, 6H), 1.70 (dt, *J* = 14.9, 7.5 Hz, 6H), 1.20 (d, *J* = 7.5 Hz, 36H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 148.9* (C), 1478.0* (C), 142.3* (C), 133.5** (C), 139.0** (C), 124.9** (C), 116.3** (CH), 19.2 (6 × CH_3), 13.3 (3 × CH), 8.8 (2 × CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{34}H_{51}S_2Se_4Si_2$ 896.9648, Found 896.9635.

*Tentative assignment based on ^{13}C NMR of **290**

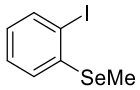
****Obtained from 2D NMR (S56-57)

2-(2,2-Dibromovinyl)-5-hexyl-3-(methylselanyl)benzo[b]thiophene (318):



To a RBF under $N_{2(g)}$ was added **262**(108.2 mg, 0.2599 mmol) and DCM (2 mL). The solution was then cooled to 0 °C before **280** (0.65 mL of a 0.6 M solution in DCM) was slowly added. The reaction was allowed to stir for 1 h at 0 °C. After this time the reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown semi-solid (128 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.85 (dd, J = 1.7, 0.8 Hz, 1H), 7.72 (dd, J = 8.2, 0.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.19 (s, 3H), 1.70 (ddd, J = 9.2, 4.9, 1.8 Hz, 2H), 1.43 – 1.30 (m, 6H), 0.93 – 0.88 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.35 (C), 140.33 (C), 140.18 (C), 136.69 (C), 132.72 (CH), 127.50 (CH), 125.27 (C), 123.88 (CH), 122.13 (CH), 90.56 (C), 36.15 (CH_2), 31.96 (CH_2), 31.87 (CH_2), 29.15 (CH_2), 22.78 (CH_2), 14.26 (CH_3), 9.72 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

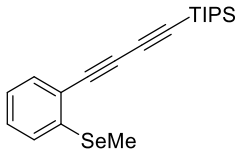
(2-Iodophenyl)(methyl)selane:



To a RBF under $N_{2(g)}$ was added 2-iodoaniline (2.00 g, 9.13 mmol), dimethyl diselenide (2.59 mL, 27.39 mmol), isopentyl nitrite (3.6 mL, 27.39 mmol), and DCE (45 mL). The reaction mixture was then refluxed for 1 h at 70 – 80 °C. After this time the reaction was concentrated

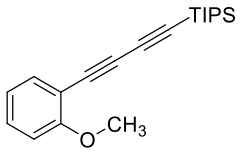
under reduced pressure before being diluted with H_2O (25 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 25 mL), washed with H_2O (2 × 20 mL) and brine (2 × 15 mL). The combined organics were dried with $MgSO_4$, filtered and concentrated under reduced pressure to give a crude oil. This material was then subject to further concentration under reduced pressure whilst heating to 110 °C for 6 h, to remove any residual volatiles. The title compound was obtained as a dark orange oil (2.57 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.30 (ddd, *J* = 7.9, 7.3, 1.4 Hz, 1H), 7.18 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.89 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 2.33 (s, 3H). This data is consistent with that previously reported for this compound.[246]

Triisopropyl((2-(methylselanyl)phenyl)buta-1,3-diyn-1-yl)silane (321):



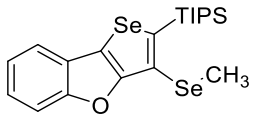
To a RBF under $N_{2(g)}$ was added **(2-iodophenyl)(methyl)selane** (1.0 g, 3.3 mmol), $Pd(PPh_3)_4$ (116.6 mg, 0.1009 mmol) and DIPA (16.8 mL). The reaction was degassed with $N_{2(g)}$ × 3 before CuI (38.46 mg, 0.2018 mmol) was added. The reaction was then heated to 60 °C. A DIPA solution of **225** (2.0 g, 10 mmol) was added slowly to the reaction mixture over 4 h. The reaction was allowed to stir for 1 h at 60 °C. After this time the reaction was quenched through gradual addition of a sat. aq. NH_4Cl solution (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) and washed with a sat. aq. NH_4Cl solution (2 × 10 mL) and brine (2 × 10 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (silica gel, 1% Et_3N in hexanes) to give the title compound as a brown oil (787 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (ddd, J = 7.6, 1.3, 0.7 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.12 (ddd, J = 7.6, 6.6, 2.1 Hz, 1H), 2.36 (s, 3H), 1.12 (d, J = 1.6 Hz, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 137.7 (C), 133.9 (CH), 129.6 (CH), 127.9 (CH), 125.3 (CH), 122.2 (C), 89.8 (C), 89.4 (C), 80.0 (C), 73.7 (C), 18.6 (6 × CH_3), 11.4 (3 × CH), 6.4 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

Triisopropyl((2-methoxyphenyl)buta-1,3-diyn-1-yl)silane (322):



To a RBF under $N_{2(g)}$ was added **1-ethynyl-2-methoxybenzene** (119.7 mg, 0.9719 mmol), *n*-butylamine (0.24 mL, 2.4 mmol), CuCl (2.4 mg, 0.024 mmol), $HONH_2.HCl$ (16.88 mg, 0.2429 mmol) and MeOH (2 mL). A MeOH (2 mL) solution of **222** (211.6 mg, 0.8099 mmol) was added and the reaction allowed to stir for 18 h at 22 °C. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with Et_2O (5 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 10 mL) before being washed with 10% citric acid solution (10 mL) and brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil (178 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 6.93 – 6.84 (m, 2H), 3.89 (s, 3H), 1.11 (s, 21H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 161.72 (C), 134.94 (CH, 130.82 (CH), 120.66 (CH), 110.90 (CH), 110.74 (C), 89.86 (C), 88.42 (C), 78.62 (C), 72.12 (C), 55.95 (CH_3), 18.73 (6 × CH_3), 11.48 (3 × CH); LCMS: t_R = 4.2 min *m/z*: 313.1 [$M+H^+$].

Triisopropyl(3-(methylselanyl)selenopheno[3,2-b]benzofuran-2-yl)silane (324):

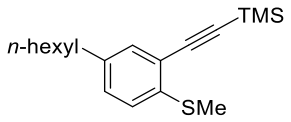


To a RBF under $N_{2(g)}$ was added **322** (95.6 mg, 0.305 mmol) and DCM (2 mL). A DCM solution of **280** (1.15 mL, 0.8 M) was then added and the reaction was allowed to stir for 2 h at 22 °C. After this time the reaction was quenched through addition of H_2O (10 mL) and diluted with DCM (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 15 mL) and washed with a sat. solution of sodium metabisulfite (1 × 10 mL) and brine (2 × 15 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil (198.7 mg) was subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as a light brown solid (4 mg, <10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.38 – 7.25 (m, 2H), 2.46 (s, 3H), 1.68 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.25 – 1.16 (m, 18H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 163.3 (C), 158.4 (C),

144.9 (C), 126.7 (C), 124.9 (CH), 123.1 (CH), 122.4 (C), 119.9 (CH), 117.0 (C), 112.7 (CH), 19.1 (6 × CH_3), 13.1 (3 × CH), 8.2 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{20}H_{29}Se_2Si$ 471.0327, Found 471.0312.

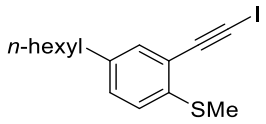
5.3 Chapter 3 Experimental

((5-Hexyl-2-(methylthio)phenyl)ethynyl)trimethylsilane (351):



To a RBF under $N_{2(g)}$ was added **245** (3.0 g, 8.9 mmol), CuI (17.09 mg, 0.0897 mmol), $Pd(PPh_3)_2Cl_2$ (125.9 mg, 0.1795 mmol) and Et_3N (30 mL). The reaction was degassed with $N_{2(g)}$ × 3 before trimethylsilylacetylene (1.5 mL, 10.77 mmol) was added dropwise. The reaction was allowed to stir at 22 °C for 18 h. The reaction mixture was concentrated under reduced pressure before being taken up into Et_2O and filtered over a pad of Celite®, which was washed with additional Et_2O. The organic solution was washed with H_2O (2 × 15 mL) and brine (2 × 15 mL). The organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as an orange oil (2.3 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.11 – 7.04 (m, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 1.57 (s, 2H), 1.28 (m, 6H), 0.88 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.3 (C), 138.6 (C), 132.8 (CH), 129.5 (CH), 124.7 (CH), 121.4 (C), 102.7 (C), 100.7 (C), 35.2 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 15.4 (CH_3), 14.2 (CH_3), 0.1 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. for $C_{18}H_{29}SSi$: 305.1662, Found 305.1675.

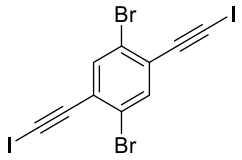
(352):



To a RBF under $N_{2(g)}$ was added **351** (3.59 g, 11.7 mmol) and MeOH (58.5 mL). The solution was then cooled to 0 °C before NIS (3.99 g, 17.6 mmol) and KOH (2.64 g, 47.1 mmol) were added. The reaction was warmed to 22 °C before being allowed to stir at this temperature for 1 h. After this time the reaction was concentrated under reduced pressure before being diluted with Et_2O (50 mL) and H_2O (50 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 30 mL) and washed with brine (2 × 20 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown semi-solid (4.2 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 1.7, 0.7 Hz,

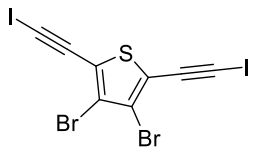
1H), 7.09 (dd, J = 2.2, 1.3 Hz, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.59 – 1.52 (m, 4H), 1.32 – 1.25 (m, 7H), 0.90 – 0.85 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 139.4 (C), 139.0 (C), 133.4 (CH), 129.7 (CH), 124.9 (CH), 121.8 (C), 92.2 (C), 66.0 (C), 35.1 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.6 (CH_3), 14.2 (CH_3). HRMS *m/z* $[M+H]^+$ Calcd. for $C_{15}H_{20}IS$ 359.0325, Found 359.0332.

1,4-Dibromo-2,5-bis(iodoethynyl)benzene (353):



To a RBF under $N_{2(g)}$ was added **267** (1.0 g, 2.3 mmol) and MeOH (23.5 mL). The solution was then cooled to 0 °C before NIS (1.36 g, 6.04 mmol) and KOH (1.0 g, 17 mmol) were added. The reaction was warmed to 22 °C before being allowed to stir at this temperature for 1 h. After this time the reaction was concentrated under reduced pressure before being dilute with DCM (50 mL) and H_2O (50 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 30 mL) and washed with brine (2 × 20 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as a brown solid (772 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 2H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 137.1 (CH), 127.0 (C), 124.1 (C), 91.3 (C), 16.7 (C). Mass spec. data could not be obtained due to poor ionisation/solubility.

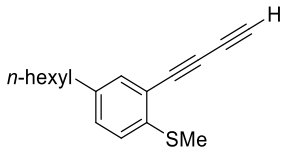
3,4-Dibromo-2,5-bis(iodoethynyl)thiophene (361):



To a RBF under $N_{2(g)}$ was added **360** (600 mg, 1.38 mmol) and MeOH (14 mL). The solution was then cooled to 0 °C before NIS (808 mg, 3.59 mmol) and KOH (619.9 mg, 11.04 mmol) were added. The reaction was warmed to 22 °C before being allowed to stir at this temperature for 1 h. After this time the reaction was concentrated under reduced pressure before being

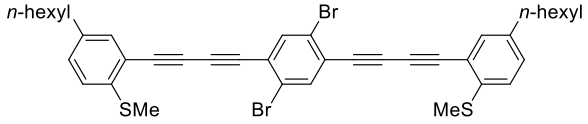
diluted with DCM (50 mL) and H_2O (50 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 30 mL) and washed with brine (2 × 20 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as a brown solid (481 mg, 64%). ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 121.8 (C), 120.0 (C), 85.2 (C), 19.3 (C). Mass spec. data could not be obtained due to poor ionisation/solubility.

(2-(Buta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (273):



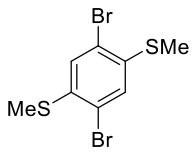
To a RBF under $N_{2(g)}$ was added **262** (6.2 g, 15.1 mmol) and anhydrous THF (151 mL). The solution was then cooled to -78 °C before *n*-BuLi (21 mL of a 1.44 M solution in hexanes) was slowly added and the reaction allowed to stir at -78 °C for 30 mins. After this time the reaction was quenched through slow addition of NH_4Cl sat. solution (100 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 50 mL) and washed with brine (2 × 50 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil in Et_2O to avoid decomposition. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.6 Hz, 1H), 7.13 (dt, J = 19.2, 5.0 Hz, 2H), 2.59 (s, 1H), 2.56 (t, J = 7.7 Hz, 2H), 2.48 (s, 3H), 1.61 – 1.51 (m, 2H), 1.51 – 1.37 (m, 2H), 1.31 – 1.24 (m, 4H), 0.88 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.2 (C), 139.5 (C), 133.8 (CH), 130.3 (CH), 125.2 (CH), 119.4 (C), 78.9 (C), 72.9 (C), 67.9 (C), 35.0 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 28.8 (CH_2), 22.6 (CH_2), 15.5 (CH_3), 14.0 (CH_3); LCMS: t_R = 7.9 min *m/z*: 256.2 [M^+]; HRMS (APCI) *m/z* [M+H]$^+$ Calcd. for $C_{17}H_{21}S$ 257.1358, Found 257.1356.

(((2,5-Dibromo-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(4-hexyl-2,1-phenylene))bis(methylsulfane) (354):



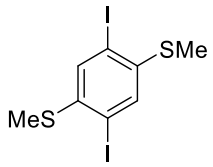
To a RBF under $N_{2(g)}$ was added 1,2-dibromo-3,4-diiodobenzene (322 mg, 0.660 mmol), CuI (7.5 mg, 0.03 mmol, $Pd(PPh_3)_4$ (45.77 mg, 0.0396 mmol), THF (8 mL) and DIPA (8 mL). A DIPA solution of **273** (2 mL, 0.73 M) was then added before the reaction was allowed to stir at 22 °C for 1 h. Further **273** (2 mL of a 0.73 M solution in DIPA) was added before the reaction was again allowed to stir at 22 °C for 1 h. After this time the reaction was diluted with Et_2O and filtered through a Celite® pad. The organic solution was then washed with H_2O (20 mL) and brine (2 × 20 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as a brown oil (334 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.38 – 7.32 (m, 2H), 7.20 – 7.09 (m, 4H), 2.52 (t, *J* = 7.5 Hz, 4H), 2.51 (s, 6H), 1.63 – 1.55 (m, 4H), 1.30 (s, 12H), 0.90 – 0.86 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.2 (C), 139.7 (C), 137.3 (CH), 133.8 (CH), 130.6 (CH), 126.2 (C), 125.3 (CH), 124.3 (C), 119.7 (C), 83.0 (C), 81.6 (C), 79.7 (C), 78.8 (C), 35.1 (CH_2), 31.8 (CH_2), 31.2 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.7 (CH_3), 14.2 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

(2,5-Dibromo-1,4-phenylene)bis(methylsulfane) (365):



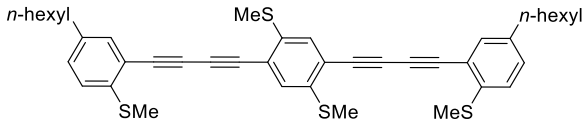
To a RBF under $N_{2(g)}$ was added 1,4-dibromo-2,5-diiodobenzene (1.0 g, 2.0 mmol), Cu (260.6 mg, 4.100 mmol), K_2CO_3 (566.7 mg, 4.100 mmol), $Pd(PPh_3)_4$ (2.6 g, 2.2 mmol) and DMF (40 mL). Dimethyl disulphide (1.86 mL, 20.5 mmol) was then added and the reaction heated to reflux for 4 h. After this time further dimethyl disulphide (1.86 mL, 20.5 mmol) was added and the reaction allowed to stir at reflux for a further 16 h. The reaction mixture was concentrated under reduced pressure then diluted with dichloromethane (20 mL) and filtered over a Celite® pad. The organic solution was then washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 10% DCM in hexanes) to give the title compound as a yellow solid (543.9 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 2.47 (s, 6H). This data is consistent with that previously reported for this compound.[247]

(2,5-Diiodo-1,4-phenylene)bis(methylsulfane) (161):



To a RBF under $N_{2(g)}$ was added **365** (1.18 g, 3.60 mmol) and anhydrous Et_2O (72 mL). The solution was then cooled to 0 °C before *n*-BuLi (4.6 mL of a 1.82 M solution in cyclohexane) was added. The reaction was allowed to stir at this temperature for 20 mins before 1,2-diiodoethane (20.31 g, 72.02 mmol) was added and the reaction then allowed to warm to 22 °C. The reaction was then quenched through addition of a saturated solution of NH_4Cl (30 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 30 mL). The combined organics were washed with brine (2 × 20 mL) and concentrated under reduced pressure. The crude material was then diluted with acetone (100 mL) and NaI (9.7 g, 64 mmol) was added to react with remaining 1,2-diiodoethane. The mixture was allowed to stir for 10 mins before being quenched through addition of a saturated solution of $Na_2S_2O_3$ (100 mL). The aqueous layer was again extracted with additional DCM (3 × 30 mL). The combined organics were then dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound as a pale yellow solid (1.5 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 2.45 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 141.2 (C), 135.2 (CH), 98.3 (C), 17.6 (CH_3); HRMS (APCI) *m/z* $[M]^+$ Calcd. For $C_8H_8I_2S_2$ 421.8151, Found 421.8138.

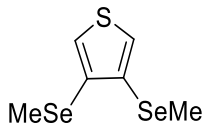
(2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-1,4-phenylene)bis(methylsulfane) (342):



To a RBF under $N_{2(g)}$ was added **161** (767.3 mg, 1.817 mmol), DIPA (6 mL), THF (6 mL), CuI (34.62 mg, 0.1817 mmol) and $Pd(PPh_3)_4$ (210 mg, 0.181 mmol). The reaction was then degassed × 3 with $N_{2g)}$ before being heated to 60 °C. Subsequently **273** (6 mL of a 0.6 M solution in DIPA) was added and the reaction allowed to stir for 1 h at 60 °C before further **273** (3 mL of a 0.6 M solution in DIPA) was added. The reaction was allowed to stir for a further 1 h at 60 °C. After this time the reaction was cooled to 22 °C before being diluted with Et_2O and filtered through a Celite® pad, washing with Et_2O followed by washing DCM which was

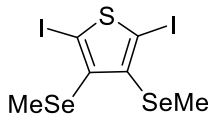
collected separately. The DCM solution was then washed with H_2O (20 mL) and brine (2 × 20 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a bright yellow solid (800 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.9, 0.6 Hz, 2H), 7.28 (s, 2H), 7.17 – 7.10 (m, 4H), 2.56 (t, *J* = 7.7 Hz, 4H), 2.50 (s, 12H), 1.57 (d, *J* = 11.1 Hz, 4H), 1.37 – 1.28 (m, 12H), 0.92 – 0.85 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.0 (C), 139.7 (C), 139.3 (C), 133.8 (CH), 130.4 (CH), 129.5 (CH), 125.4 (CH), 121.7 (C), 120.1 (C), 82.7 (C), 82.3 (C), 80.0 (C), 79.1 (C), 35.1 (CH_2) , 31.8 (CH_2), 31.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 15.8 (CH_3), 14.2 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

3,4-Bis(methylselanyl)thiophene (374):



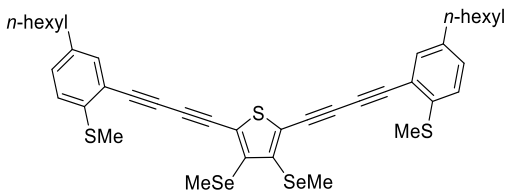
To a RBF under $N_{2(g)}$ was added 3,4-dibromothiophene (0.92 mL, 8.2 mmol) and anhydrous Et_2O (40 mL). The reaction was then cooled to -78 °C before *n*-BuLi (6.8 mL of a 1.82 M solution in cyclohexane) was added and the solution was allowed to stir for 1 h at -78 °C. Dimethyl diselenide (1.2 mL, 12.4 mmol) was then added and the reaction allowed to stir at -78 °C for 30 min before being warmed to 22 °C. The reaction was re-cooled to -78 °C before further *n*-BuLi (6.8 mL of a 1.82 M solution in cyclohexane) was added and the solution allowed to stir for 1 h at -78 °C. Dimethyl diselenide (1.2 mL, 12.4 mmol) was then added and the reaction allowed to stir at -78 °C for 30 min before being warmed to 22 °C. The reaction was then quenched through addition of a saturated solution of NH_4Cl (40 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 20 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 100% hexanes) to give the title compound as an orange oil (1.9 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 128.9 (C), 124.4 (CH), 8.5 (CH_3). These data are consistent with that previously reported for this compound [248]

2,5-Diiodo-3,4-bis(methylselanyl)thiophene (375):



To a RBF under $N_{2(g)}$ was added DIPA (3.7 mL, 26 mmol) and anhydrous Et_2O (40 mL). This solution was cooled to 0 °C before *n*-BuLi (13 mL, of a 1.82 M solution in cyclohexane) was then slowly added and the reaction allowed to stir at this temperature for 30 mins. After this time this lithium DIPA solution was transferred to a RBF containing **374** (1.98 g, 7.34 mmol) in anhydrous Et_2O (20 mL) at 0 °C. The reaction mixture was then allowed to stir at 0 °C for 1 h before being warmed to 22 °C and then subsequently cooled to -78 °C before 1,2-diiodoethane (12.42 g, 44.09 mmol) was added and allowed to warm to 22 °C. After this time the reaction was quenched through addition of a saturated solution of NH_4Cl (30 mL). After separation, the aqueous layer was extracted with additional Et_2O (3 × 30 mL). The combined organics were washed with brine (2 × 20 mL) and concentrated under reduced pressure. The crude material was diluted with acetone (100 mL) and NaI (4.4 g, 29 mmol) was added to react with remaining 1,2-diiodoethane. The mixture was allowed to stir for 10 mins before being quenched through addition of a saturated solution of Na_2SO_3 (100 mL). The aqueous layer was again extracted with additional Et_2O (3 × 30 mL). The combined organics were then dried over $MgSO_4$, filtered and concentrated under reduced pressure before being subject to column chromatography (silica gel, 0-10% EtOAc in hexanes) and then titrated from Et_2O with hexanes to give the title compound as a pink-cream solid (2.6 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 138.7 (C), 90.2 (C), 11.3 (CH_3); HRMS (APCI) *m/z* $[M]^+$ Calcd. For $C_6H_6I_2SSe_2$ 521.6614, Found 521.6600.

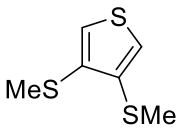
2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-3,4-bis(methylselanyl)thiophene (344):



To a RBF under $N_{2(g)}$ was added **375** (750 mg, 1.43 mmol), DIPA (7 mL), THF (7 mL), CuI (41.10 mg, 0.2158 mmol) and $Pd(PPh_3)_4$ (249.4 mg, 0.2158767 mmol). The reaction mixture

was then degassed with $N_{2(g)}$ × 3 before heating the reaction to 60 °C. Subsequently **273** (4.8 mL of a 0.6 M solution in DIPA) was added and the reaction allowed to stir for 1 h at 60 °C before further **273** (4.8 mL of a 0.6 M solution in DIPA) was added and the reaction allowed to stir for 1 h at 60 °C. After this time the reaction was cooled to 22 °C before being diluted with Et_2O and filtered through a Celite® pad. The organic solution was washed with H_2O (20 mL) and brine (2 × 20 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to column chromatography (silica gel, 0-20% DCM in hexanes) to give the title compound as an orange-brown oil (809 mg, 72%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.11 – 7.02 (m, 4H), 2.48 (t, *J* = 7.9 Hz, 4H), 2.43 (s, 6H), 2.42 (s, 6H), 1.52 (p, *J* = 7.1 Hz, 4H), 1.29 – 1.19 (m, 12H), 0.86 – 0.79 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 140.1 (C), 139.4 (C), 137.3 (C), 133.4 (CH), 130.5 (CH), 124.9 (CH), 124.6 (C), 119.4 (C), 83.9 (C), 82.9 (C), 79.0 (C), 75.1 (C), 34.9 (CH_2), 31.6 (CH_2), 31.0 (CH_2), 28.7 (CH_2), 22.5 (CH_2), 15.5 (CH_3), 14.1 (CH_3), 9.5 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 174.9. Mass spec. data could not be obtained due to poor ionisation/solubility.

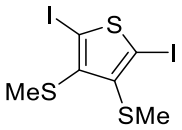
3,4-Bis(methylthio)thiophene (384):



To a RBF under $N_{2(g)}$, 3,4-dibromothiophene (2 mL, 18.1 mmol) and anhydrous Et_2O (45 mL) were added. The flask was cooled to -78 °C and *n*-BuLi (22.6 mL of a 1.6 M solution in hexane) was added dropwise. Following this, the reaction was stirred for 1 h. Subsequently dimethyl disulfide (4 mL, 45.2 mmol) was added, and the mixture was stirred for additional 35 min at −78°C before being slowly warmed to 22 °C. After warming up to 22 °C, the reaction mixture was quenched with 1 M HCl (20 mL) and extracted with Et_2O (3 × 10 mL). The combined organics were washed with H_2O (30 mL) and brine (3 × 30 mL) successively before being dried over $MgSO_4$ and concentrated under reduced pressure to yield 3-bromo-4-(methylthio)thiophene (**382)** as a yellow oil. Due to its volatility, the compound was used in the following reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 3.4 Hz, 1H), 6.90 (d, *J* = 3.4 Hz, 1H), 2.46 (s, 3H); LCMS: t_R = 3.8 min *m/z* (%): 207.9 (100, $M^{37}[Br]^+$), 209.9 (90, $M^{39}[Br]^+$). These data are consistent with that previously reported for this compound.[249] To a RBF under $N_{2(g)}$, was added **382** (18.1 mmol, material from previous step)

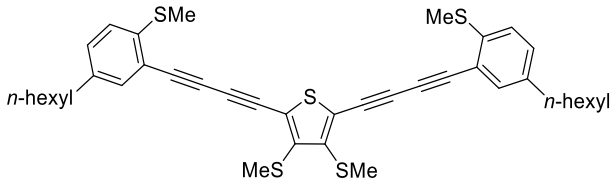
and anhydrous Et_2O (45 mL). The flask was cooled to −78°C and *n*-BuLi (22.6 mL of a 1.6 M solution in hexane) was added dropwise. Following this, the reaction was stirred for 1 h. Subsequently dimethyl disulfide (4 mL, 45.2 mmol) was added and the mixture was stirred for additional 35 min at −78°C before being slowly warmed to 22 °C. After warming to 22 °C, the reaction mixture was quenched with 1 M HCl (20 mL) and extracted with Et_2O (3 × 10 mL). The combined organics were washed with H_2O (30 mL) and brine (3 × 30 mL) successively before being dried over $MgSO_4$ and concentrated under reduced pressure to yield a pale-yellow oil as the crude. The crude material was purified with flash column chromatography (silica gel, 100% hexanes) to give the title compound as a pale-yellow oil (2.63 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 2H), 2.46 (s, 6H); LCMS: t_R = 3.8 min *m/z*: 176.0 [M^+], 177.0 [$M+H^+$], 130.0 [$M+H-[SCH_3]^+$]. These data are consistent with that previously reported for this compound.[250]

2,5-Diiodo-3,4-bis(methylthio)thiophene (385):



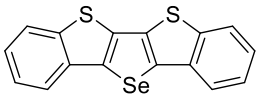
To a RBF under $N_{2(g)}$ in the dark, **384** (2.0 g, 11.3 mmol), NIS (5.6 g, 25.0 mmol), *p*-toluenesulfonic acid (0.22 g, 1.1 mmol) and EtOH (60 mL) were added. The flask was then degassed × 3 with $N_{2(g)}$ before stirred for 3 h at 22 °C. Following this, the reaction was quenched with a saturated $Na_2S_2O_3$ solution (20 mL) and the aqueous layer extracted with DCM (3 × 20 mL). The combined organics were washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield yellow crystals. The crude material was purified *via* trituration with hexanes from DCM to give the title compound as pale-yellow cubic crystals (4.18 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 142.3 (C), 89.8 (C), 20.0 (CH_3); LCMS: t_R = 3.9 min, *m/z*: 427.8 [M^+], 301.8 [$M+H-[I]^+$]; HRMS (APCI) *m/z* [$M]^+$ Calcd. For $C_6H_6I_2S_3$ 427.7700, Found 427.7709.

2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-3,4-bis(methylthio)thiophene (346):



To a RBF under $N_{2(g)}$ in the dark, **385** (0.68 g, 1.6 mmol), $Pd(PPh_3)_4$ (0.091 g, 0.08 mmol), CuI (0.030 g, 0.16 mmol) and DIPA (7 mL) were added. The reaction flask was then degassed × 3 with $N_{2(g)}$ and heated to 60 °C before **273** (16 mL of a 0.24 M Et_2O solution) was added dropwise over 6 h. The reaction was stirred for an additional 12 h at 60 °C. The reaction mixture was filtered over a pad of Celite®, eluting with Et_2O. The organic solution was then washed with H_2O (30 mL) and brine (3 × 30 mL), before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 10% Et_2O in hexanes) to give the title compound as small light-yellow needle-crystals (0.87 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.9 Hz, 2H), 7.09 (dd, *J* = 8.2 Hz, 1.9 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 2.53 (s, 6H), 2.56 (t, *J* = 7.7 Hz, 4H), 2.43 (s, 6H), 1.58 (p, *J* = 2.9 Hz, 4H), 1.29 – 1.17 (m, 12H), 0.85 – 0.77 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 142.5 (C), 140.1 (C), 139.7 (C), 133.7 (C), 130.6 (C), 125.3 (C), 123.8 (C), 119.8 (C), 84.1 (C), 83.5 (C), 79.1 (C), 74.7 (C), 35.1 (CH_2), 31.7 (CH_2), 31.2 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 18.6 (CH_3), 15.7 (CH_3), 14.2 (CH_3); HRMS (APCI) *m/z* $[M]^+$ Calcd. for $C_{40}H_{44}S_5$ 685.2119, Found 685.2122.

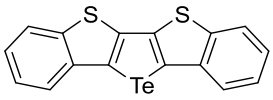
Selenocycle (387):



To a round bottom flask under $N_{2(g)}$, DCE (5 mL) was added. The flask was heated to 80 °C and **386** (0.074 g, 0.25 mmol) in DCE (3 mL) and $SeCl_2$ (0.25 mmol, material titrated from previous step) in DCE (3 mL) were simultaneously added to the flask dropwise over 6 h. The reaction was stirred for an additional 12 h. Following this, the reaction was cooled to RT and quenched with a saturated $Na_2S_2O_3$ solution (70 mL) and diluted with DCM (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and the combined organics were washed with a saturated $Na_2S_2O_3$ solution (40 mL), H_2O (40 mL) and

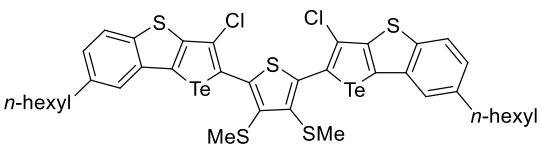
brine (3 × 40 mL) successively. The organic solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a red solid. Trituration of this solid with DCM yielded the product in the supernatant as dark-red solid (71 mg, 86%). Recrystallisation in $CHCl_3$ yields long dark-red needle-crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 4H), 7.48 (ddd, J = 8.1, 7.2, 1.1 Hz, 2H), 7.40 ppm (ddd, J = 8.3, 7.2, 1.3 Hz, 2H). This data is consistent with that previously reported for this compound.[9]

Tellurocycle (389):



To a round bottom flask under $N_{2(g)}$, DCE (5 mL) was added. The flask was heated to 80 °C and **1386** (0.074 g, 0.25 mmol) in DCE (3 mL) and $TeCl_4$ (0.068 g, 0.25 mmol) in anhydrous dioxane (3 mL) were simultaneously added to the flask dropwise over 6 h. The reaction was stirred for an additional 12 h. Following this, the reaction was cooled to RT and quenched with a saturated $Na_2S_2O_3$ solution (70 mL) and diluted with DCM (10 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 10 mL) and the combined organics were washed with a saturated $Na_2S_2O_3$ solution (40 mL), H_2O (40 mL) and brine (3 × 40 mL) successively. The organic solution was then dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a yellow solid. Trituration of this solid with hexanes from $CHCl_3$ yielded small light-yellow needle-crystals (63 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.79 – 7.65 (m, 2H), 7.50 – 7.34 (m, 4H); LCMS: t_R = 4.5 min *m/z*: 391.9 [M^+], 395.9 [$M+H^+$]. These data are consistent with that previously reported for this compound.[9]

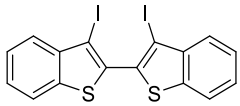
2,2'-(3,4-Bis(methylthio)thiophene-2,5-diyl)bis(3-chloro-7-hexylbenzo[*b*]telluropheno[2,3-*d*]thiophene) (393):



To a round bottom flask under N_2(g), DCE (5 mL) was added and the solution was heated to 80 °C. To this flask, **346** (77 mg, 0.11 mmol in 2.5 mL dioxane) and $TeCl_4$ (60 mg, 0.05 mmol

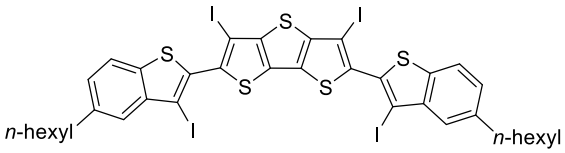
in 2.5 mL dioxane) were added simultaneously over 6 h and stirred for an additional 12 h at 80 °C. Following this, the reaction was quenched with a saturated $Na_2S_2O_3$ solution (30 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 5 mL) and the combined organics were washed with a saturated $Na_2S_2O_3$ solution (2 × 30 mL), H_2O (30 mL) and brine (3 × 30 mL). The organic solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the title compound as a deep-yellow solid (98 mg, 88%). This solid rapidly degrades in hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 1.7 Hz, 2H), 7.17 (dd, *J* = 8.3, 1.7 Hz, 2H), 2.74 – 2.65 (m, 4H), 2.57 (s, 6H), 1.67 (p, *J* = 7.0, 4H), 1.43 – 1.29 (m, 12H), 0.93 – 0.88 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 145.2 (C), 141.4 (C), 140.9 (C), 134.0 (C), 138.5 (C), 133.3 (C), 128.3 (C), 126.3 (CH), 122.9 (CH), 122.6 (CH), 121.9 (C), 121.3 (C), 36.1 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.2 (CH_2), 22.8 (CH_2), 22.4 (CH_2), 18.3 (CH_3). Mass spec. data could not be obtained due to poor stability.

3,3'-Diiodo-2,2'-bibenzo[b]thiophene (407):



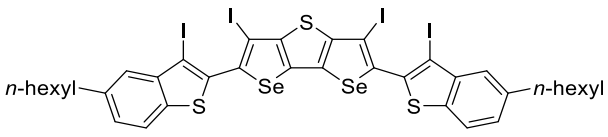
To a RBF under $N_{2(g)}$ was added **386** (1.0 g, 3.3 mmol), and DCE (34 mL). NIS (3.05 mg, 14.5 mmol) and triphenylphosphine resin (890 mg, 0.801 mmol) were then added and the reaction was heated to 60 °C and allowed to stir at this temperature for 18 h. The reaction mixture was diluted with DCM and filtered over a Celite® pad. The organics were washed with a saturated $Na_2S_2O_3$ solution (2 × 20 mL), 1.0 M NaOH (2 × 20 mL) and brine (2 × 20 mL) successively. The organic solution was then dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield an off-white powder (1.3 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (tt, *J* = 7.7, 0.7 Hz, 4H), 7.55 – 7.44 (m, 4H); LCMS: t_R = 4.6 min *m/z*: 517.8 [M^+]. These data are consistent with that previously reported for this compound.[131]

2,6-Bis(5-hexyl-3-iodobenzo[*b*]thiophen-2-yl)-3,5-diiododithieno[3,2-*b*:2',3'-d]thiophene (408):



To a RBF under $N_{2(g)}$ was added **346** (146.1 mg, 0.2132 mmol), and DCE (4.3 mL). NIS (383.8 mg, 1.706 mmol) and triphenylphosphine resin (111.8 mg, 0.1006 mmol) were then added and the reaction was heated to 70 °C and allowed to stir at this temperature for 18 h. The reaction mixture was diluted with DCM and filtered over a Celite® pad. The organics were washed with a saturated $Na_2S_2O_3$ solution (2 × 20 mL), 1.0 M NaOH (2 × 20 mL) and brine (2 × 20 mL) successively. The organic solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the title compound as a red-orange semi-solid (201 mg, 84%). Recrystallisation in MeOH and $CHCl_3$ yielded thin clear needle-crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 1.6 Hz, 2H), 7.32 (dd, *J* = 8.3, 1.6 Hz, 2H), 2.88 – 2.75 (m, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.46–1.29 (m, 12H), 0.97–0.88 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 147.1 (C) 141.2 (C), 137.7 (C), 136.1 (C), 134.5 (C), 132.1 (C), 127.9 (CH), 126.1 (CH), 122.1 (CH), 87.3 (C), 78.1 (C), 36.14 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

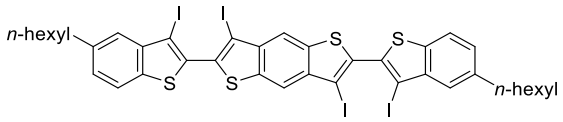
2,6-Bis(5-hexyl-3-iodobenzo[b]thiophen-2-yl)-3,5-diiododiselenopheno[3,2-b:2',3'-d]thiophene (409):



To a RBF under $N_{2(g)}$ was added **344** (220.1 mg, 0.2825 mmol), and DCE (6 mL). NIS (508.4 mg, 2.259 mmol) and triphenylphosphine resin (148.1 mg, 0.1332 mmol) were then added and the reaction was heated to 60 °C and allowed to stir at this temperature for 18 h. The reaction mixture was diluted with DCM and filtered over a Celite® pad. The organics were then washed with a saturated $Na_2S_2O_3$ solution (2 × 20 mL), 1.0 M NaOH (2 × 20 mL) and brine (2 × 20 mL) successively. The organic solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a red solid (290 mg, 84%). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 1.5 Hz, 2H), 7.31 (dd, J = 8.2, 1.6 Hz, 2H), 2.81 (t, J = 7.8 Hz, 4H), 1.77 – 1.66 (m, 4H), 1.43 – 1.34 (m, 12H), 0.96 – 0.87 (m, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 148.0 (C), 141.2 (C), 141.1 (C), 138.8 (C), 137.7 (C), 136.8 (C), 135.3 (C), 127.8 (CH), 126.0 (CH), 122.1 (CH), 86.9 (C), 79.6 (C), 36.1 (CH_2), 31.9 (CH_2), 31.9 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 655.27. Mass spec. data could not be obtained due to poor ionisation/solubility.

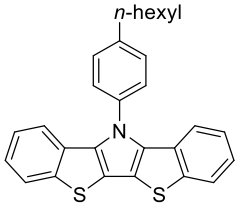
2,6-Bis(5-hexyl-3-iodobenzo[b]thiophen-2-yl)-3,7-diiodobenzo[1,2-b:4,5-b']dithiophene (410):



To a RBF under $N_{2(g)}$ in the dark was added **342** (118.2 mg, 0.1740 mmol) and DCE (8.7 mL). Iodine (397.6 mg, 1.566 mmol) was then added and the reaction heated to 80 °C and allowed to stir at this temperature for 18 h. The reaction was then cooled to 22 °C before being quenched through addition of a saturated $Na_2S_2O_3$ solution (20 mL). After separation, the aqueous layer was extracted with DCM (3 × 20 mL) and the combined organics were washed with brine (2 × 20 ml), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material underwent trituration with hexanes from DCM to give the title compound as a cream-coloured powder (190.4 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.65 (m, 3H), 7.33 (dd, J = 8.1, 1.6 Hz, 3H), 2.82 (t, *J* = 7.8 Hz, 4H), 1.72 (d, *J* = 8.1 Hz, 4H), 1.45 – 1.32 (m, 12H), 0.94 – 0.88 (m, 6H). ^{13}C NMR* (DEPT-Q, 100 MHz, $CDCl_3$) δ 127.8 (CH), 125.9 (CH), 122.1 (CH), 120.1 (CH), 36.1 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 39.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3). Mass spec. data could not be obtained due to poor ionisation/solubility.

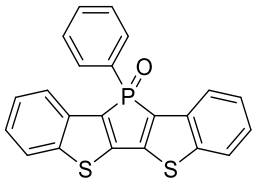
*Quaternary carbon resonances could not be obtained due to poor solubility.

11-(4-Hexylphenyl)-11H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-d]pyrrole (414):



To a RBF under $N_{2(g)}$ was added **407** (58.1 mg, 0.112 mmol), anhydrous toluene (3.7 mL), *n*-hexylaniline (0.32 mL, 0.16 mmol), Cs_2CO_3 (146 mg, 0.448 mmol), Xantphos (25.94 mg, 0.0448 mmol) and $Pd_2(dba)_3$ (20.53 mg, 0.0224 mmol). The reaction mixture was heated at reflux for 40 h. After this time the reaction was cooled to 22 °C before being quenched through addition of 10% citric acid aqueous solution (5 mL). The aqueous layer was then extracted with DCM (3 × 20 mL) and the combined organics were then washed with brine (2 × 20 ml), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was subject to column chromatography (silica gel, 0-25% DCM in hexanes) to give the title compound as a pink-red crystal (48.7 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 8.1, 0.9 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.23 (ddd, *J* = 8.1, 6.7, 1.8 Hz, 2H), 7.19 – 7.10 (m, 4H), 2.87 – 2.80 (m, 2H), 1.85 – 1.75 (m, 2H), 1.51 – 1.37 (m, 6H), 0.98 – 0.91 (m, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 144.4 (C), 141.9 (C), 138.2 (C), 135.9 (C), 129.8 (CH), 127.8 (CH), 127.5 (C), 124.3 (CH), 124.1 (CH), 123.5 (CH), 119.2 (CH), 115.4 (C), 35.9 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. For $C_{28}H_{26}NS_2$ 440.1501, Found 440.1490. These data are consistent with that previously reported for this compound.[251]

(423):

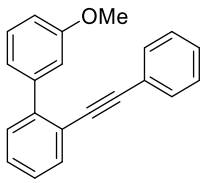


To a RBF under $N_{2(g)}$ was added **407** (30.0 mg, 0.057 mmol) and anhydrous Et_2O (3 mL). The solution was then cooled to 0 °C before *n*-BuLi (0.06 mL of a 2.0 M solution in hexanes) was slowly added. The reaction mixture was allowed to stir at this temperature for 1 h. After this

time phenylphosphonic dichloride (0.01 mL, 0.06 mmol) was added before the reaction was allowed to warm to 22 °C and stir at this temperature for 18 h. The reaction was quenched through addition of H_2O (5 mL) and diluted with DCM (5 mL). After separation, the aqueous layer was extracted with additional DCM (3 × 5 mL) and washed with brine (2 × 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was triturated from DCM with hexanes to give the title compound as a yellow solid (15.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 6H), 7.56 – 7.49 (m, 1H), 7.46 – 7.33 (m, 6H); LCMS: t_R = 3.3 min *m/z*: 389.0 [M+H$^+$]. These data are consistent with that previously reported for this compound.[252]

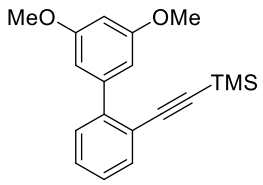
5.4 Chapter 4 Experimental

3'-Methoxy-2-(phenylethynyl)-1,1'-biphenyl (460):



To a RBF under $N_{2(g)}$ was added iodobenzene (0.19 mL, 1.6 mmol), CuI (19.07 mg, 0.1001 mmol), $Pd(PPh_3)_4$ (96.45 mg, 0.0834 mmol) and DIPA (4 mL). Compound **469** (173.8 mg, 0.8347 mmol) was then added before the reaction mixture was allowed to stir at 22 °C for 18 h. After this time, the solution was diluted with Et_2O before being filtered over a Celite® pad. The organics were then washed with H_2O (1 × 15 mL) and brine (2 × 20 ml) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 0-10% EtOAc in hexanes) to give the title compound as a brown semi-solid (168.9 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (ddd, J = 7.6, 1.5, 0.6 Hz, 1H), 7.46 – 7.33 (m, 6H), 7.29 (dt, J = 4.2, 2.8 Hz, 3H), 7.26 – 7.22 (m, 2H), 6.95 (ddd, J = 8.2, 2.5, 1.1 Hz, 1H), 3.83 (s, 3H); LCMS: t_R = 3.8 min *m/z*: 285.2 [M+H$^+$]. These data are consistent with that previously reported for this compound.[227]

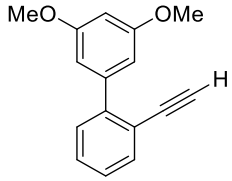
((3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)ethynyl)trimethylsilane (473):



To a RBF under $N_{2(g)}$ was added **471** (4.0 g, 15.7 mmol), 3,5-dimethoxyphenylboronic acid (11.48 g, 63.16 mmol), $Pd(PPh_3)_4$ (1.82 g, 1.57 mmol), Cs_2CO_3 (51.44 g, 157.7 mmol), toluene (160 mL), EtOH (40 mL) and H_2O (40 mL). The reaction mixture was heated to reflux and allowed to stir at this temperature for 18 h. After this time the solution was then filtered through a Celite® pad, washing with Et_2O. The organic solution was washed with brine (2 × 40 mL), dried over $MgSO_4$, filtered and concentrated under educed pressure. The crude material was then subject to flask column chromatography (silica gel, 0-20% EtOAc in hexanes) and subject to reverse phase column chromatography (C18 silica, 0-100% ACN in H_2O) to give the title compound as a light orange oil (3.5 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (ddd, *J*

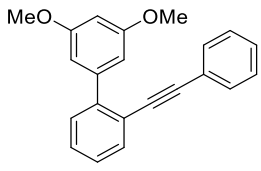
= 7.6, 1.4, 0.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.16 (ddd, *J* = 7.6, 7.0, 2.0 Hz, 1H), 6.65 (d, *J* = 2.3 Hz, 2H), 6.38 (t, *J* = 2.3 Hz, 1H), 3.72 (s, 6H), 0.04 (s, 9H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.3 (C), 144.3 (C), 142.3 (C), 133.5 (CH), 129.3 (CH), 128.7 (CH), 127.1 (CH), 121.5 (C), 107.6 (CH), 104.7 (C), 99.8 (CH), 97.8 (C), 55.4 (2 × CH_3), -0.1 (CH_3). LCMS: t_R = 3.6 min *m/z*: 311.1 [M+H$^+$]; HRMS *m/z* [M+H]$^+$ Calcd. for $C_{19}H_{23}O_2Si$ 311.1462, Found 311.1472.

2-Ethynyl-3',5'-dimethoxy-1,1'-biphenyl (474):



To a RBF under $N_{2(g)}$ was added **473** (500 mg, 1.61 mmol), K_2CO_3 (333.8 mg, 2.415 mmol), THF (11 mL) and MeOH (11 mL). The reaction was stirred overnight at 22 °C, before being quenched through addition of H_2O. The organics were extracted with EtOAc (3 × 20 mL), washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. This gave the title compound as a yellow oil (372 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.30 (ddd, *J* = 7.7, 5.5, 3.3 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 2H), 6.49 (t, *J* = 2.3 Hz, 1H), 3.83 (s, 6H), 3.09 (s, 1H); LCMS: t_R = 3.0 min *m/z*: 239.2 (100, M+H$^+$), 240.1 [M+2H$^+$]. These data are consistent with that previously reported for this compound.[253]

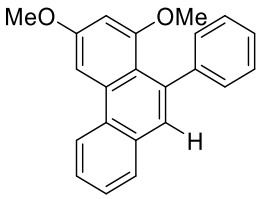
3',5'-Dimethoxy-2-(phenylethynyl)-1,1'-biphenyl (462):



To a RBF under $N_{2(g)}$ was added 1-iodobenzene (0.7 mL, 6.2 mmol), CuI (29.76 mg, 0.1563 mmol), $Pd(PPh_3)_2Cl_2$ (54.85 mg, 0.0781 mmol) and DIPA (10.4 mL). Compound **474** (372.5 mg, 1.563 mmol) was added before the reaction mixture was allowed to stir at 22 °C for 18 h. After this time, the solution was dilute with diethyl ether before being filtered over a Celite®

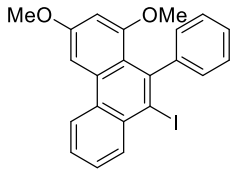
pad. The organics were washed with H_2O (1 × 15 mL) and brine (2 × 20 ml) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 0-75% DCM in hexanes) to give the title compound as a brown semi-solid (407 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 (dt, *J* = 4.5, 2.8 Hz, 3H), 6.83 (d, *J* = 2.3 Hz, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 3.81 (s, 6H); LCMS: t_R = 3.6 min *m/z*: 315.1 [M+H$^+$]. These data are consistent with that previously reported for this compound.[253]

1,3-Dimethoxy-10-phenylphenanthrene (463):



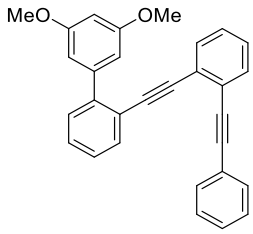
To a RBF under $N_{2(g)}$ was added **462** (74.6 mg 0.237 mmol) and anhydrous toluene (2.4 mL). $Cu(OTf)_2$ (8.57 mg, 0.023 mmol) was then added and the reaction mixture heated to 80 °C for 4 h. After this time the solution was cooled to 22 °C, concentrated under reduced pressure and diluted with DCM (15 mL). After separation, the aqueous layer was extracted with additional brine (2 × 10 mL) and the combined organics washed with H_2O (10 mL) before being dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was furnished as a brown solid (58 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.56 (m, 1H), 7.82 (dd, J = 7.0, 2.4 Hz, 1H), 7.77 (d, J = 2.4 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.41 (s, 1H), 7.39 – 7.35 (m, 4H), 6.63 (d, J = 2.3 Hz, 1H), 4.04 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 159.0 (C), 158.6 (C), 145.8 (C), 137.2 (C), 133.7 (C), 132.0 (C), 129.2 (C), 128.5 (CH), 128.4 (CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 126.1 (CH), 125.7 (CH), 117.2 (C), 99.3 (CH), 96.5 (CH), 55.5 (CH_3), 55.4 (CH_3). HRMS *m/z* [M+H]$^+$ Calcd. for $C_{22}H_{19}O_2$ 315.1380, Found 315.1387.

9-Iodo-1,3-dimethoxy-10-phenylphenanthrene (464):



To a RBF under $N_{2(g)}$ in the dark was added **462** (20.7 mg, 0.065 mmol) and anhydrous DCE (0.7 mL). NIS (28.14 mg, 0.1251 mmol) and triphenylphosphine resin (8.60 mg, 0.007 mmol) were then added and the reaction allowed to stir at reflux for 2 h. After this time the reaction was cooled to 22 °C before being quenched through addition of a sat. solution of $Na_2S_2O_3$ (10 mL). The aqueous layer was extracted with DCM (3 × 20 mL), washed with brine (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to reverse phase column chromatography (C18 silica gel, 10-100% ACN in H_2O) to give the title compound as an orange solid (25 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.52 (m, 1H), 8.49 – 8.40 (m, 1H), 7.73 (d, J = 2.4 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.45 – 7.33 (m, 3H), 7.21 – 7.12 (m, 2H), 6.56 (d, J = 2.3 Hz, 1H), 4.02 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (C), 157.8 (C), 150.7 (C), 142.7 (C), 135.1 (CH), 133.6 (C), 133.2 (C), 129.8 (C), 128.8 (CH), 128.4 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 123.3 (CH), 118.6 (C), 106.5 (C), 99.8 (CH), 96.4 (CH), 55.9 (CH_3), 55.5 (CH_3); HRMS *m/z* $[M+H]^+$ Calcd. for $C_{22}H_{18}IO_2$ 441.0346 Found 441.0353.

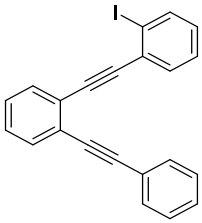
3',5'-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-1,1'-biphenyl (476):



To a RBF under $N_{2(g)}$ was added **474** (276.8 mg, 1.161 mmol), DIPA (8 mL), CuI (22.12 mg, 0.1161 mmol), $Pd(PPh_3)_4$ (67.13 mg, 0.0580 mmol) and **480** (830.6 mg, 2.731 mmol). The reaction was then allowed to stir for 18 h at 22 °C. After this time the reaction was diluted with Et_2O and filtered over a Celite® pad and washed with brine (2 × 15 mL). The organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then subject to flash column chromatography (silica gel, 0-75% DCM in hexanes) to give the

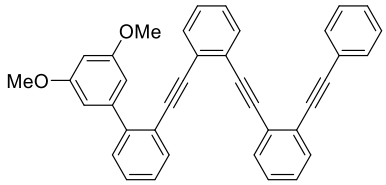
title compound as an orange semi-solid (360 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.47 – 7.38 (m, 4H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.23 – 7.15 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 2H), 6.38 (t, *J* = 2.3 Hz, 1H), 3.71 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.4 (C), 143.6 (C), 142.4 (C), 133.5 (CH), 132.0 (CH), 131.9 (CH), 131.8 (CH), 129.5 (CH), 128.8 (CH), 128.4 (CH), 128.4 (CH), 128.0 (CH), 128.0 (CH), 127.3 (CH), 126.0 (C), 125.5 (C), 123.3 (C), 121.6 (C), 107.5 (CH), 100.3 (CH), 93.5 (C), 93.5 (C), 91.7 (C), 88.3 (C), 55.5 (2 × CH_3); LCMS: t_R = 4.1 min *m/z*: 415.1 [M+H$^+$]; HRMS *m/z* [M+H]$^+$ Calcd. for $C_{30}H_{23}O_2$ 415.1693, Found 415.1695.

1-Iodo-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (483):



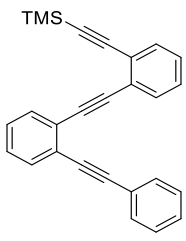
To a RBF under $N_{2(g)}$ was added 1,2-diiodobenzene (2.47g, 7.50 mmol), CuI (23.83 mg, 0.1251 mmol), $Pd(PPh_3)_4$ (144.6 mg, 0.1251 mmol) and DIPA (6.3 mL). A DIPA solution of **482** (253.1 mg, 1.251 mmol) was then added and the reaction allowed to stir at 22 °C for 18 h. After this time the reaction was dilute with EtOAc (10 mL) and brine (10 mL). After separation, the aqueous layer was extracted with additional EtOAc (3 × 20 mL) and the combined organics washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 15% DCM in hexanes) to give the title compound as an off white solid (288 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.60 – 7.55 (m, 4H), 7.37 – 7.29 (m, 6H), 7.04 – 7.00 (m, 1H); LCMS: t_R = 4.2 min *m/z*: 404.0 [M$^+$], 405.0 [M+H$^+$]. These data are consistent with that previously reported for this compound.[254]

3',5'-Dimethoxy-2-((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,1'-biphenyl (477):



To a RBF under $N_{2(g)}$ was added **483** (398.8 mg, 0.9865 mmol), CuI (37.5 mg, 0.197 mmol), $Pd(PPh_3)_4$ (227.9 mg, 0.1973 mmol) and DIPA (20 mL). Compound **474** (352.6 mg, 1.479 mmol) was added, and the reaction heated to 60 °C and allowed to stir at this temp for 2 hours. After this time the reaction was diluted with Et_2O (20 mL) and filtered over a pad of Celite®. The organics were washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 0-10% DCM in hexanes) to give the title compound as a dark yellow oil (385 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.46 (m, 3H), 7.43 – 7.39 (m, 1H), 7.37 – 7.22 (m, 9H), 6.84 (d, J = 2.3 Hz, 2H), 6.41 (t, J = 2.3 Hz, 1H), 3.77 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.4 (C), 143.5 (C), 142.4 (C), 133.7 (CH), 132.2 (CH), 132.2 (CH), 132.0 (CH), 131.8 (CH), 131.8 (CH), 129.3 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.0 (C), 125.9 (C), 125.9 (C), 125.6 (C), 123.4 (C), 121.5 (C), 107.5 (CH), 100.2 (CH), 93.8 (C), 93.7 (C), 92.3 (C), 92.3 (C), 91.6 (C), 88.4 (C), 55.5 (2 × CH_3); HRMS *m/z* $[M+H]^+$ Calcd. for $C_{38}H_{27}O_2$ 515.2006, Found 515.2008.

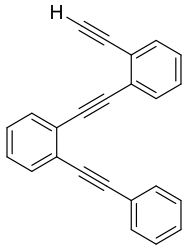
Trimethyl((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)silane (484):



To a RBF under $N_{2(g)}$ was added **483** (288.9 mg, 0.7146 mmol), CuI (13.6 mg, 0.071 mmol), $Pd(PPh_3)_2Cl_2$ (50.16 mg, 0.0714 mmol) and DIPA (4 mL). Trimethylsilylacetylene (0.3 mL, 2.1 mmol) was then added and the reaction allowed to stir at 22 °C for 18 h. After this time the reaction was diluted with Et_2O (10 mL) and filtered over a pad of Celite. The organics were

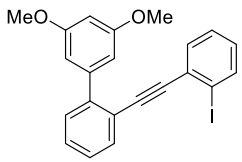
then washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 0-15% DCM in hexanes) to give the title compound as a brown oil (265 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 6H), 7.36 – 7.27 (m, 7H), 0.21 (s, 9H); LCMS: t_R = 4.7 min *m/z*: 375.2 [M+H$^+$]. These data are consistent with that previously reported for this compound.[255]

1-Ethynyl-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (485):



To a RBF under $N_{2(g)}$ was added MeOH (3.5 mL), Et_2O (3.5 mL) and **484** (265 mg, 0.714 mmol). K_2CO_3 (197.5 mg, 1.429 mmol) was then added before the reaction mixture was allowed to stir at 22 °C for 18 h. The reaction solution was concentrated under reduced pressure before being diluted with EtOAc (10 mL) and H_2O (10 mL). After separation, the aqueous layer was extracted with additional EtOAc (3 × 20 mL) and washed with brine (2 × 20 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a brown oil (155 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 6H), 7.38 – 7.28 (m, 7H), 3.20 (s, 1H); LCMS: t_R = 3.8 min *m/z*: 302.2 [M$^+$]. These data are consistent with that previously reported for this compound.[255]

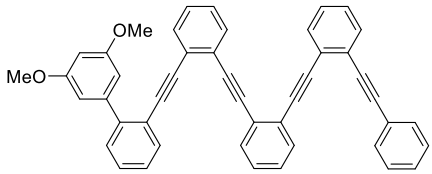
2-((2-Iodophenyl)ethynyl)-3',5'-dimethoxy-1,1'-biphenyl (486):



To a RBF under $N_{2(g)}$ was added 1,2-diiodobenzene (830.6 mg, 2.517 mmol), CuI (23.97 mg, 0.1258 mmol), $Pd(PPh_3)_2Cl_2$ (88.13 mg, 0.1258 mmol) and DIPA (6.3 mL). Compound **474** (300 mg, 1.25 mmol) was then added and the reaction was allowed to stir for 18 h at 22 °C.

After this time the reaction was dilute with Et_2O (20 mL) and filtered over a pad of Celite®. The organics were washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 10% DCM in hexanes) to give the title compound as a dark yellow oil (291 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.75 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.46 – 7.24 (m, 4H), 6.97 (td, *J* = 7.6, 1.8 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.5 (C), 143.9 (C), 142.5 (C), 138.8 (CH), 133.4 (CH), 132.7 (CH), 130.1 (C), 129.5 (CH), 129.3 (CH), 128.9 (CH), 127.8 (CH), 127.3 (CH), 121.3 (C), 107.7 (CH), 100.4 (C), 100.2 (CH), 94.5 (C), 92.9 (C), 55.6 (2 × CH_3); HRMS *m/z* $[M+H]^+$ Calcd. for $C_{22}H_{18}IO_2$ 441.0346, Found 441.0360.

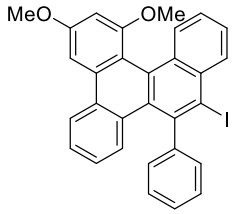
3',5'-Dimethoxy-2-((2-((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,1'-biphenyl (478):



To a RBF under $N_{2(g)}$ was added **486** (68.2 mg, 0.154 mmol), CuI (2.95 mg, 0.015 mmol), $Pd(PPh_3)_4$ (17.89 mg, 0.0154 mmol), DIPA (4 mL), and toluene (4 mL). The reaction mixture was then heated to 80 °C before **485** (94 mg, 0.31 mmol) was added as a DIPA solution. The reaction was allowed to stir at this temperature for 2.5 h. After this time the reaction was quenched through addition of H_2O (10 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organics washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (50-100% DCM in hexanes) to give the title compound as a brown oil (57 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.55 – 7.49 (m, 6H), 7.42 – 7.39 (m, 1H), 7.37 – 7.27 (m, 8H), 7.26 – 7.17 (m, 4H), 6.84 (d, *J* = 2.3 Hz, 2H), 6.41 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 6H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.3 (C), 143.5 (C), 142.4 (C), 133.7 (CH), 132.3 (CH), 132.3 (CH), 132.2 (CH), 131.9 (CH), 131.8 (CH), 129.3 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128. (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.2 (CH), 125.9 (C), 125.9 (C), 125.9 (C), 125.9 (C), 125.8 (C), 125.5 (C), 123.4 (C), 121.5 (C), 107.6 (CH), 100.1 (CH), 93.7 (C), 93.6 (C), 92.5 (C), 92.5 (C),

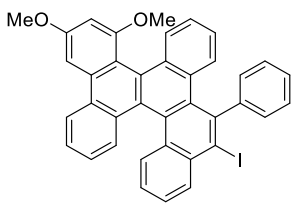
92.4 (C), 92.2 (C), 91.7 (C), 88.4 (C), 55.5 (2 × CH_3); HRMS *m/z* $[M+H]^+$ Calcd. for $C_{46}H_{31}O_2$ 615.2319, Found 615.2311.

6-Iodo-11,13-dimethoxy-5-phenylbenzo[g]chrysene (488):



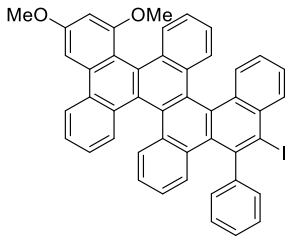
To a RBF under $N_{2(g)}$ in the dark was added **476**(100 mg, 0.241 mmol) and anhydrous DCE (12 mL). NIS (119.4 mg, 0.5307 mmol) and triphenylphosphine resin (63.27 mg, 0.0569 mmol) were then added and the reaction allowed to stir at 22 °C for 18 h. After this time the reaction was quenched through addition of a sat. solution of $Na_2S_2O_3$ (20 mL). The aqueous layer was then extracted with DCM (3 × 20 mL) and the combined organics were washed with brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 25% DCM in hexanes) to give the title product as a pink solid (116 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.42 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.59 – 7.37 (m, 5H), 7.34 – 7.28 (m, 1H), 7.10 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 2.3 Hz, 1H), 4.09 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.1 (C), 158.0 (C), 147.7 (C), 141.7 (C), 134.0 (C), 133.4 (CH), 132.8 (C), 132.4 (CH), 130.8 (CH), 130.7 (C), 130.5 (C), 130.5 (C), 130.3 (CH), 129.0 (CH), 128.8 (C), 128.8 (C), 128.7 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 126.4 (CH), 126.1 (CH), 124.3 (CH), 123.6 (CH), 113.6 (C), 106.0 (C), 98.8 (CH), 97.7 (CH), 55.7 (CH_3), 54.9 (CH_3). HRMS *m/z* $[M+H]^+$ Calcd. for $C_{30}H_{22}IO_2$ 541.0659 Found 541.0642.

10-Iodo-2,4-dimethoxy-9-phenyltribenzo[c,g,p]chrysene (489):



To a RBF under $N_{2(g)}$ in the dark was added anhydrous DCE (7 mL), **477** (35.0 mg, 0.068 mmol), NIS (48.96 mg, 0.2176 mmol) and triphenylphosphine resin (35.6 mg, 0.032 mmol). The reaction was allowed to stir at 22 °C for 20 h before being quenched through addition of a sat. solution of $Na_2S_2O_3$ (10 mL). The aqueous layer was extracted with DCM (3 × 20 mL) and the combined organics washed with brine (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subject to flash column chromatography (silica gel, 25% DCM in hexanes) to give the title compound as a yellow solid (27 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.5, 1.2 Hz, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.82 – 7.66 (m, 3H), 7.60 – 7.38 (m, 6H), 7.25 – 7.16 (m, 3H), 7.03 (dt, J = 7.6, 1.6 Hz, 1H), 6.94 – 6.84 (m, 2H), 4.13 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 159.9 (C), 157.8 (C), 149.3 (C), 143.2 (C), 134.4 (CH), 134.0 (C), 133.6 (C), 133.1 (C), 132.7 (CH), 132.6 (C), 131.1 (CH), 130.5 (C), 130.5 (C), 130.2 (CH), 129.4 (CH), 129.4 (CH), 129.2 (CH), 129.2 (C), 128.7 (C), 128.6 (C), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.6 (C), 126.8 (C), 126.5 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 124.0 (CH), 123.7 (CH), 113.3 (C), 111.4 (C), 99.1 (CH), 97.8 (CH), 55.8 (CH_3), 55.4 (CH_3); HRMS *m/z* $[M]^+$ Calcd. for $C_{38}H_{25}IO_2$ 640.0894, Found 640.0885.

10-Iodo-19,21-dimethoxy-9-phenyltetrabenzo[a,f,j,s]picene (490):



To a RBF under $N_{2(g)}$ was added anhydrous DCE (12 mL), **478** (70.8 mg, 0.115 mmol), NIS (155 mg, 0.690 mmol) and triphenylphosphine resin (30.16 mg, 0.0271 mmol). The reaction was allowed to stir at 22 °C for 20 h before being quenched through addition of a sat. solution of $Na_2S_2O_3$ (10 mL). The aqueous layer was extracted with DCM (3 × 20 mL), and the combined organics washed with brine (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then subject to flash column chromatography (silica gel, 25-50% DCM in hexanes) to give the title compound as a yellow solid (70 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.2 Hz, 2H), 8.13 (dd, J = 14.2,

8.1 Hz, 3H), 7.94 – 7.81 (m, 4H), 7.75 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.59 (q, J = 7.8 Hz, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.34 (dt, J = 15.4, 8.1 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.10 (t, J = 7.7 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.95 (d, J = 2.2 Hz, 1H), 4.17 (s, 3H), 4.04 (s, 3H); ^{13}C NMR (DEPT-Q, 100 MHz, $CDCl_3$) δ 160.1 (C), 157.9 (C), 147.2 (C), 141.8 (C), 134.3 (C), 133.8 (CH), 133.5 (C), 133.1 (CH), 132.4 (C), 131.8 (C), 131.5 (CH), 131.3 (C), 131.3 (CH), 131.1 (C), 131.1 (C), 130.9 (C), 130.3 (C), 130.1 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (C), 129.2 (CH), 128.9 (C), 128.8 (C), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.5 (CH), 126.3 (C), 126.2 (C), 126.1 (CH), 125.9 (CH), 125.6 (CH), 125.3 (C), 125.1 (CH), 124.6 (CH), 124.1 (CH), 123.9 (CH), 113.8 (C), 106.5 (C), 99.2 (CH), 98.0 (CH), 55.8 (CH_3), 55.6 (CH_3); HRMS (APCI) *m/z* $[M+H]^+$ Calcd. For $C_{46}H_{30}IO_2$ 741.1285, Found 741.1299.

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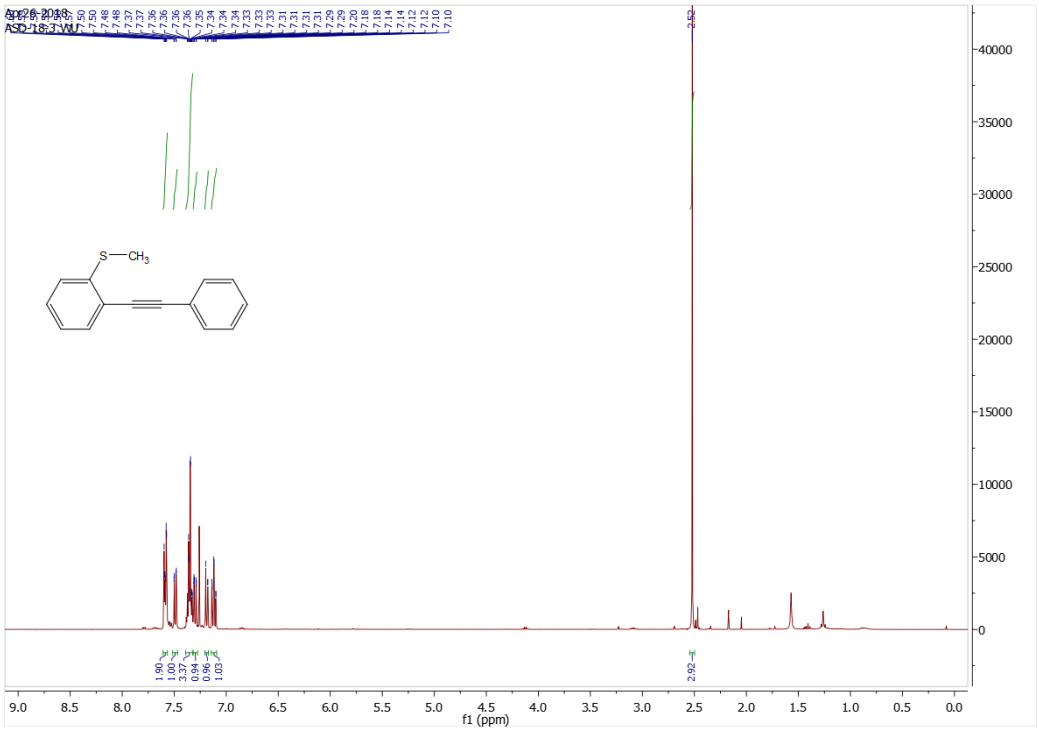
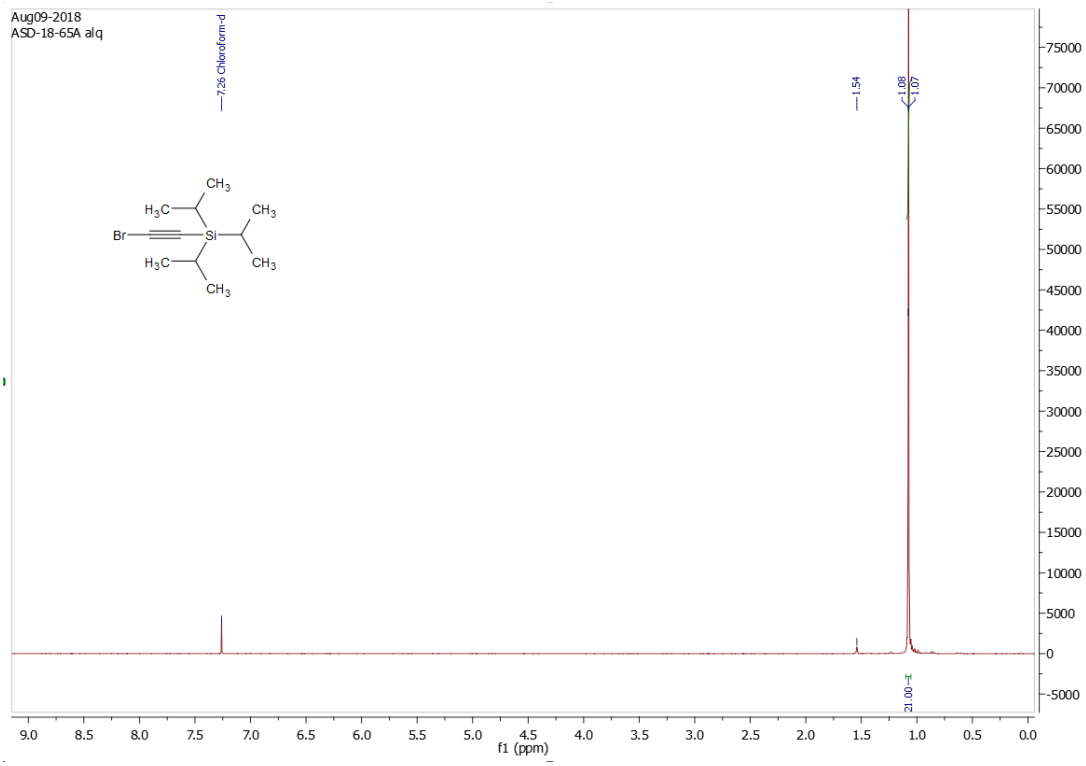
7.0 Appendices

7.1 Appendices A: NMR data

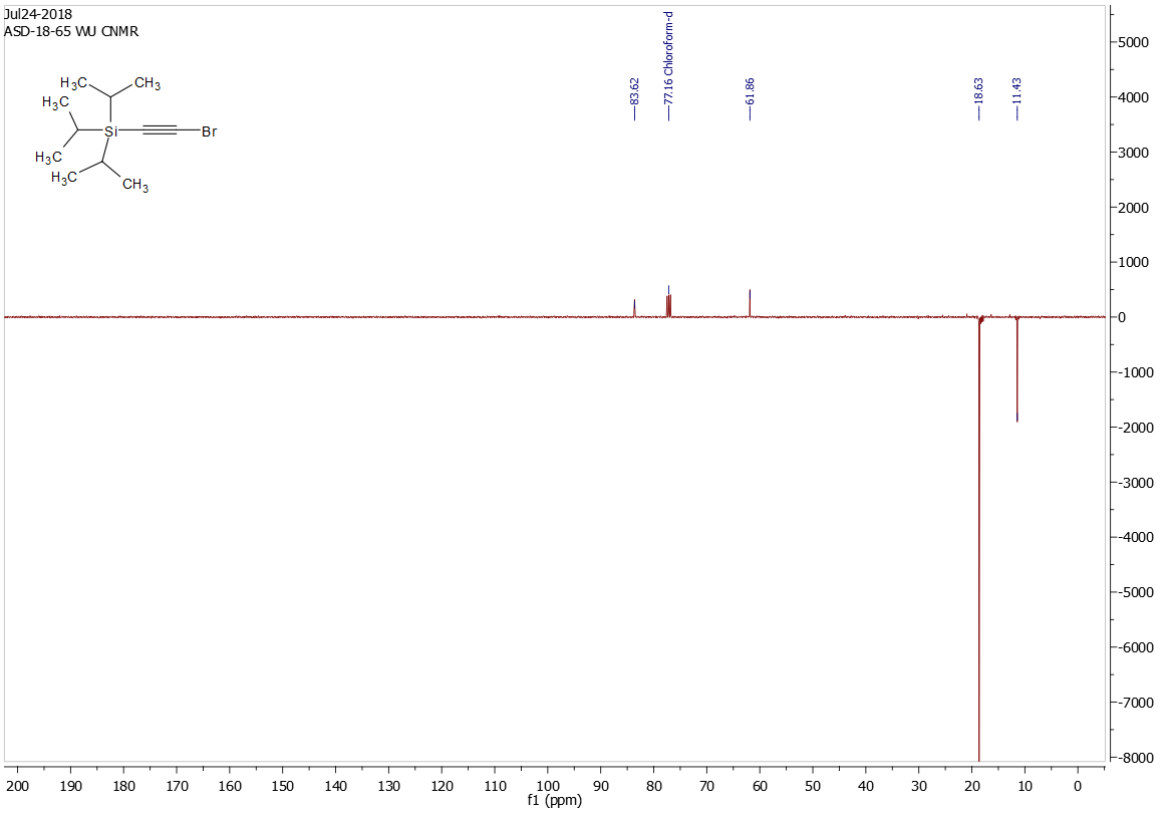
Methyl(2-(phenylethynyl)phenyl)sulfane (213): ^{1}H NMR



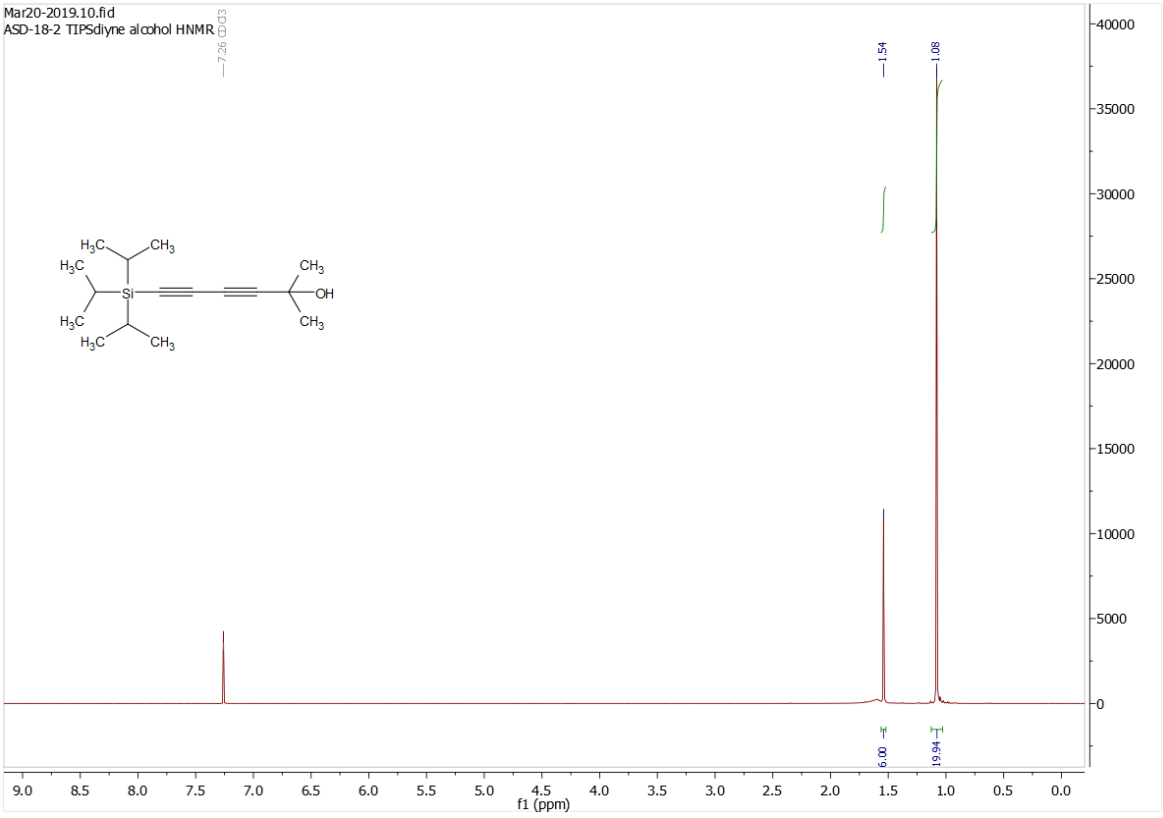
(Bromoethynyl)triisopropylsilane (222): ^{1}H NMR



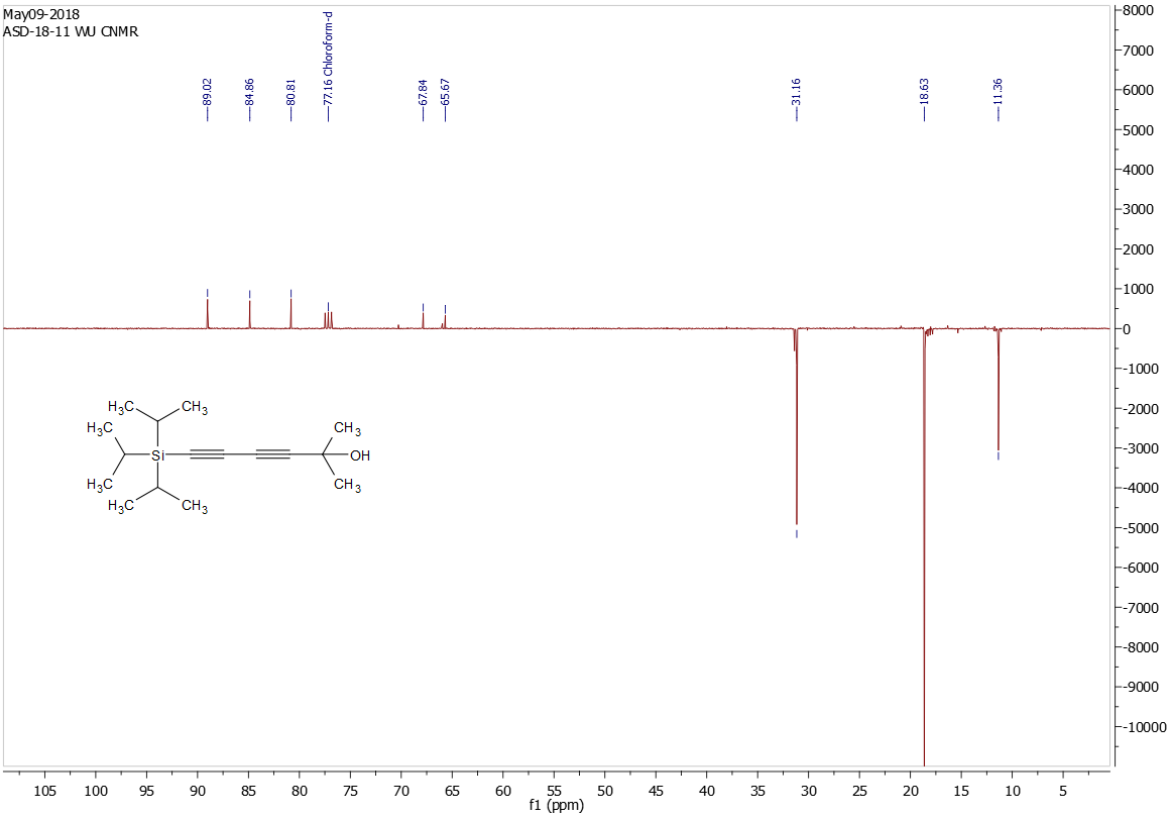
^{13}C NMR



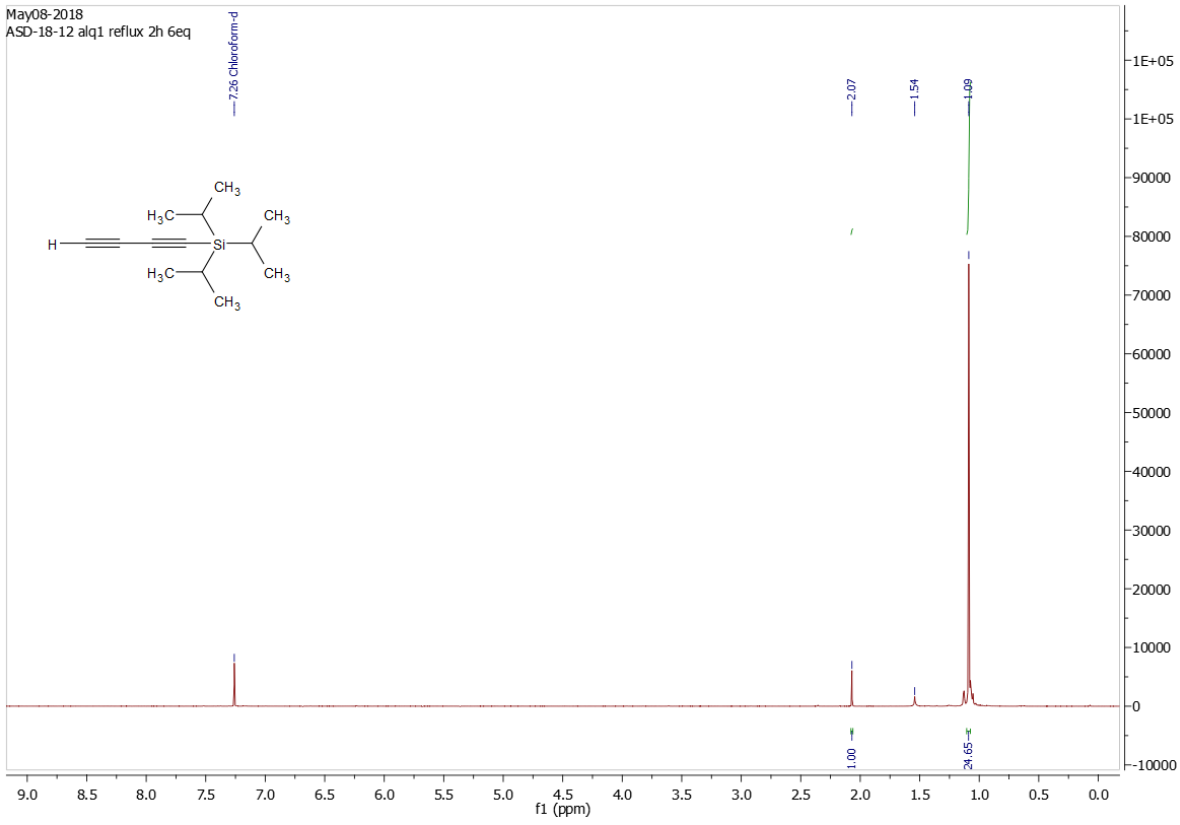
2-Methyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (224): ^{1}H NMR



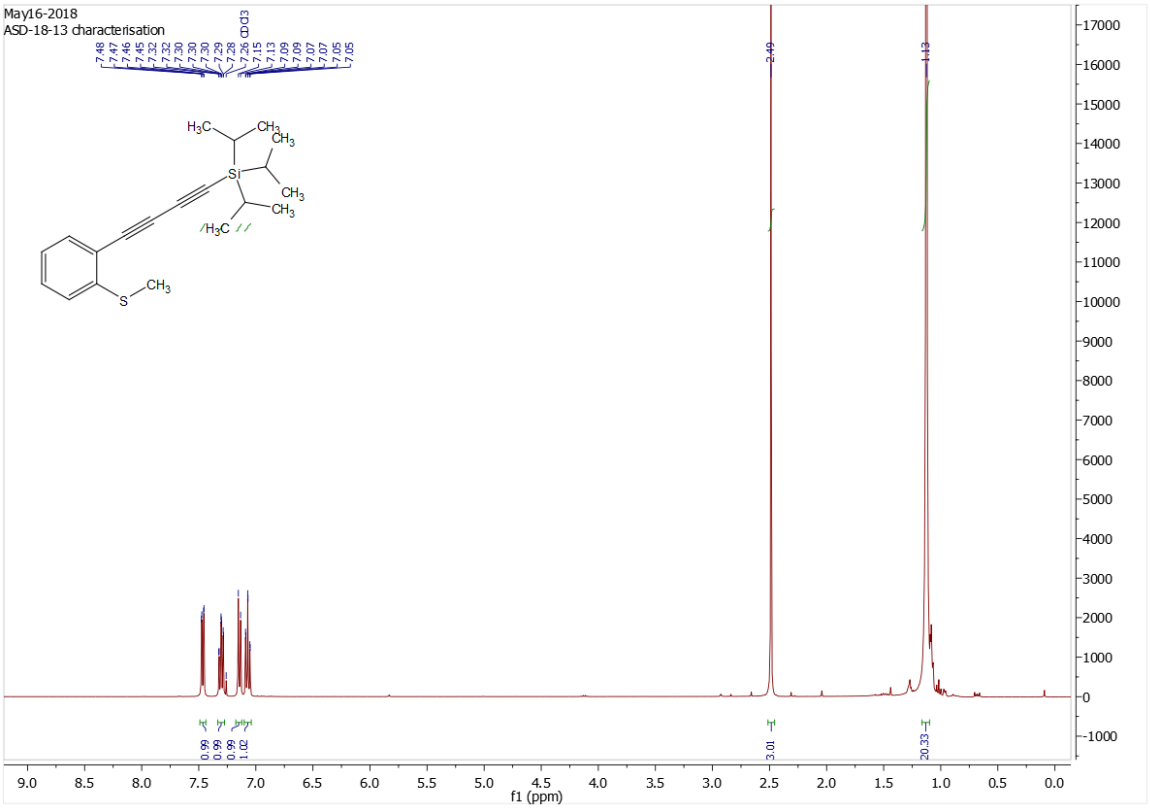
^{13}C NMR



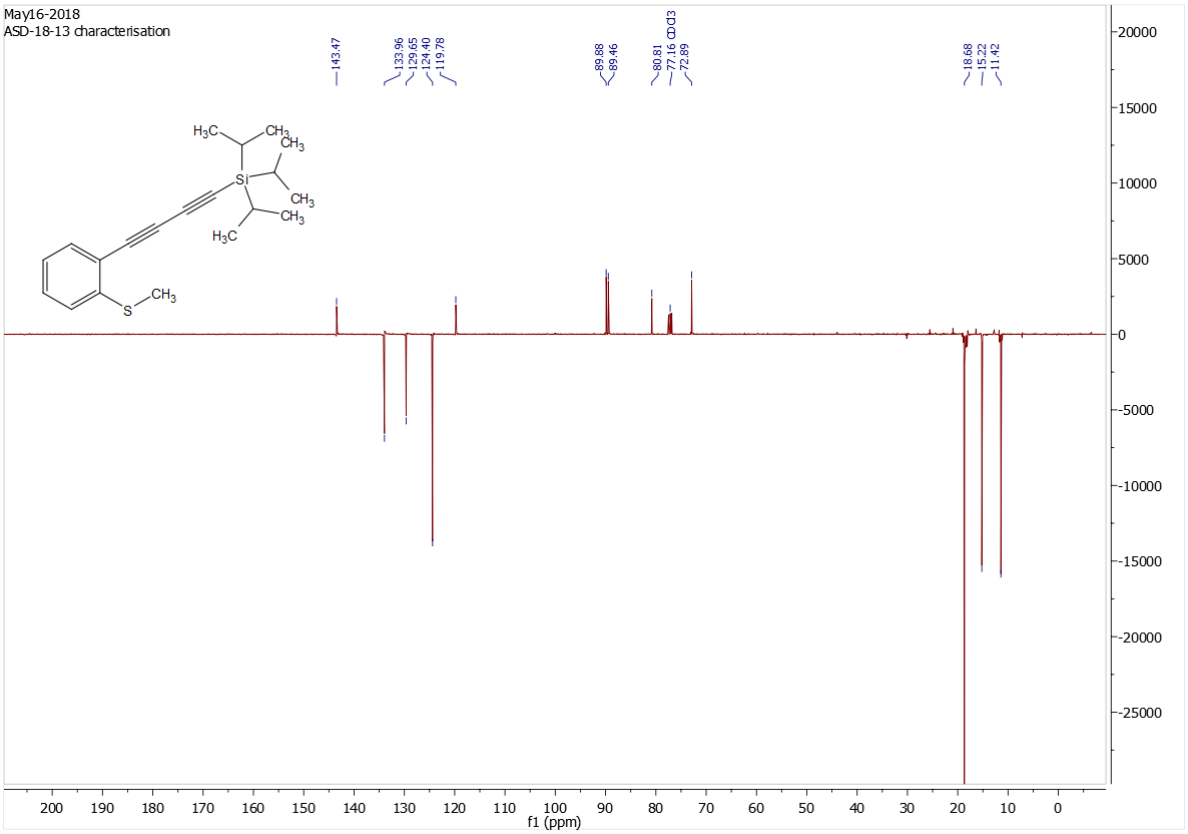
Buta-1,3-diyn-1-yltriisopropylsilane (225): ^{1}H NMR



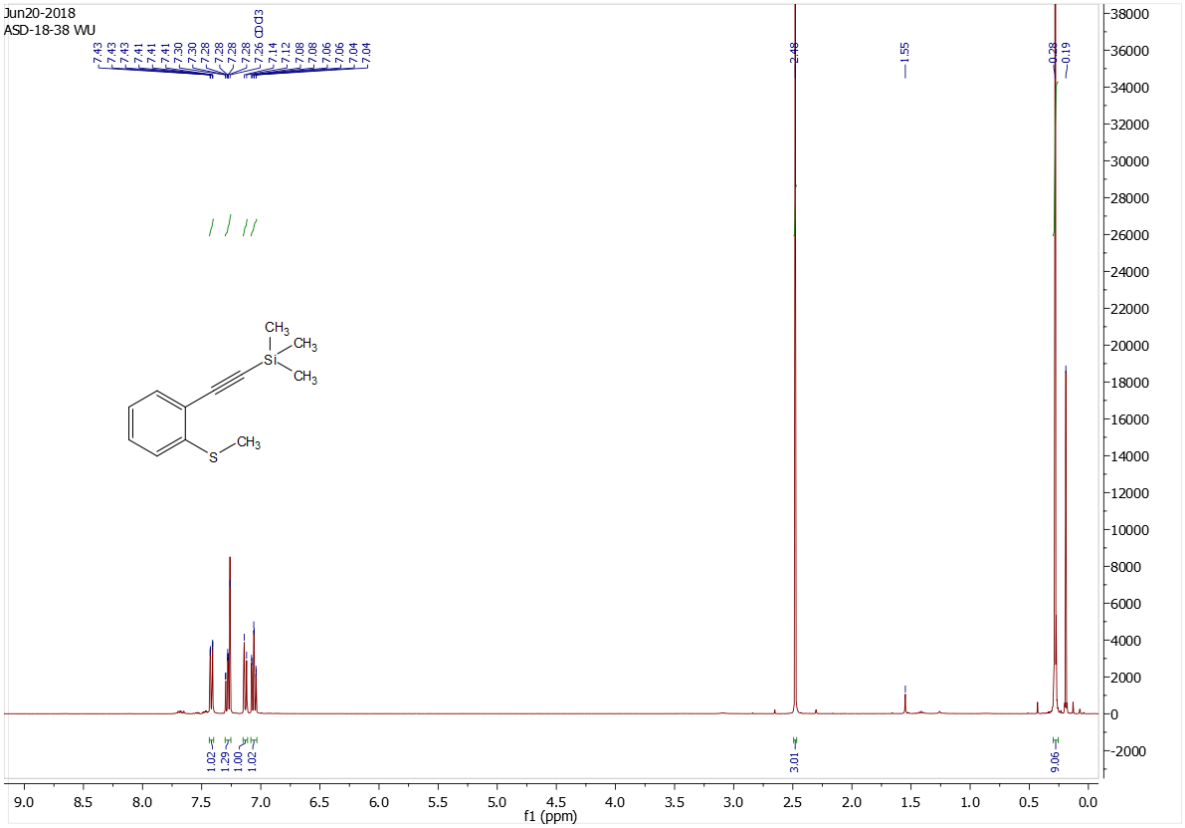
Triisopropyl((2-(methylthio)phenyl)buta-1,3-diyn-1-yl)silane (228): ^{1}H NMR



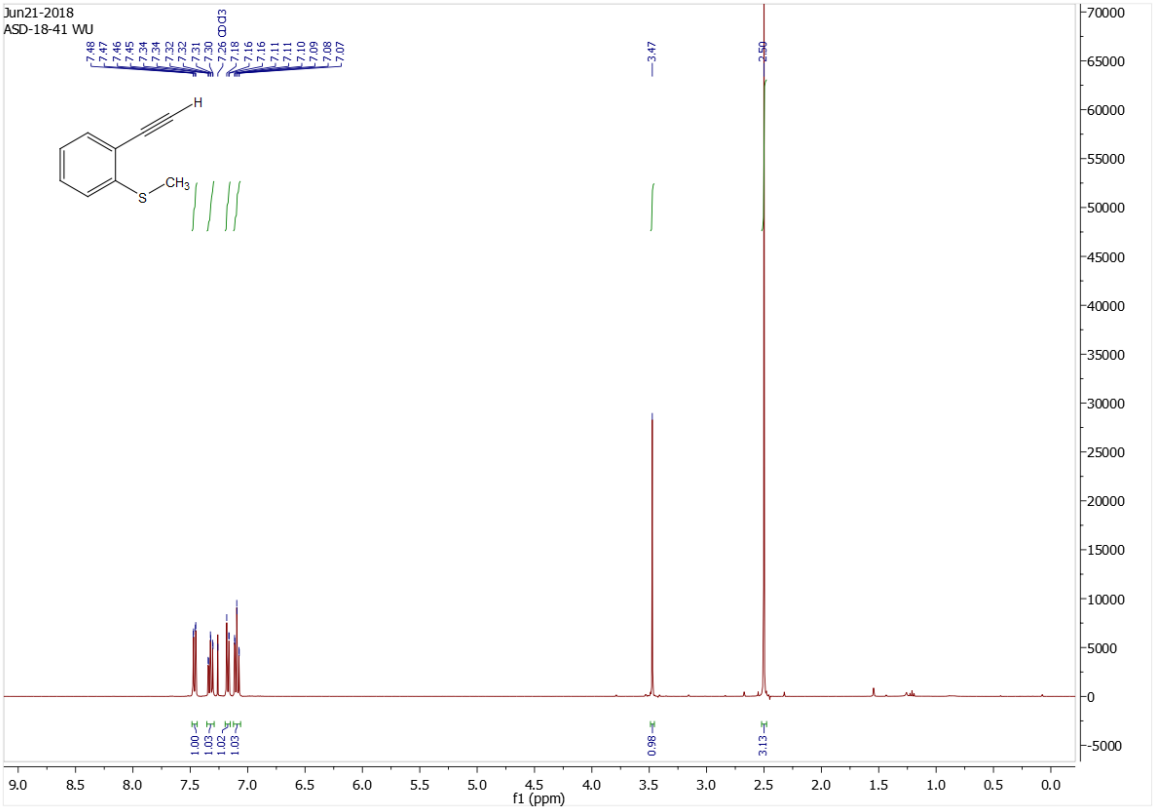
^{13}C NMR



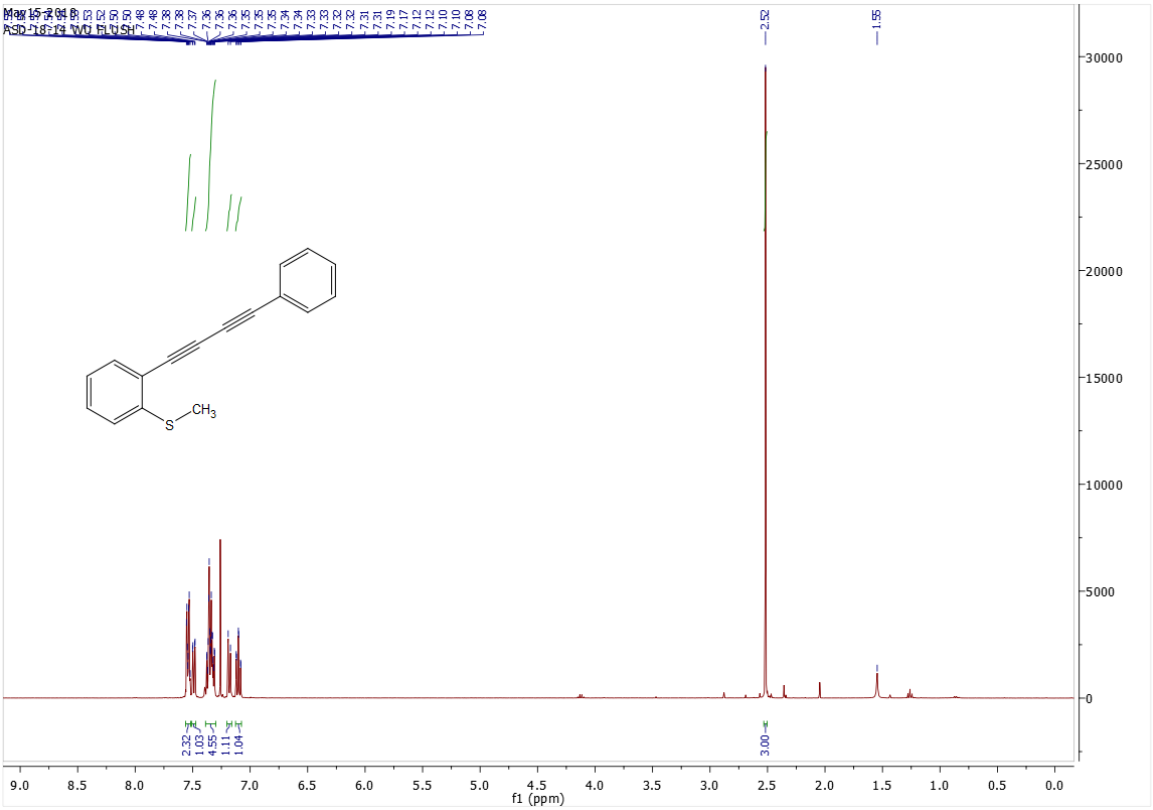
Trimethyl((2-(methylthio)phenyl)ethynyl)silane (229): ^{1}H NMR



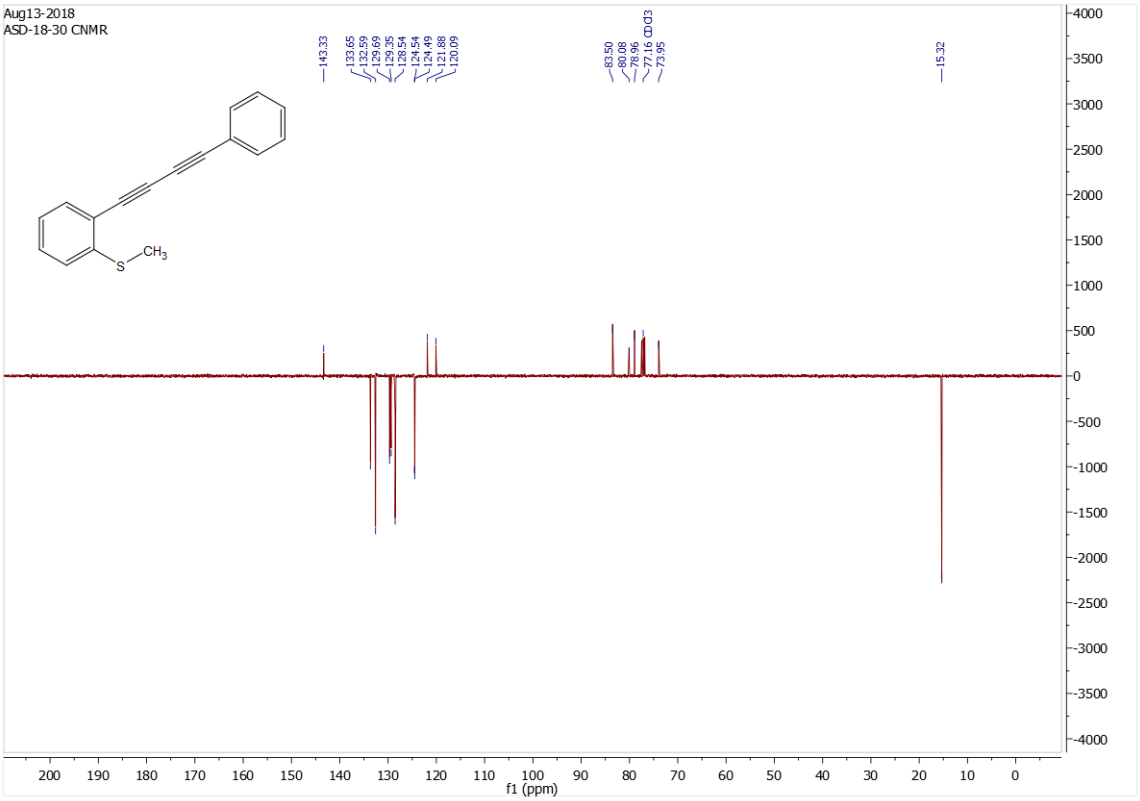
(2-Ethynylphenyl)(methyl)sulfane (129): ^{1}H NMR



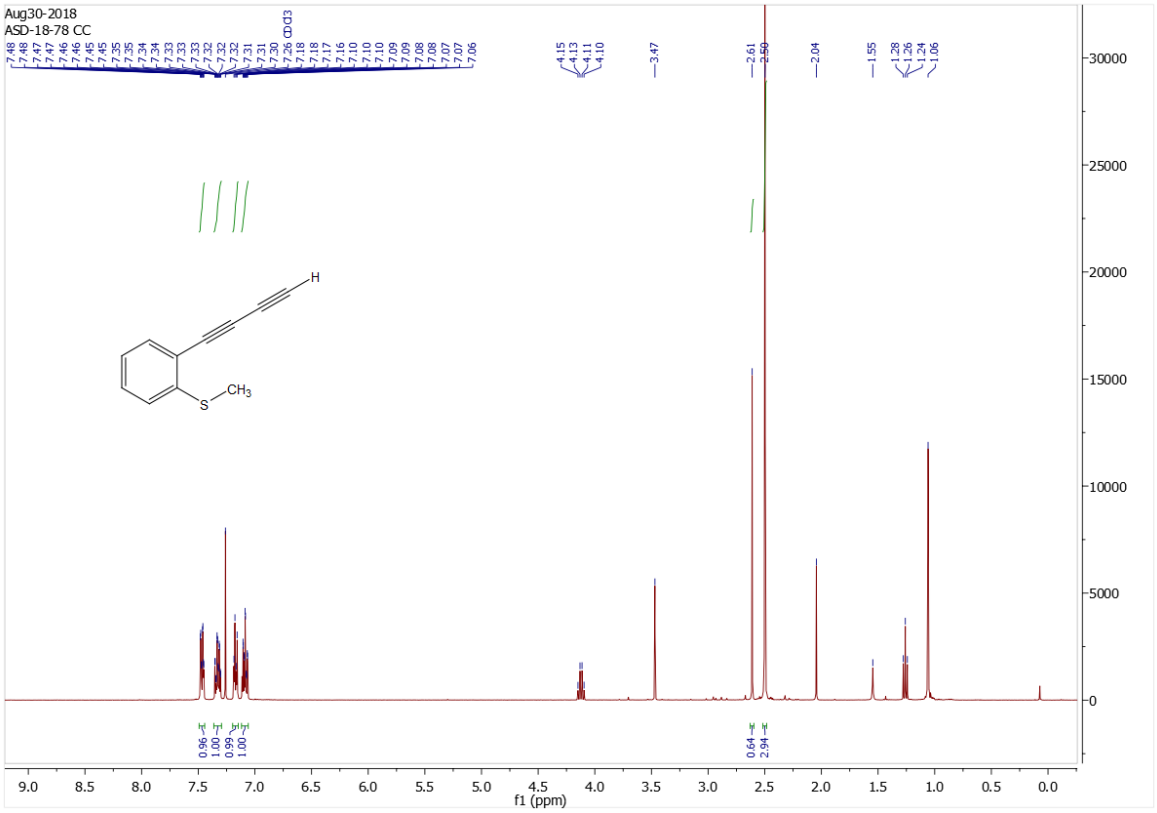
Methyl(2-(phenylbuta-1,3-diyn-1-yl)phenyl)sulfane (232): ^{1}H NMR



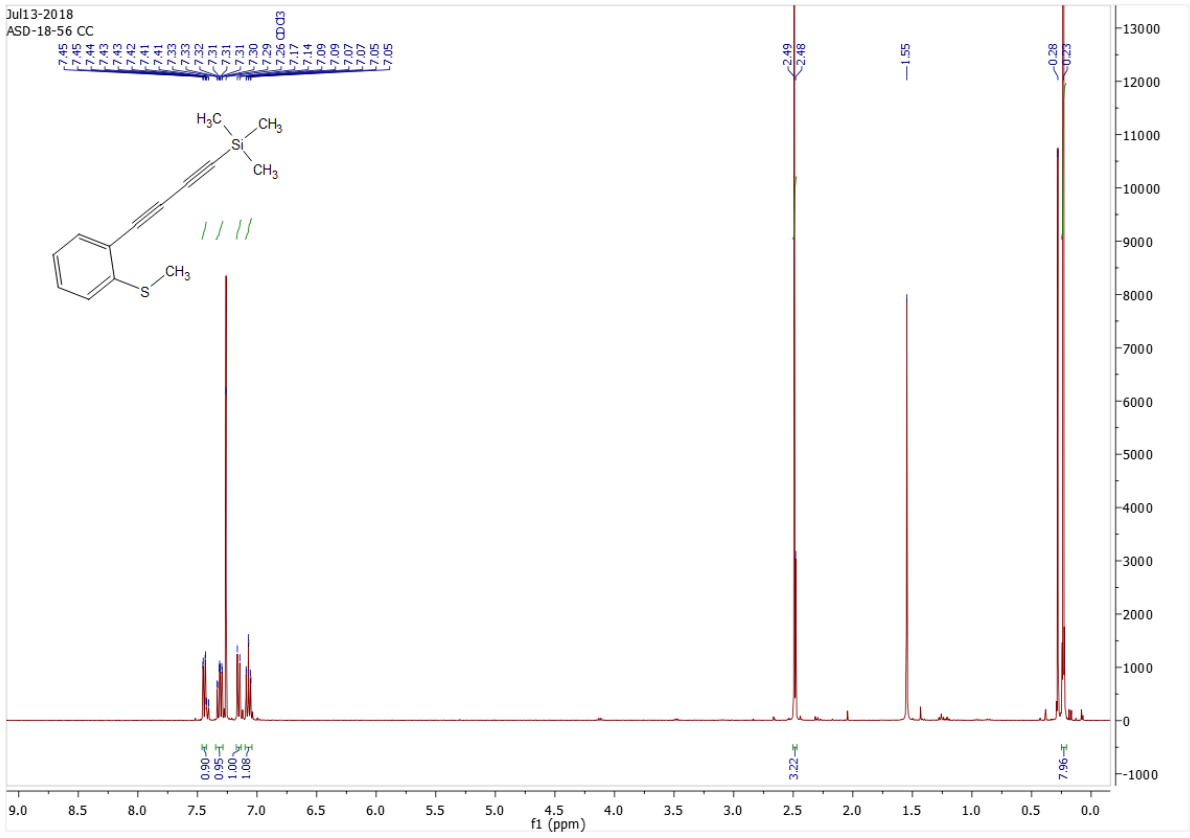
^{13}C NMR



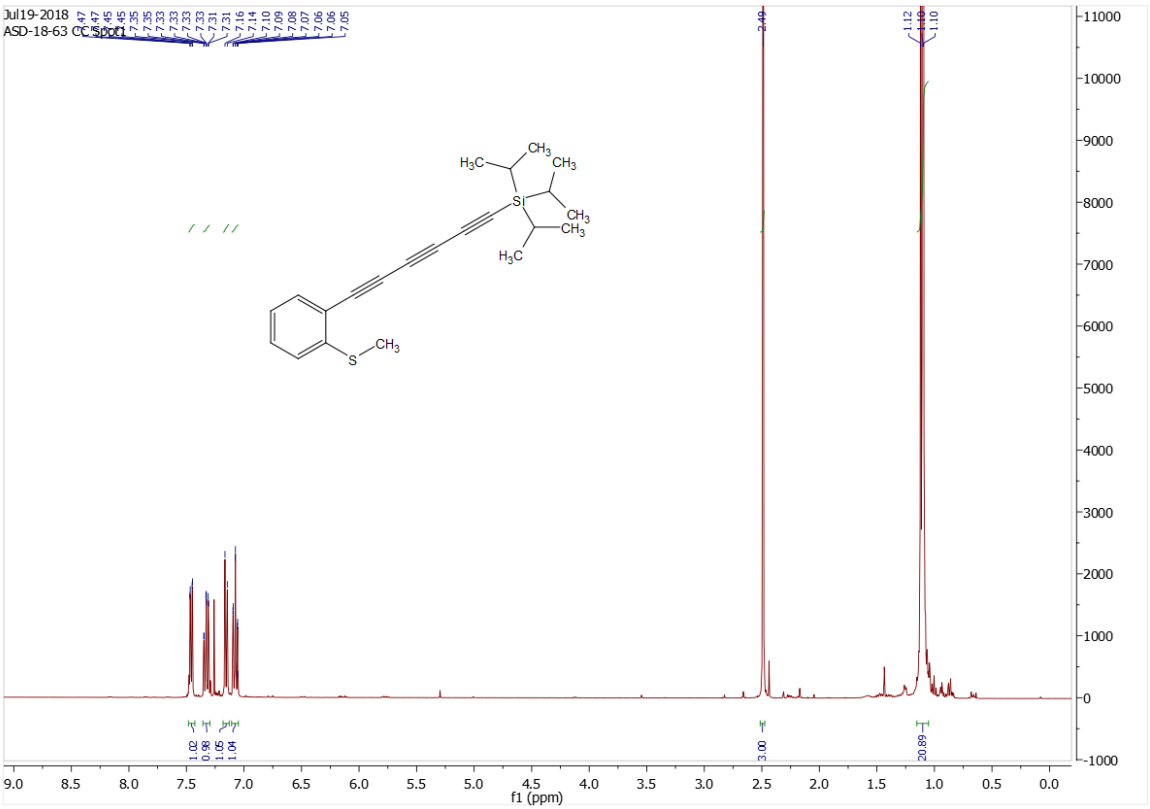
(2-(Buta-1,3-diyn-1-yl)phenyl)(methyl)sulfane (233): ^{1}H NMR



Trimethyl((2-(methylthio)phenyl)buta-1,3-diyn-1-yl)silane (234): ^{1}H NMR



Triisopropyl((2-(methylthio)phenyl)hexa-1,3,5-triyn-1-yl)silane (235): ^{1}H NMR



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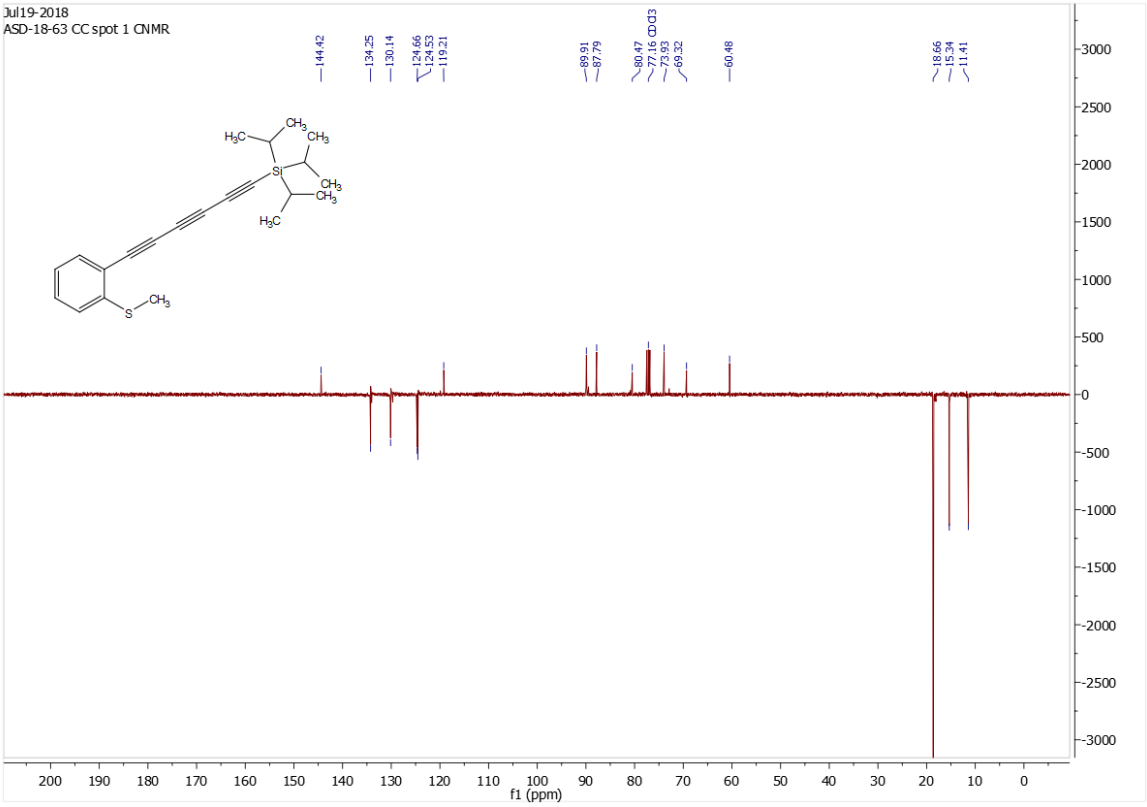
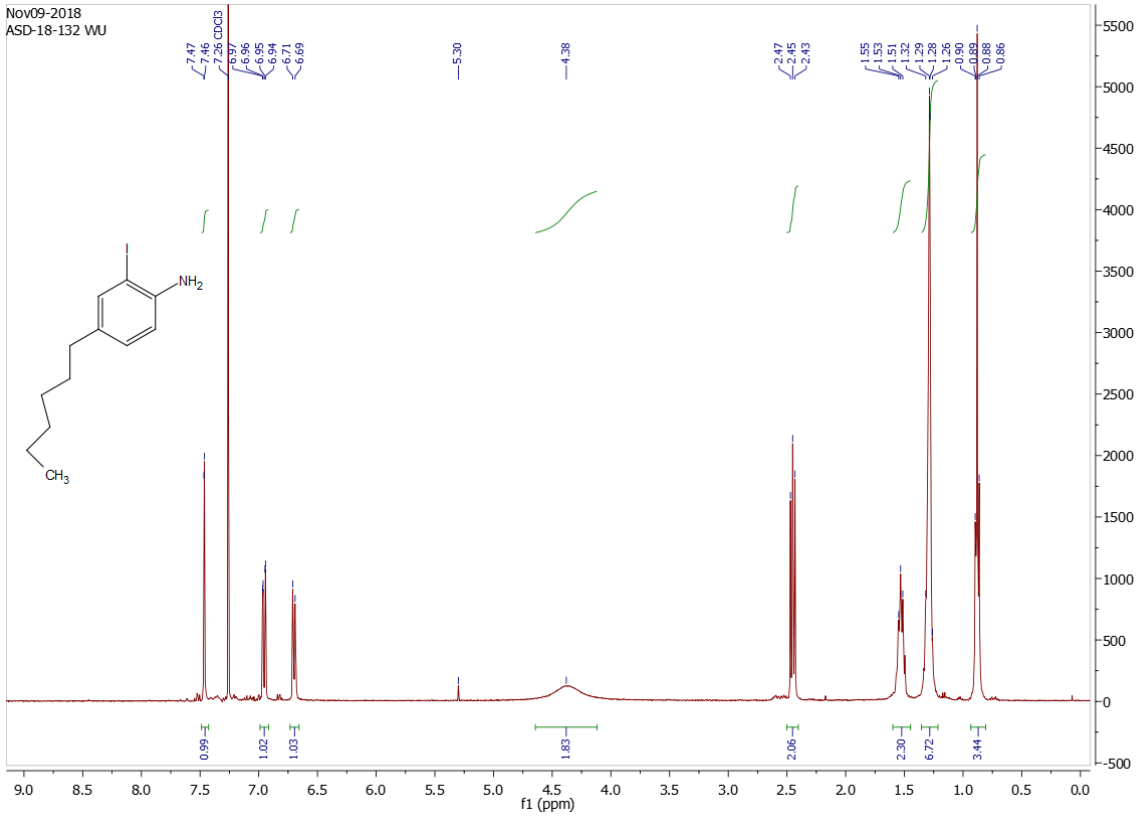


4-Hexyl-2-iodoaniline (244): ^{1}H NMR



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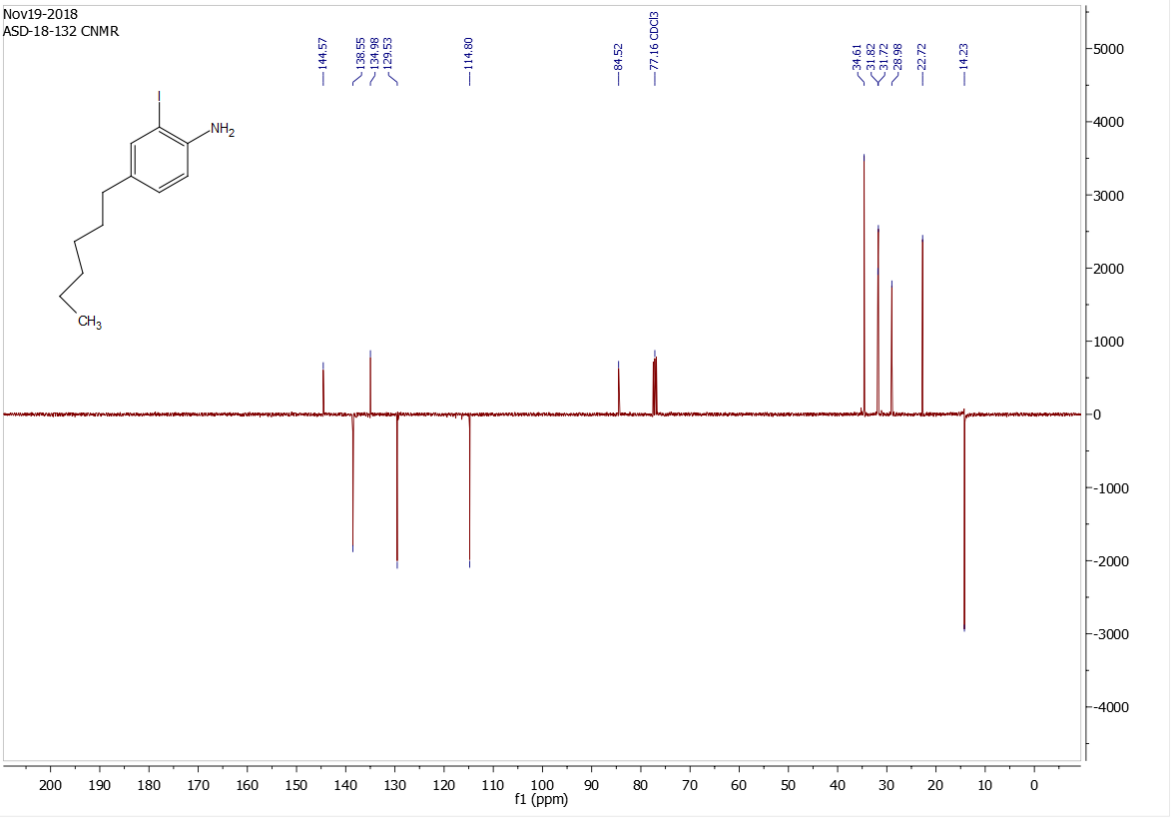
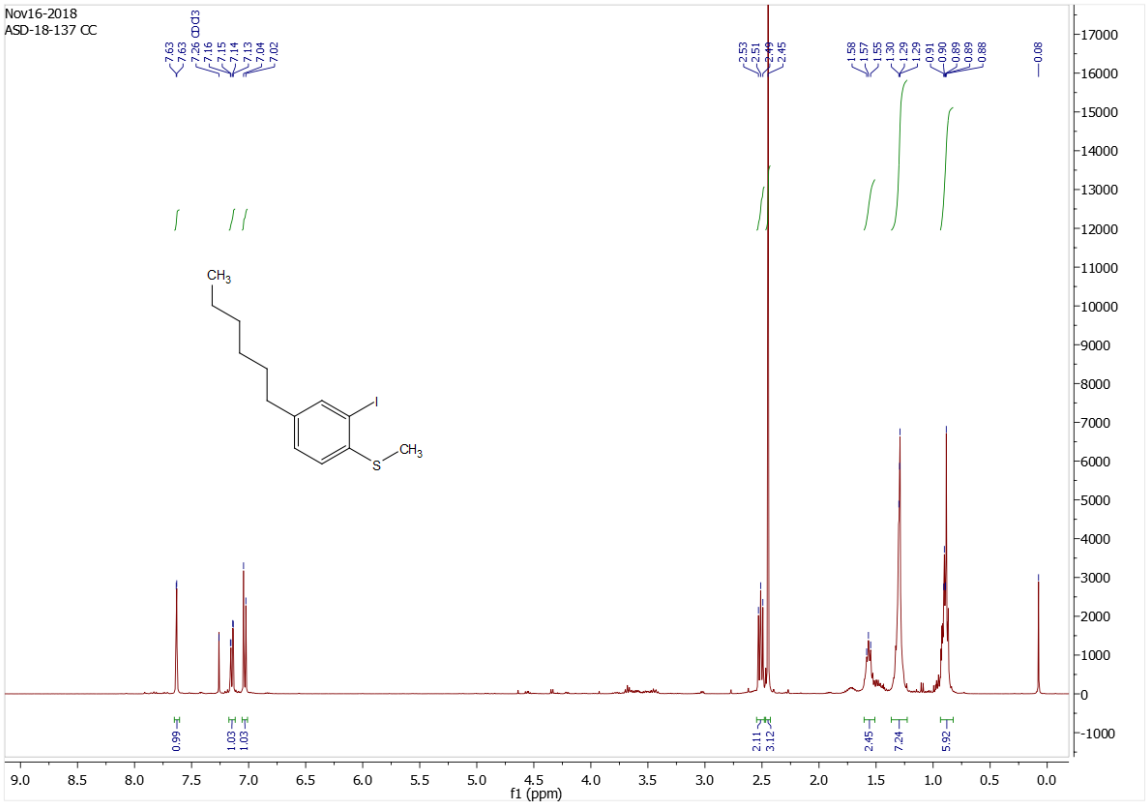


(4-Hexyl-2-iodophenyl)(methyl)sulfane (245): ^{1}H NMR



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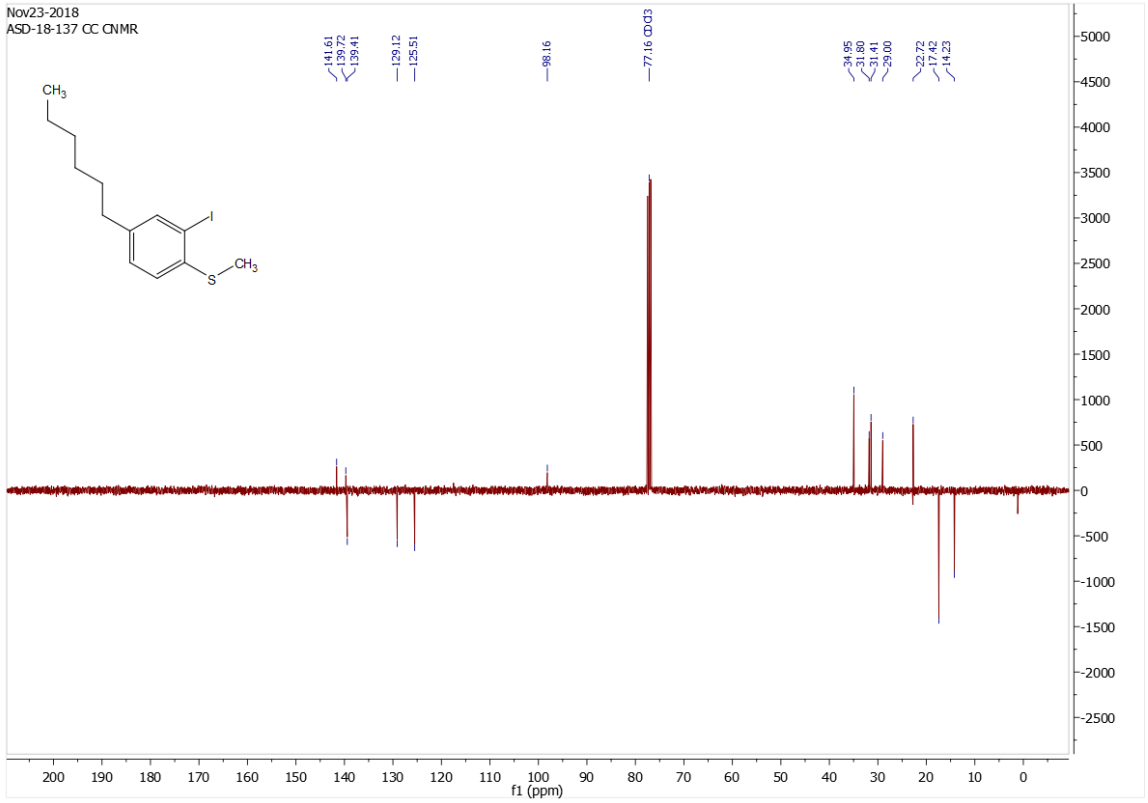
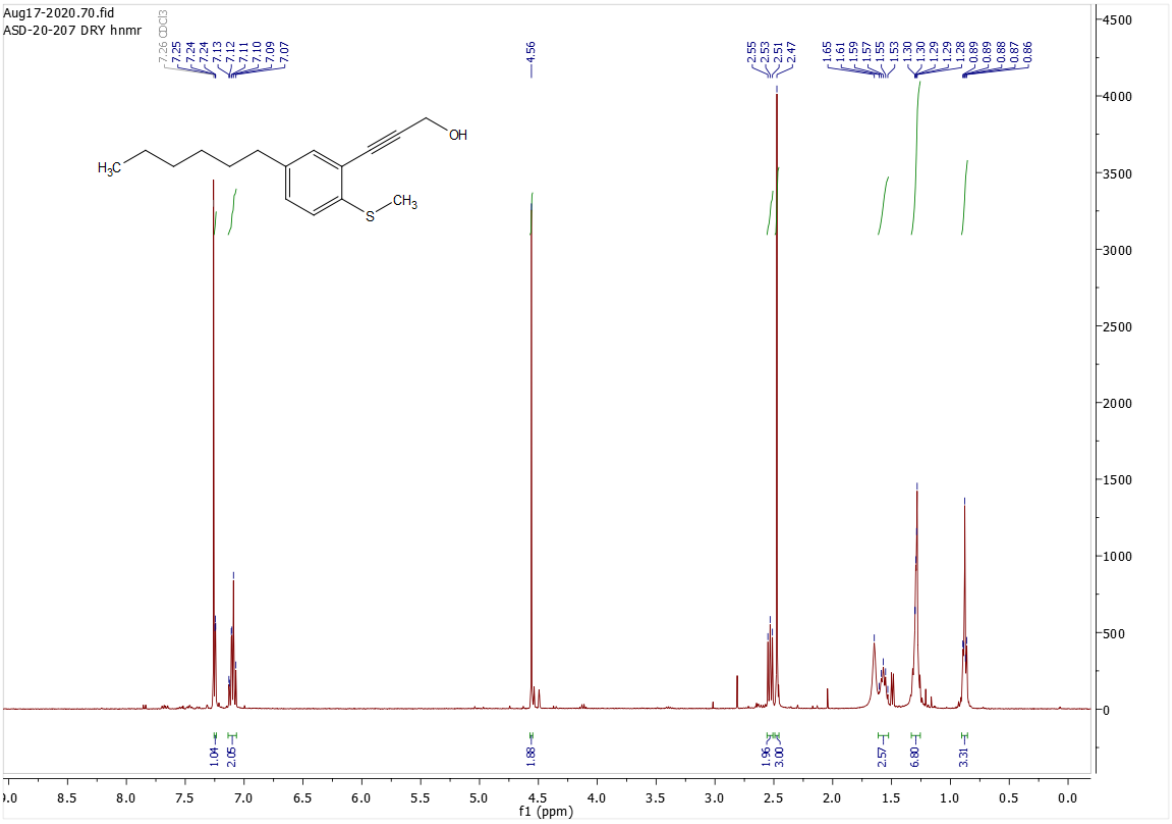
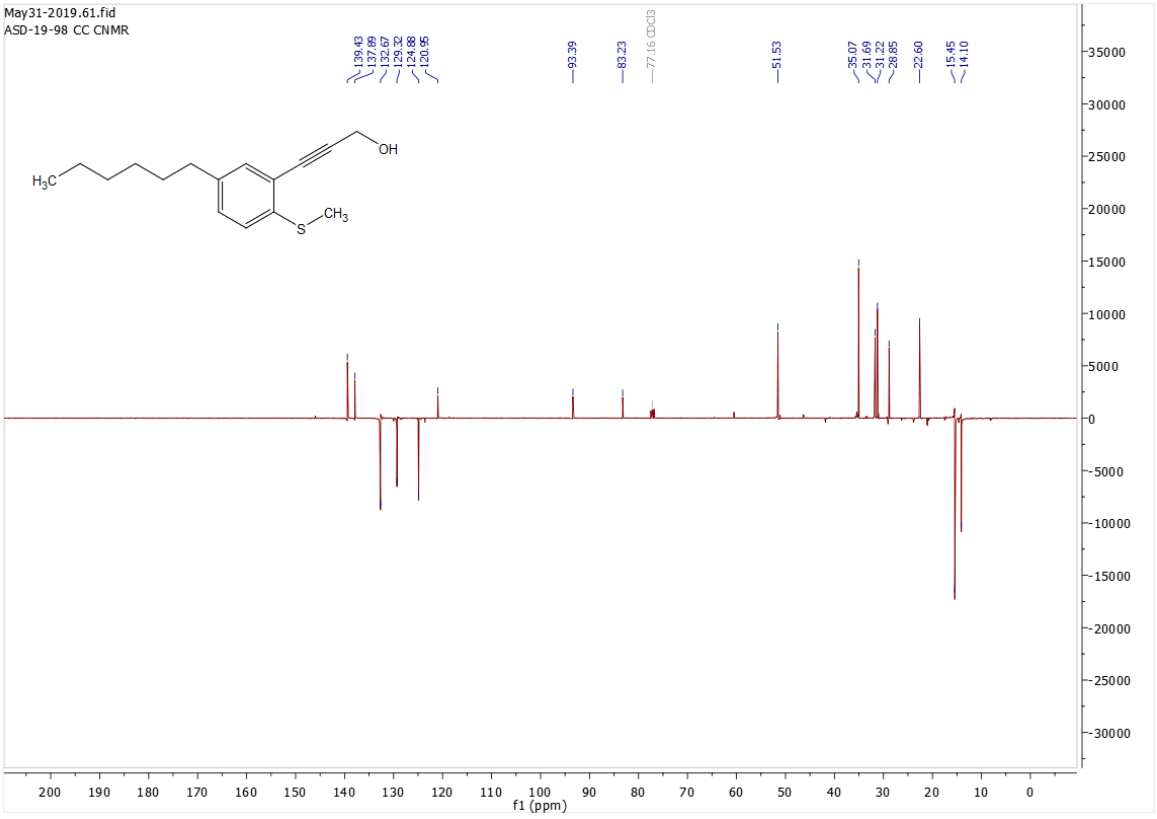


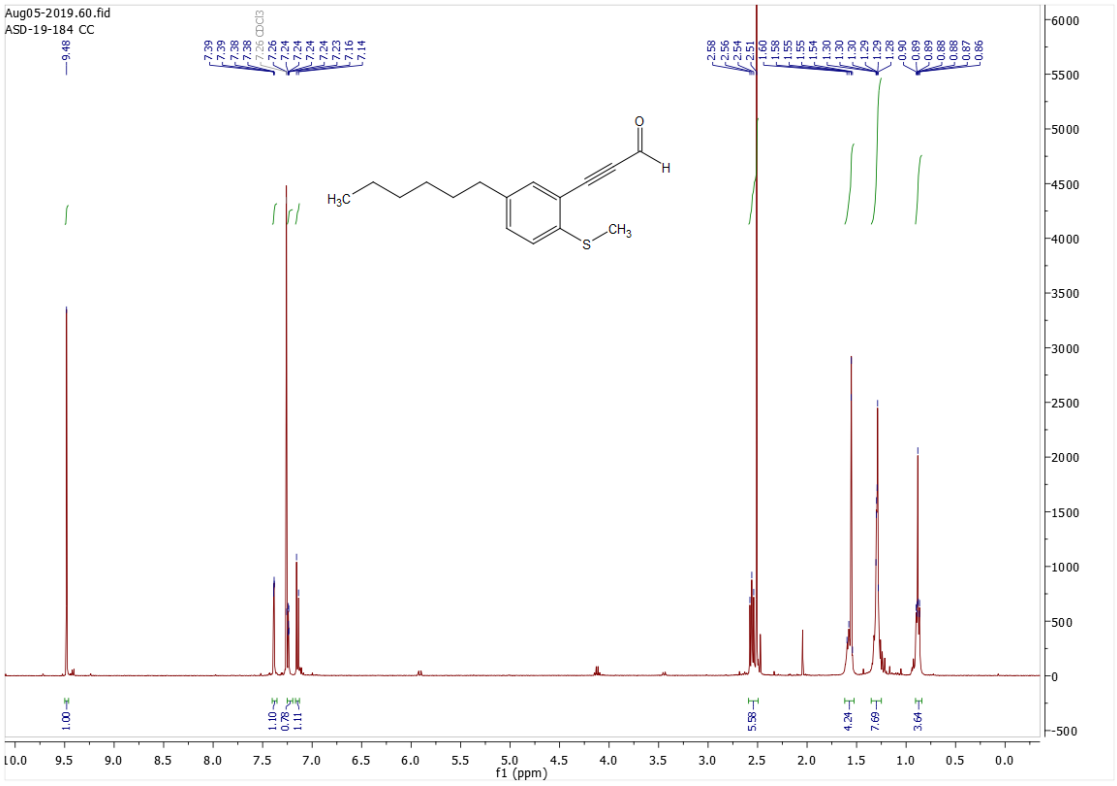
3-(5-Hexyl-2-(methylthio)phenyl)prop-2-yn-1-ol (247): ^{1}H NMR



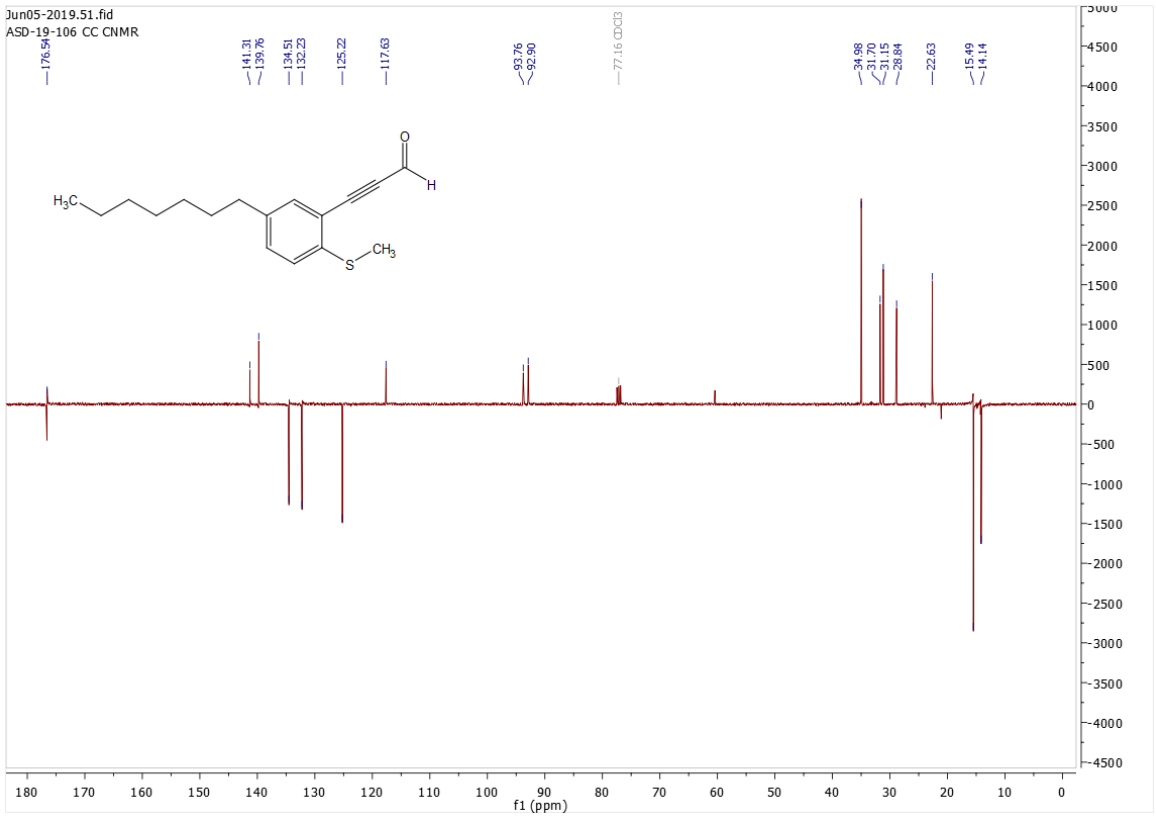
^{13}C NMR



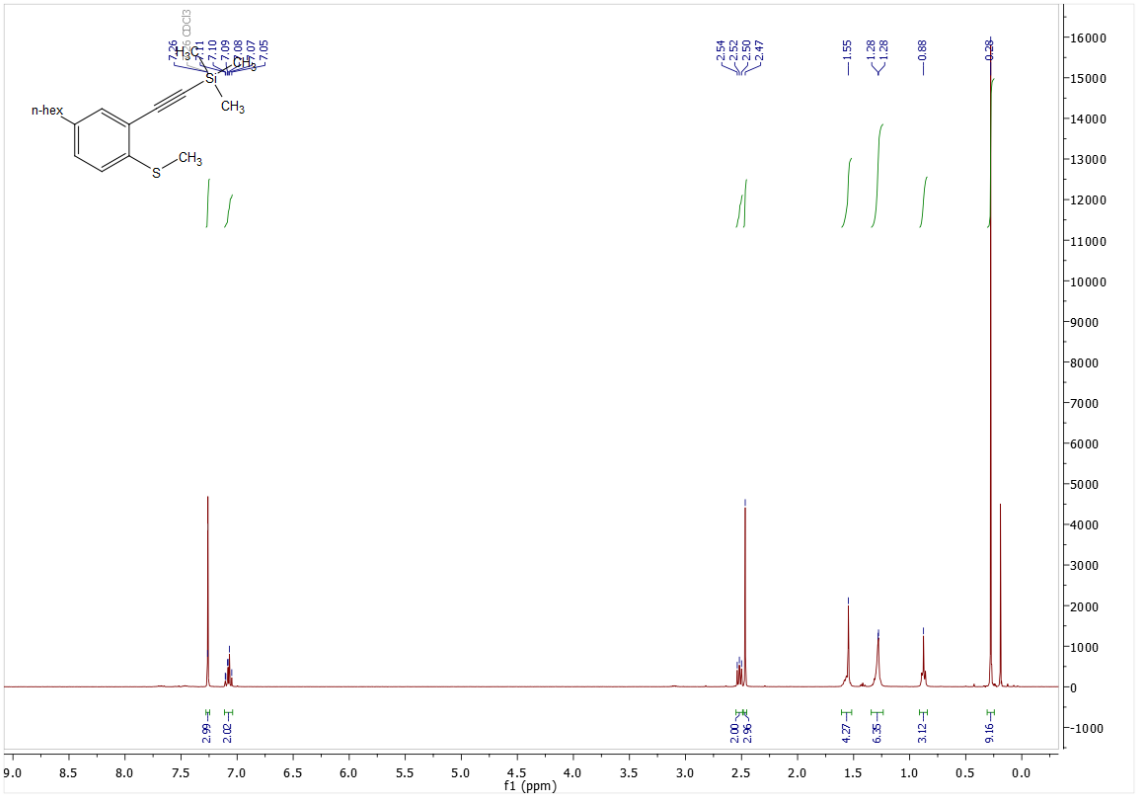
3-(5-Hexyl-2-(methylthio)phenyl)propiolaldehyde (248): ^{1}H NMR



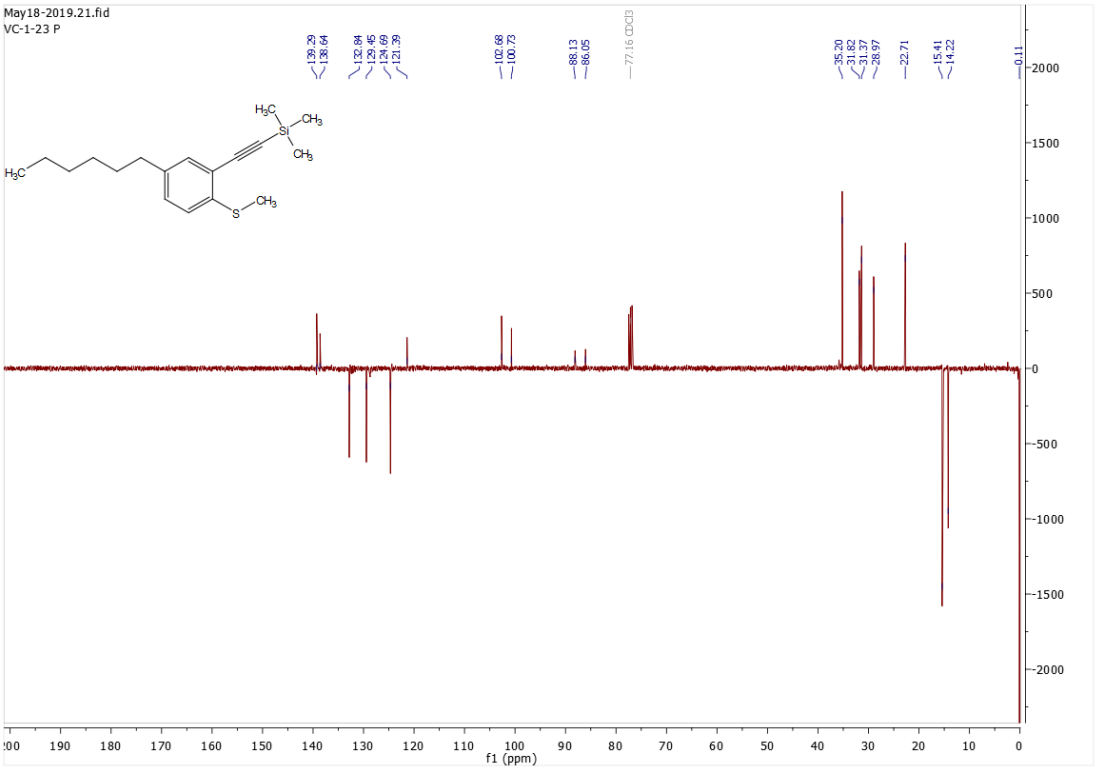
^{13}C NMR



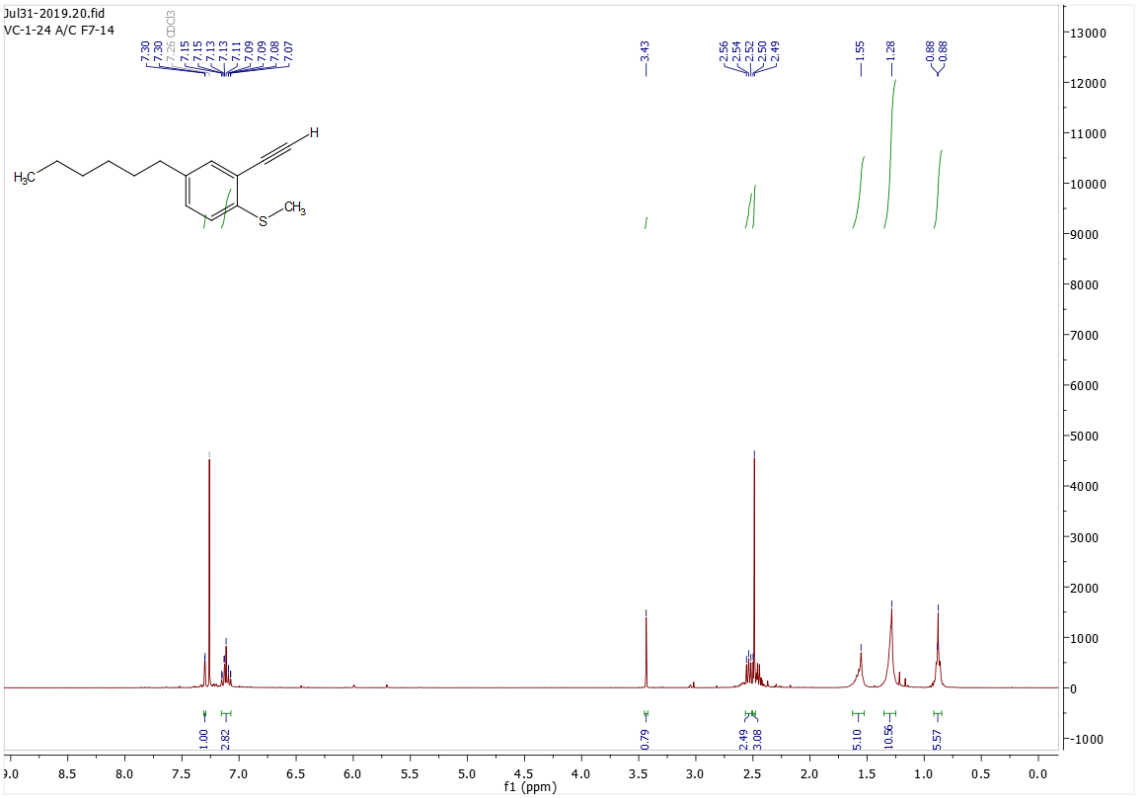
((5-Hexyl-2-(methylthio)phenyl)ethynyl)trimethylsilane (351): ^{1}H NMR



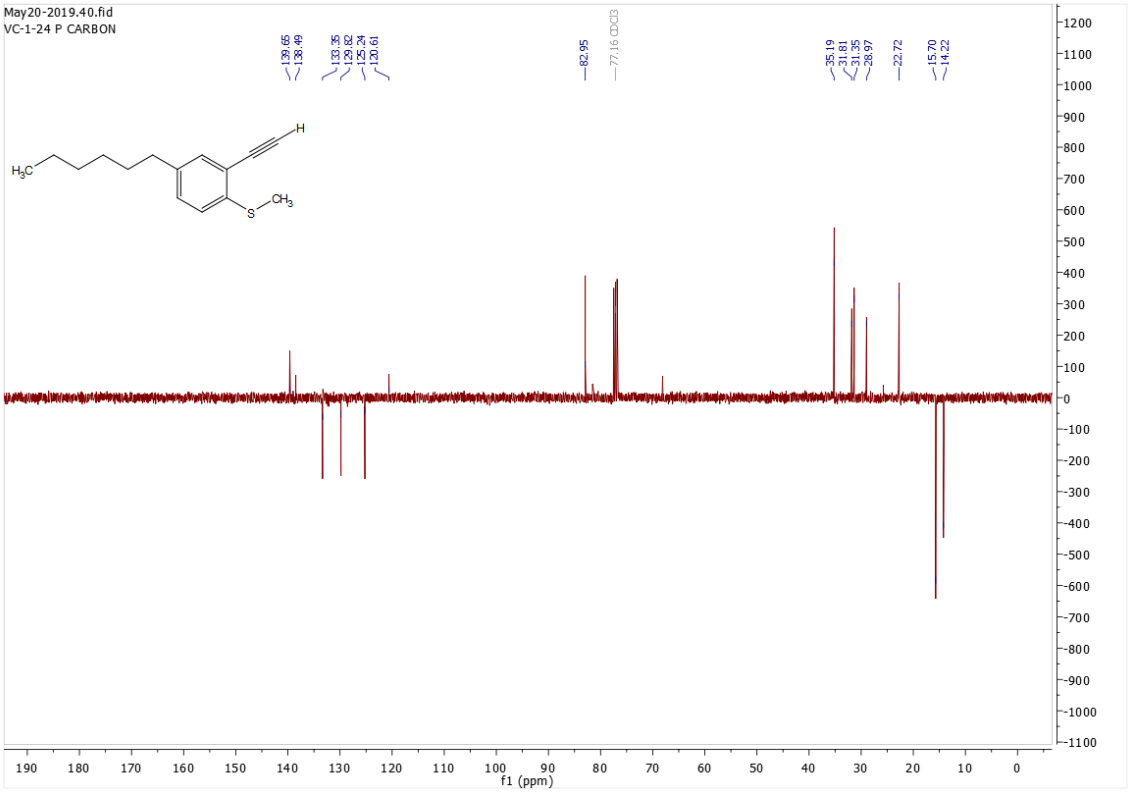
^{13}C NMR



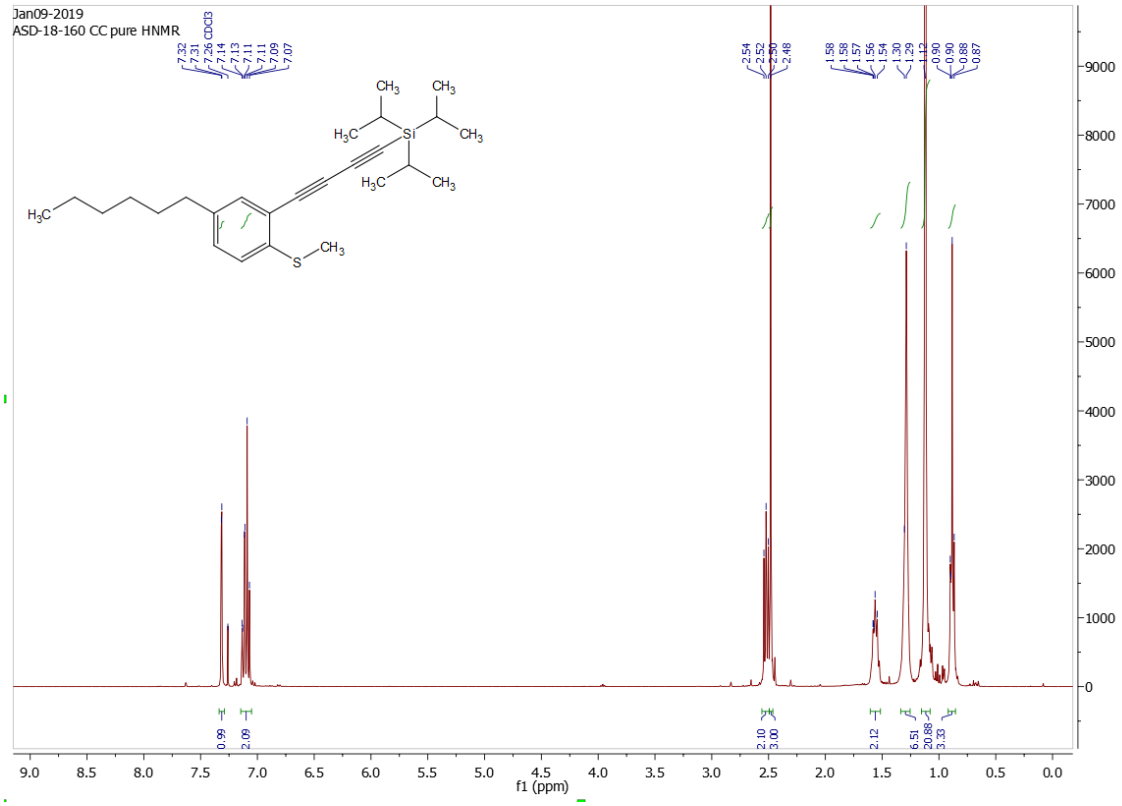
(2-Ethynyl-4-hexylphenyl)(methyl)sulfane (255): ^{1}H NMR



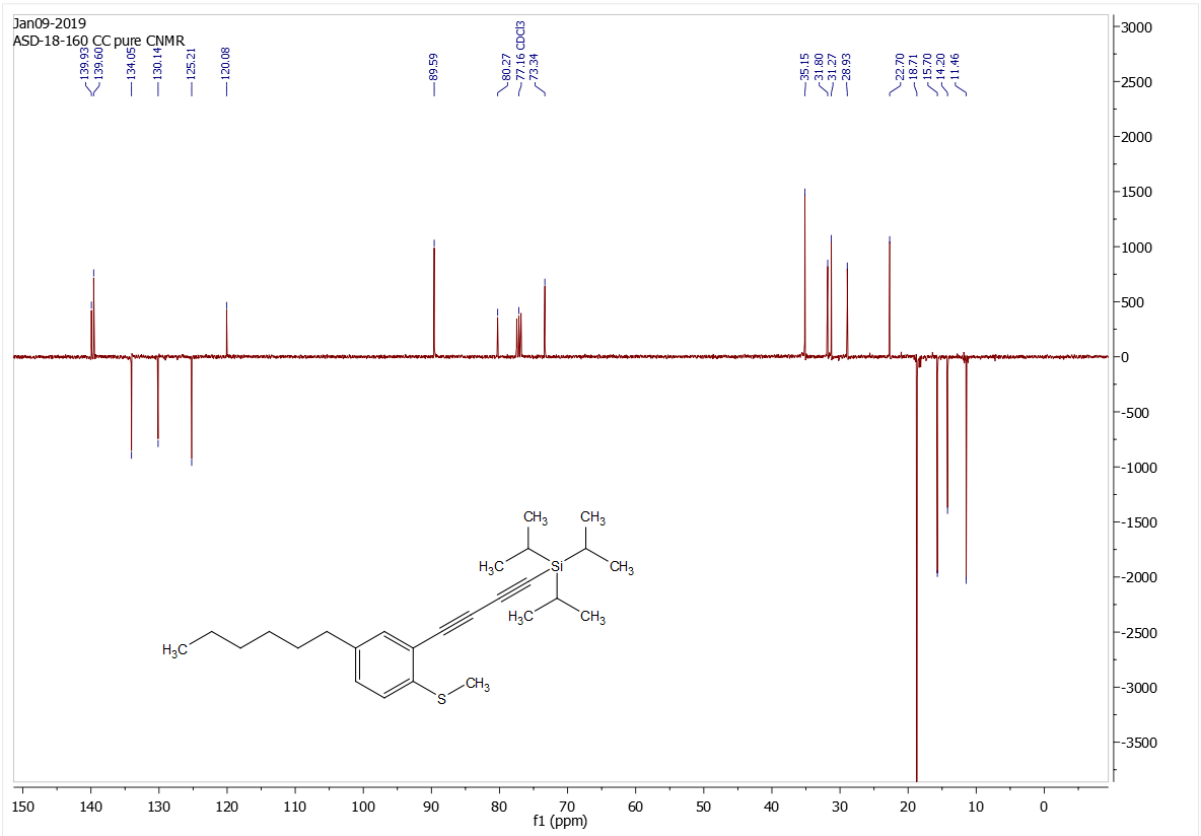
^{13}C NMR



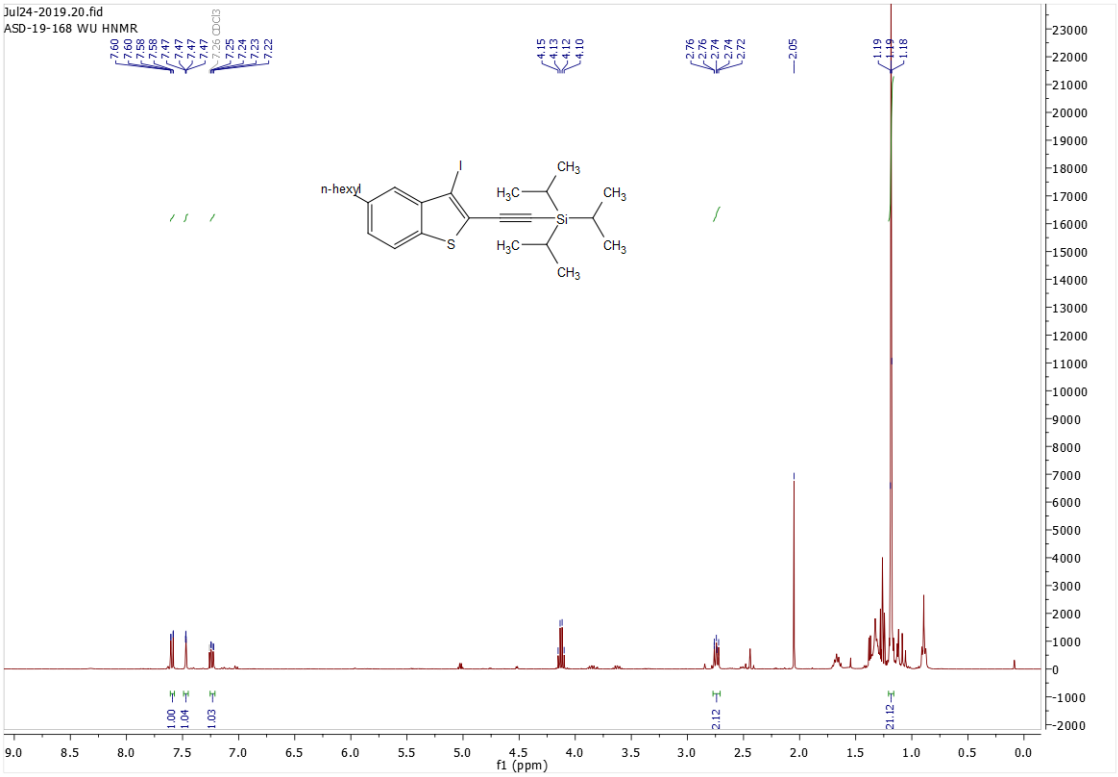
((5-Hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)triisopropylsilane (257): ^{1}H NMR



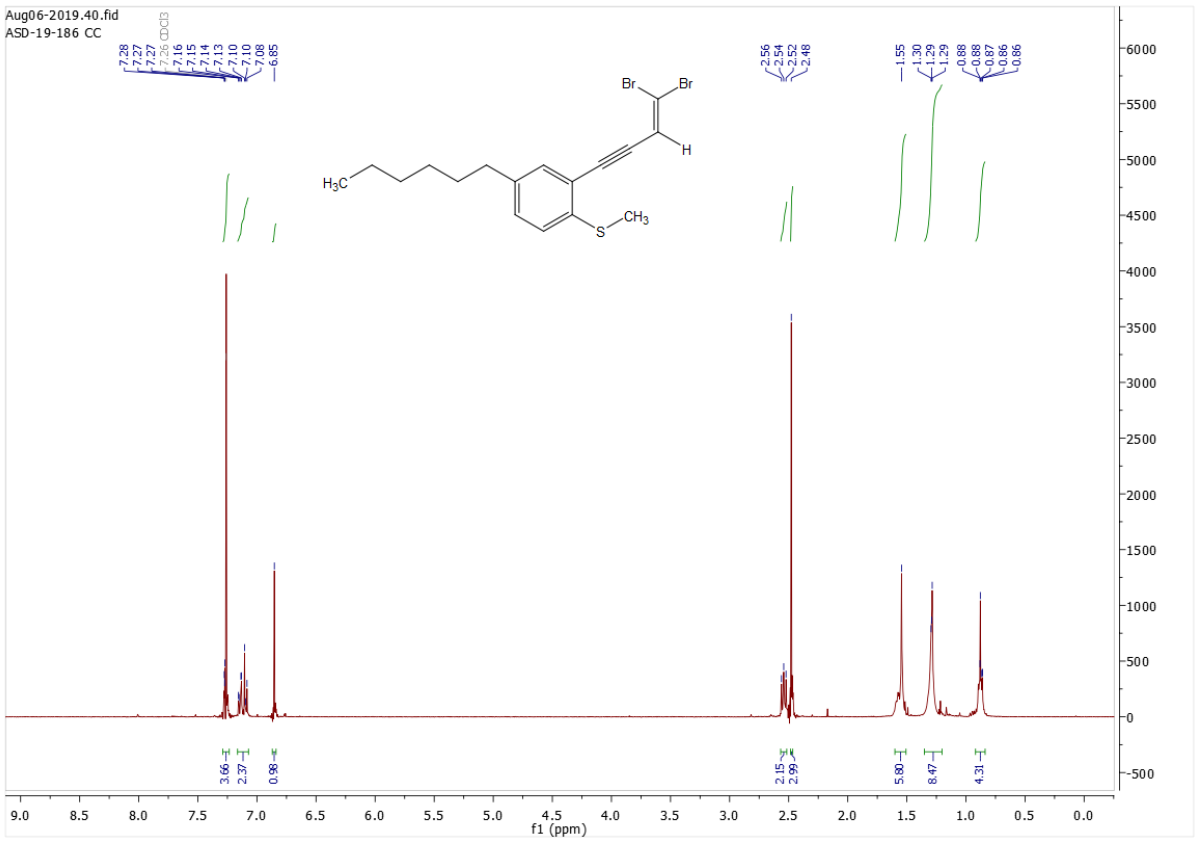
^{13}C NMR



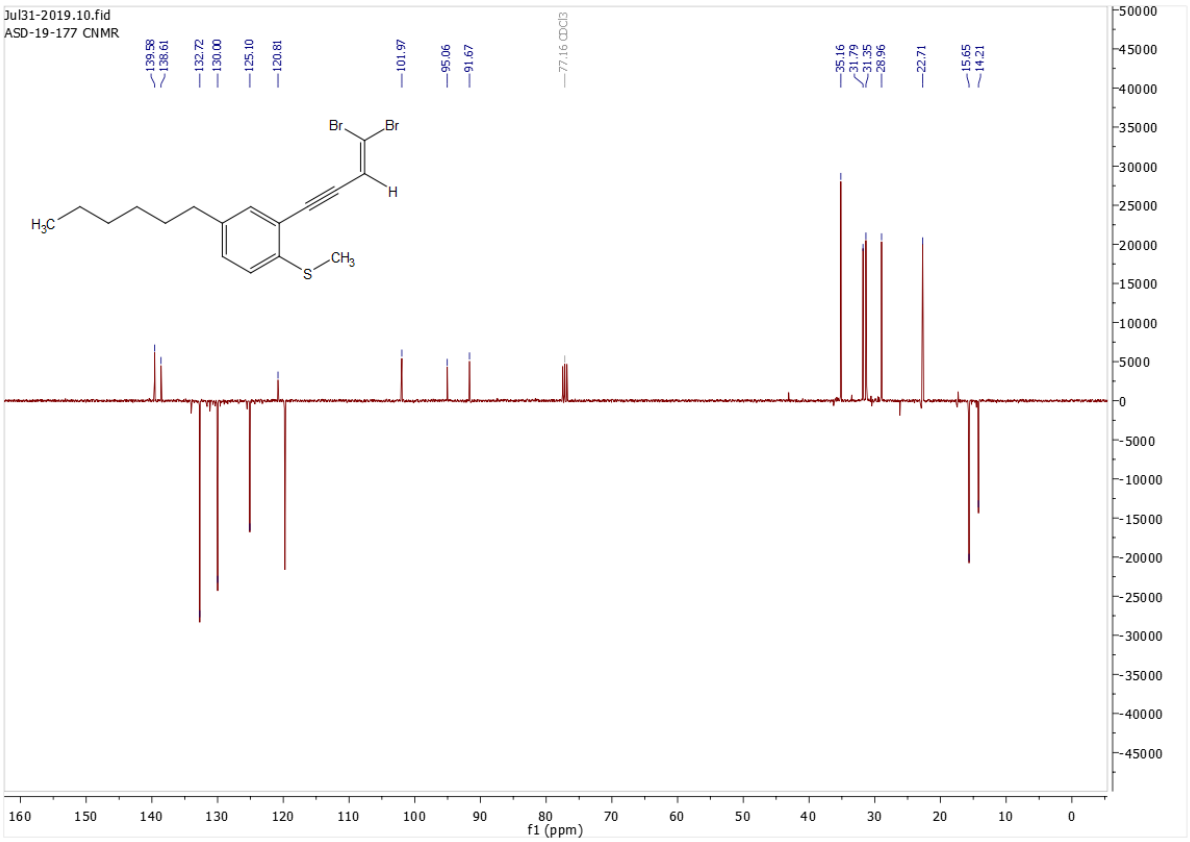
((5-Hexyl-3-iodobenzo[b]thiophen-2-yl)ethynyl)triisopropylsilane (258): ^{1}H NMR



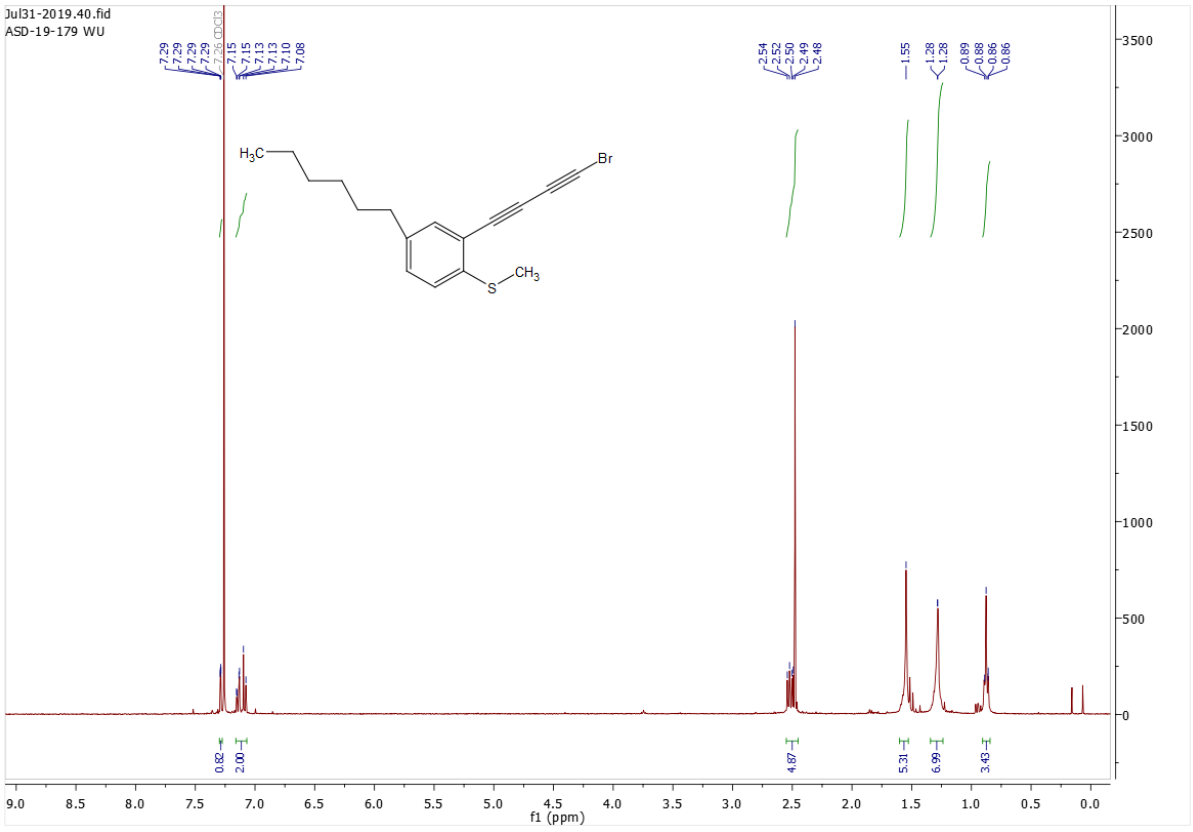
(2-(4,4-Dibromobut-3-en-1-yn-1-yl)-4-hexylphenyl)(methyl)sulfane (262): ^{1}H NMR



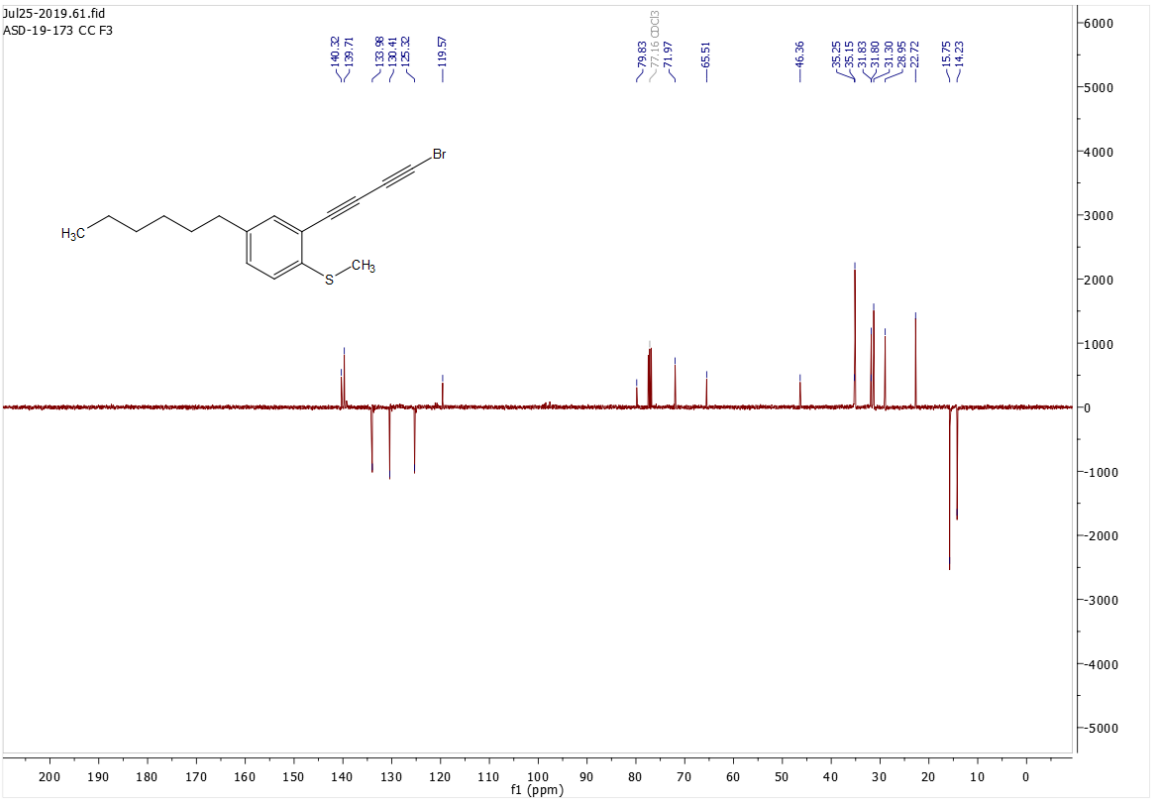
^{13}C NMR



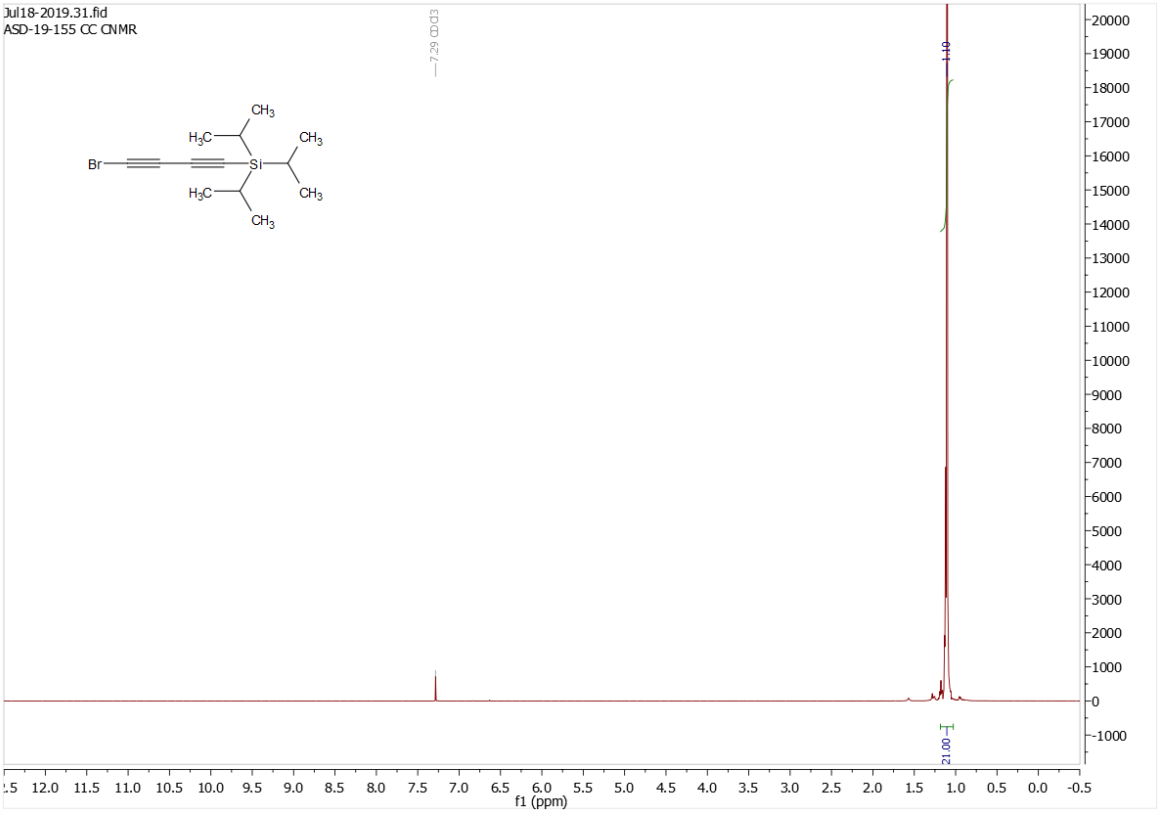
(2-(Bromobuta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (263): ^{1}H NMR



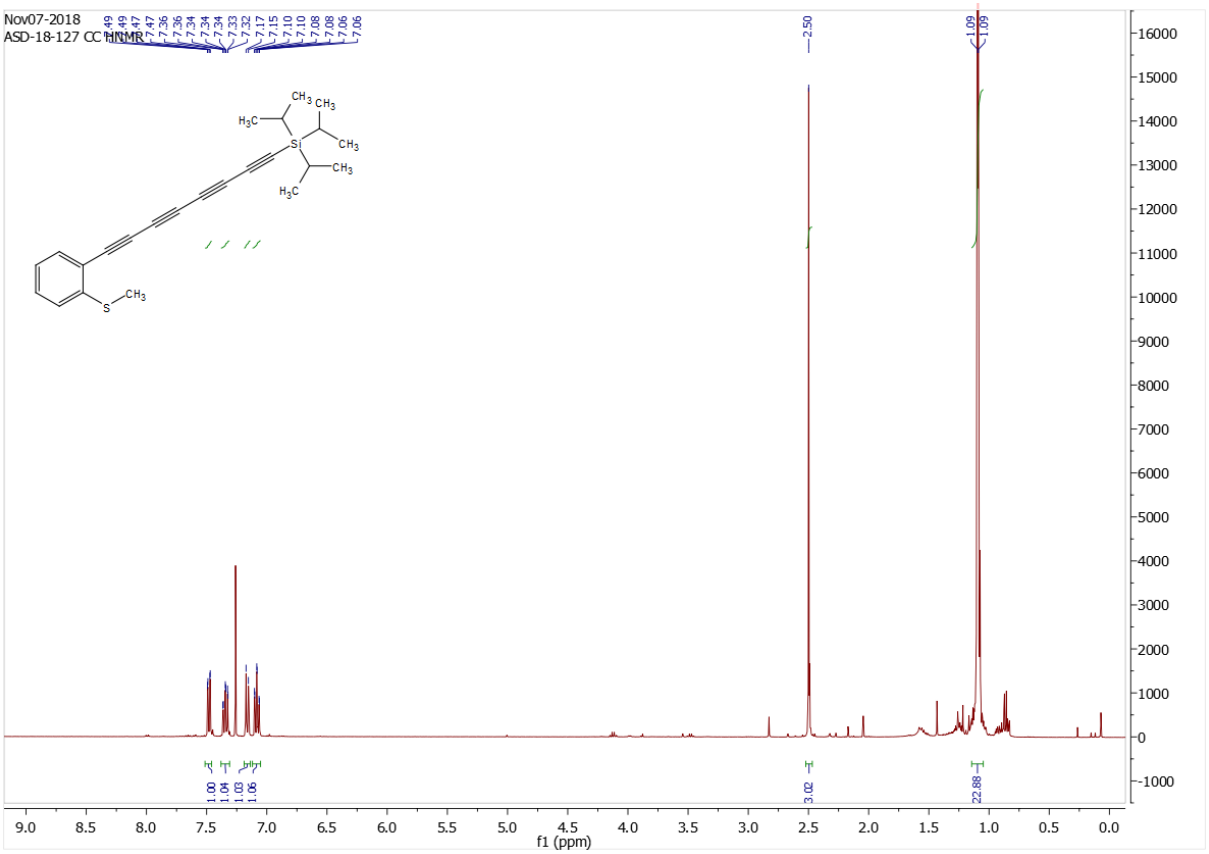
^{13}C NMR



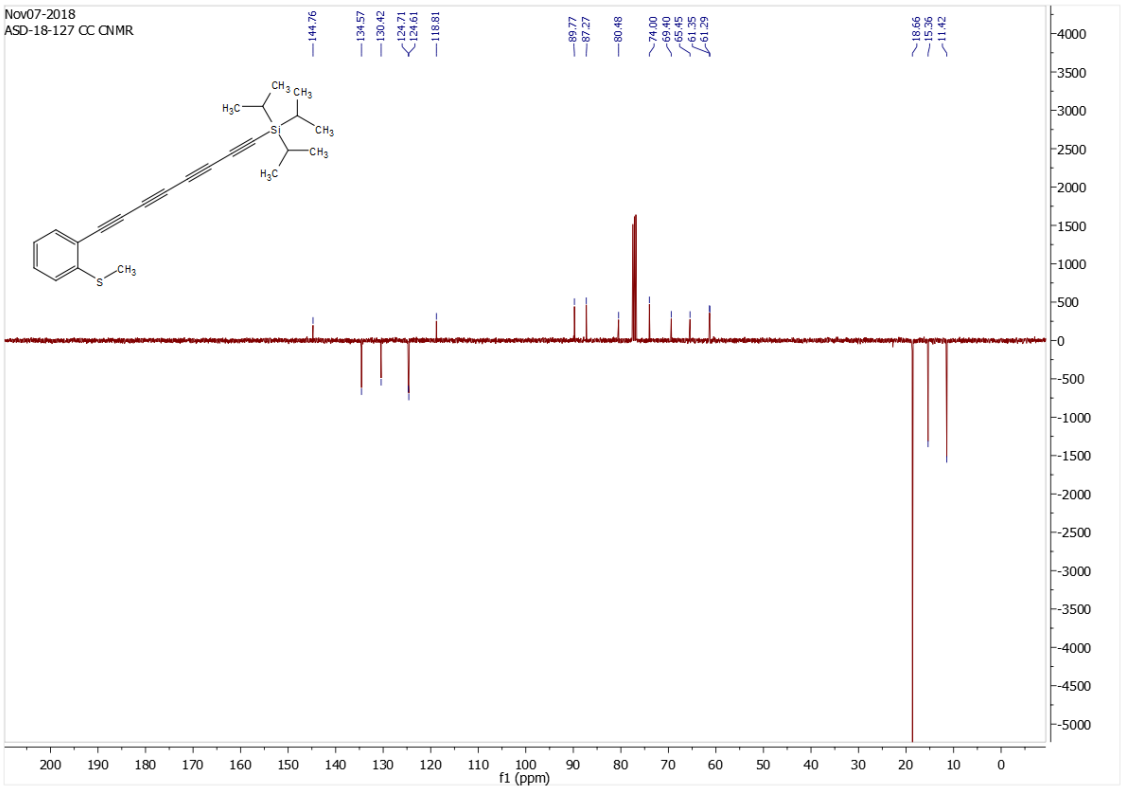
(Bromobuta-1,3-diyn-1-yl)triisopropylsilane (264): ^{1}H NMR



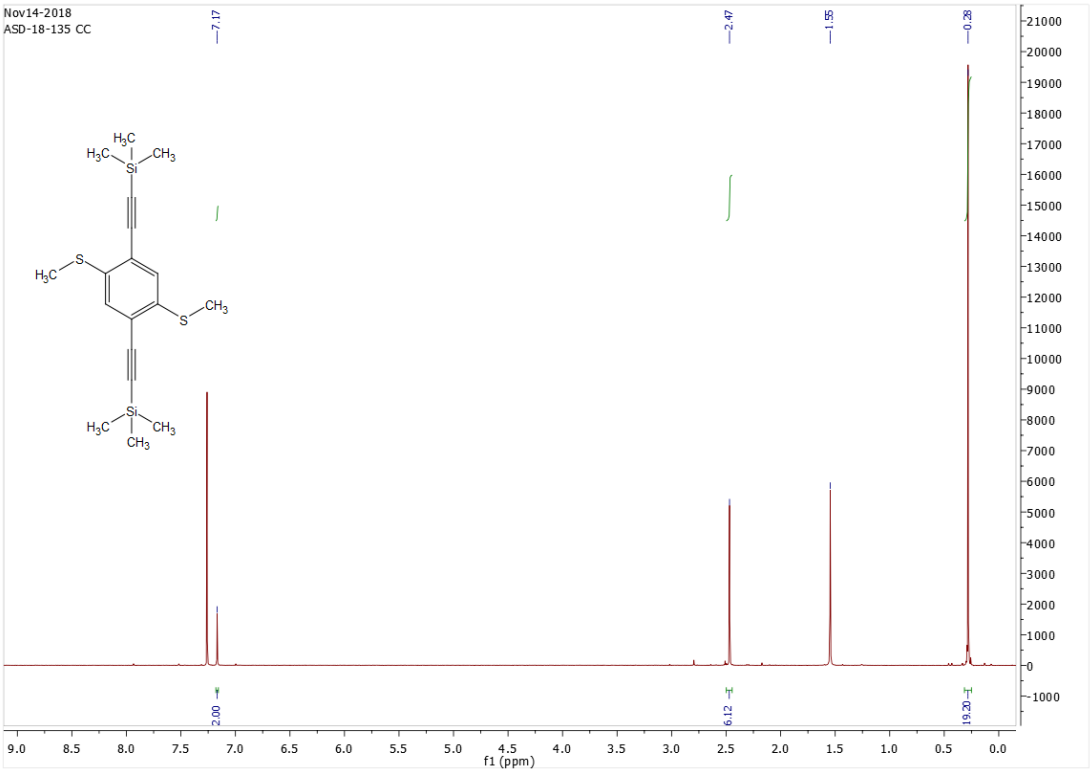
Triisopropyl((2-(methylthio)phenyl)octa-1,3,5,7-tetrayn-1-yl)silane (237): ^{1}H NMR



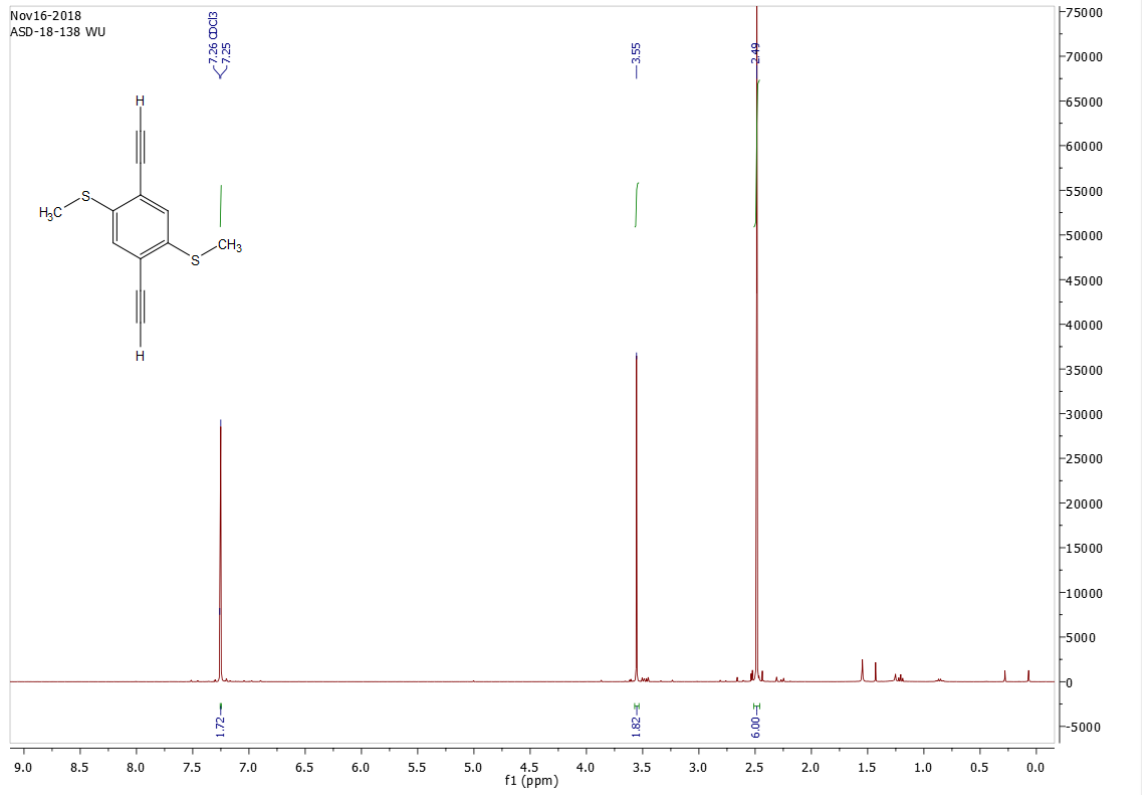
^{13}C NMR



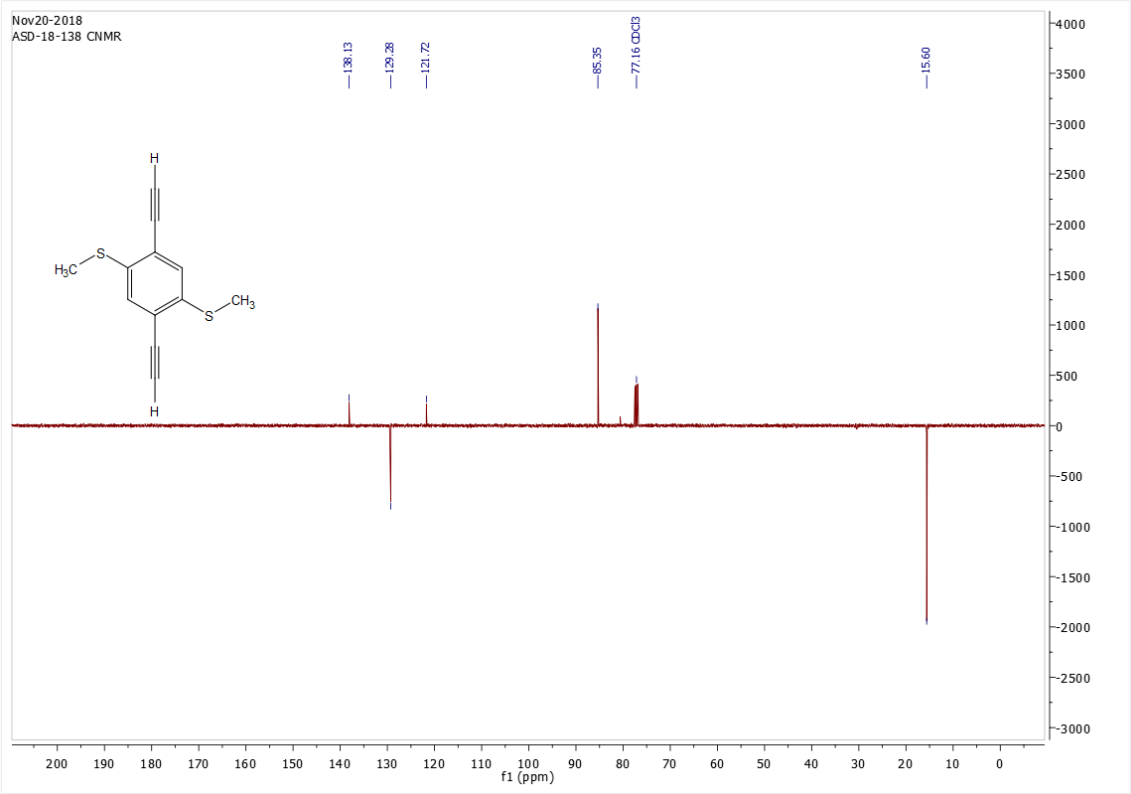
((2,5-Bis(methylthio)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (108): ^{1}H NMR



(2,5-Diethynyl-1,4-phenylene)bis(methylsulfane) (270): ^{1}H NMR

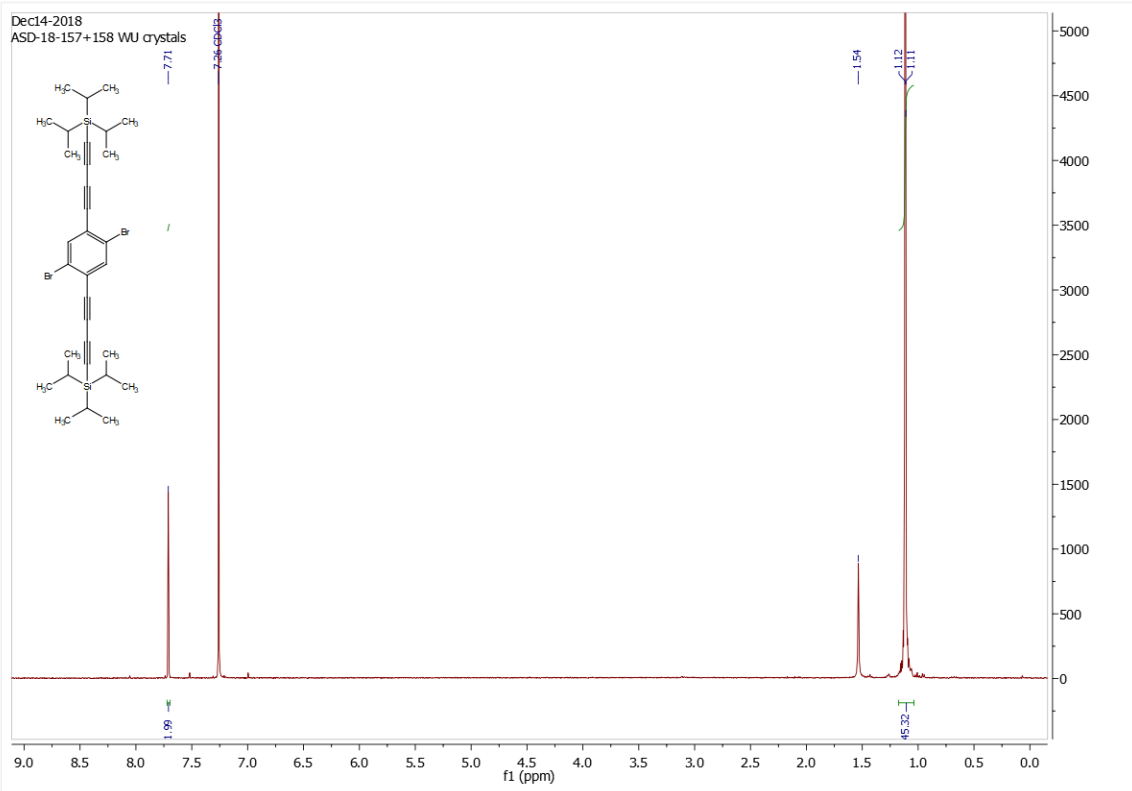


^{13}C NMR

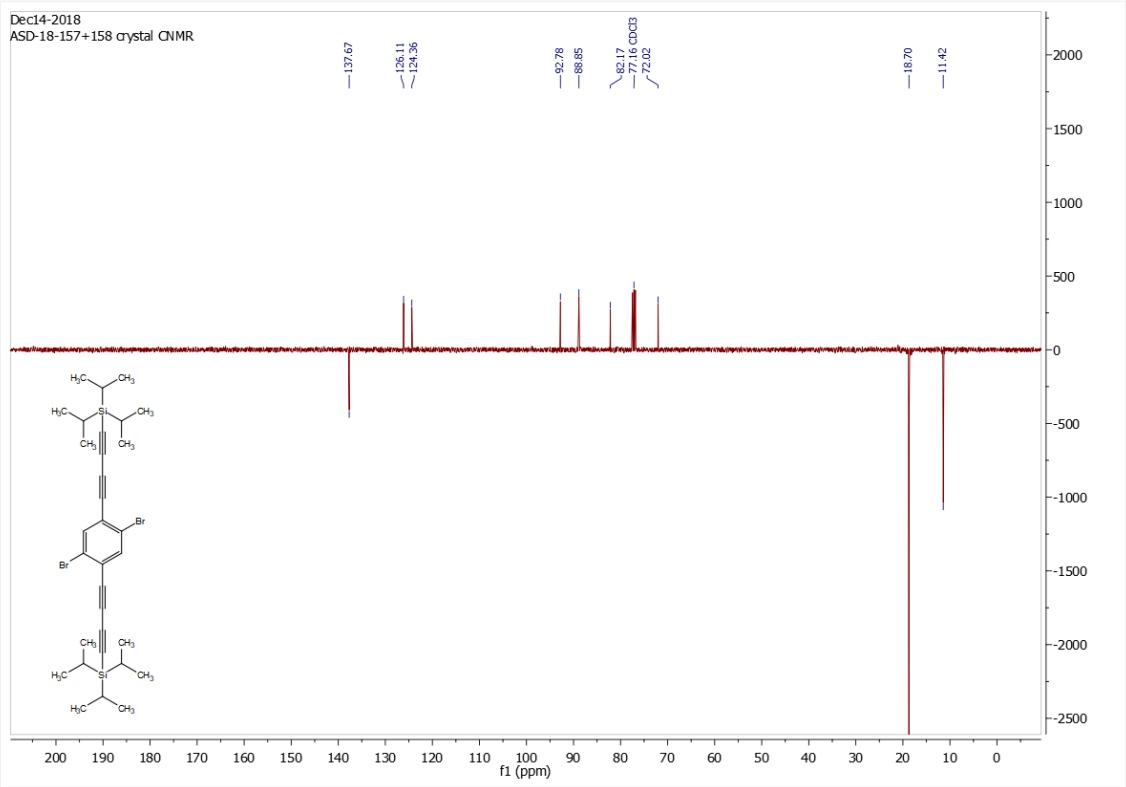


((2,5-Dibromo-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(triisopropylsilane) (271):

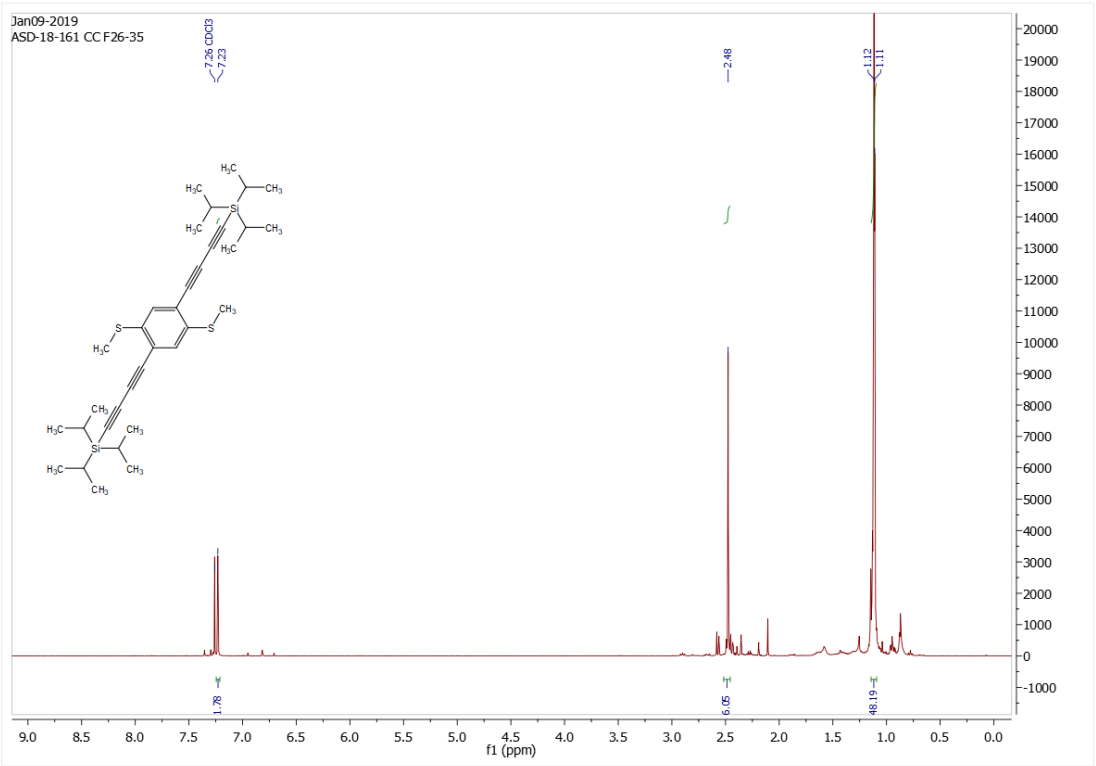
^{1}H NMR



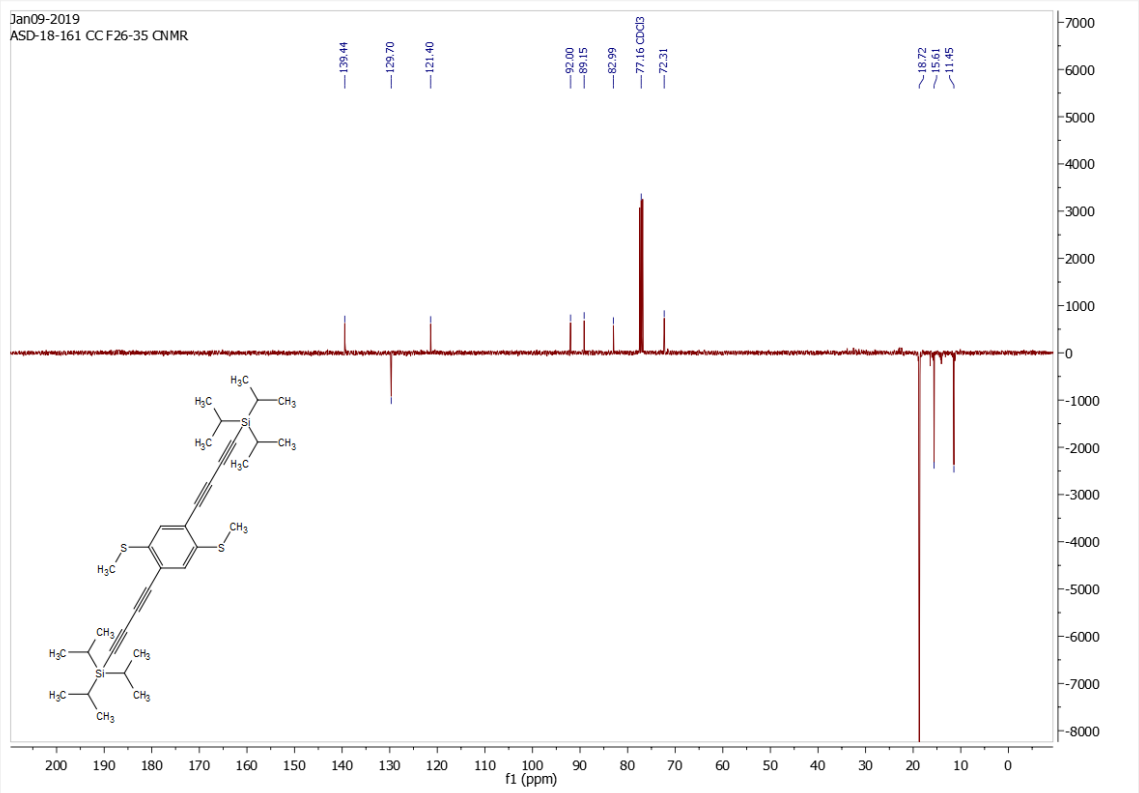
^{13}C NMR



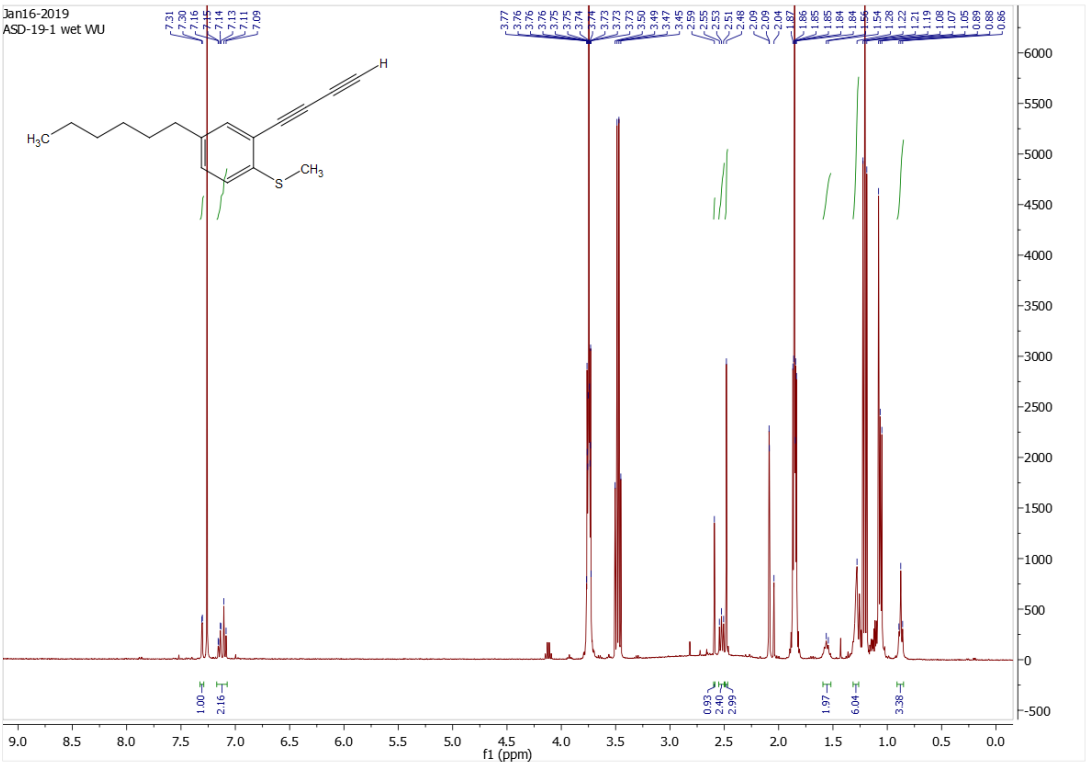
((2,5-Bis(methylthio)-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(triisopropylsilane) (265): ^{1}H NMR



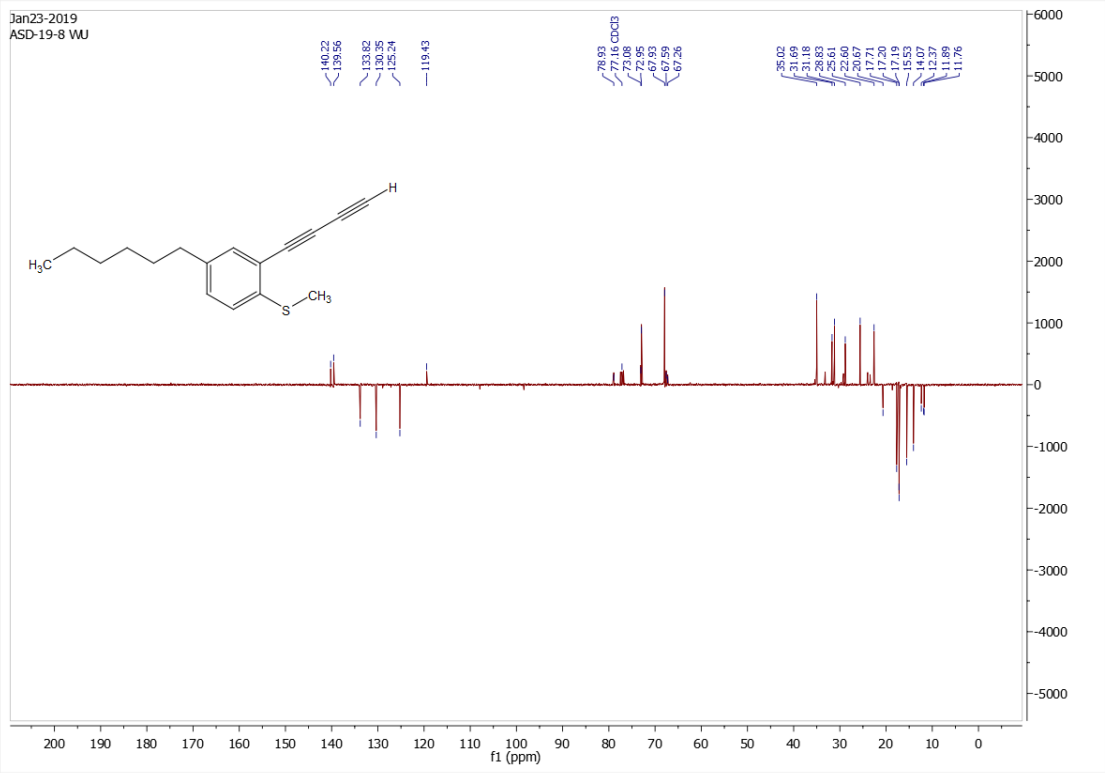
^{13}C NMR



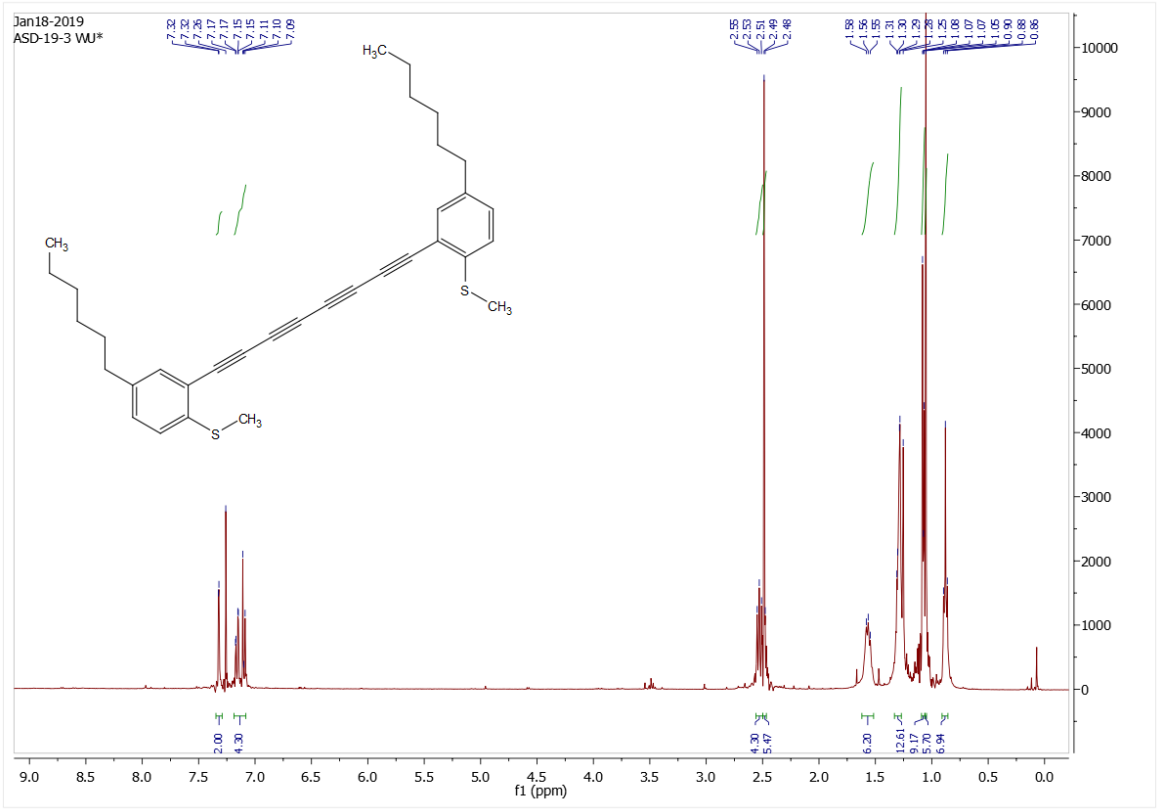
(2-(Buta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (273): ^{1}H NMR



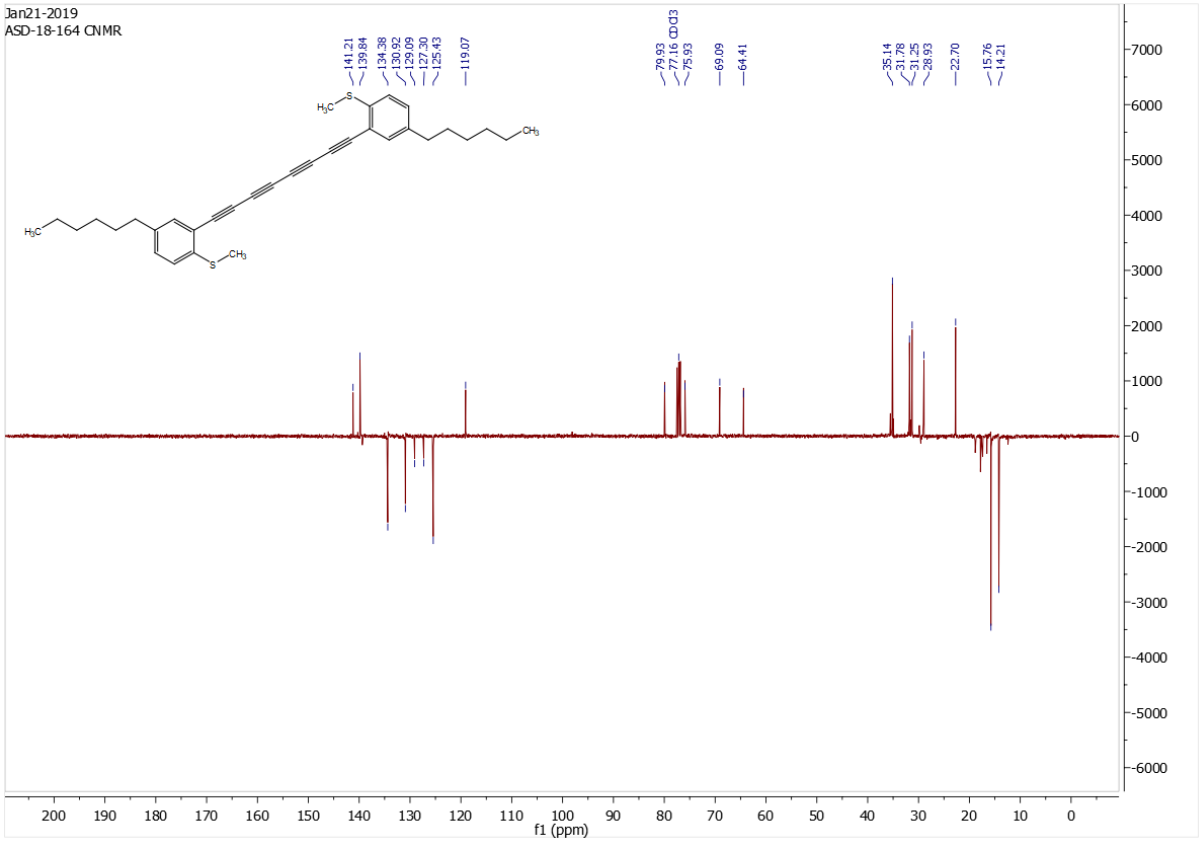
^{13}C NMR



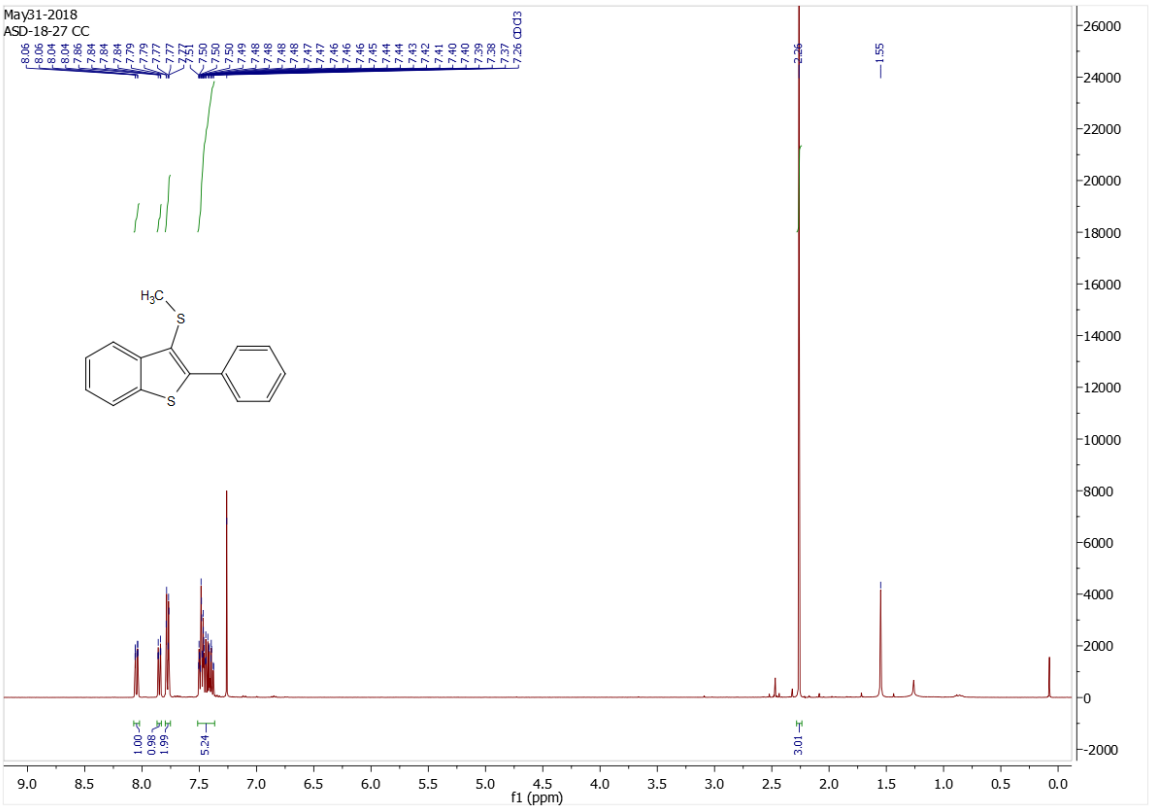
1,8-Bis(5-hexyl-2-(methylthio)phenyl)octa-1,3,5,7-tetrayne (266): ^{1}H NMR



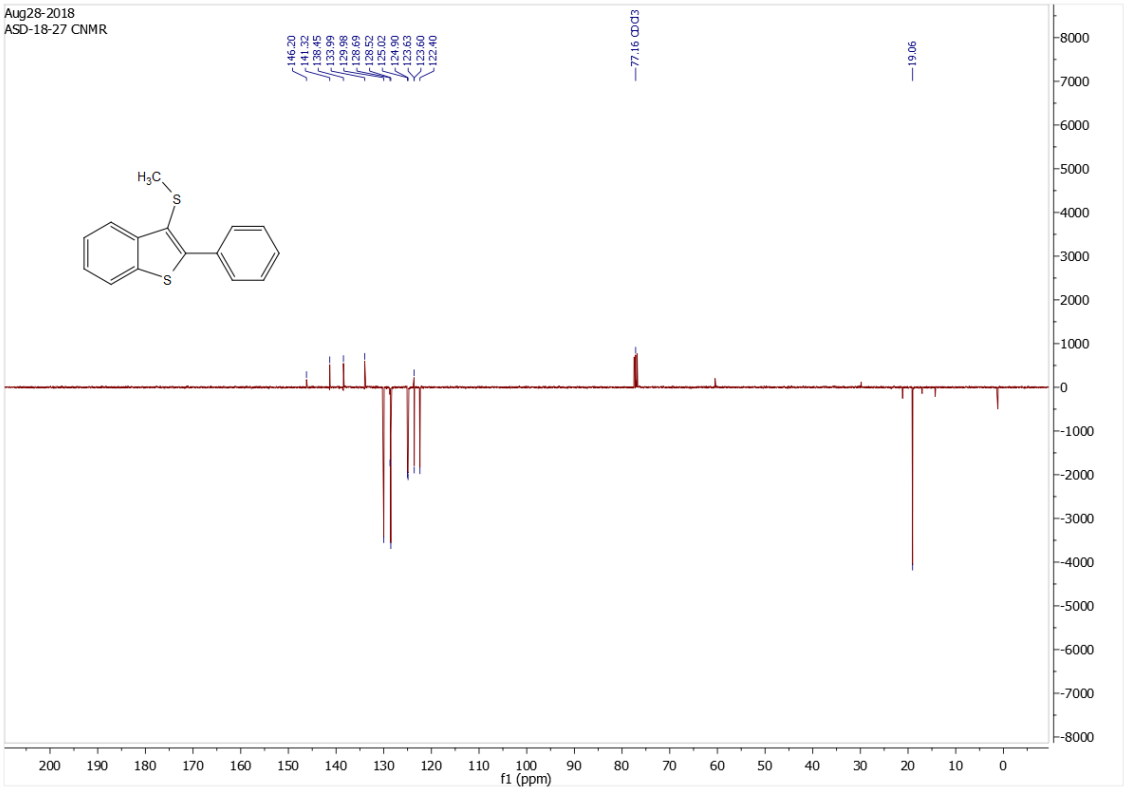
^{13}C NMR



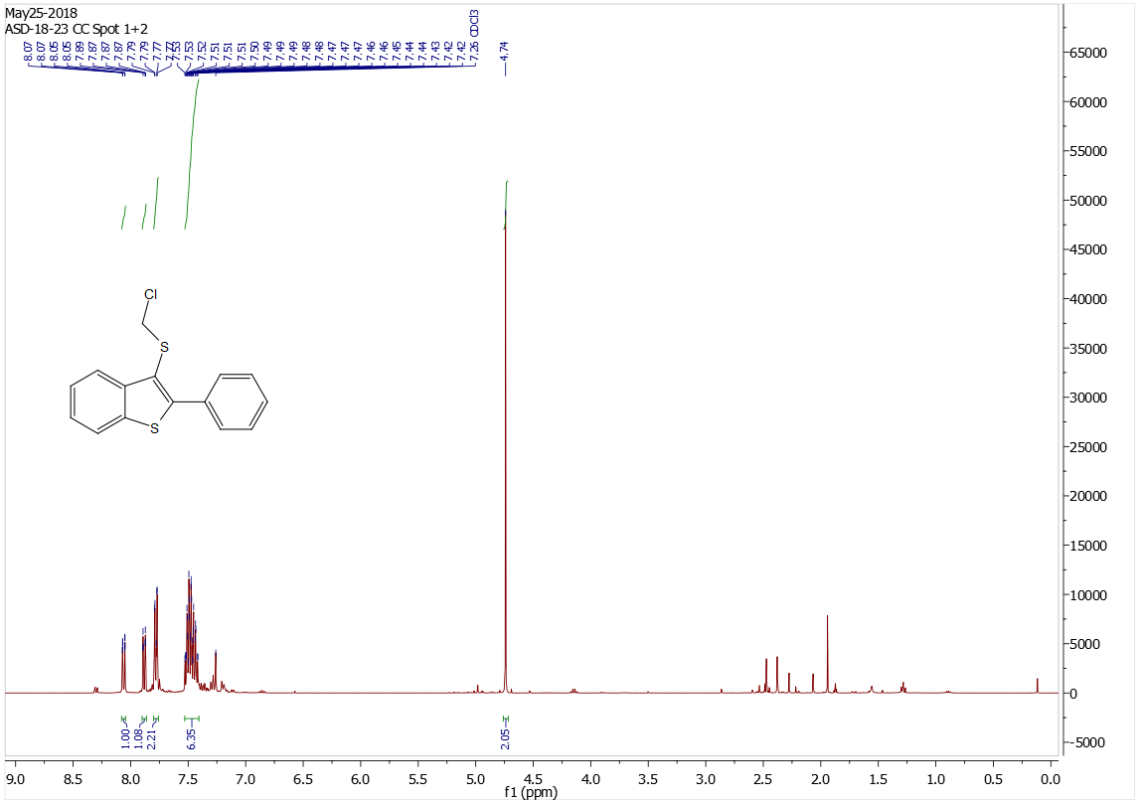
3-(Methylthio)-2-phenylbenzo[*b*]thiophene (276): ^{1}H NMR



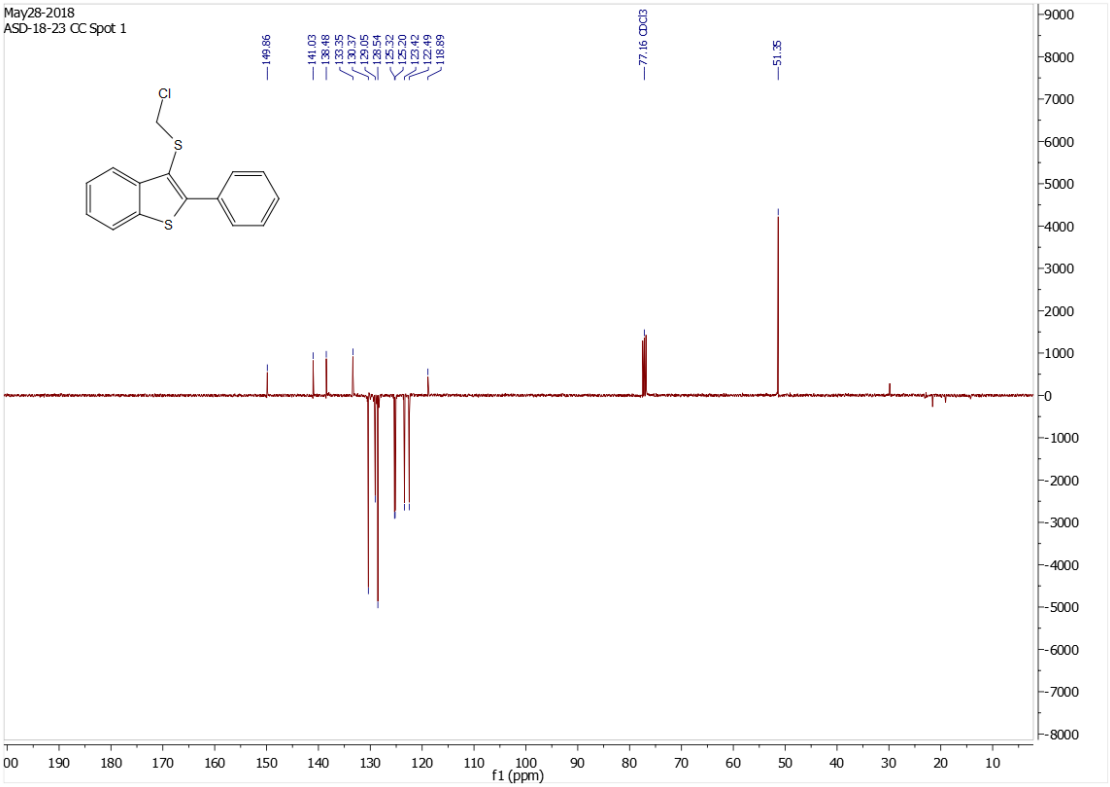
^{13}C NMR



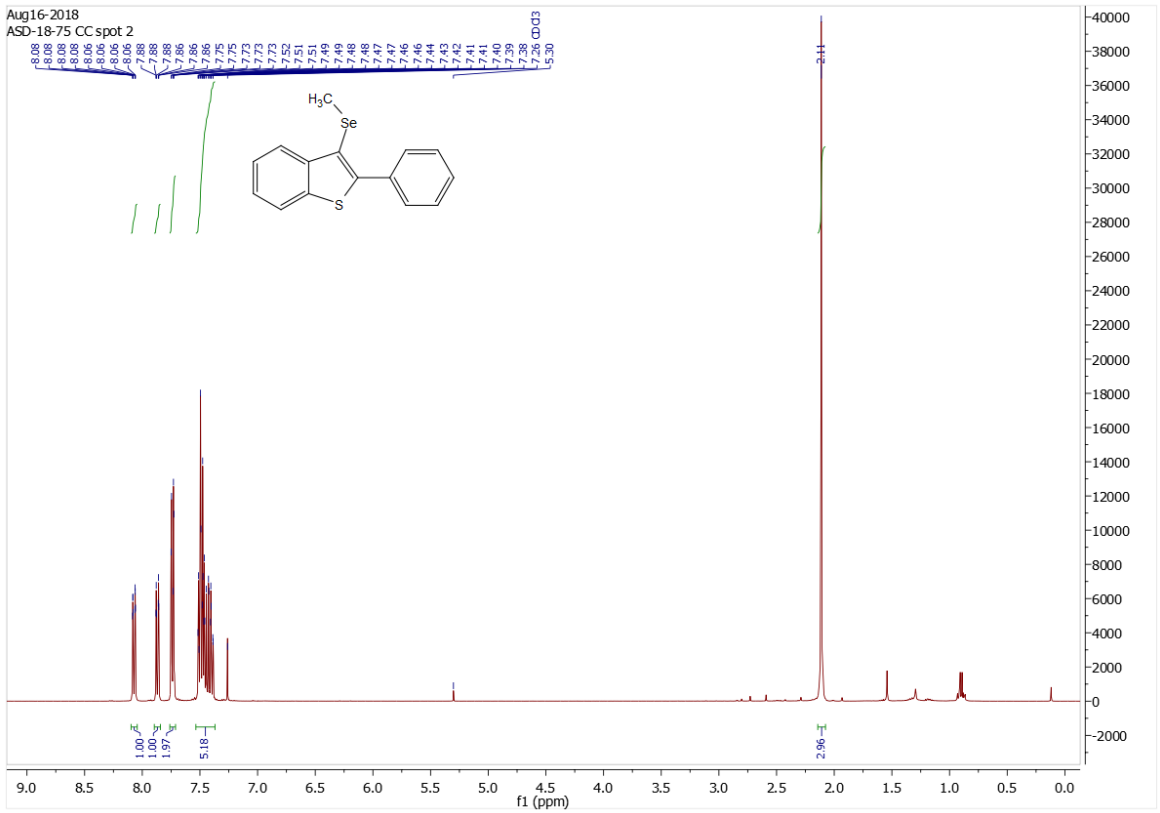
3-((chloromethyl)thio)-2-phenylbenzo[b]thiophene (278): ^{1}H NMR



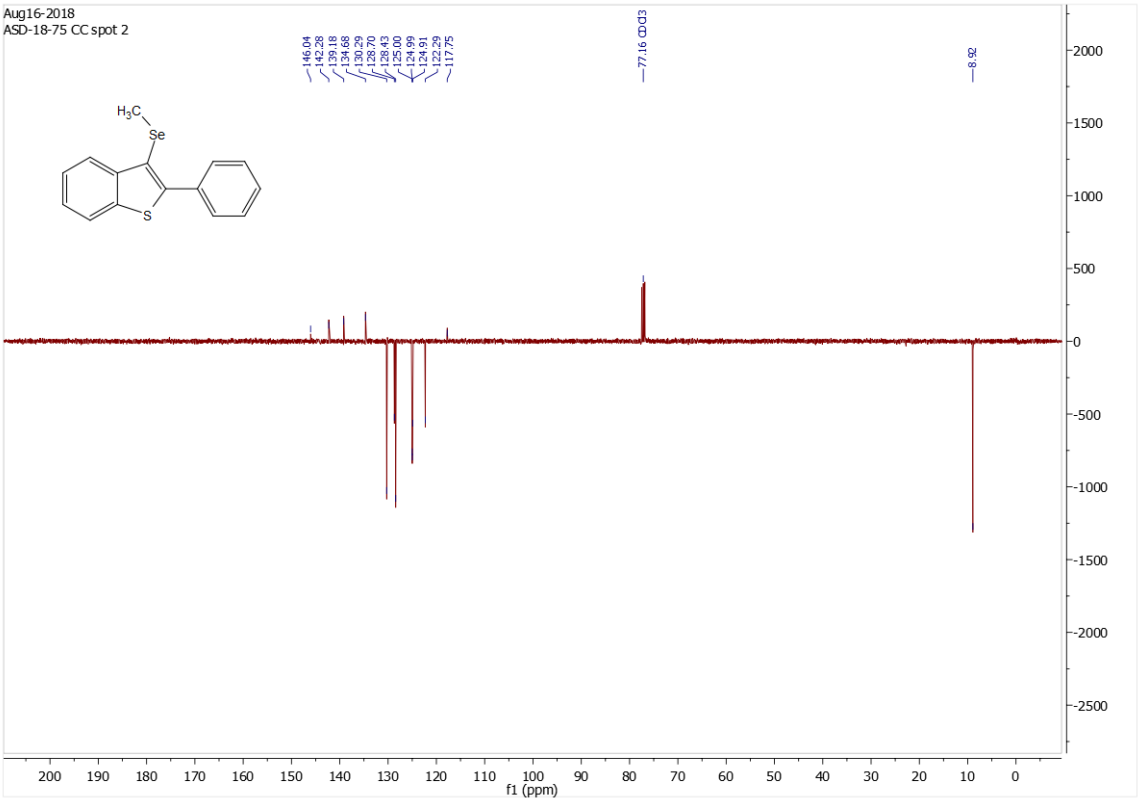
^{13}C NMR



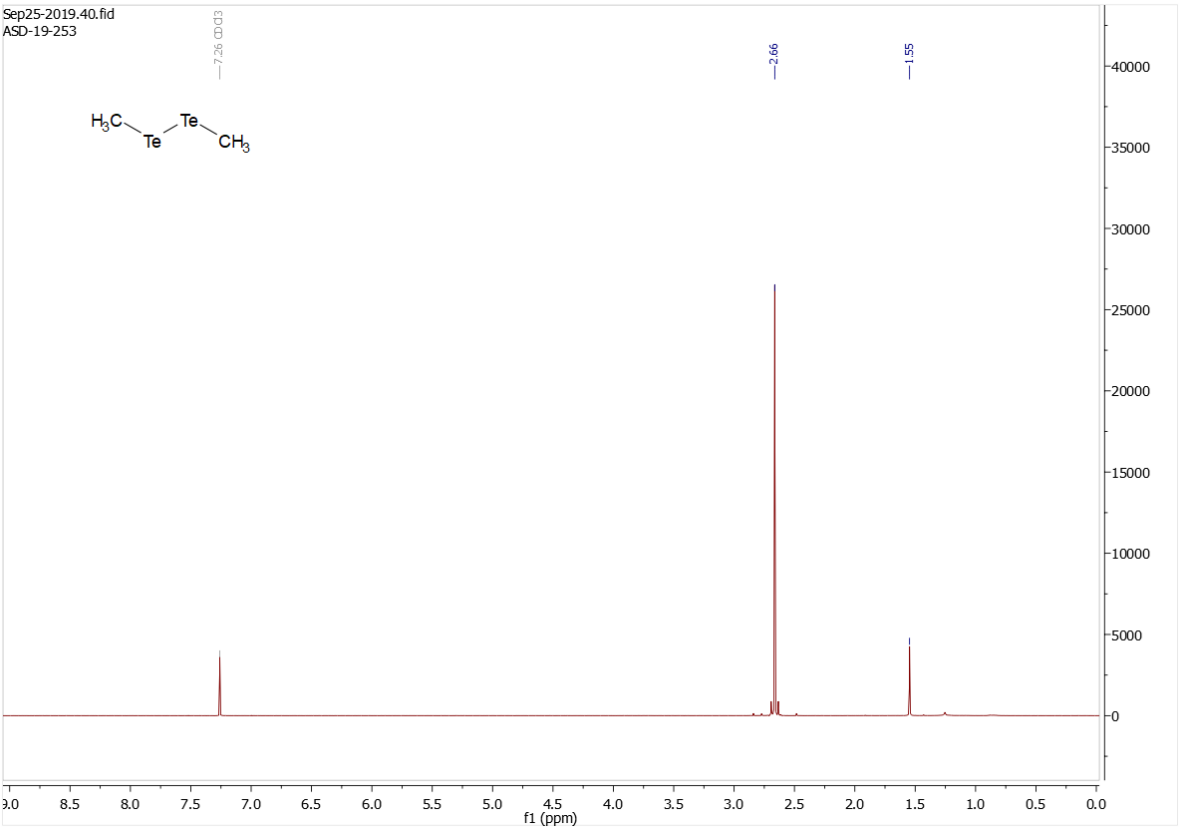
3-(Methylselanyl)-2-phenylbenzo[*b*]thiophene (281): ^{1}H NMR



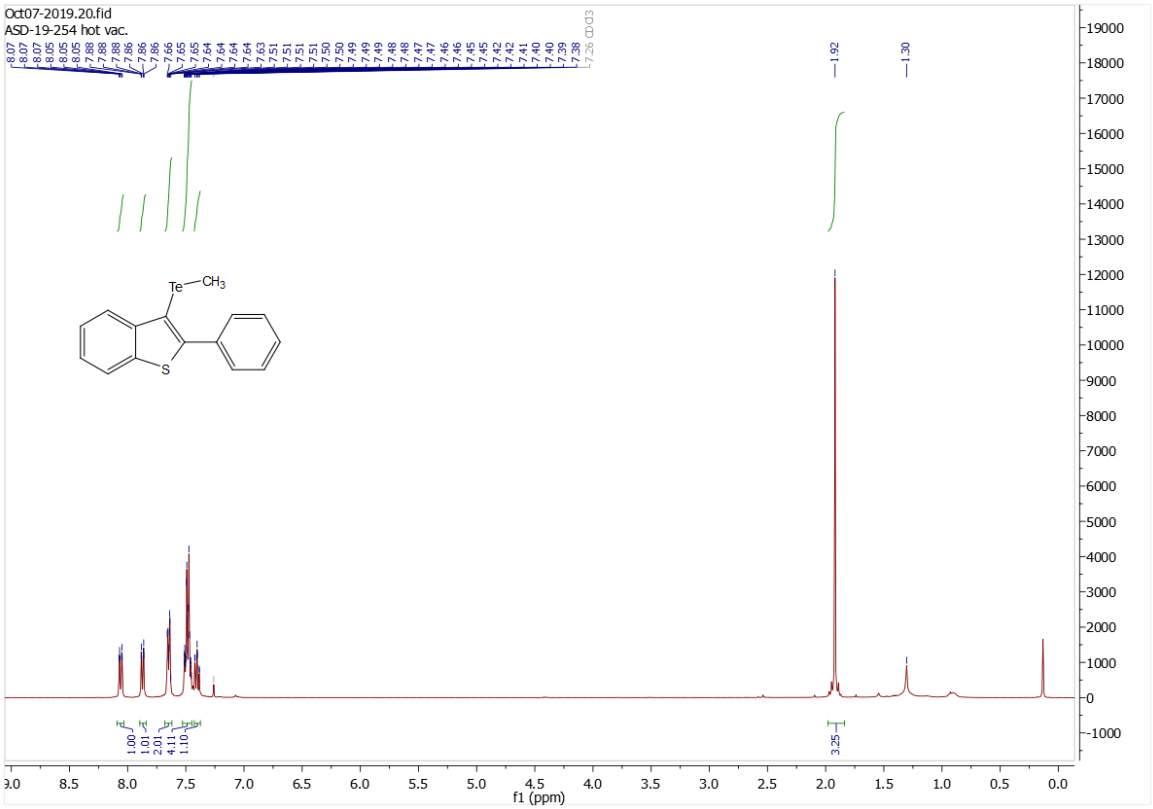
^{13}C NMR



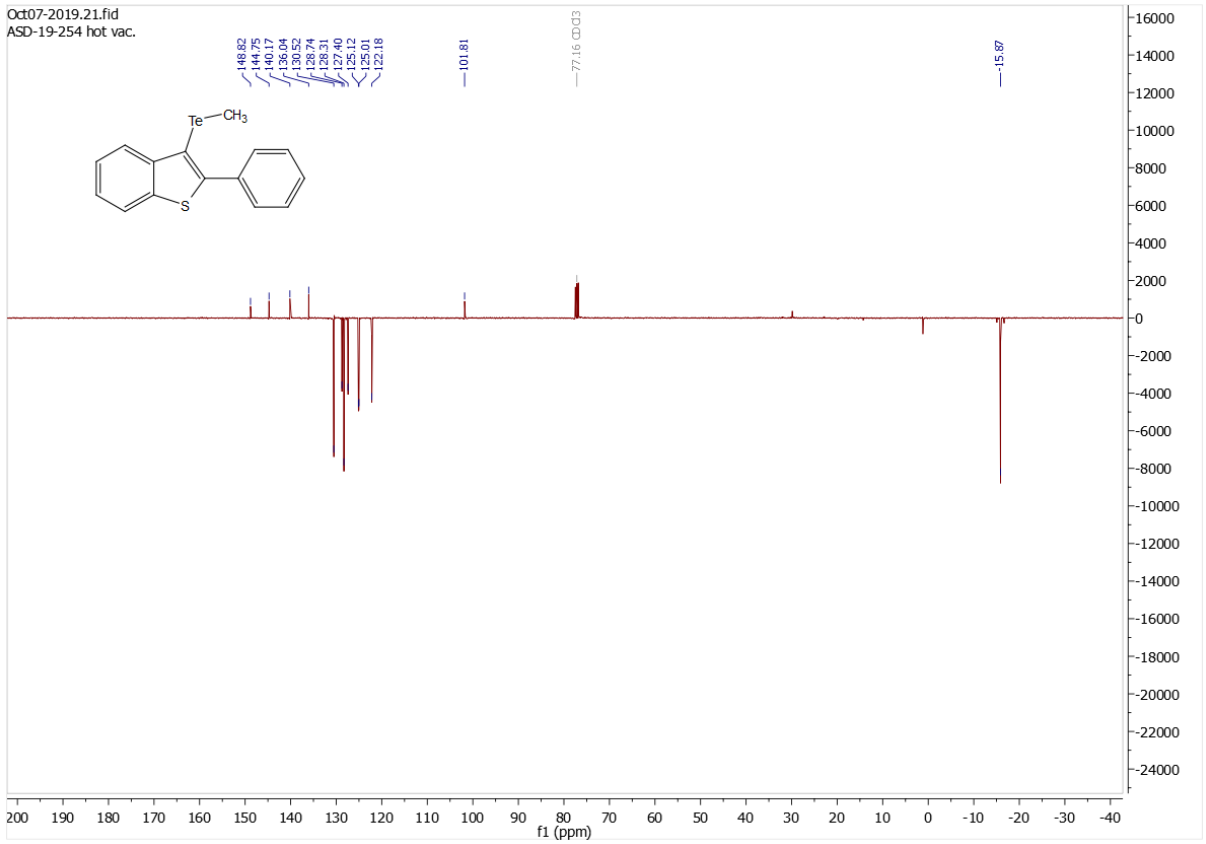
1,2-Dimethylditellane (283): ^{1}H NMR



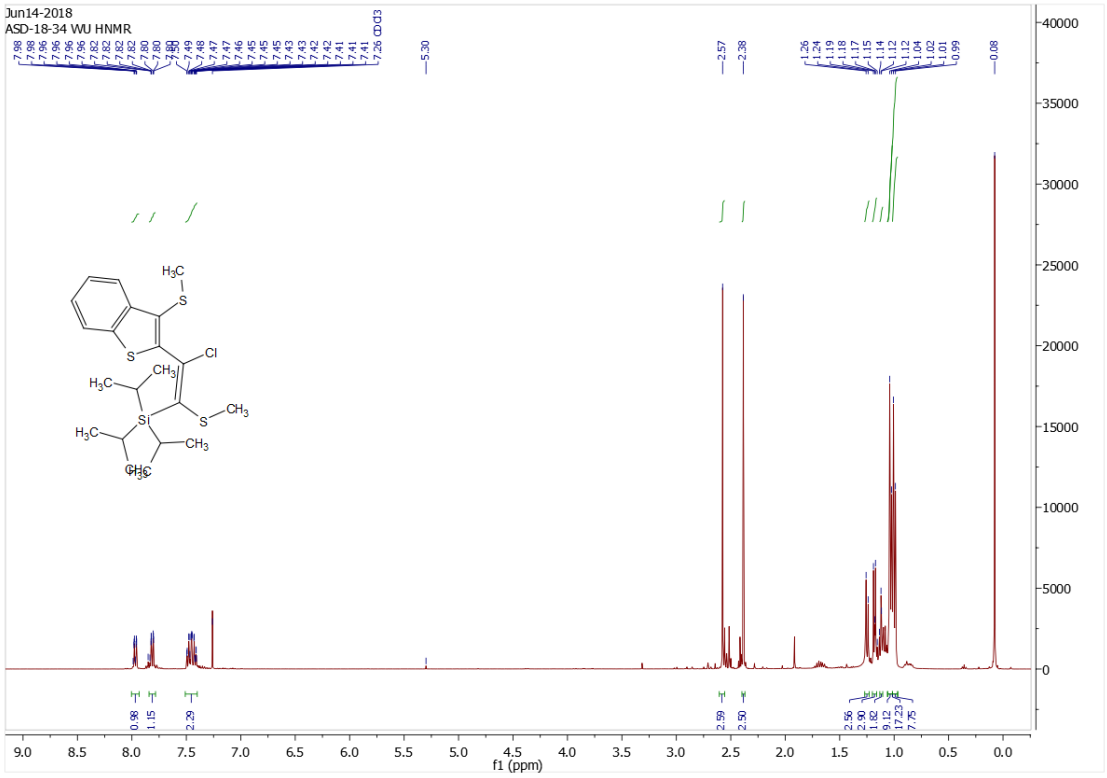
3-(Methyltellanyl)-2-phenylbenzo[b]thiophene (285): ^{1}H NMR



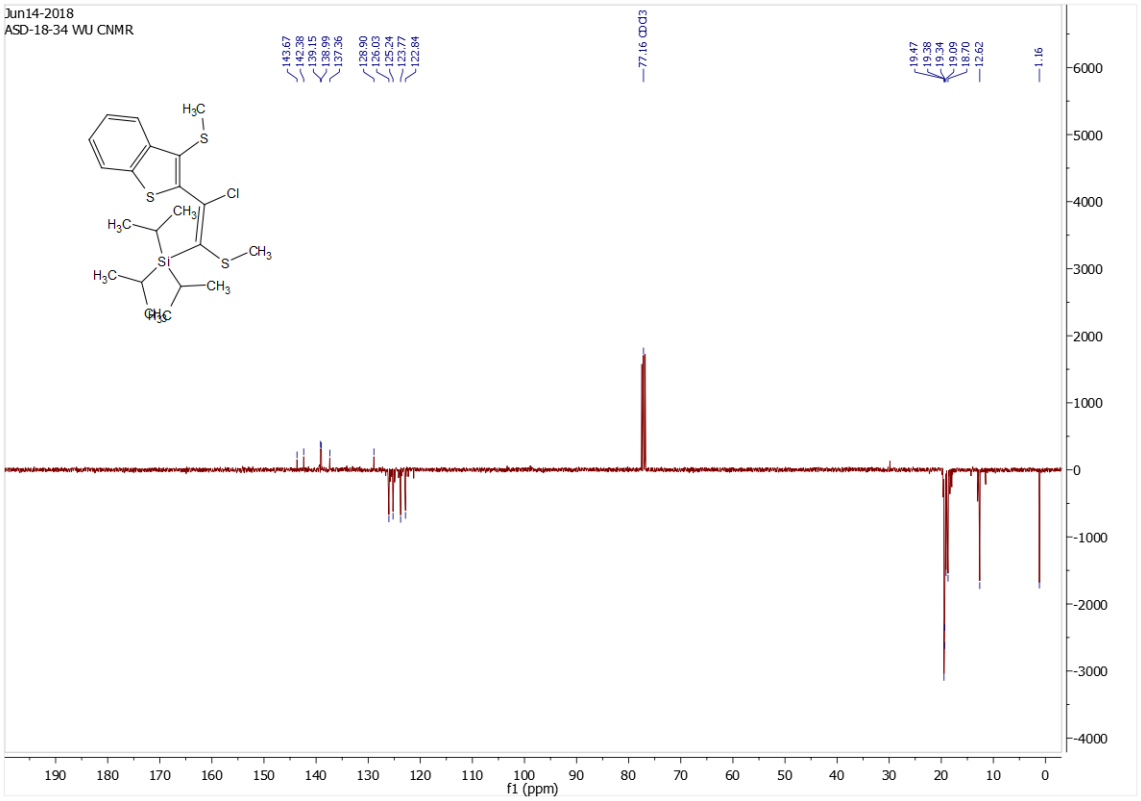
^{13}C NMR



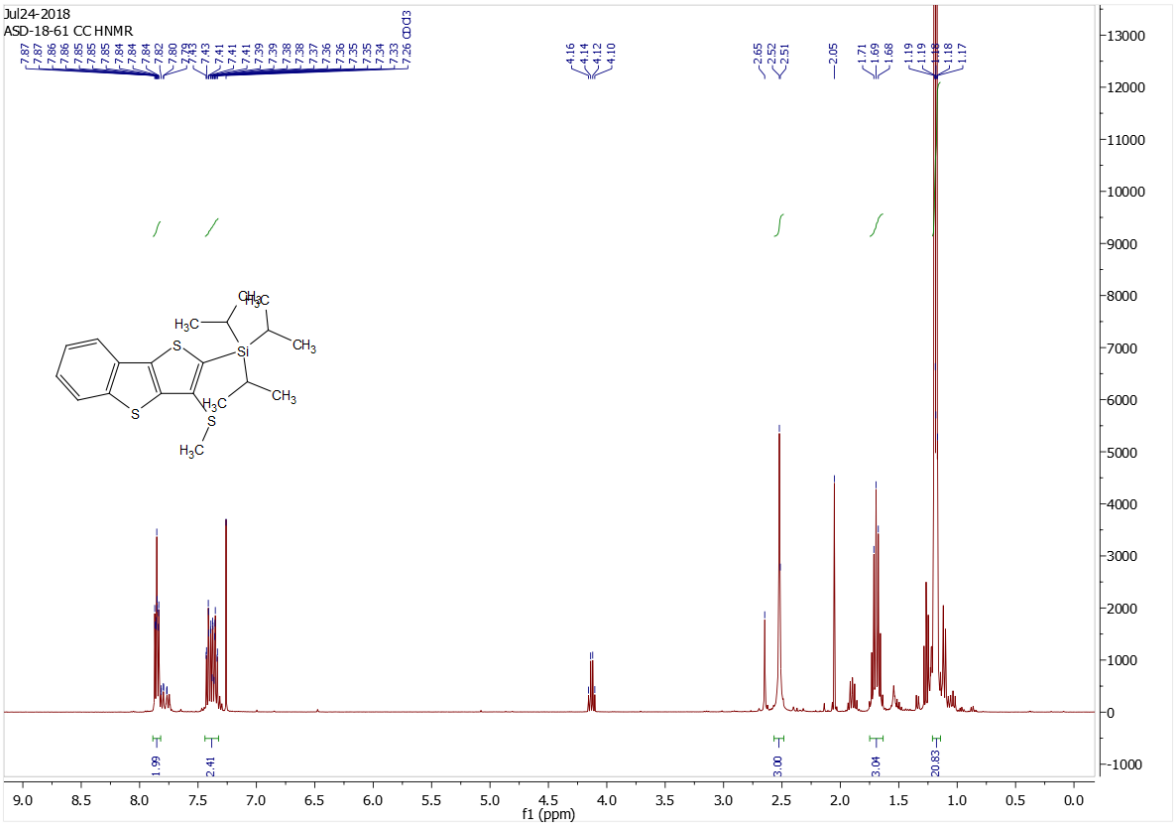
(*Z*)-(2-Chloro-1-(methylthio)-2-(3-(methylthio)benzo[b]thiophen-2-yl)vinyl)triisopropylsilane (286): ^{1}H NMR



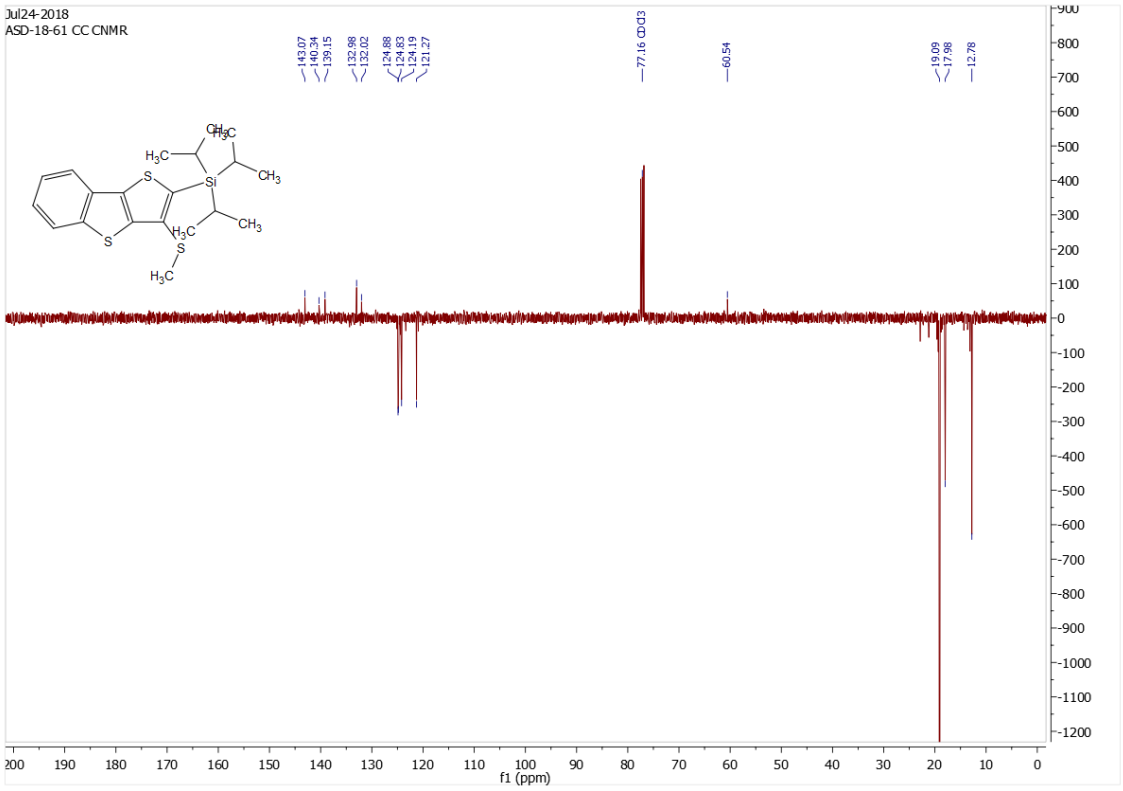
^{13}C NMR



Benzo[*b*]thieno[2,3-d]thiophen-2-yltriisopropylsilane (287): ^{1}H NMR

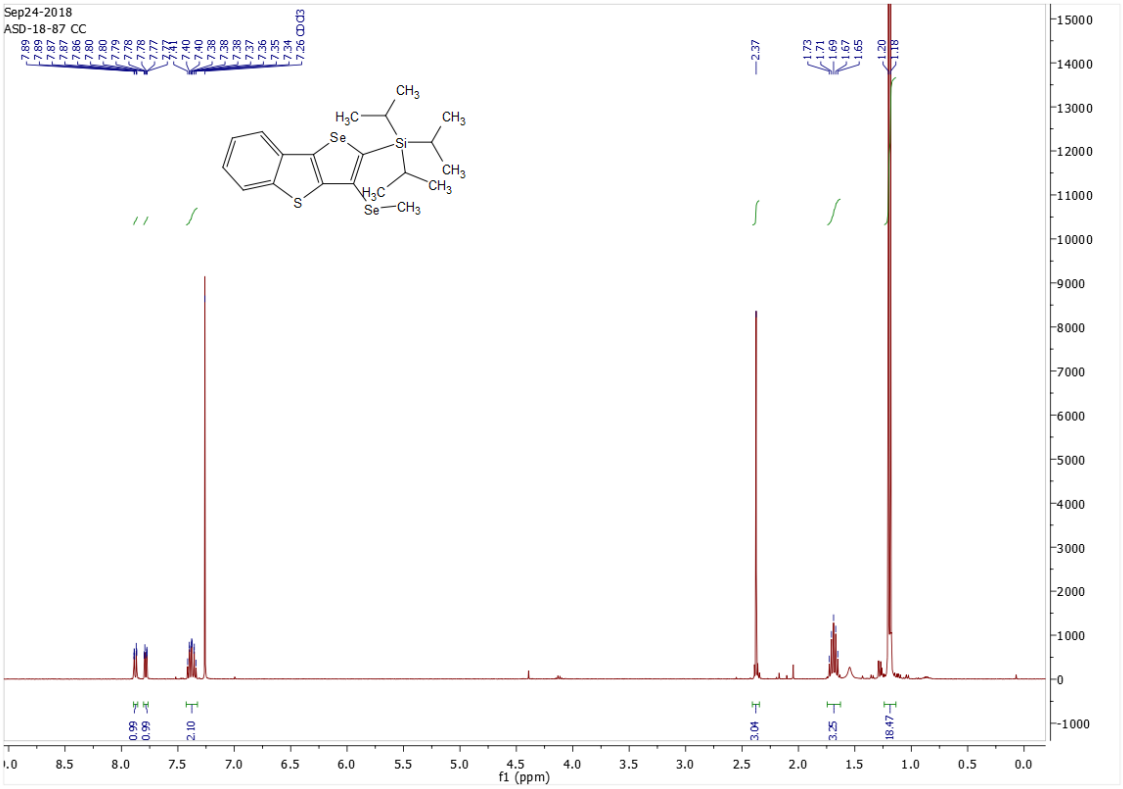


^{13}C NMR

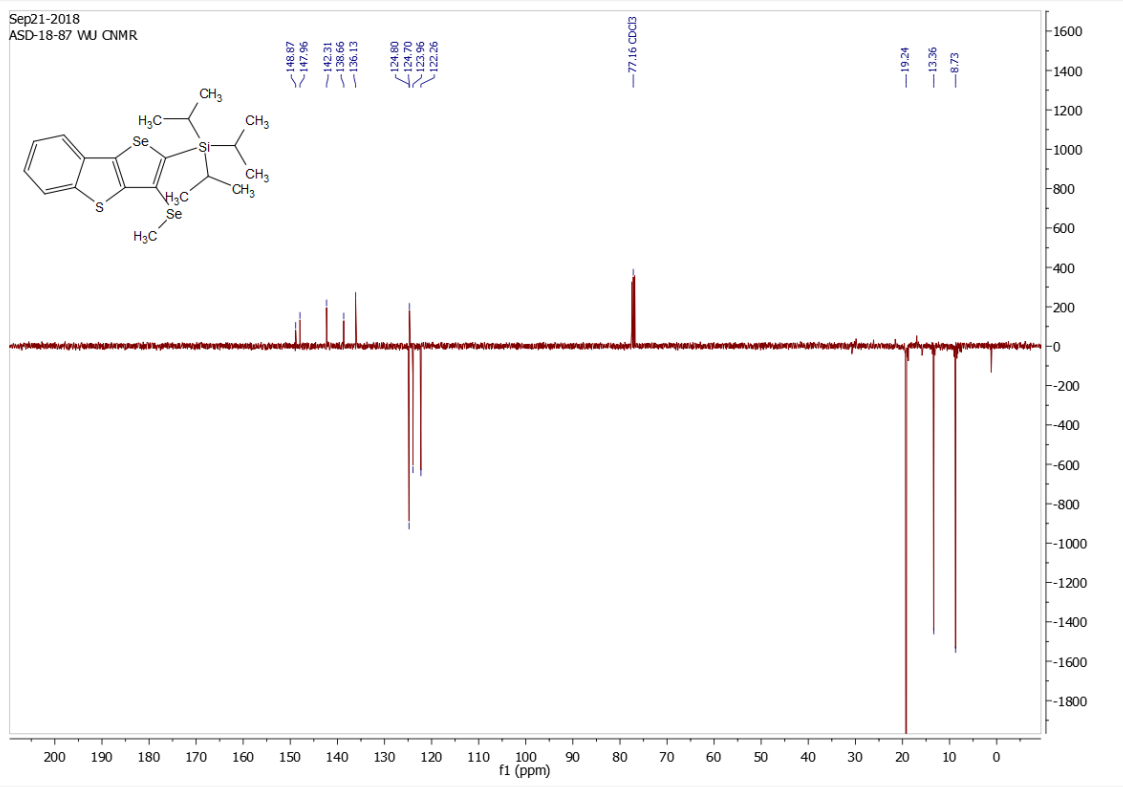


Triisopropyl(3-(methylselanyl)benzo[*b*]selenopheno[2,3-d]thiophen-2-yl)silane (290):

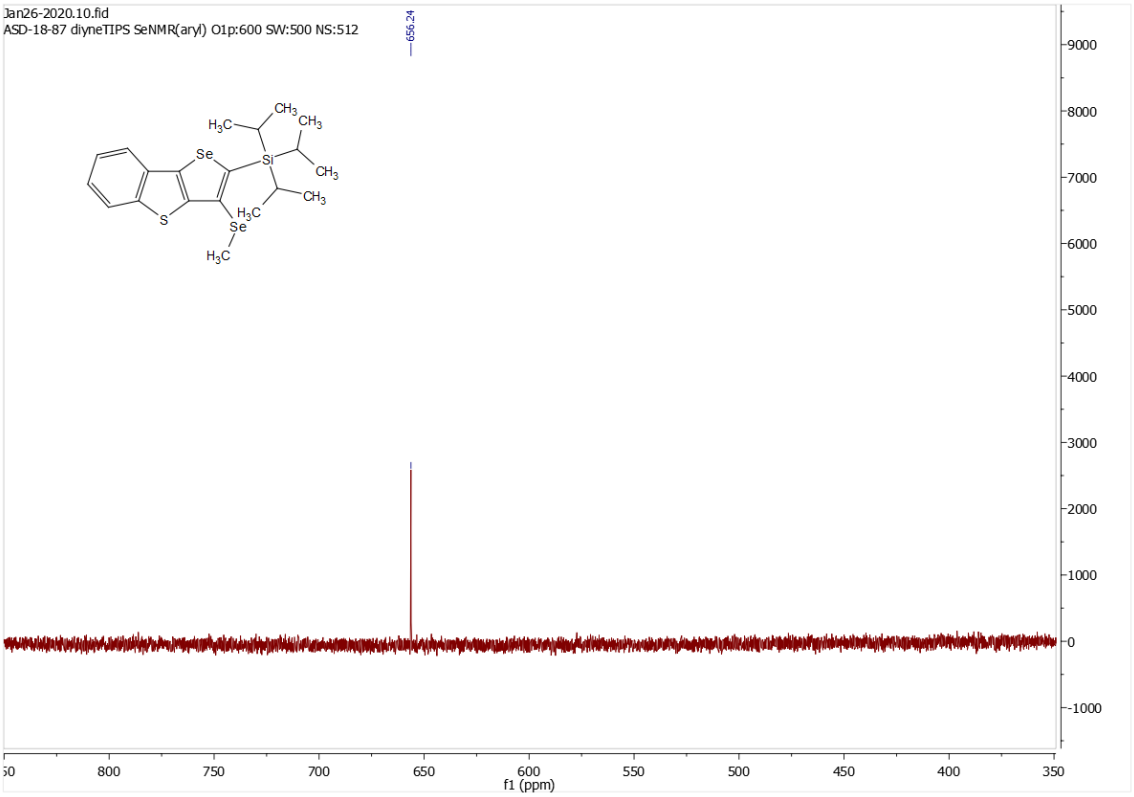
^{1}H NMR



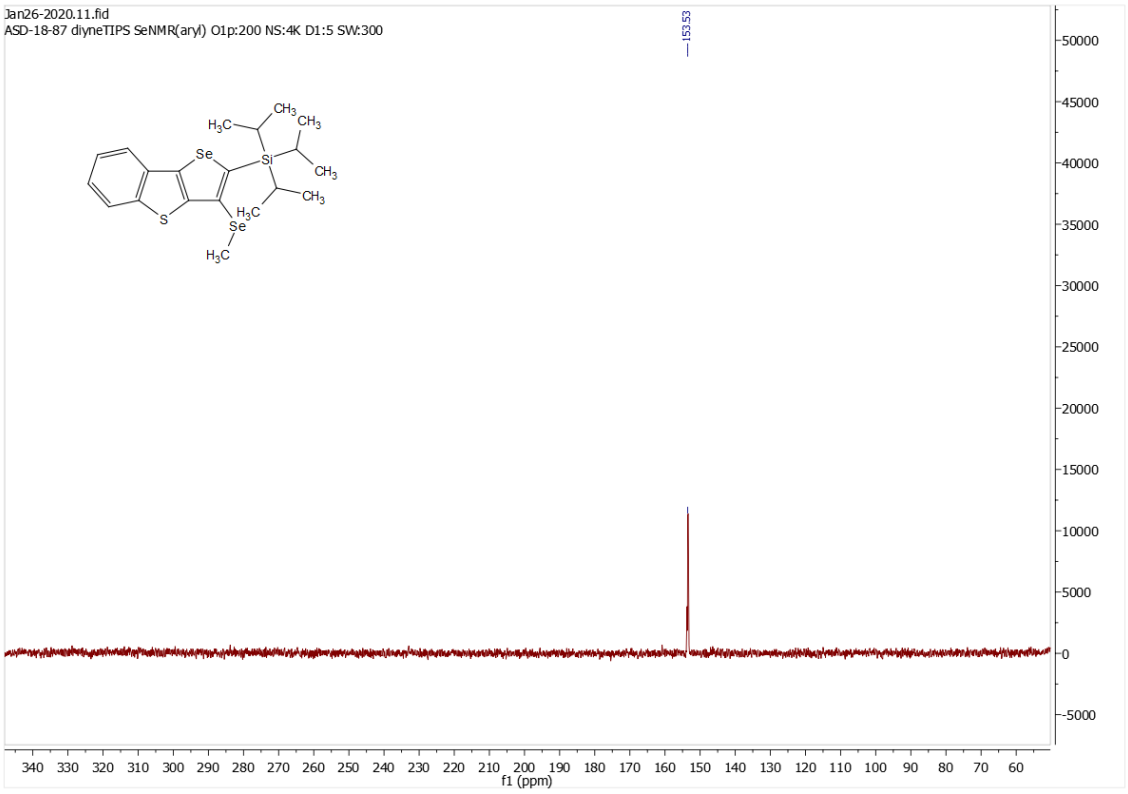
^{13}C NMR



^{77}Se NMR Aromatic Region

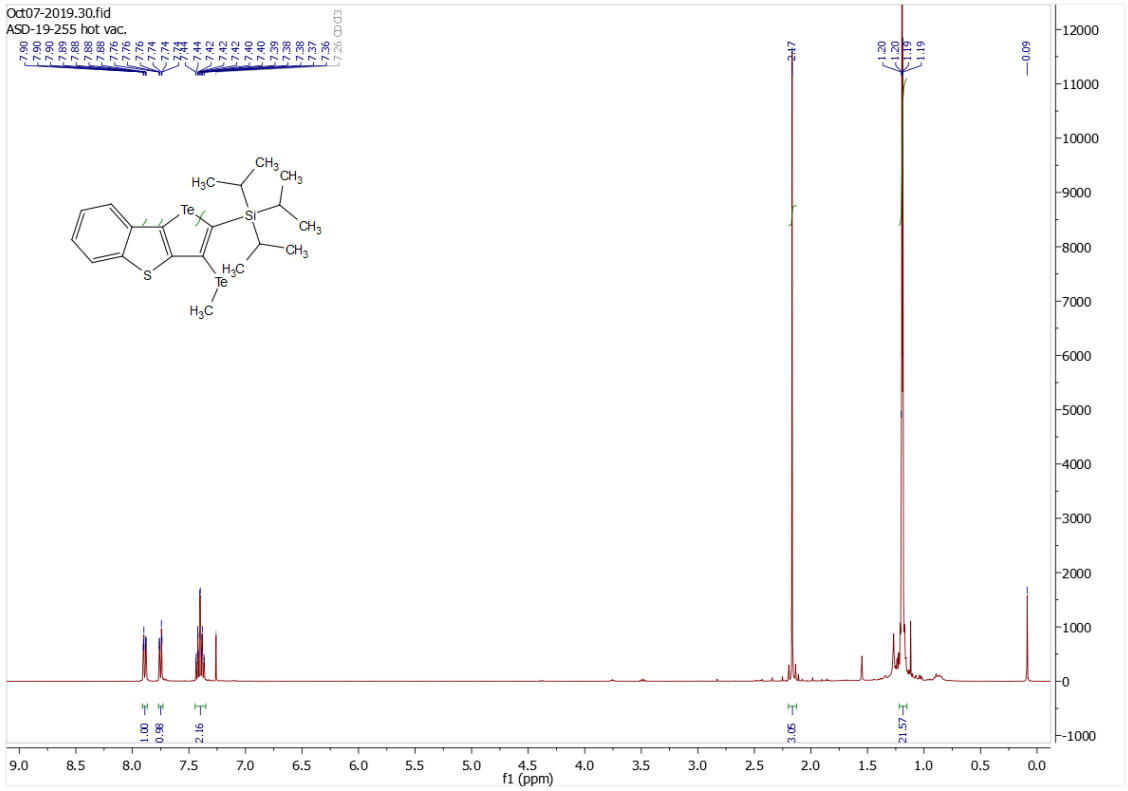


^{77}Se NMR Aliphatic Region

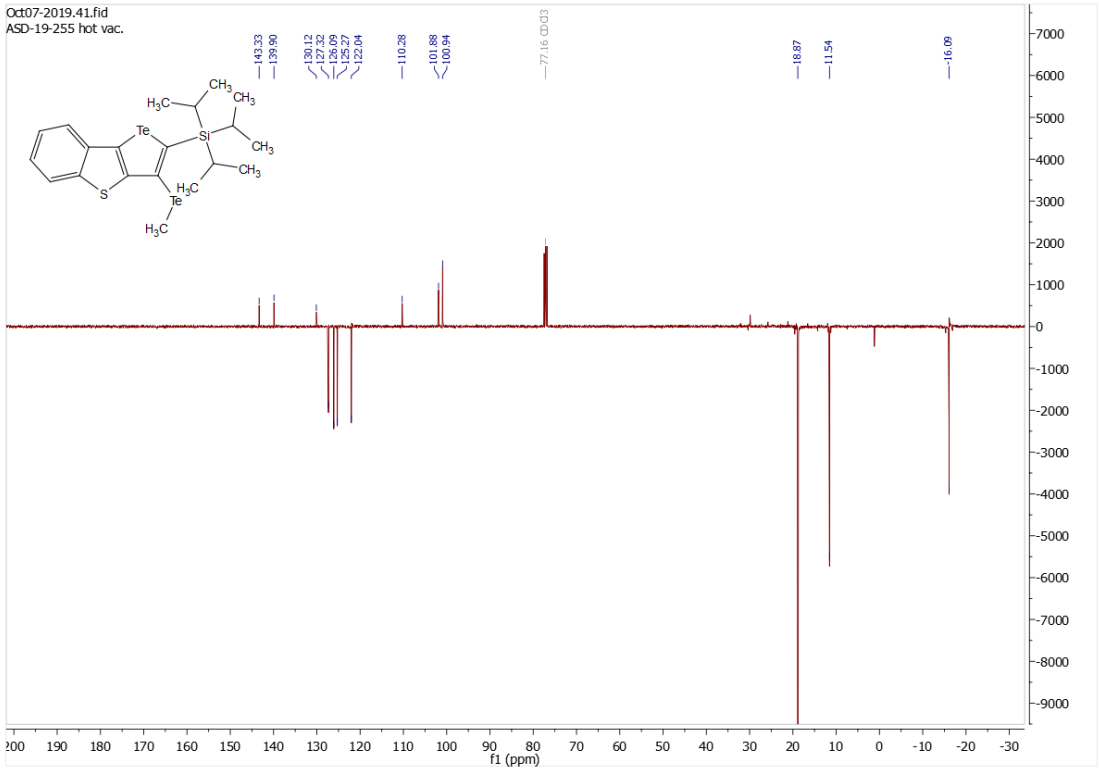


Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2,3-d]thiophen-2-yl)silane (291):

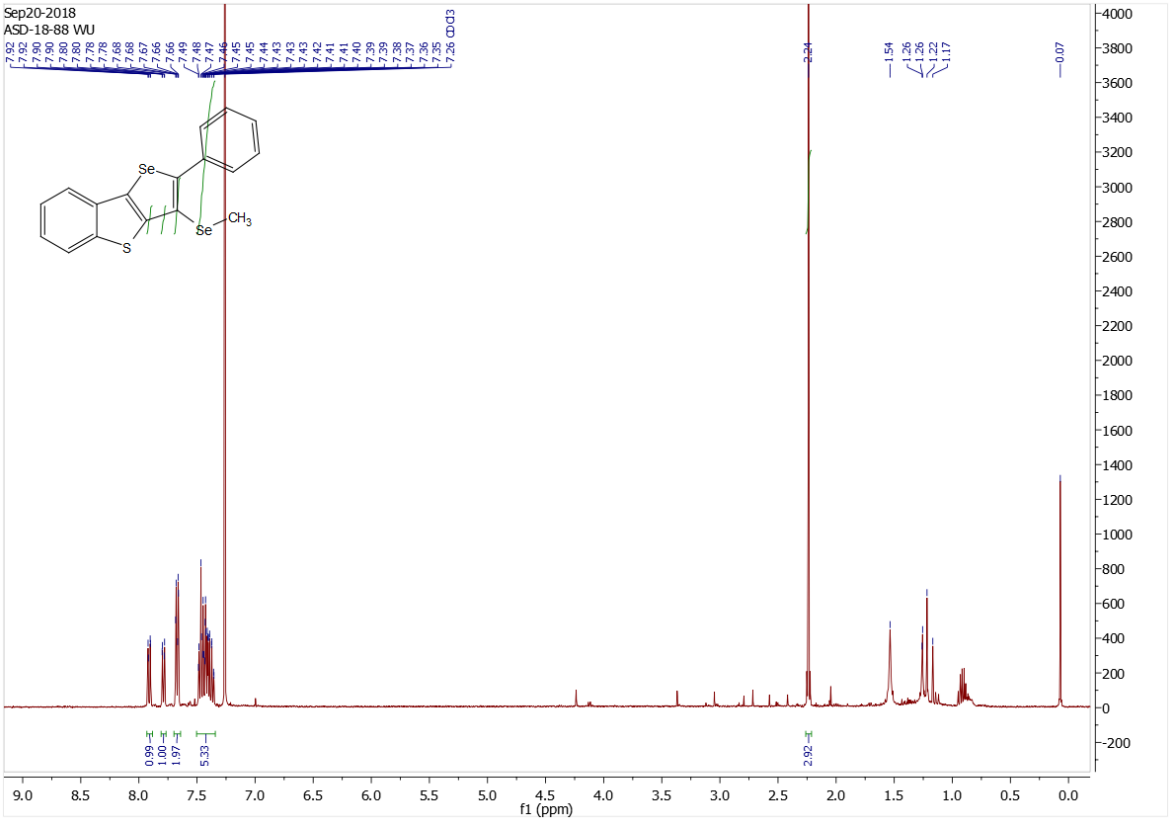
^{1}H NMR



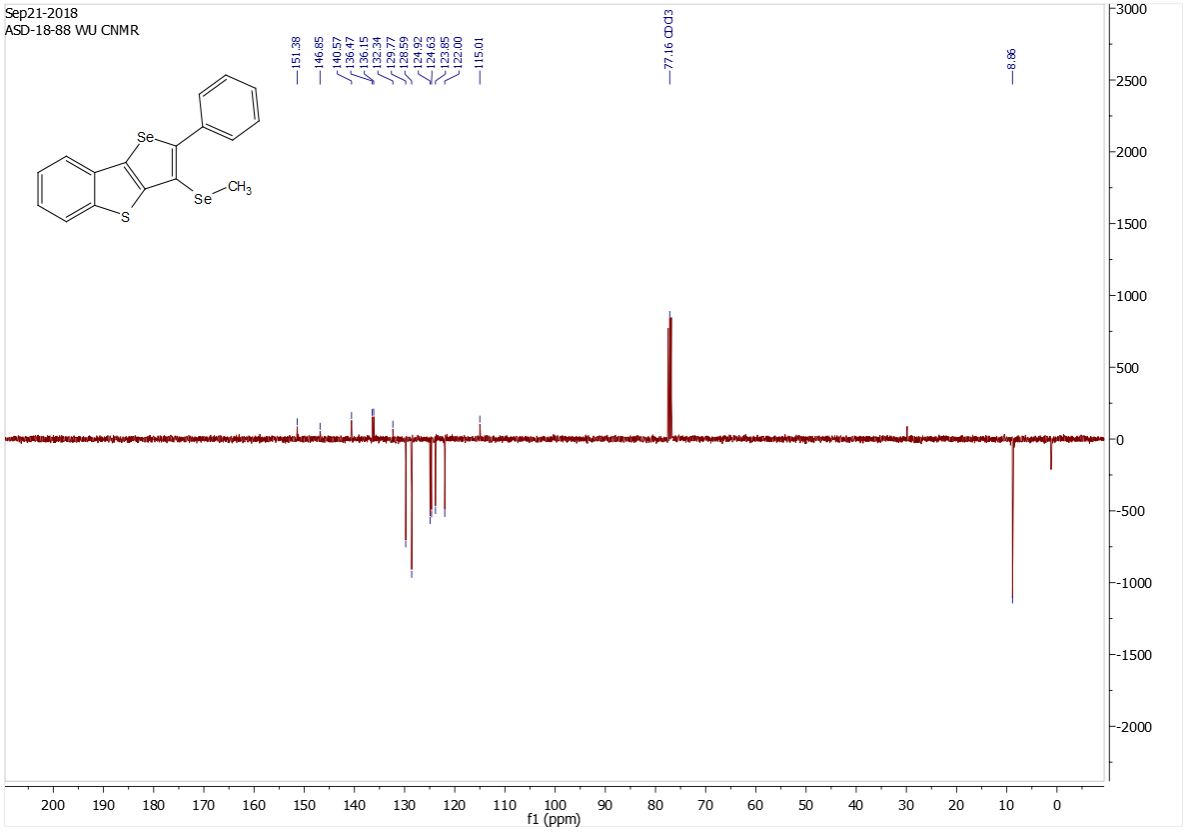
^{13}C NMR



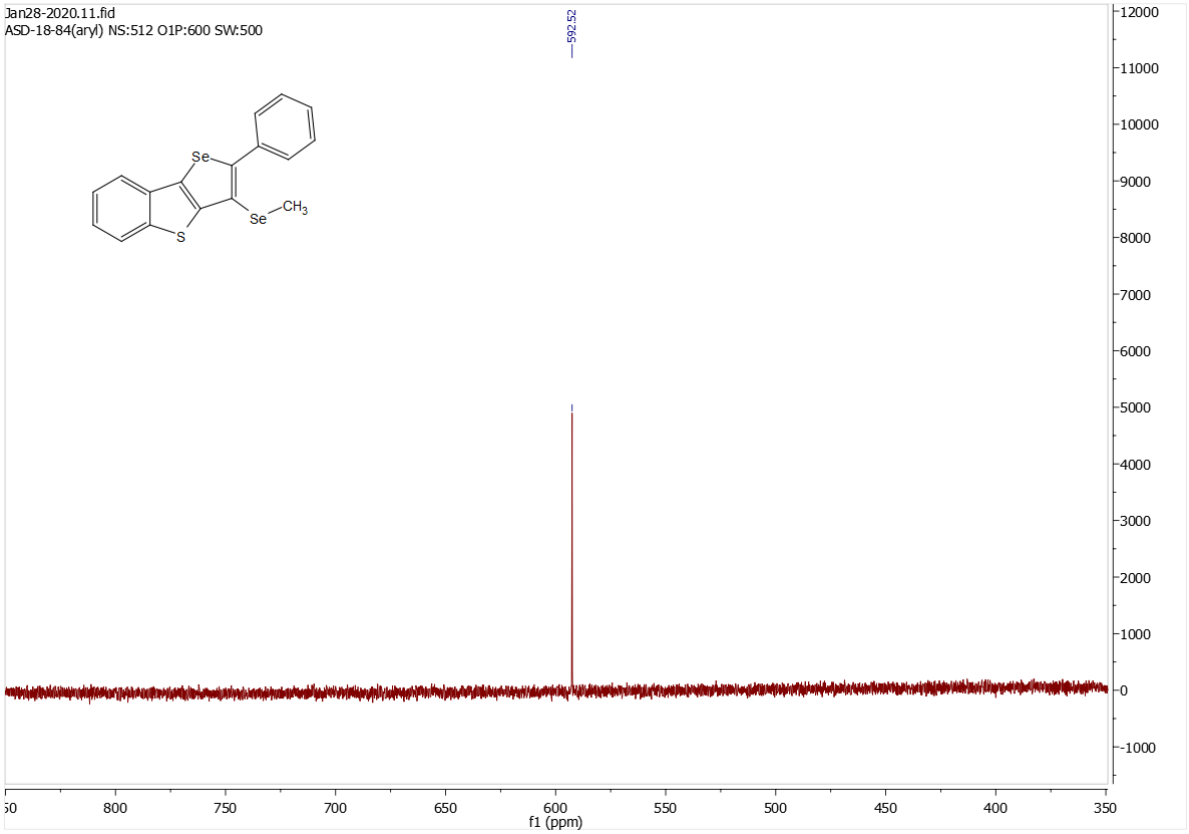
3-(Methylselanyl)-2-phenylbenzo[*b*]selenopheno[2,3-*d*]thiophene (292): ^{1}H NMR



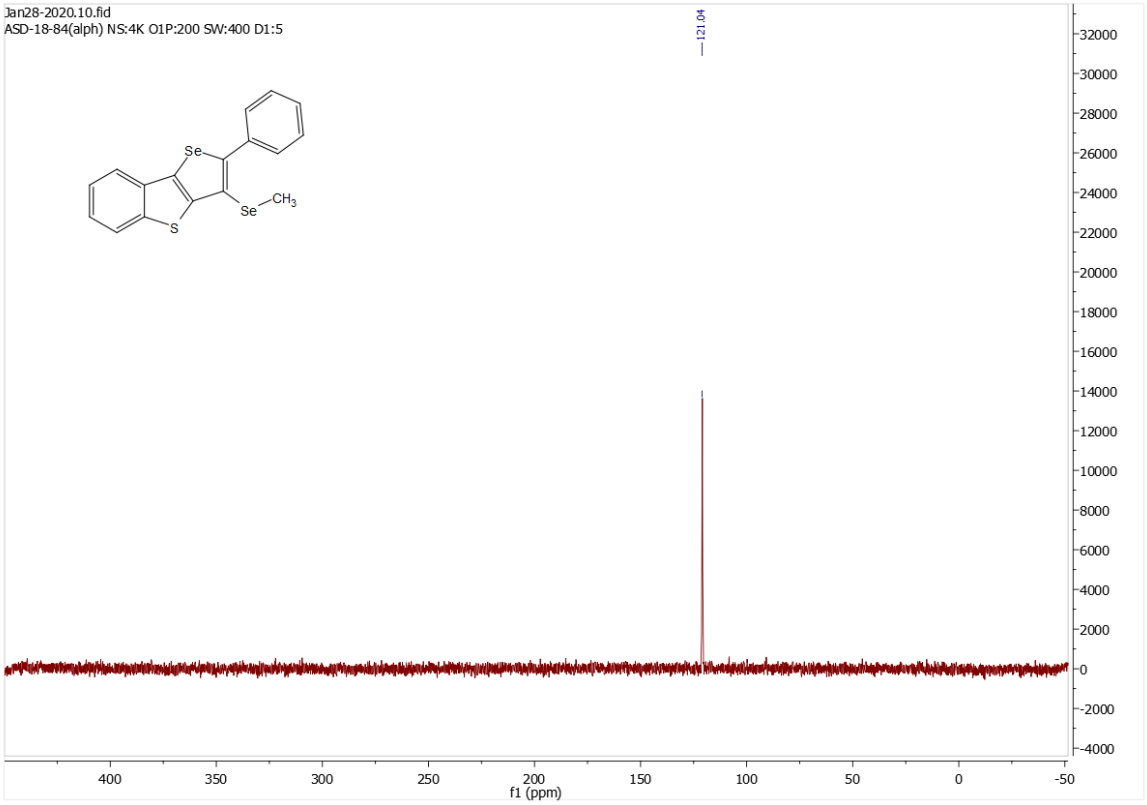
^{13}C NMR



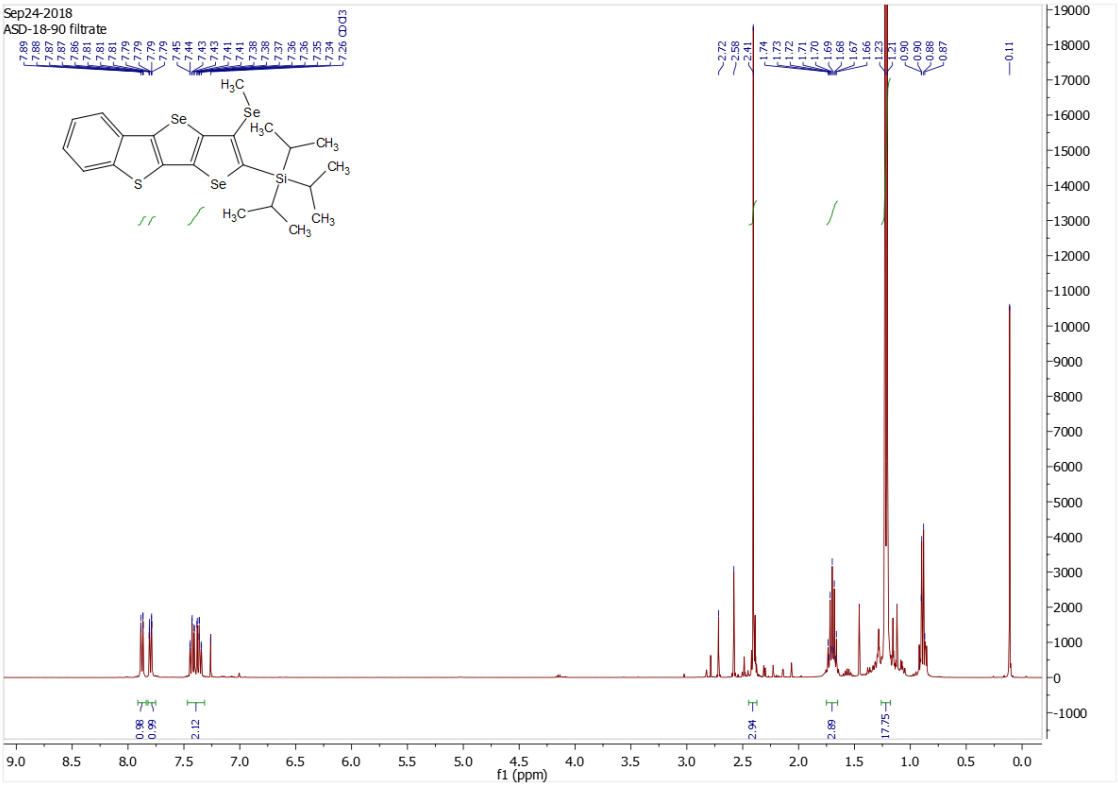
^{77}Se NMR Aromatic Region



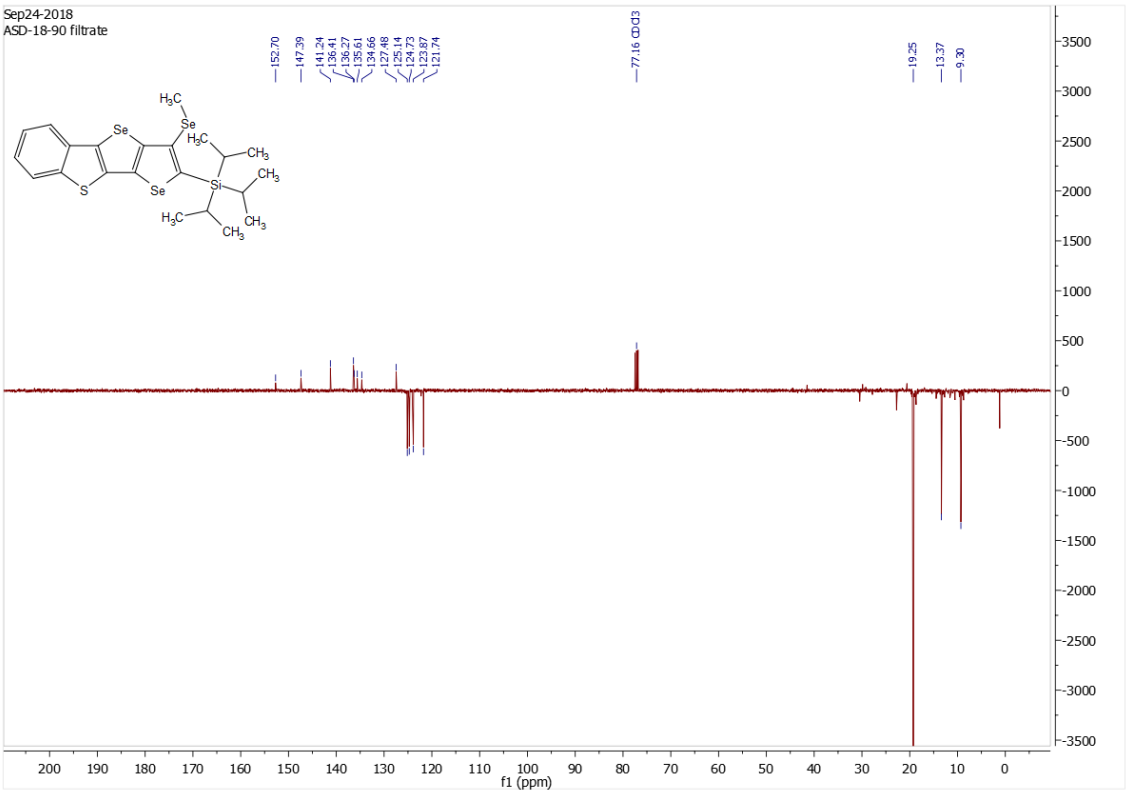
^{77}Se NMR Aliphatic Region



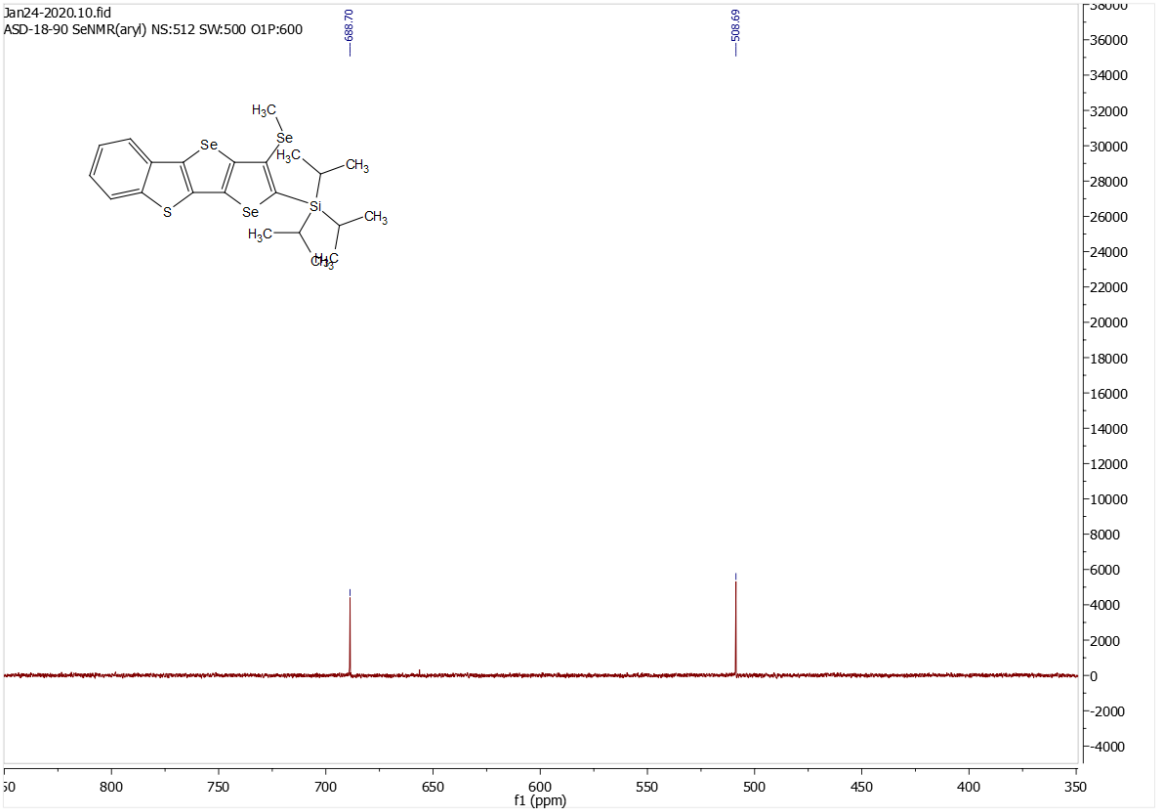
Triisopropyl(3-(methylselanyl)benzo[*b*]selenopheno[2',3':4,5]selenopheno[2,3-*d*]thiophen-2-yl)silane (295): ^{1}H NMR



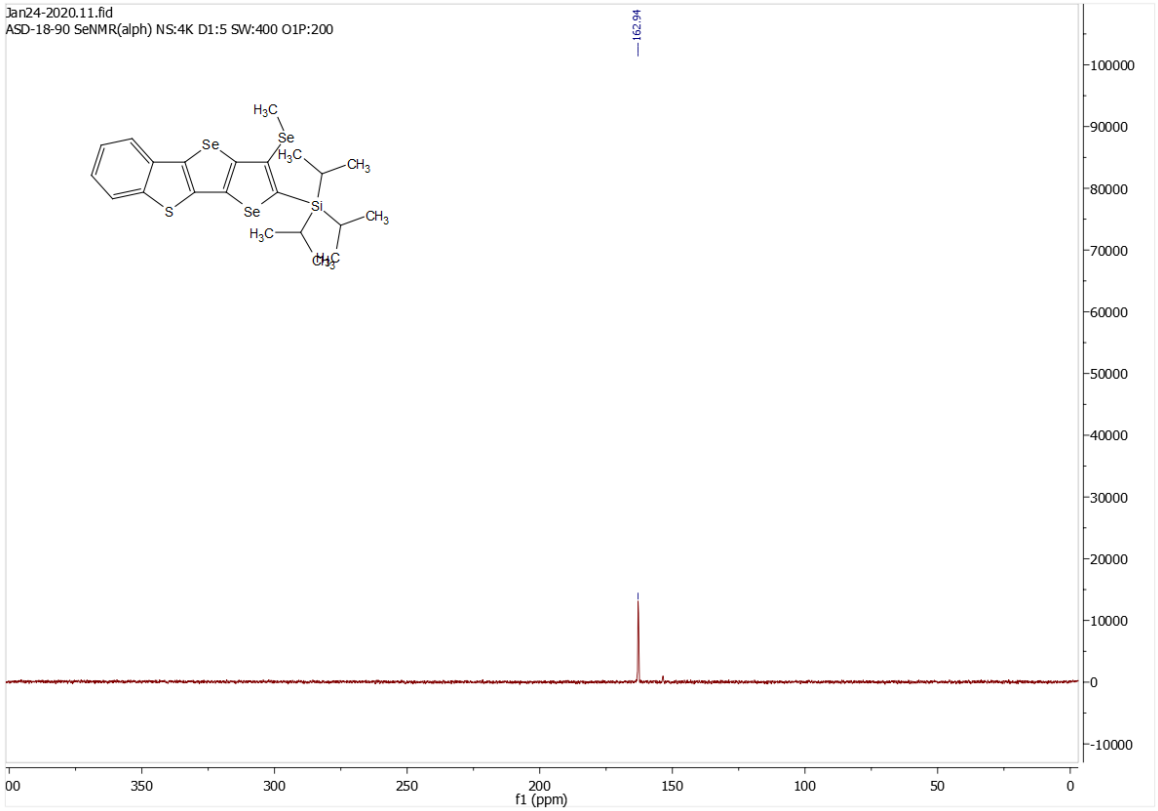
^{13}C NMR



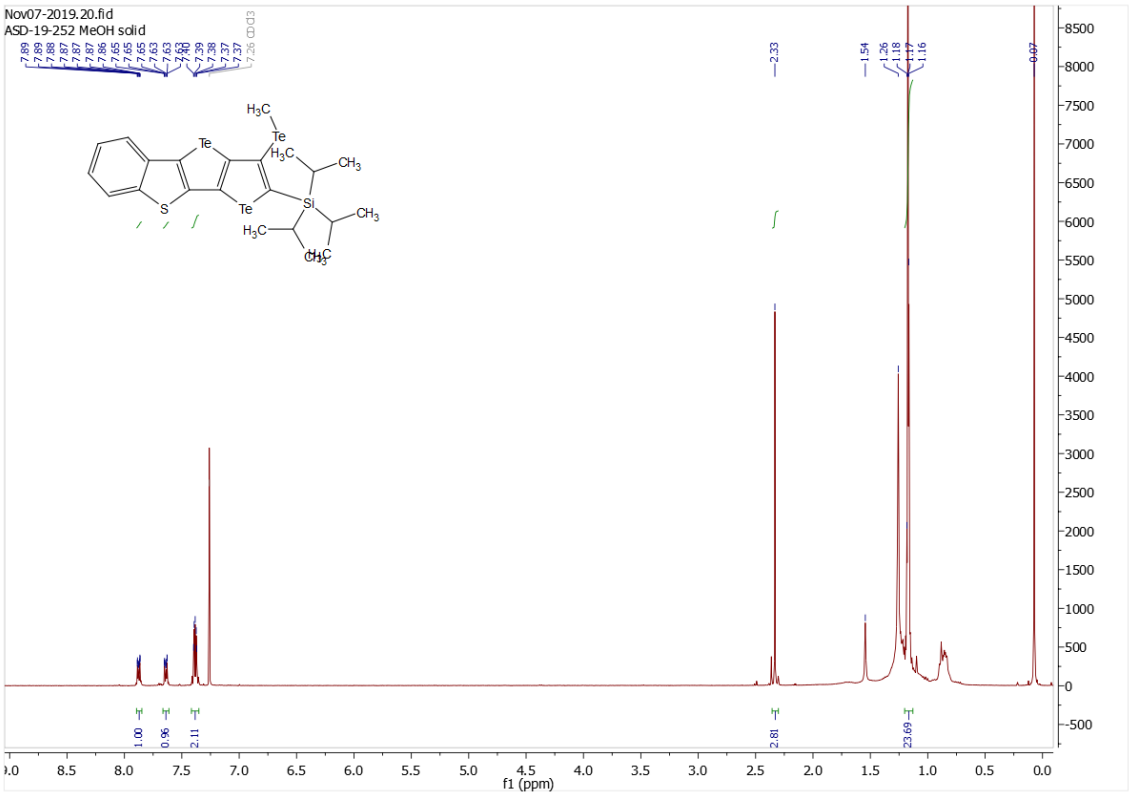
^{77}Se NMR Aromatic Region



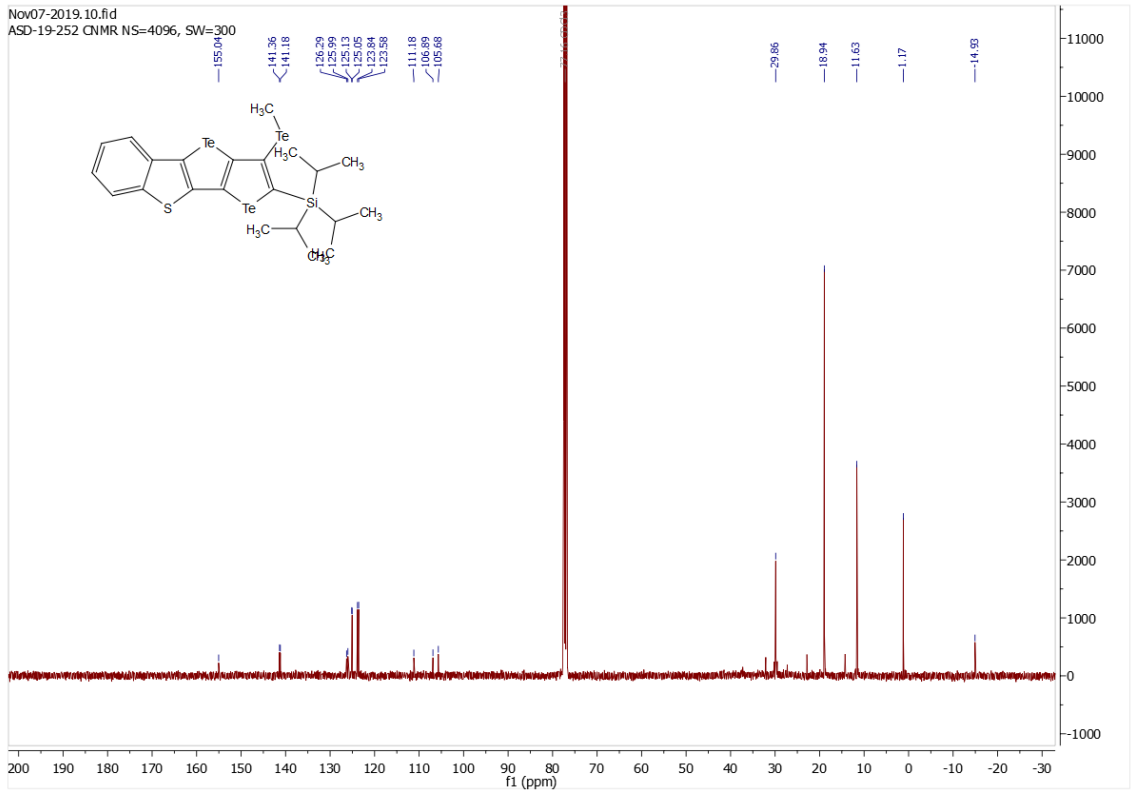
^{77}Se NMR Aliphatic Region



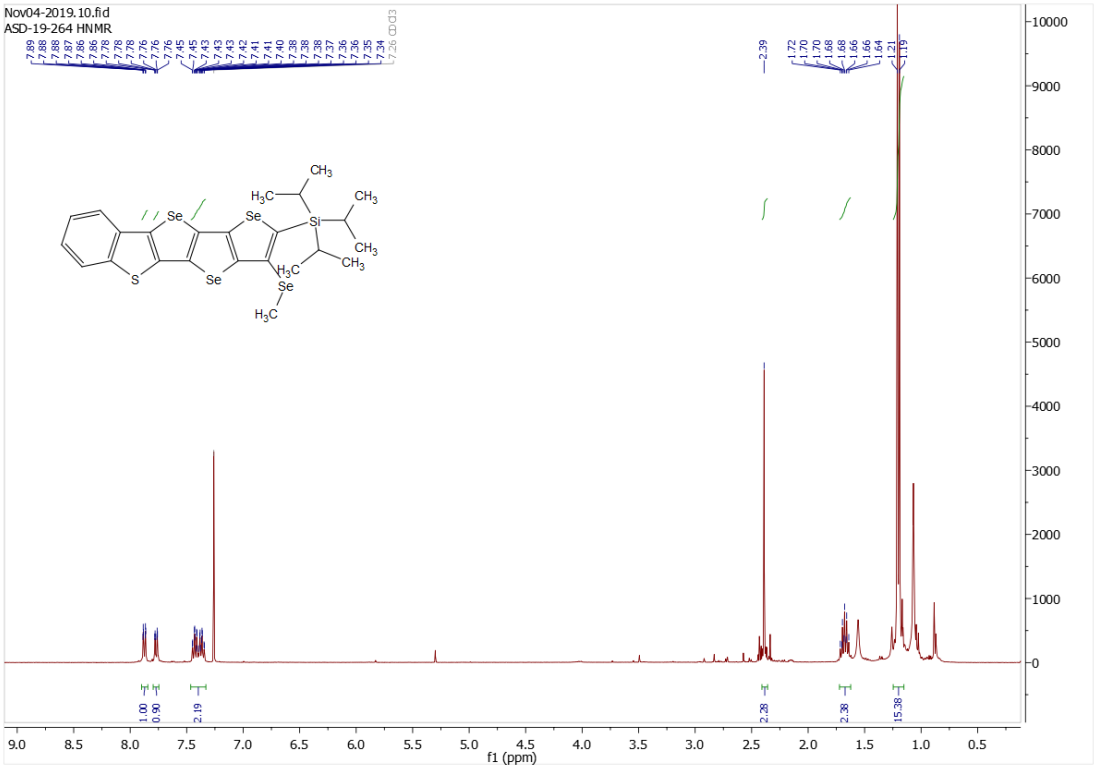
Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2',3':4,5]telluropheno[2,3-d]thiophen-2-yl)silane (296): ^{1}H NMR



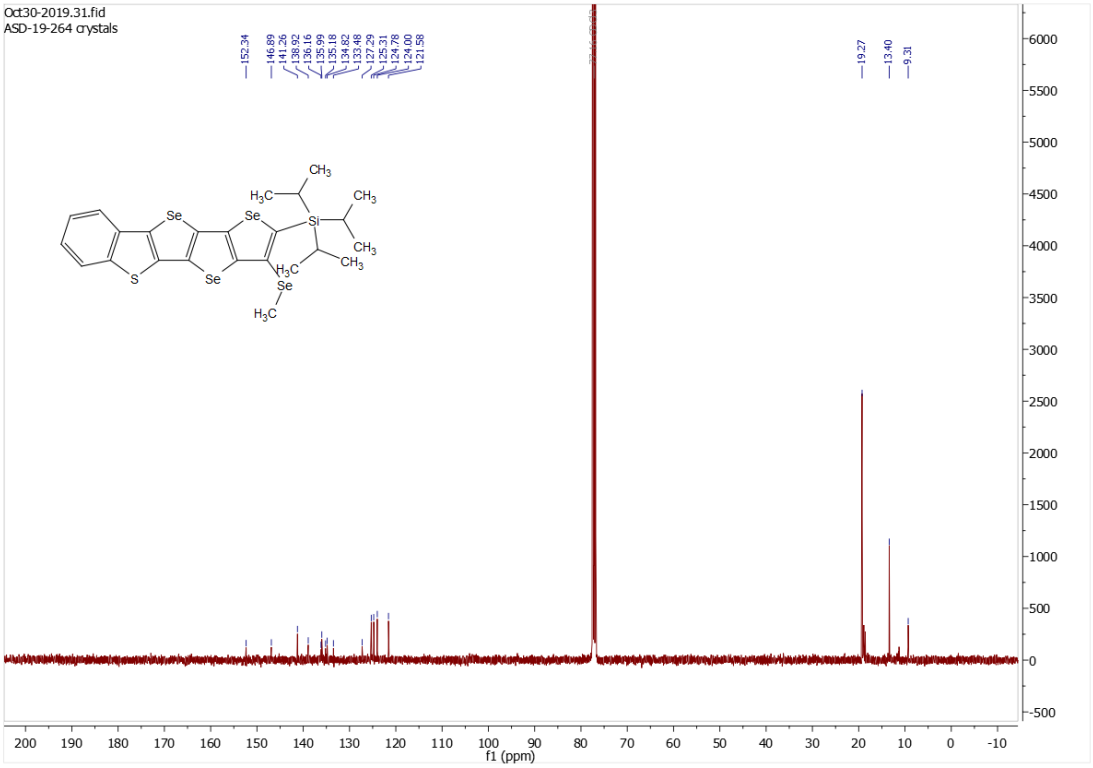
^{13}C NMR



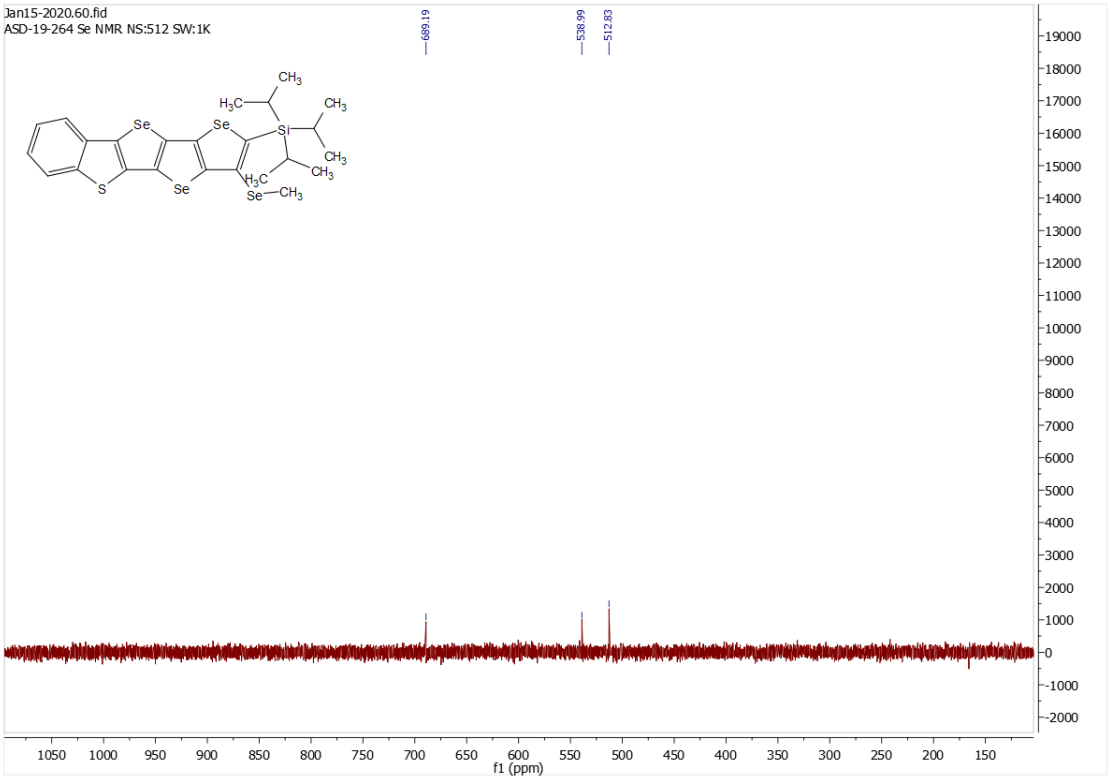
Triisopropyl(3-(methylselanyl)benzo[b]selenopheno[2'',3'':4',5']selenopheno[2',3':4,5]selenopheno[2,3-d]thiophen-2-yl)silane (297): ^{1}H NMR



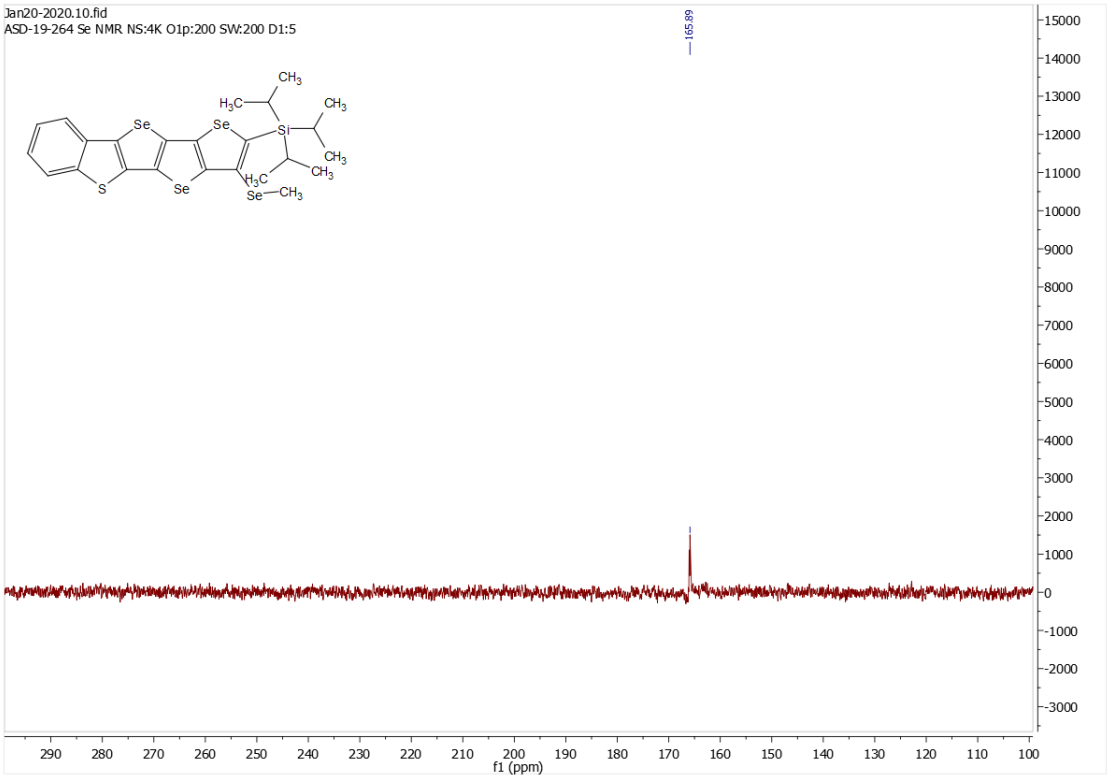
^{13}C NMR



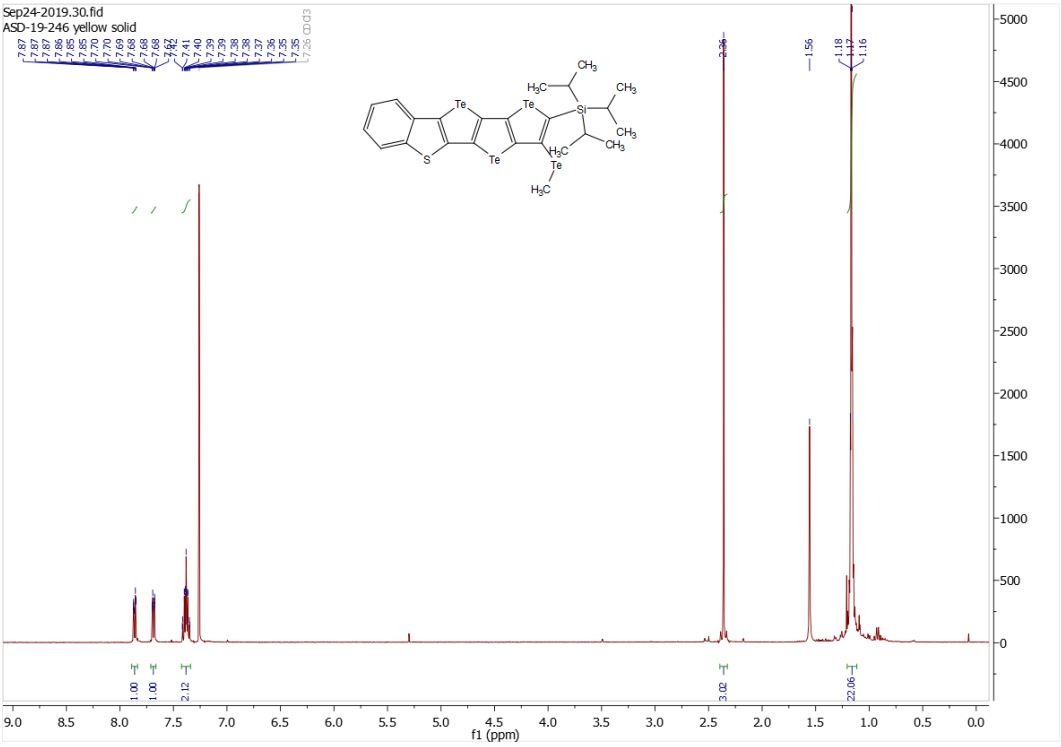
^{77}Se NMR Aromatic Region



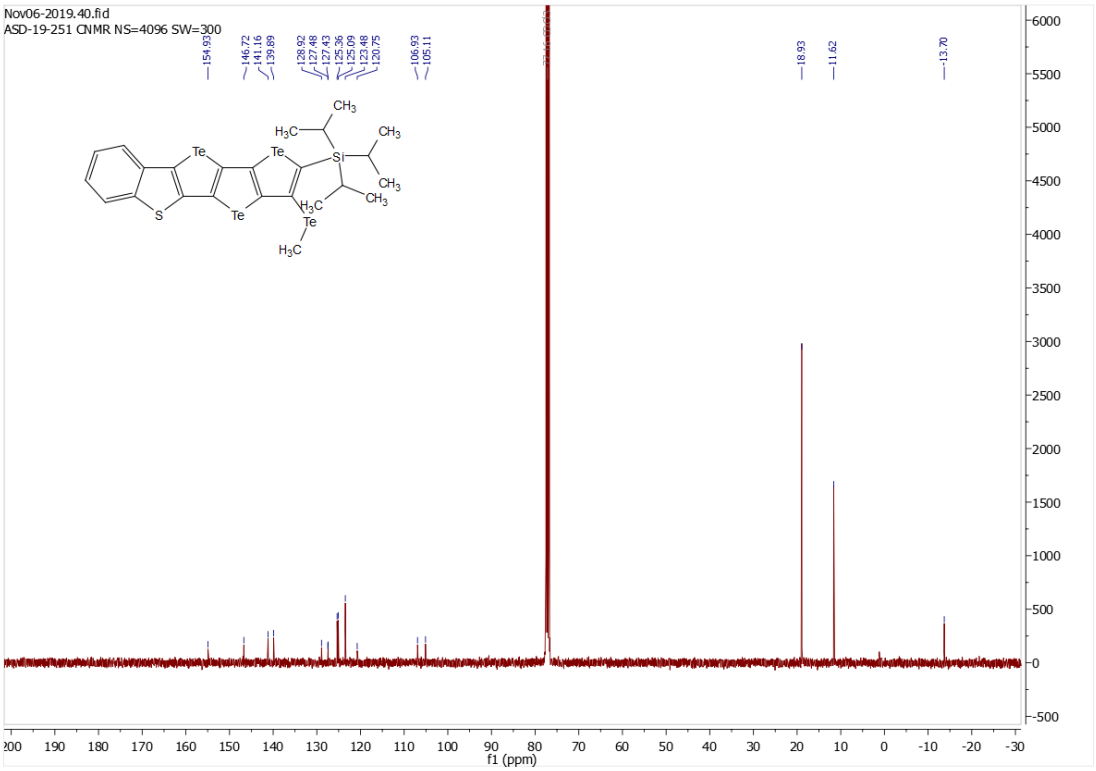
^{77}Se NMR Aliphatic Region



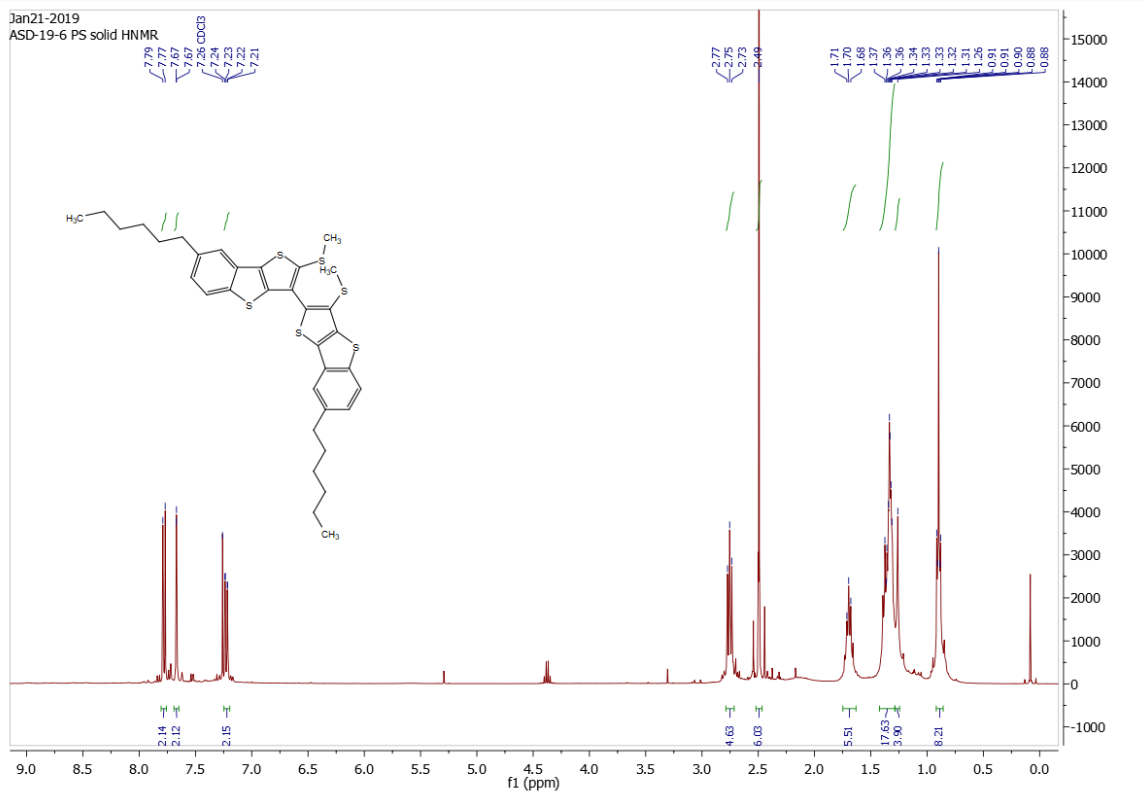
Triisopropyl(3-(methyltellanyl)benzo[b]telluropheno[2'',3'':4',5']telluropheno[2',3':4,5]telluropheno[2,3-d]thiophen-2-yl)silane (298): ^{1}H NMR



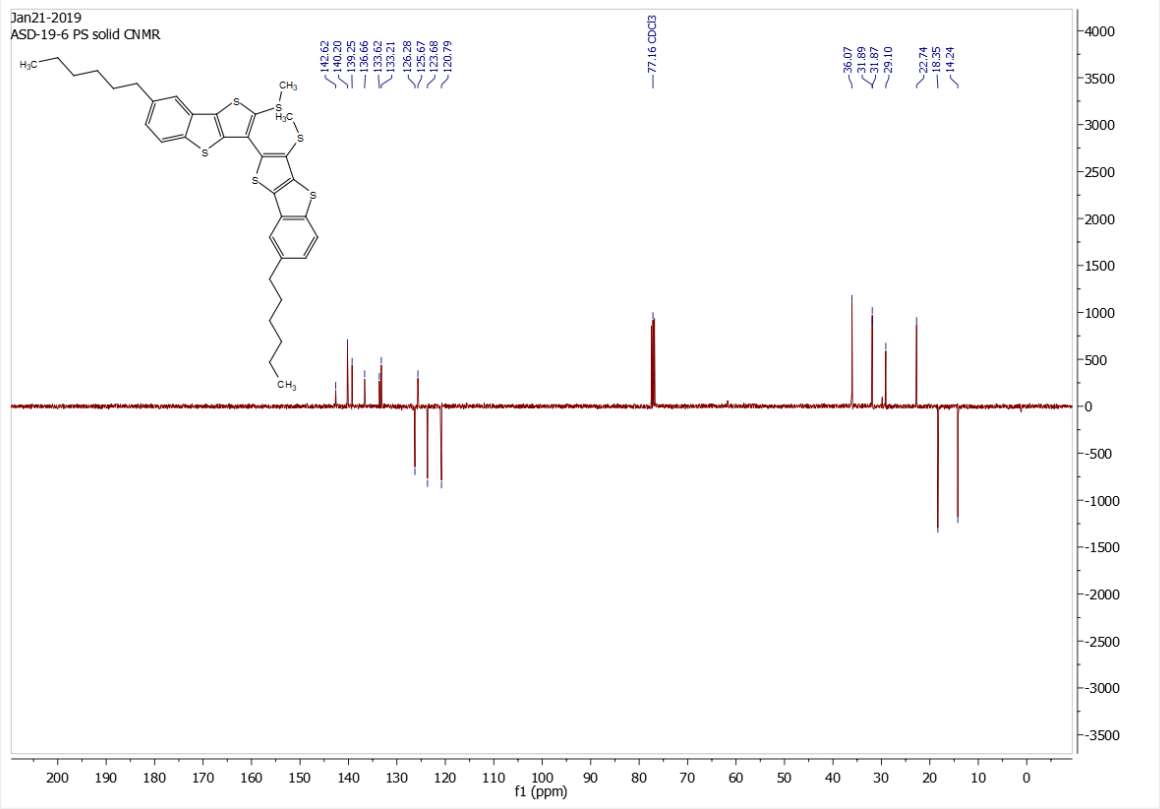
^{13}C NMR



7,7'-Dihexyl-3,3'-bis(methylthio)-2,2'-bibenzo[b]thieno[2,3-d]thiophene (299): ^{1}H NMR

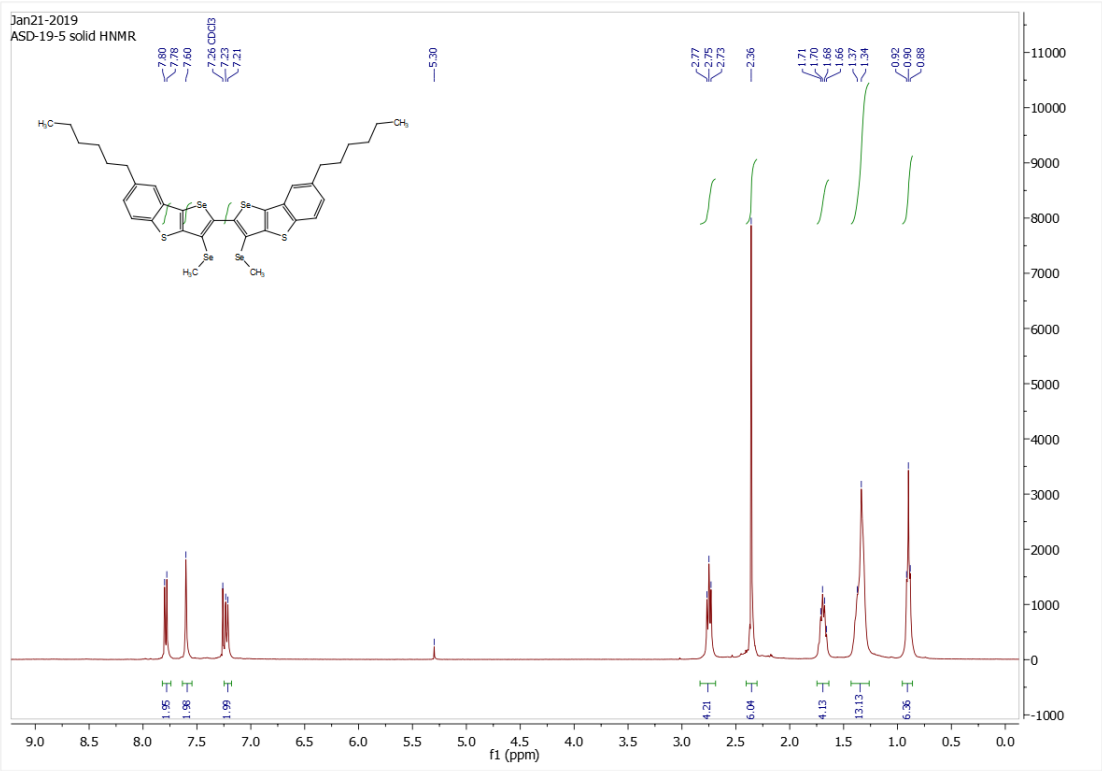


^{13}C NMR

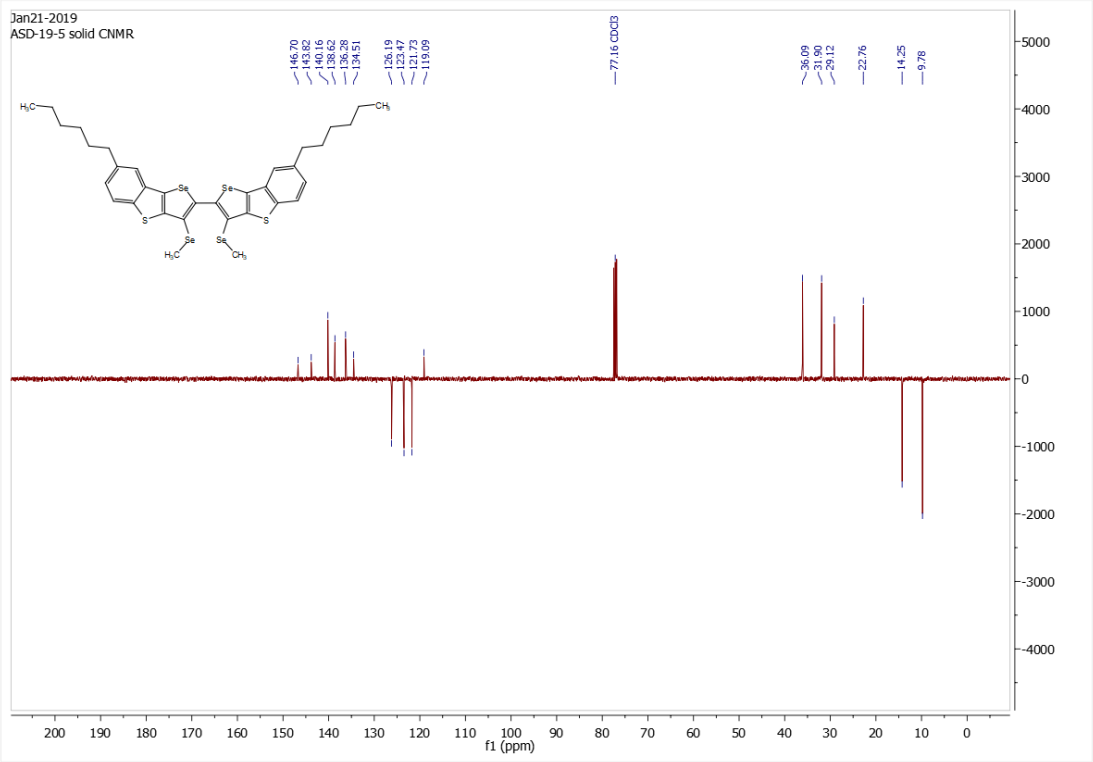


7,7'-Dihexyl-3,3'-bis(methylselanyl)-2,2'-bibenzo[b]selenopheno[2,3-d]thiophene (300):

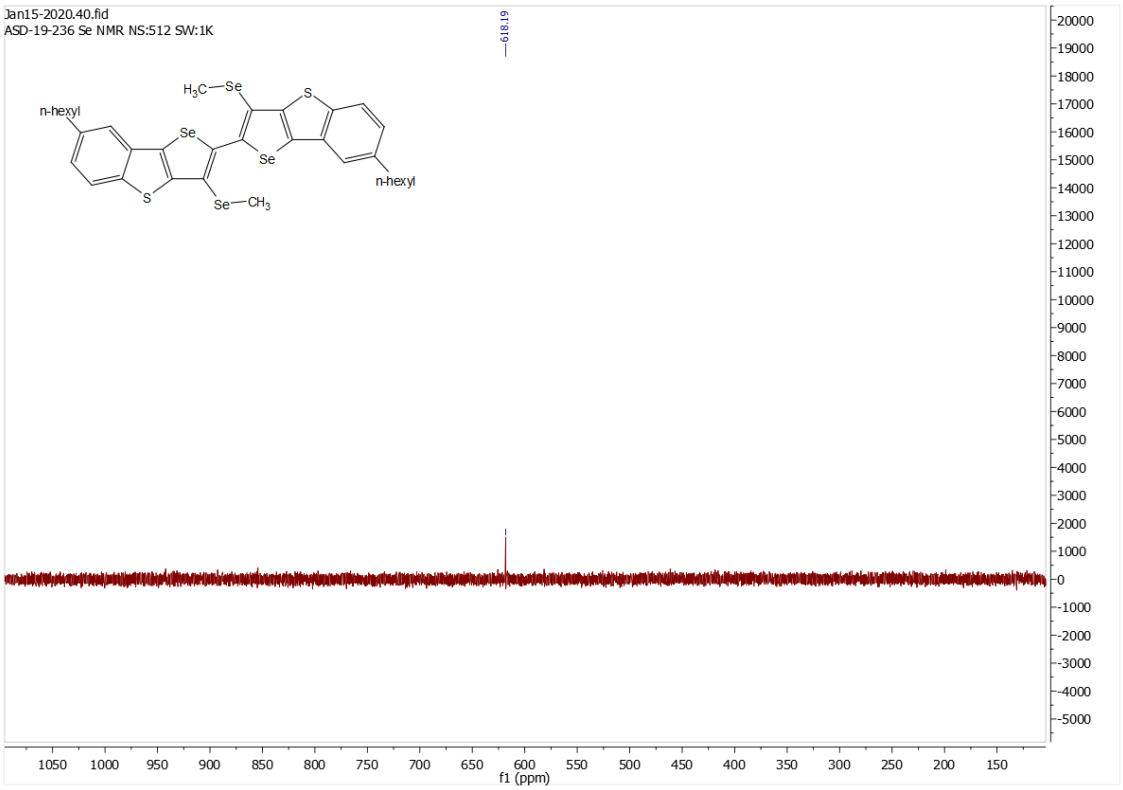
^{1}H NMR



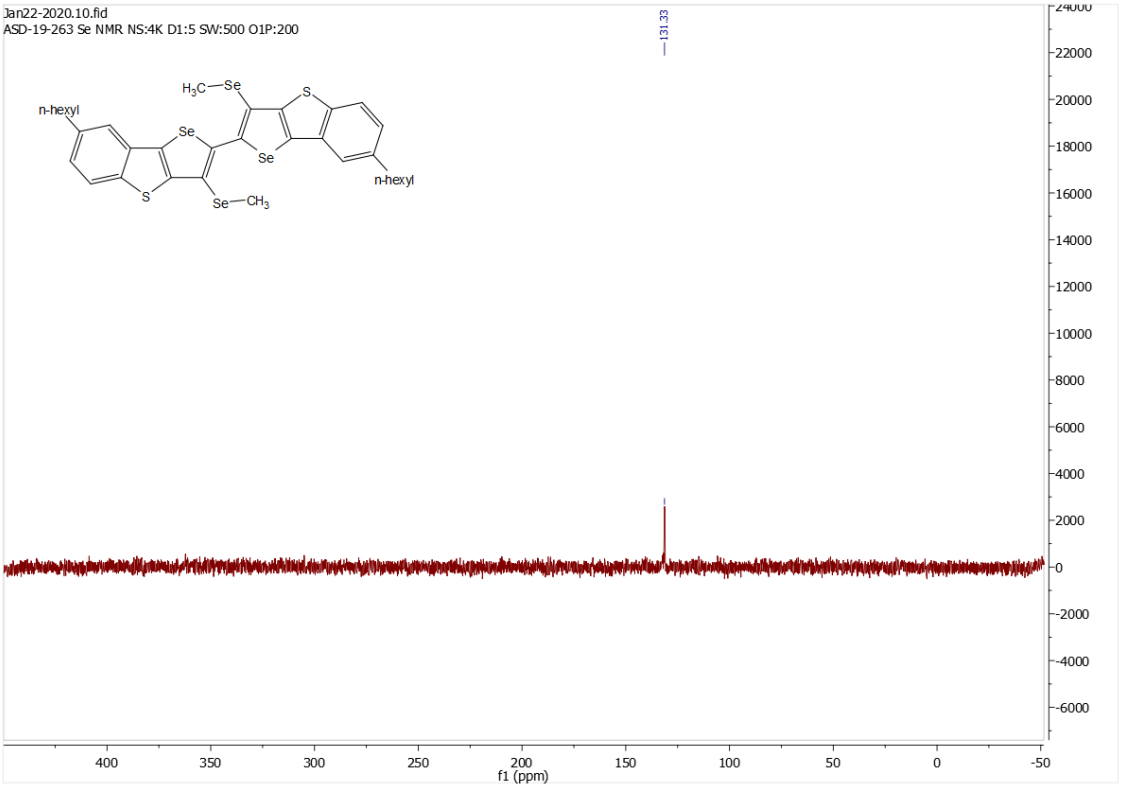
^{13}C NMR



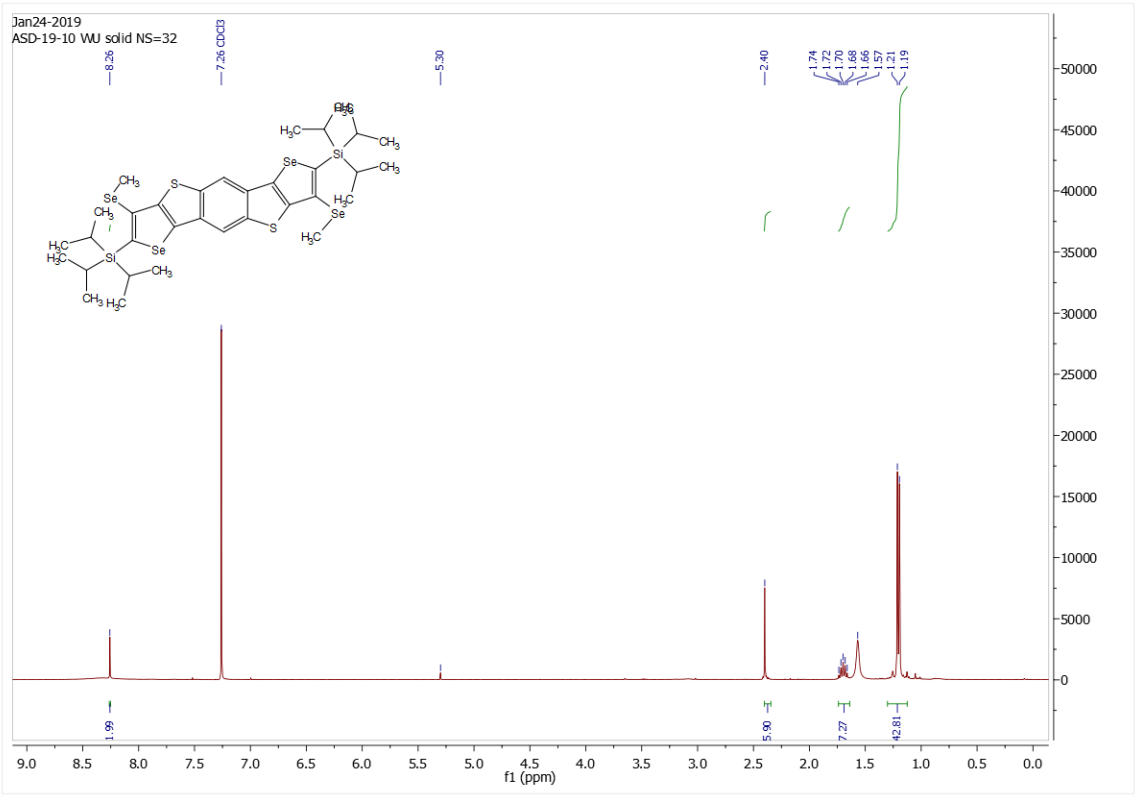
^{77}Se NMR Aromatic Region



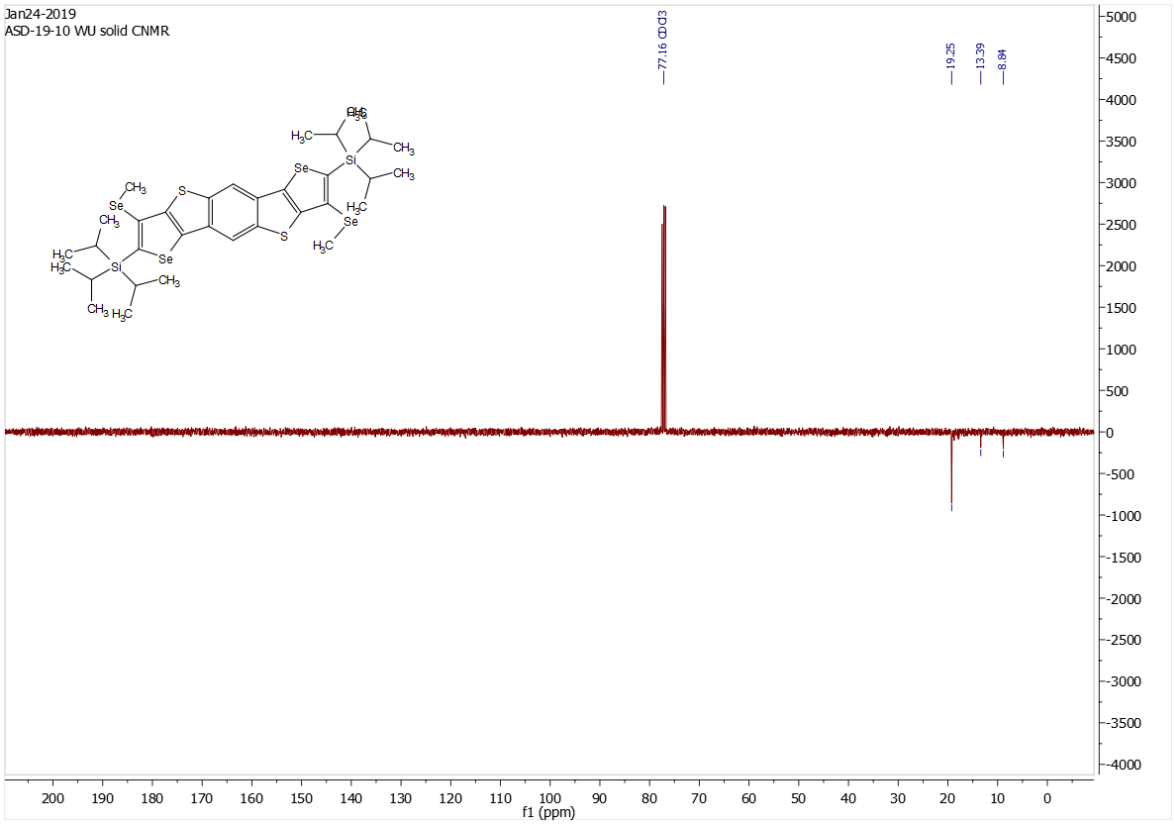
^{77}Se NMR Aliphatic Region



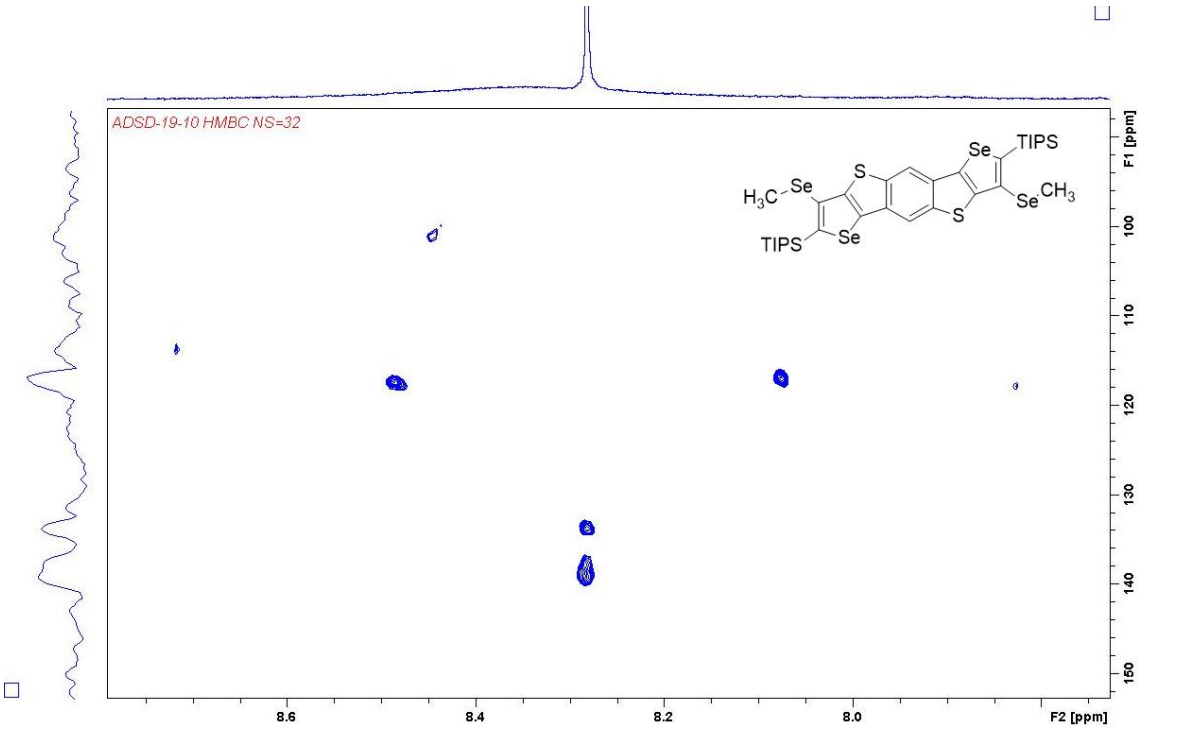
(301): ^{1}H NMR

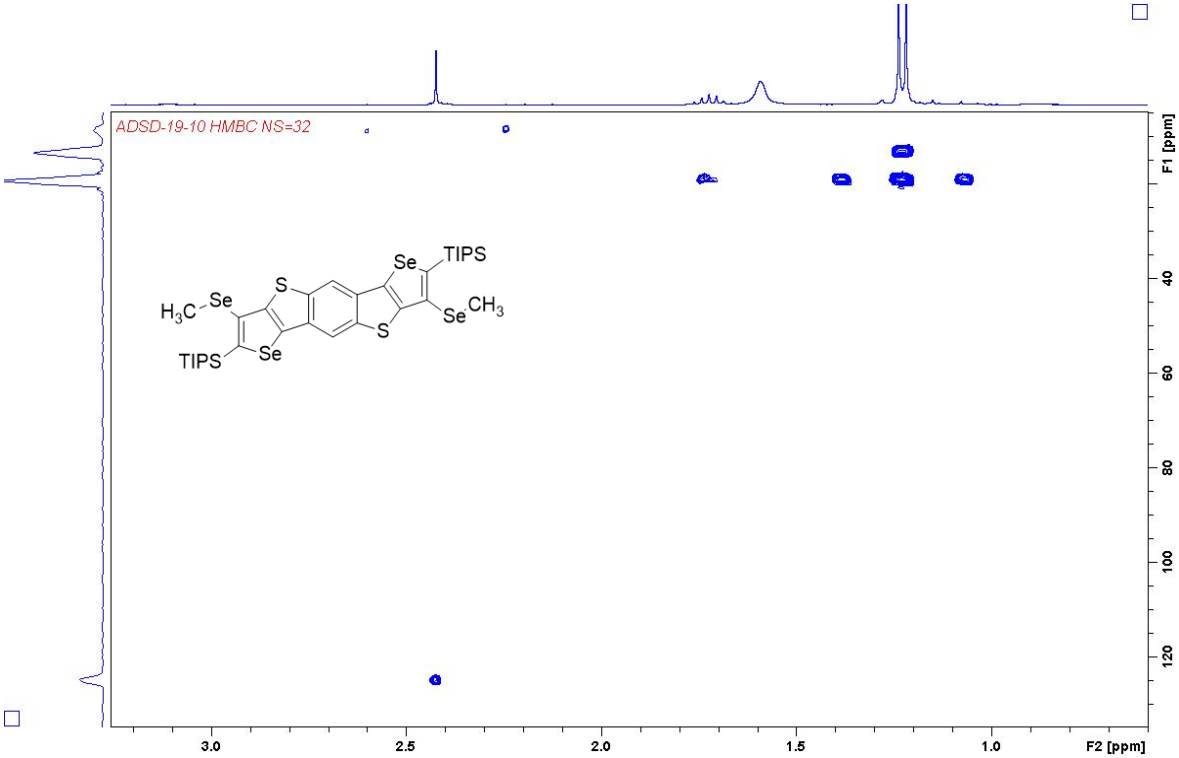


^{13}C NMR

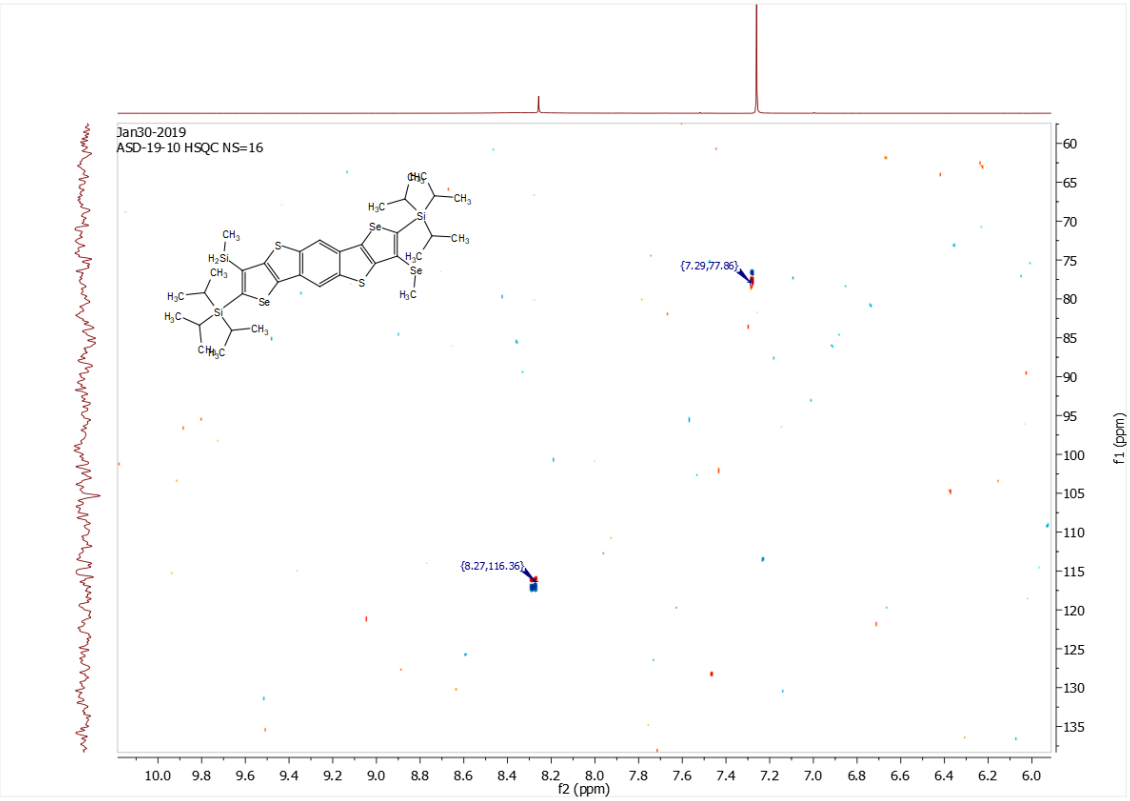


HMBC:

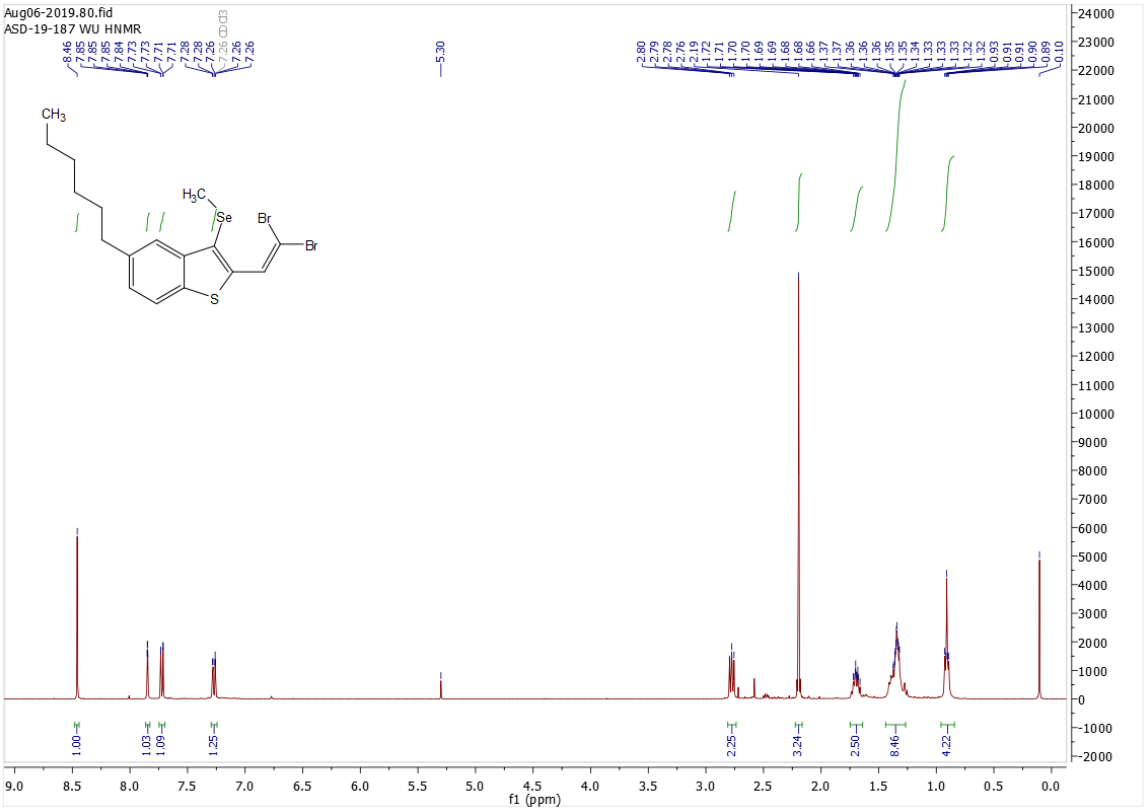

ADSD-19-10 HMBC NS=32
F1 [ppm]
F2 [ppm]
8.6
8.4
8.2
8.0
100
110
120
130
140
150
TIPS
Se
S
H_3C
CH_3


ADSD-19-10 HMBC NS=32
F1 [ppm]
F2 [ppm]
3.0
2.5
2.0
1.5
1.0
40
60
80
100
120
TIPS
Se
S
H_3C
CH_3

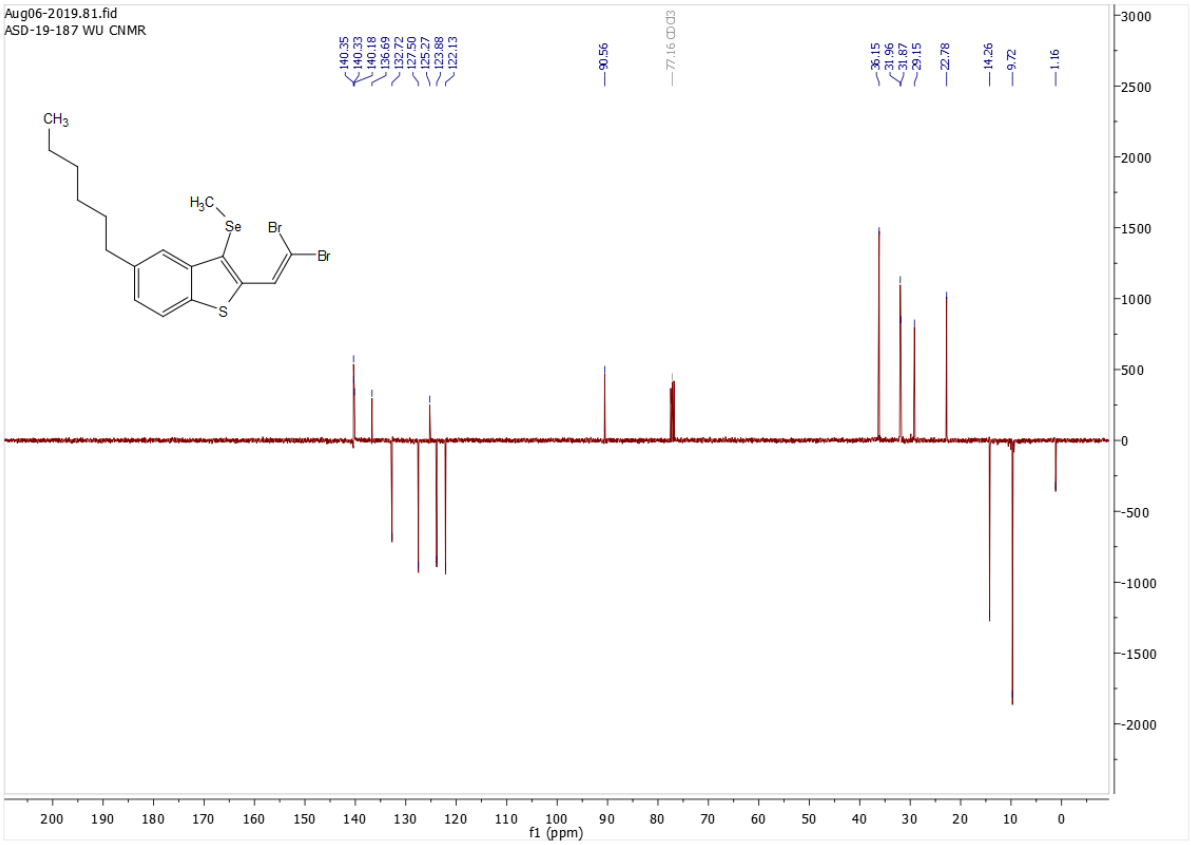
HSQC:



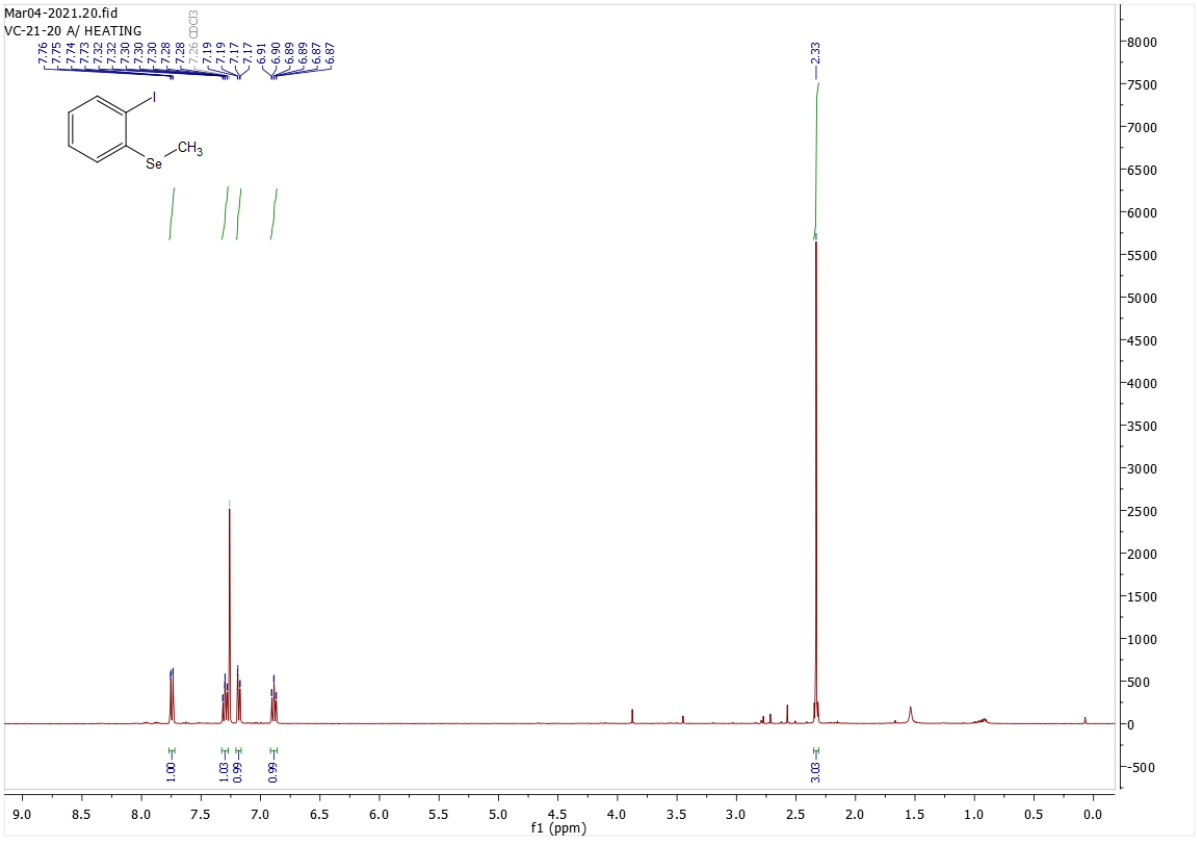
2-(2,2-Dibromovinyl)-5-hexyl-3-(methylselanyl)benzo[b]thiophene (318): ^{1}H NMR



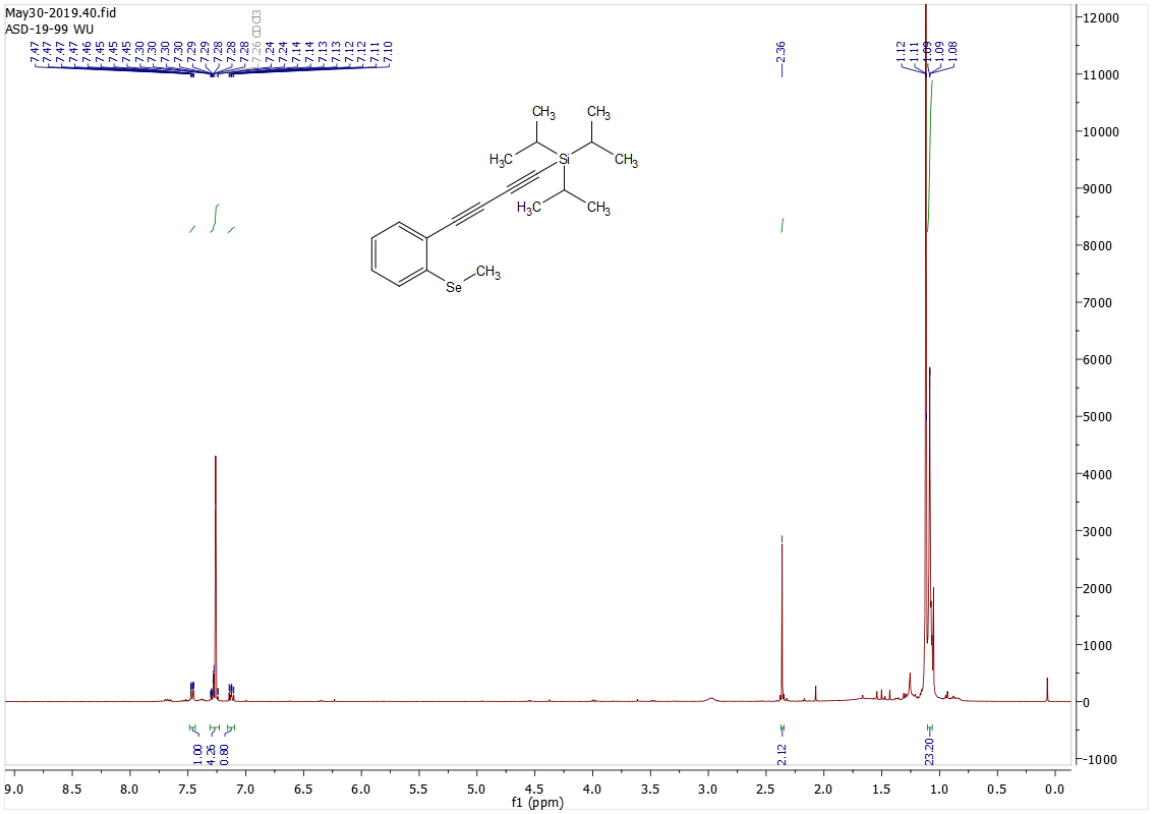
^{13}C NMR



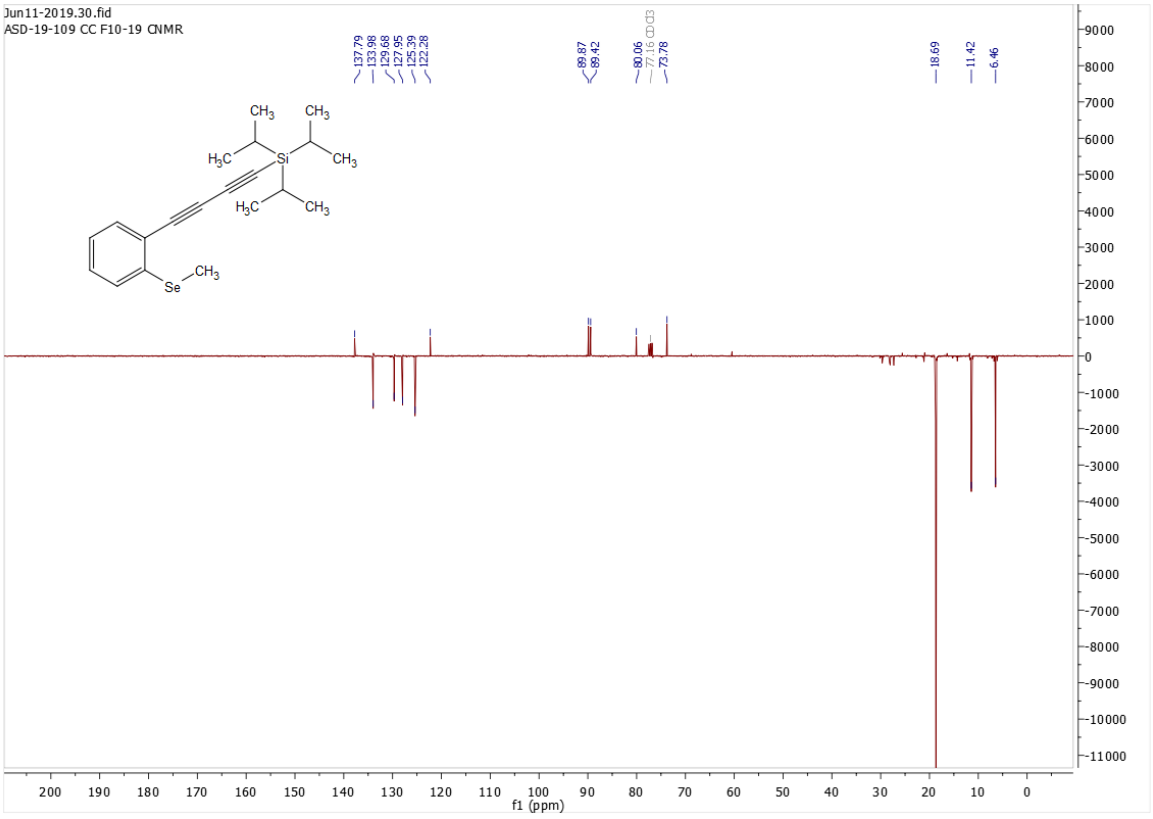
(2-Iodophenyl)(methyl)selane: ^{1}H NMR



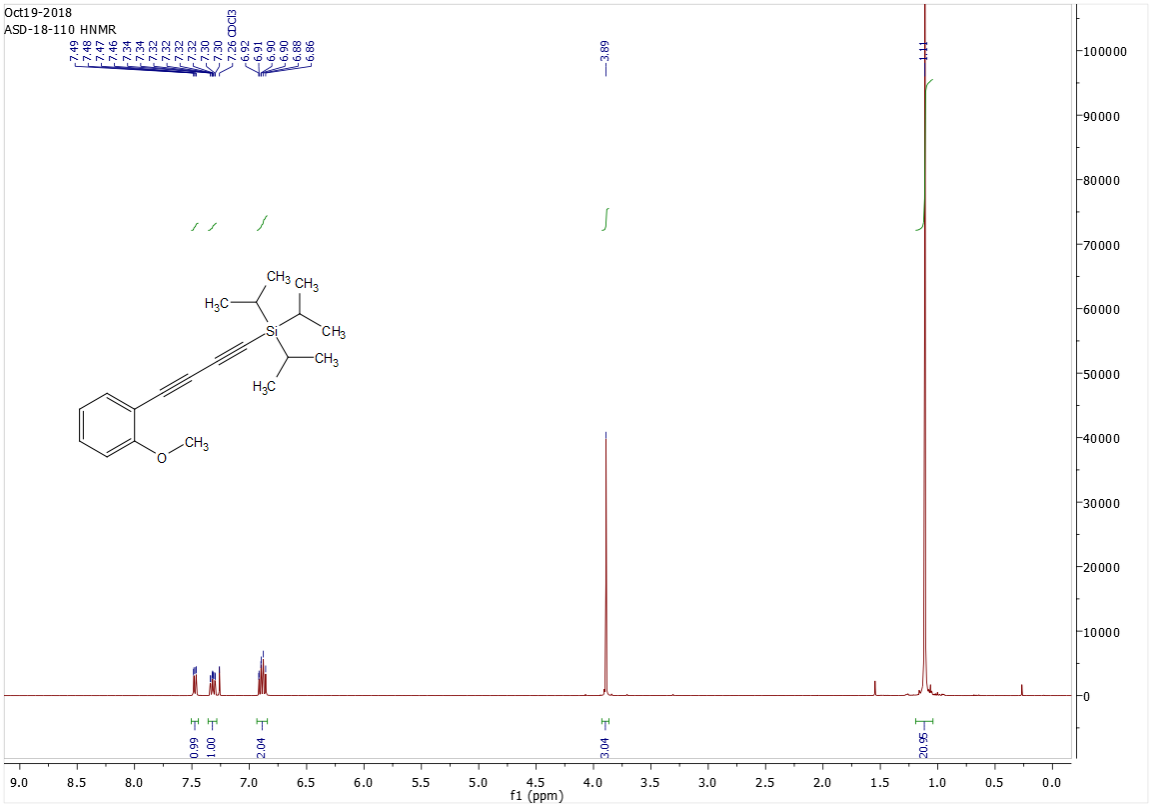
Triisopropyl((2-(methylselanyl)phenyl)buta-1,3-diyn-1-yl)silane (321): ^{1}H NMR



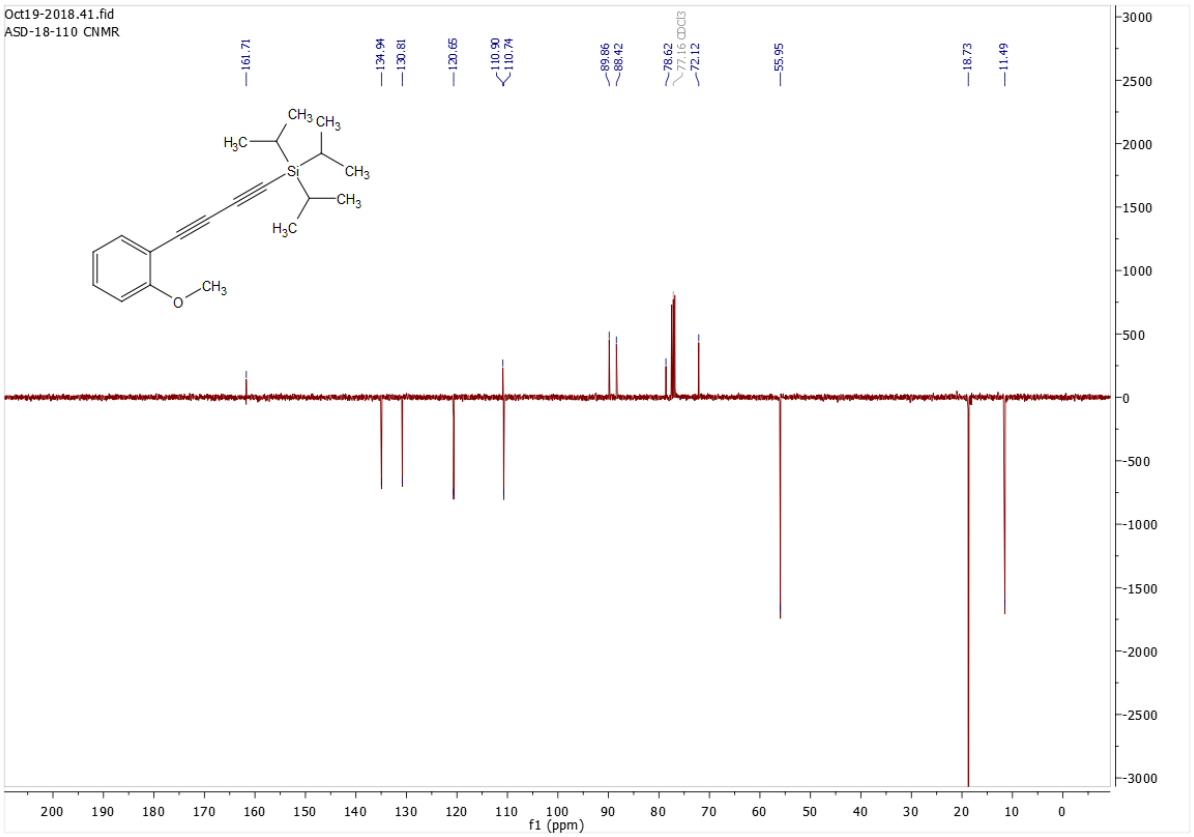
^{13}C NMR



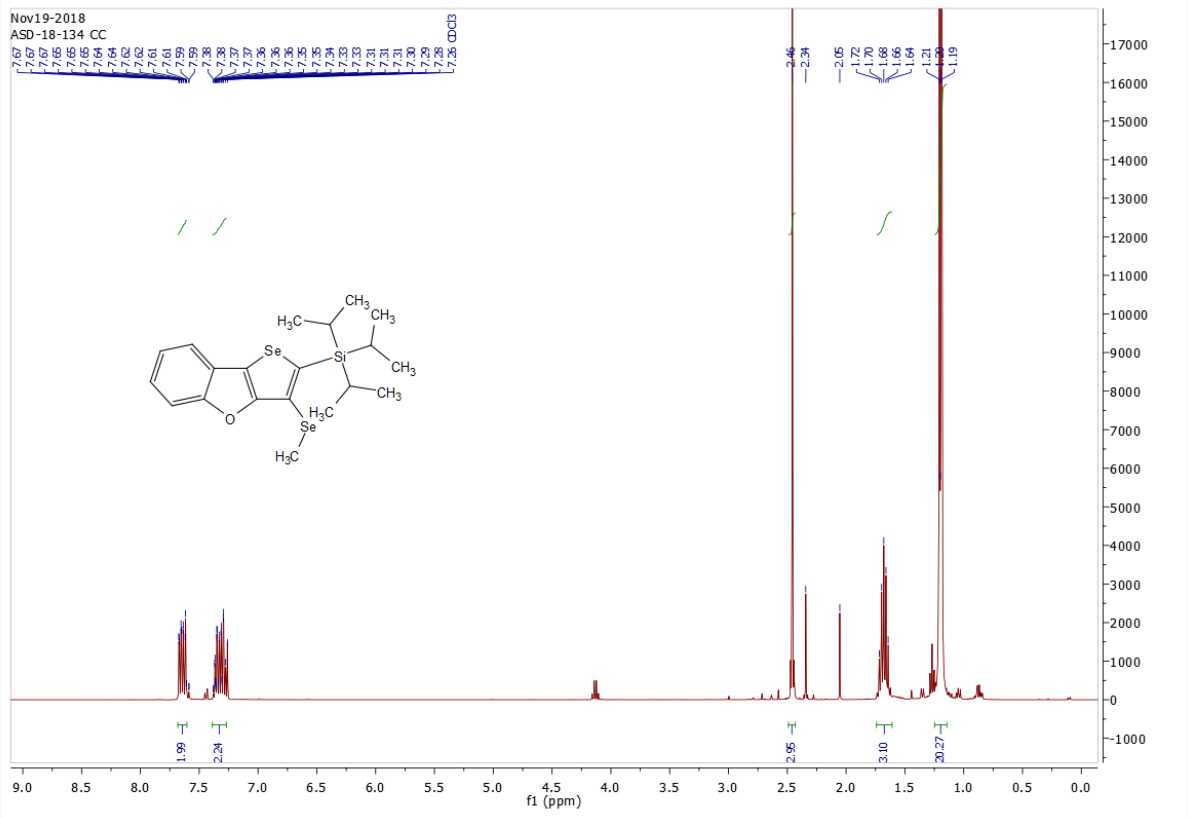
Triisopropyl((2-methoxyphenyl)buta-1,3-diyn-1-yl)silane (322): ^{1}H NMR



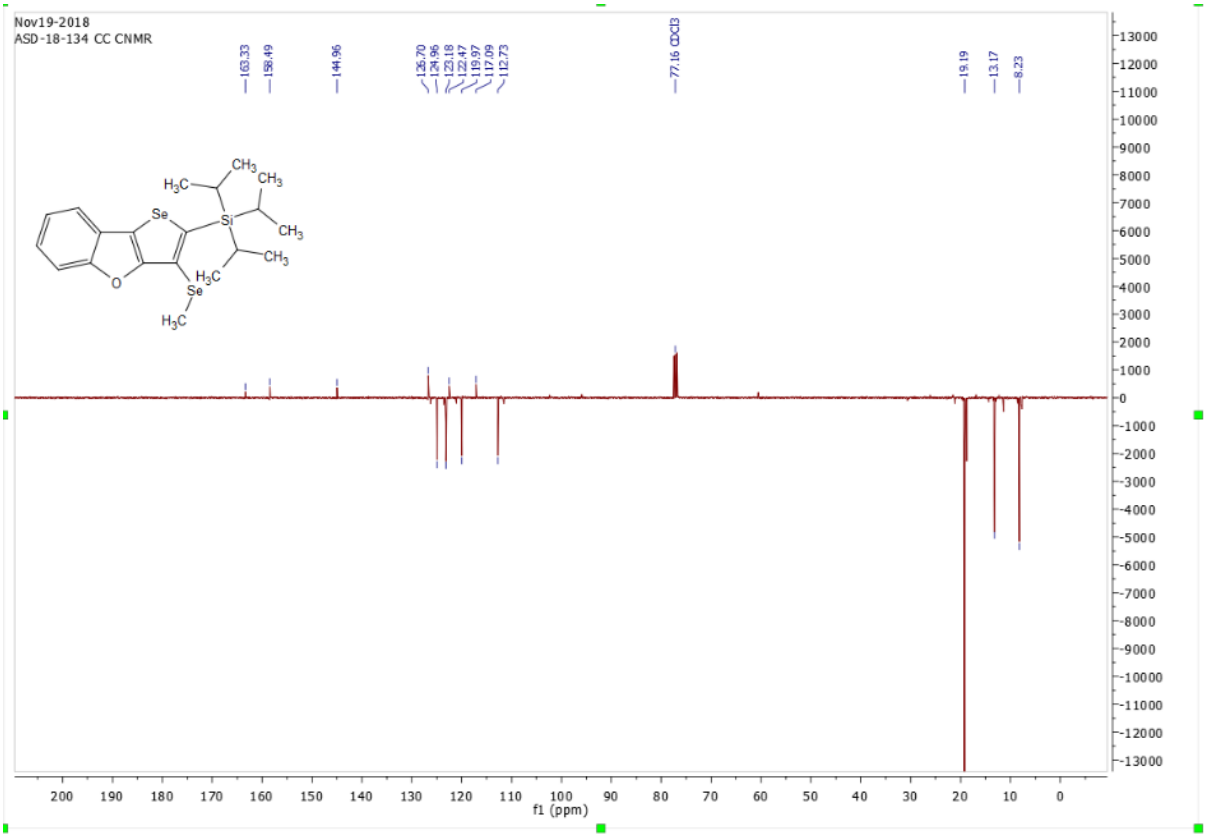
^{13}C NMR



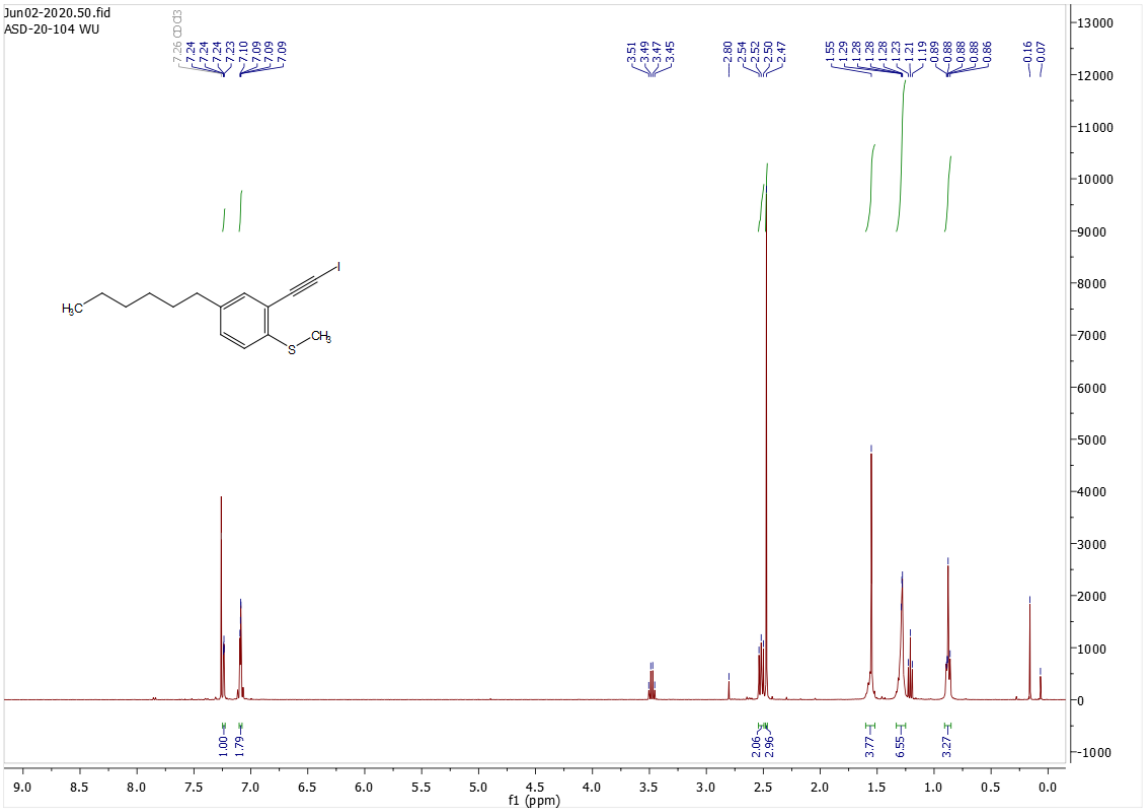
Triisopropyl(3-(methylselanyl)selenopheno[3,2-b]benzofuran-2-yl)silane (324): ^{1}H NMR



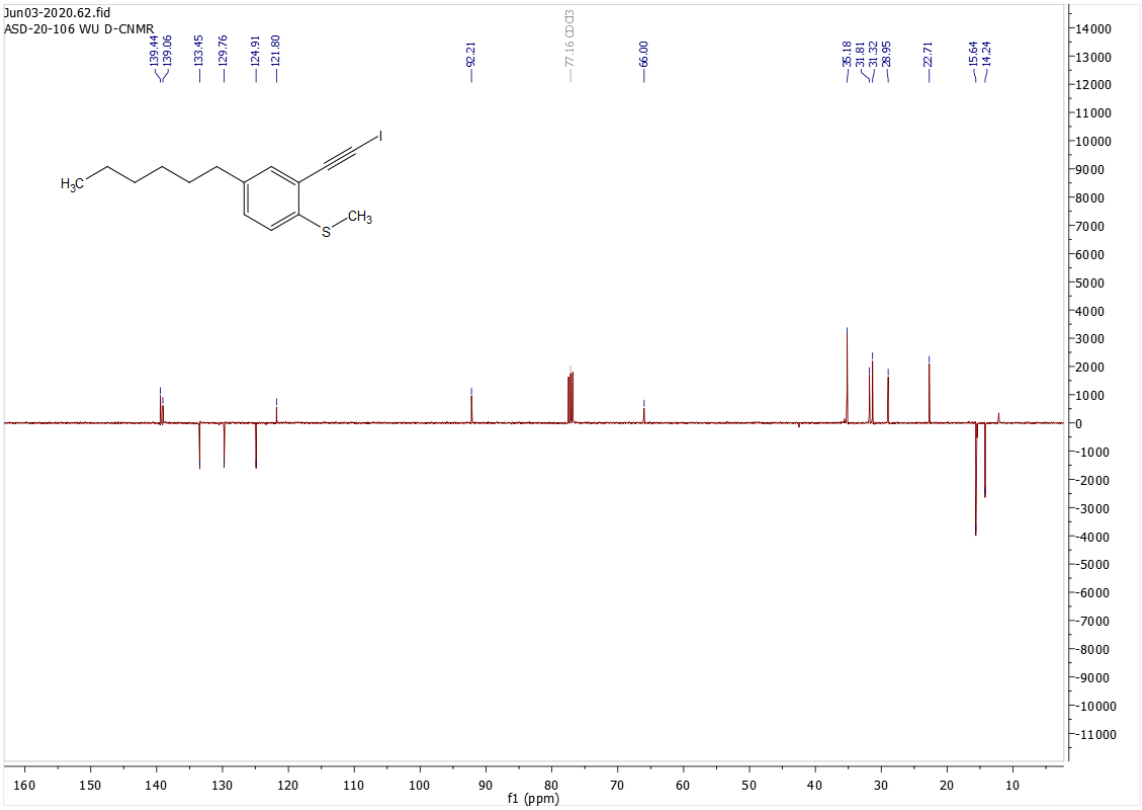
^{13}C NMR



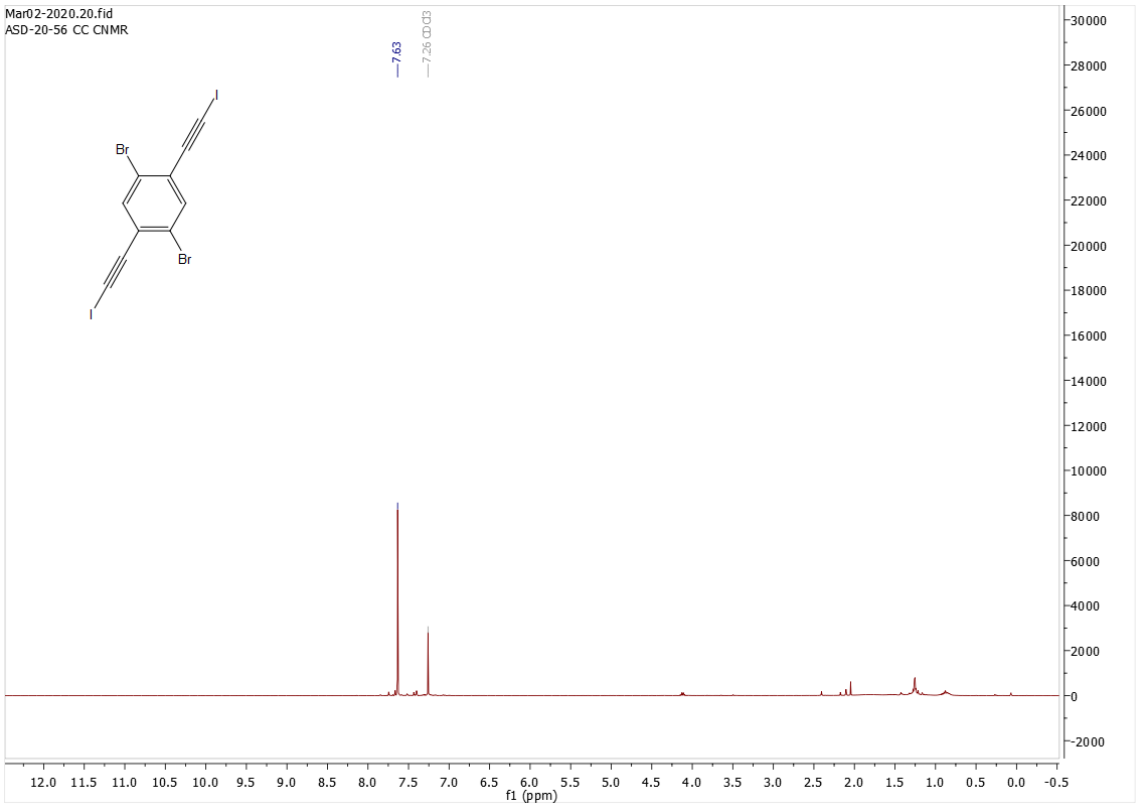
(352): ^{1}H NMR



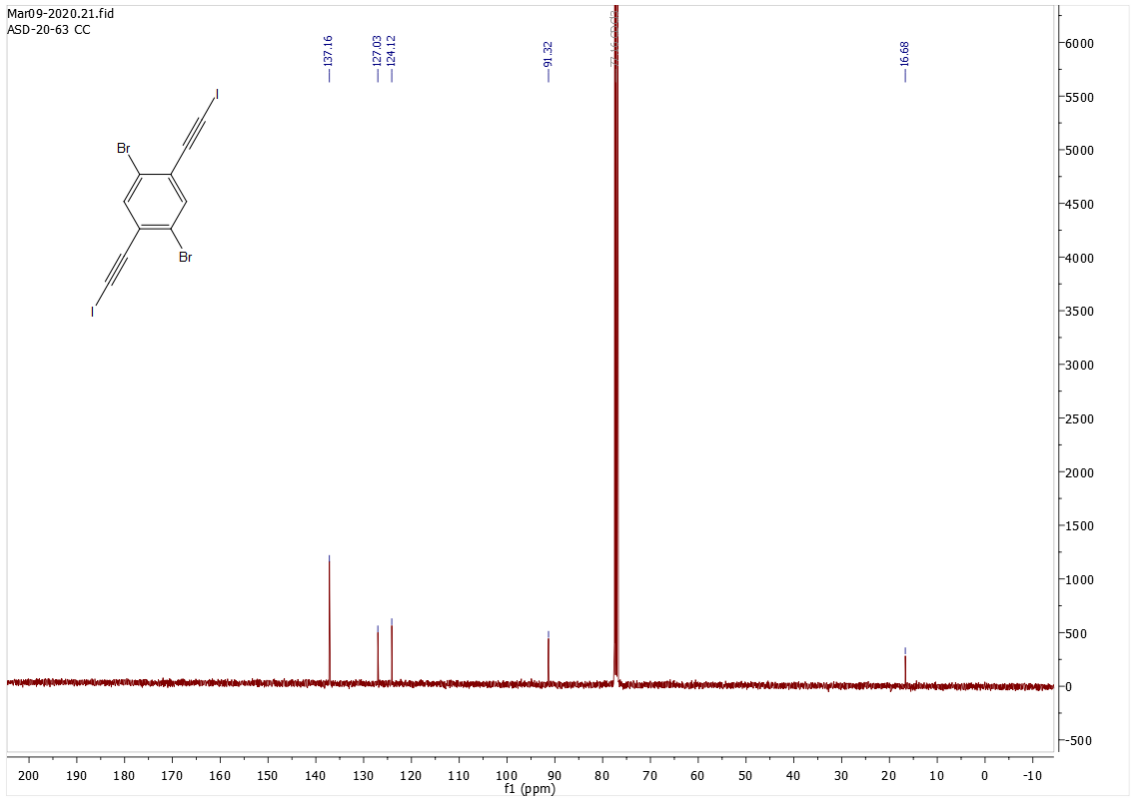
^{13}C NMR



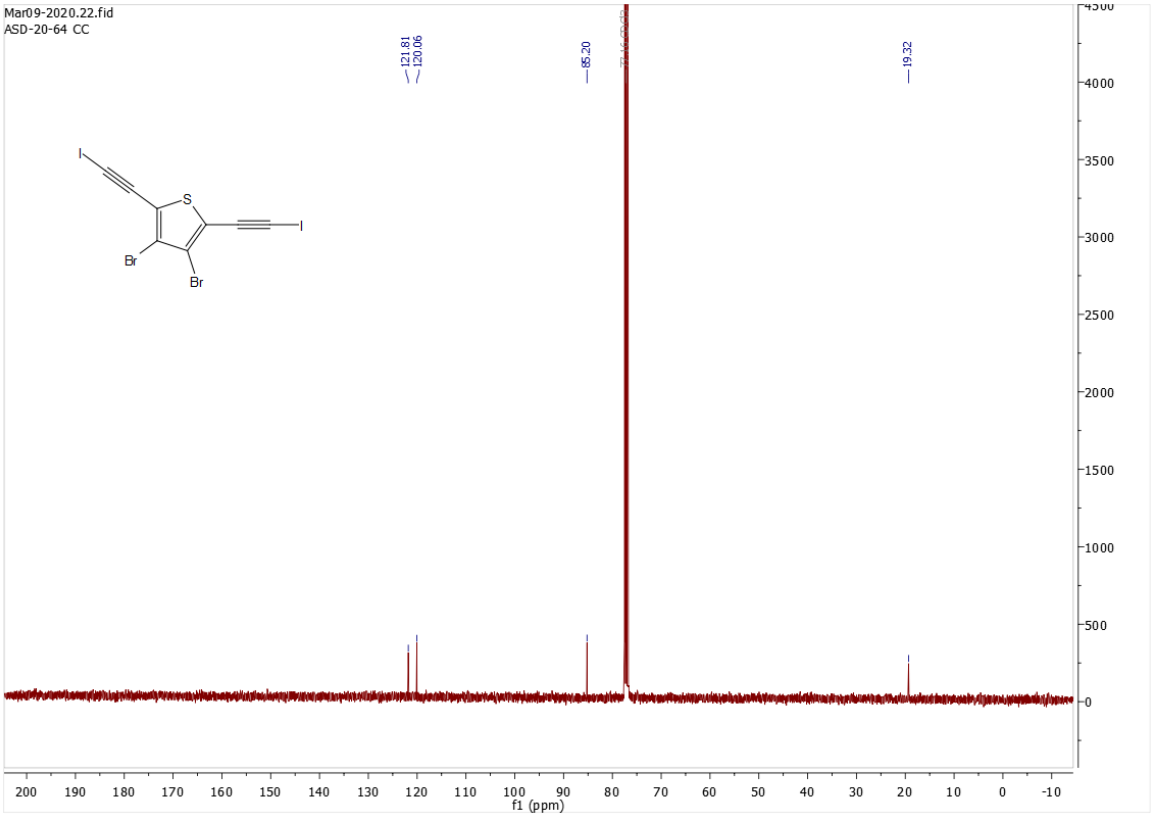
1,4-Dibromo-2,5-bis(iodoethynyl)benzene (353): ^{1}H NMR



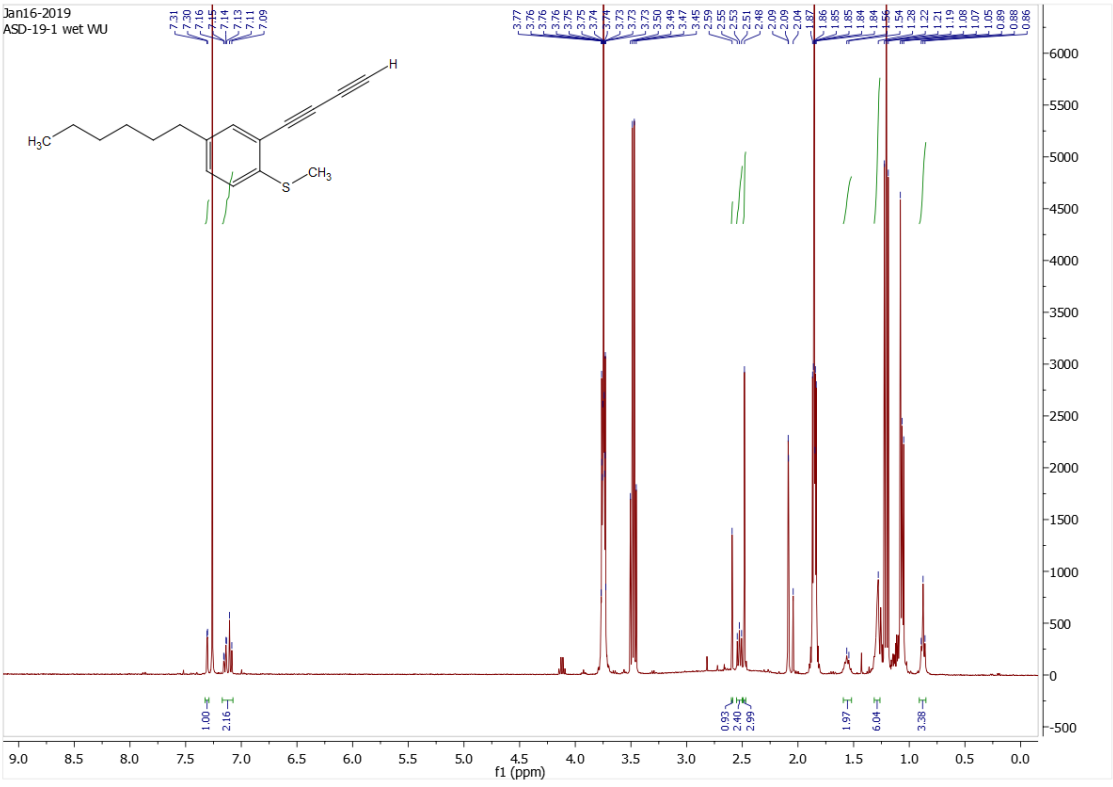
^{13}C NMR



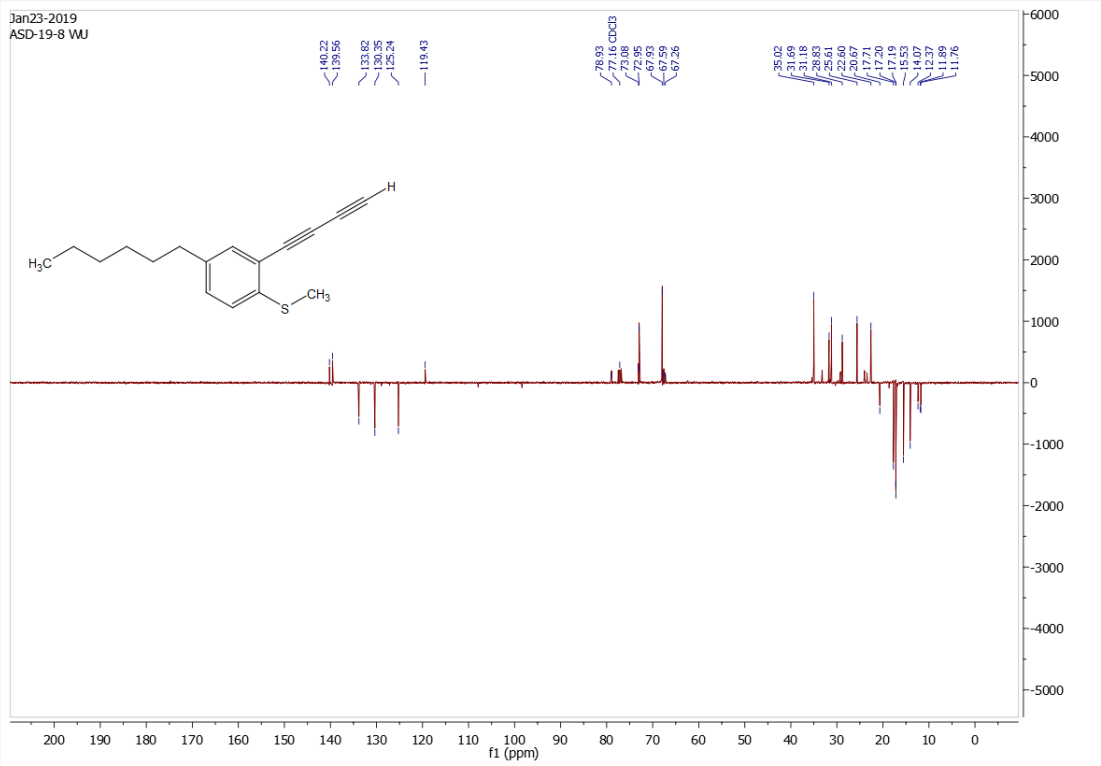
3,4-Dibromo-2,5-bis(iodoethynyl)thiophene (361): ^{13}C NMR



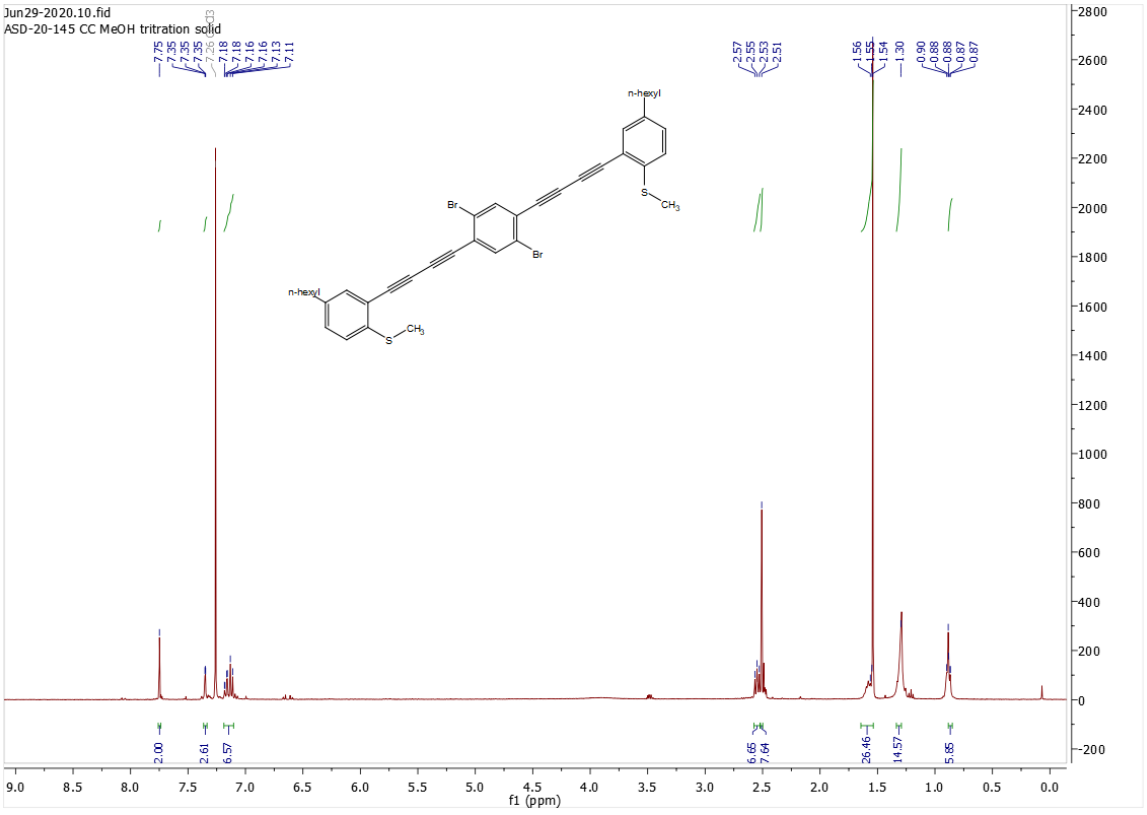
(2-(Buta-1,3-diyn-1-yl)-4-hexylphenyl)(methyl)sulfane (273): ^{1}H NMR



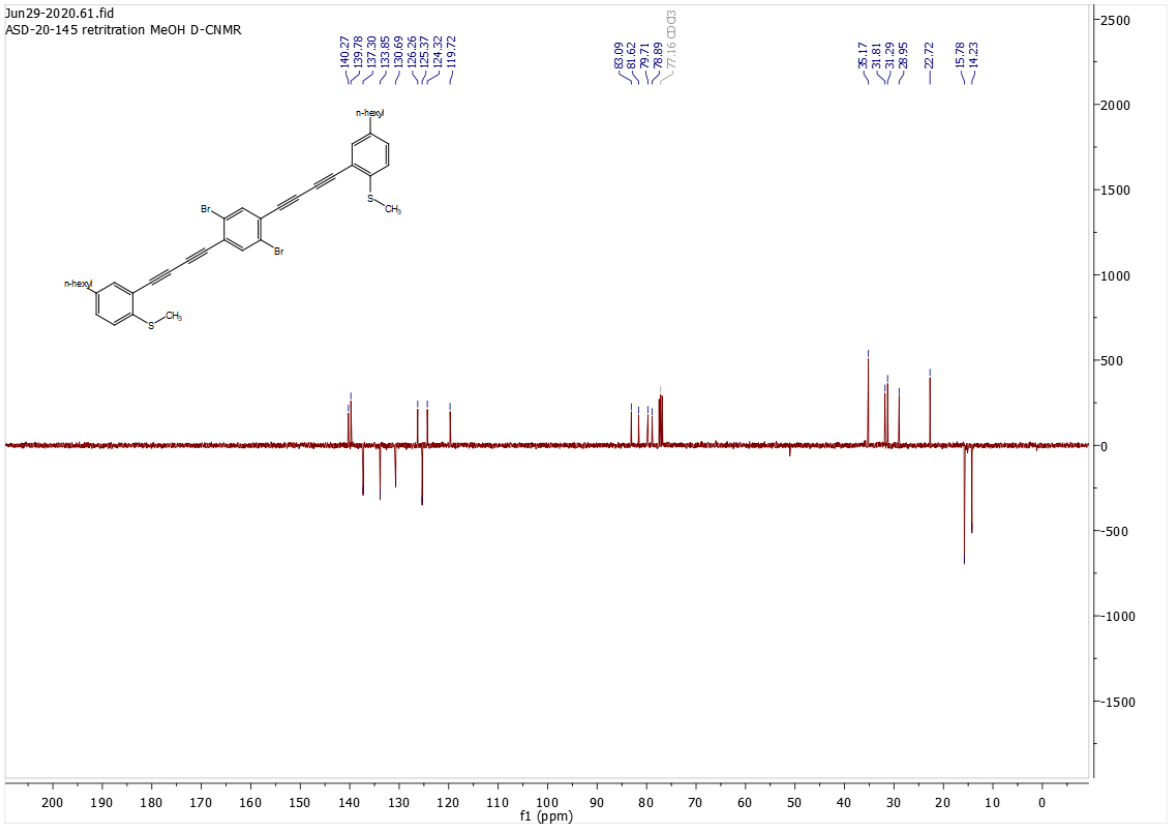
^{13}C NMR



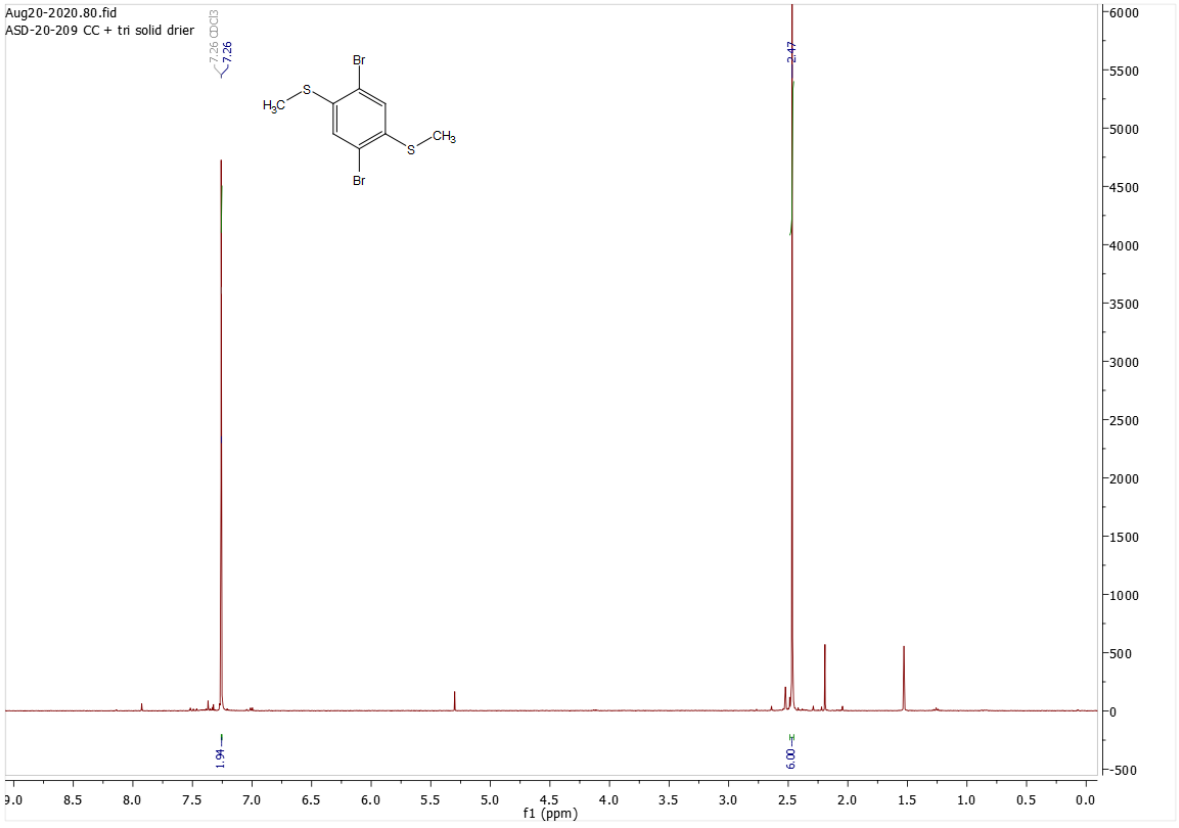
(((2,5-Dibromo-1,4-phenylene)bis(buta-1,3-diyne-4,1-diyl))bis(4-hexyl-2,1-phenylene))bis(methylsulfane) (354): ^{1}H NMR



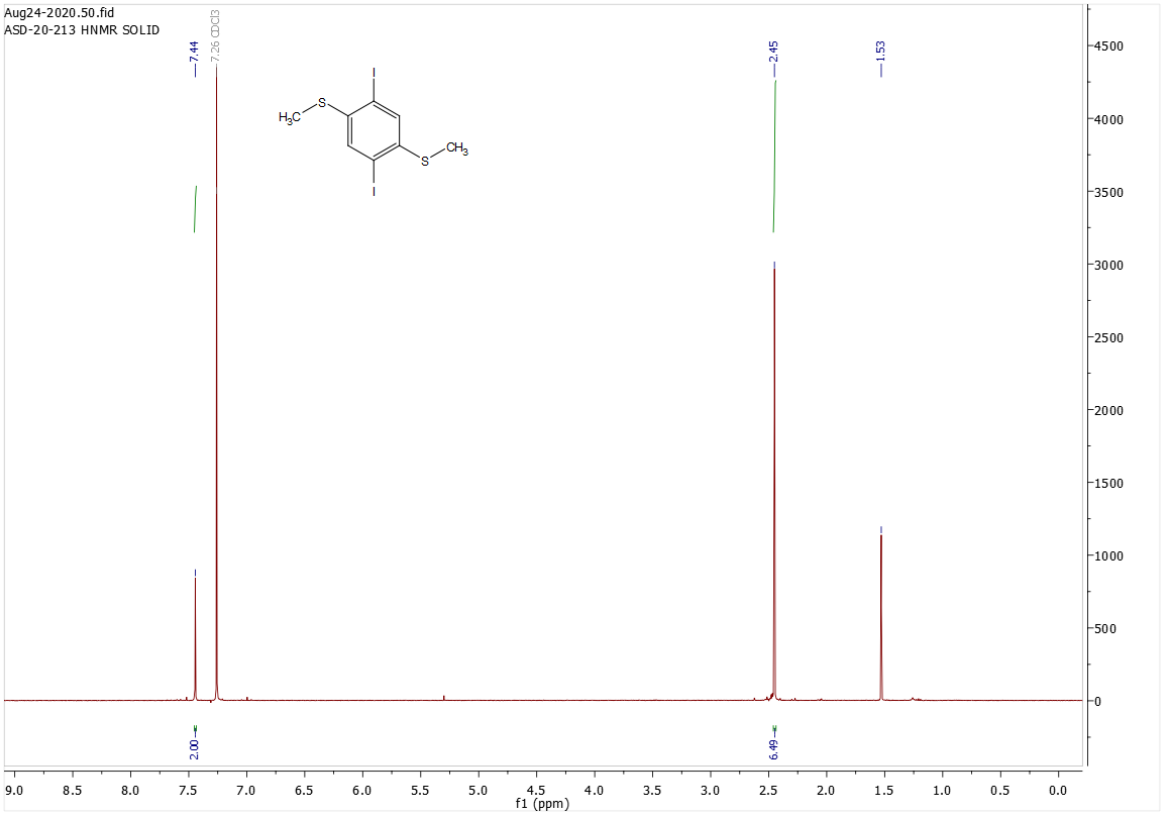
^{13}C NMR



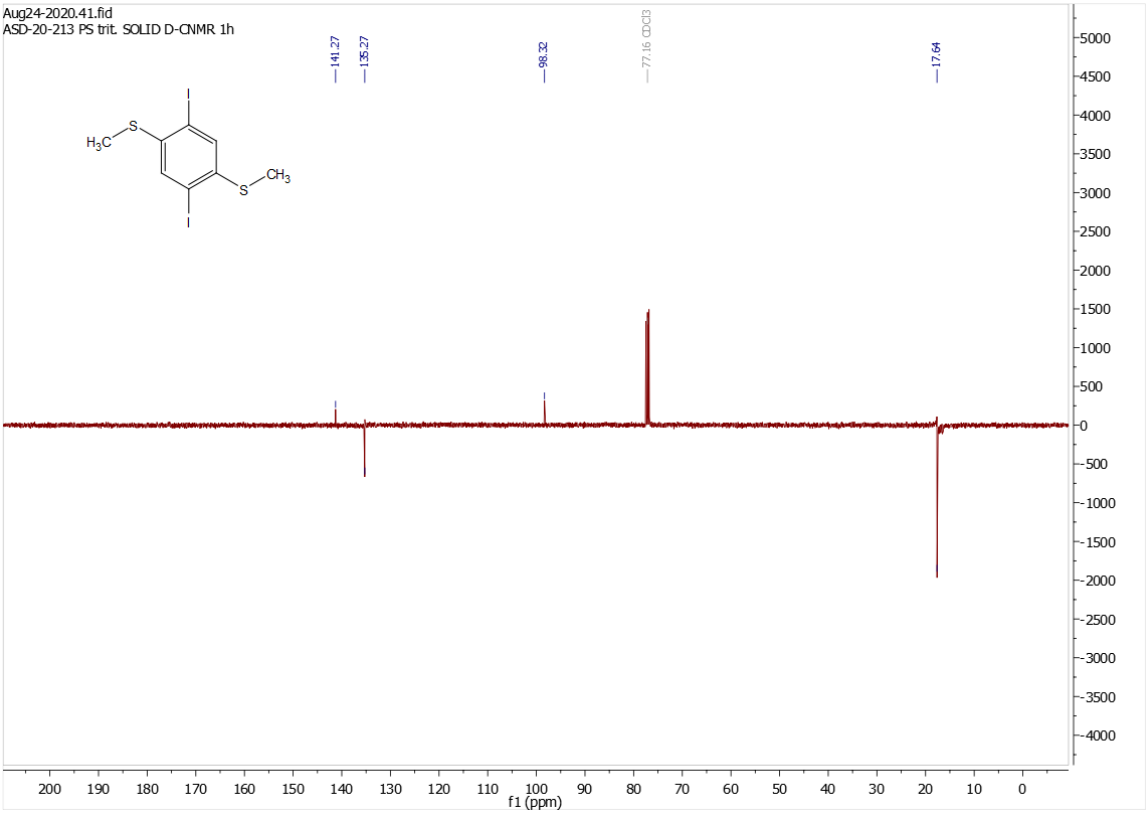
(2,5-Dibromo-1,4-phenylene)bis(methylsulfane) (365): ^{1}H NMR



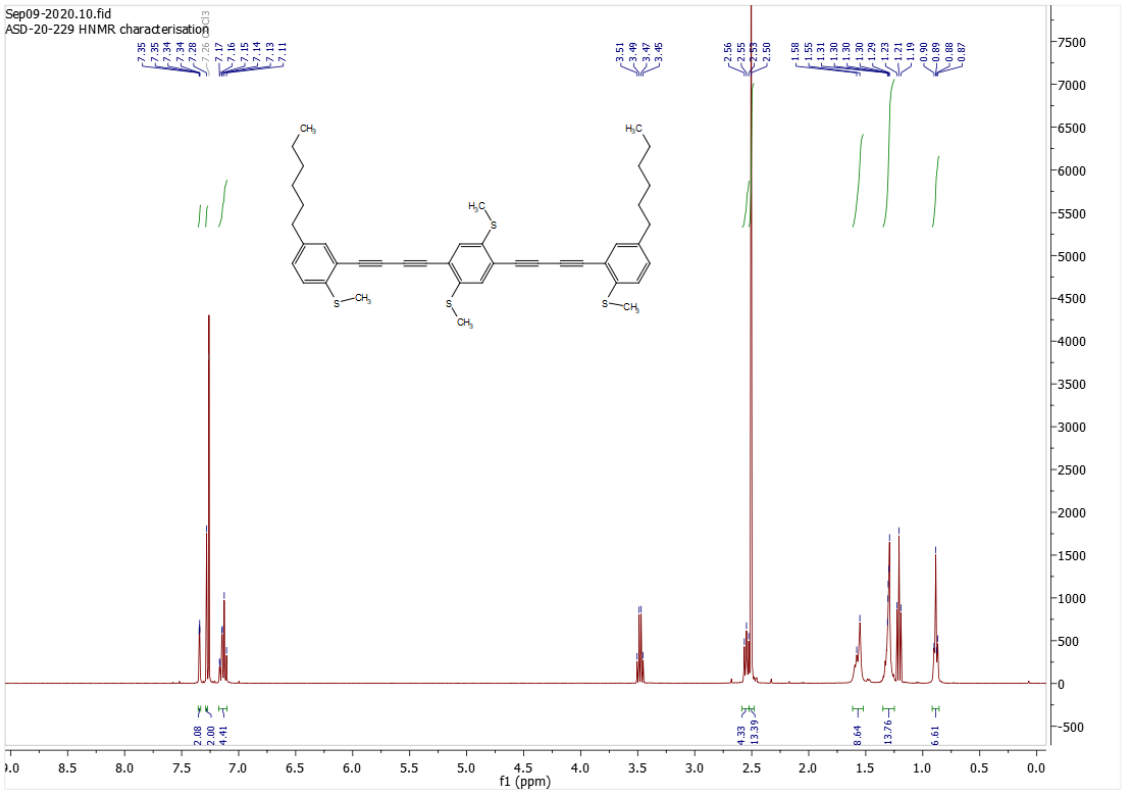
(2,5-Diiodo-1,4-phenylene)bis(methylsulfane) (161): ^{1}H NMR



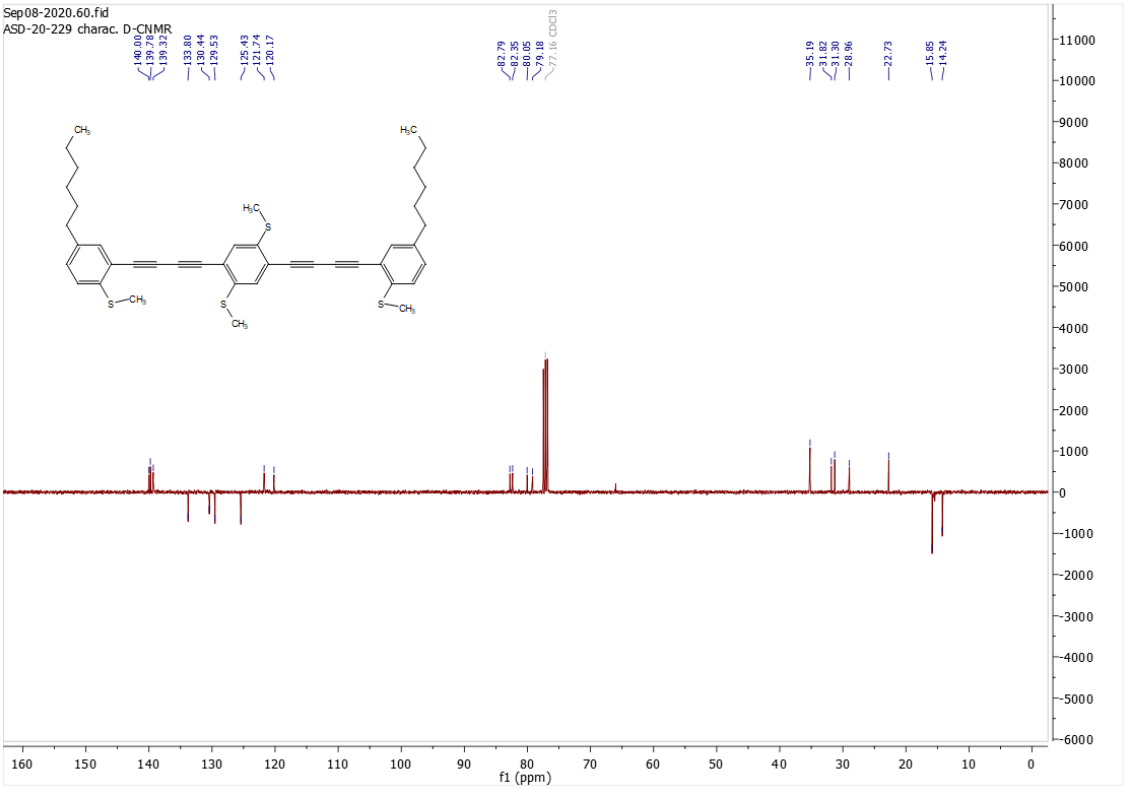
^{13}C NMR



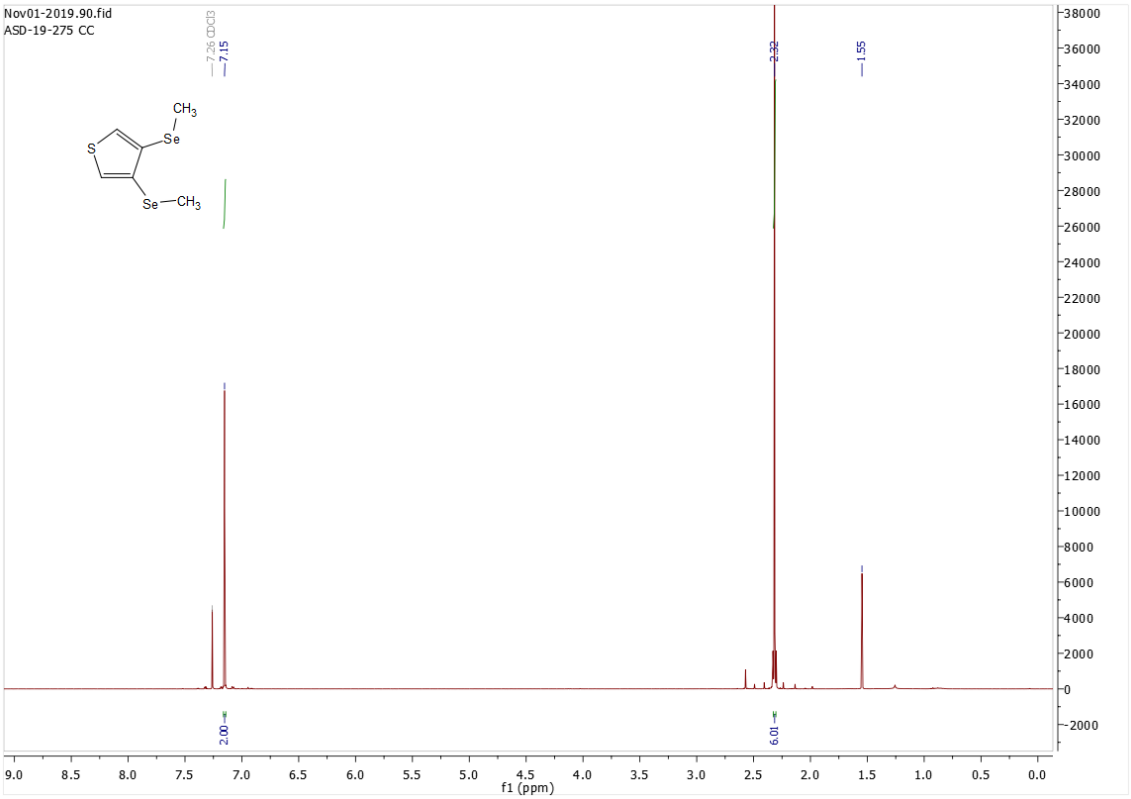
(2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-1,4-phenylene)bis(methylsulfane) (342): ^{1}H NMR



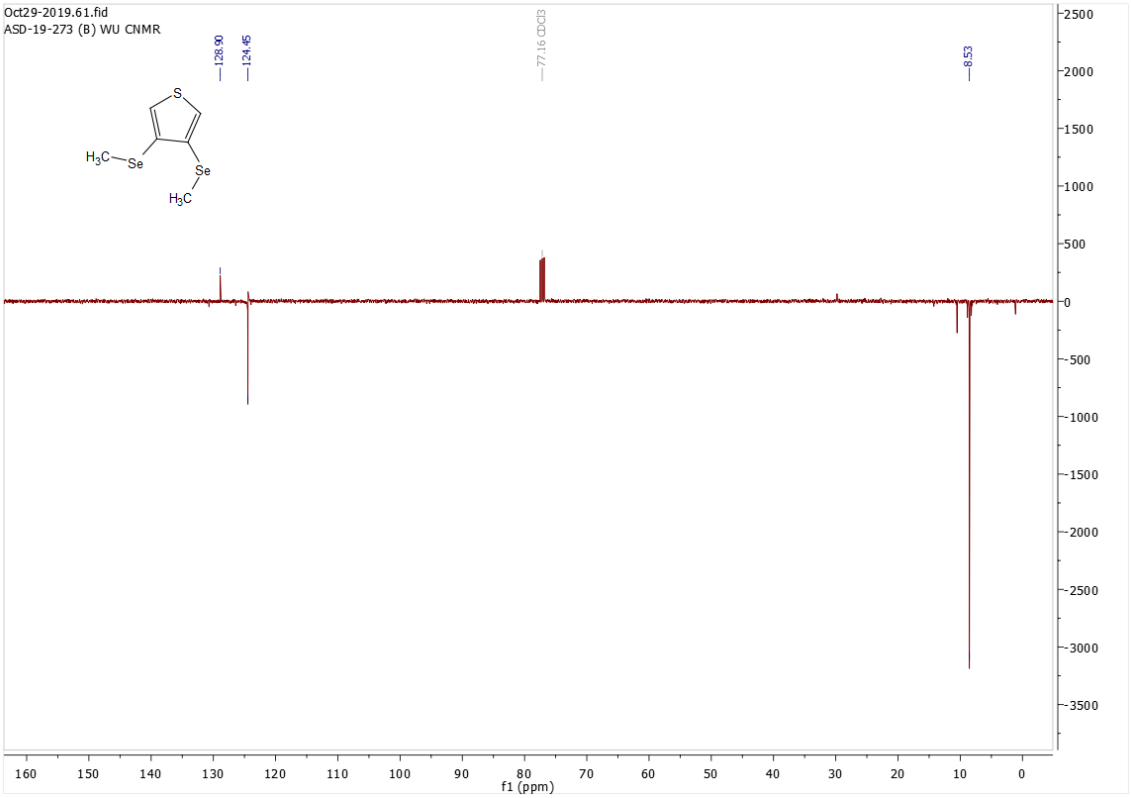
^{13}C NMR



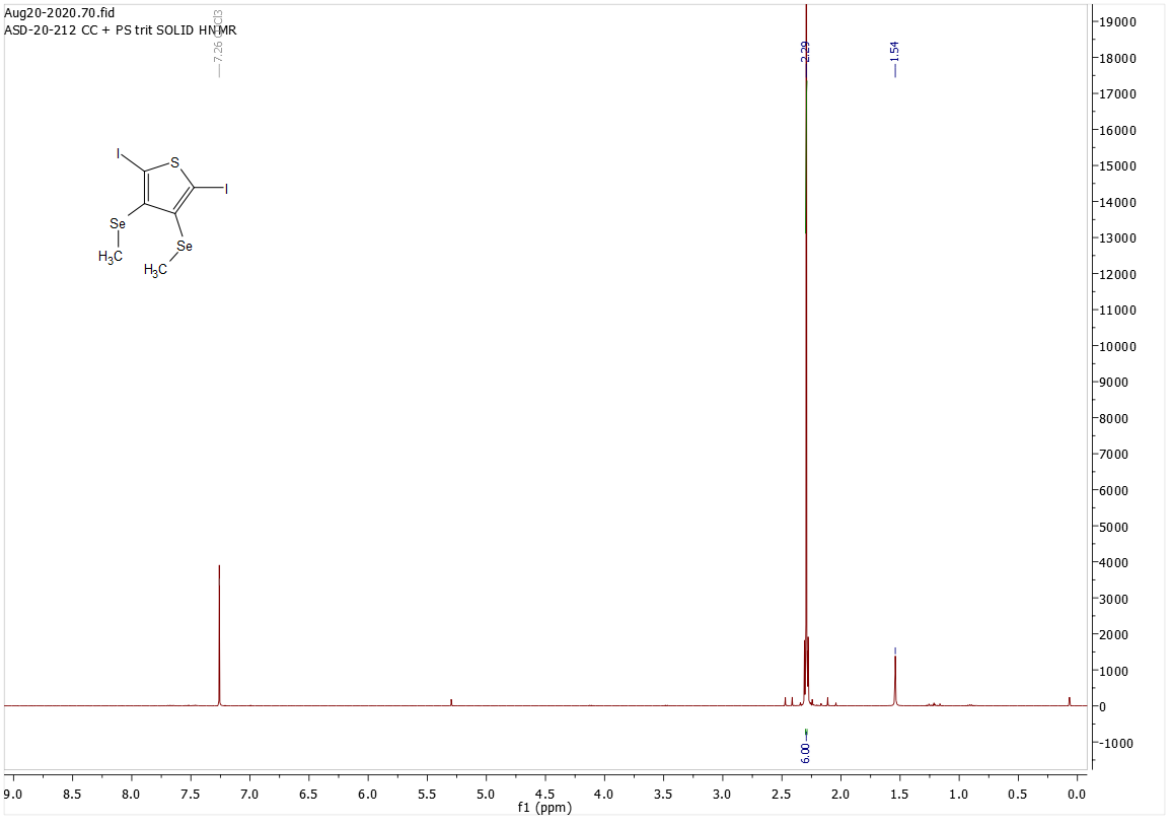
3,4-Bis(methylselanyl)thiophene (374): ^{1}H NMR



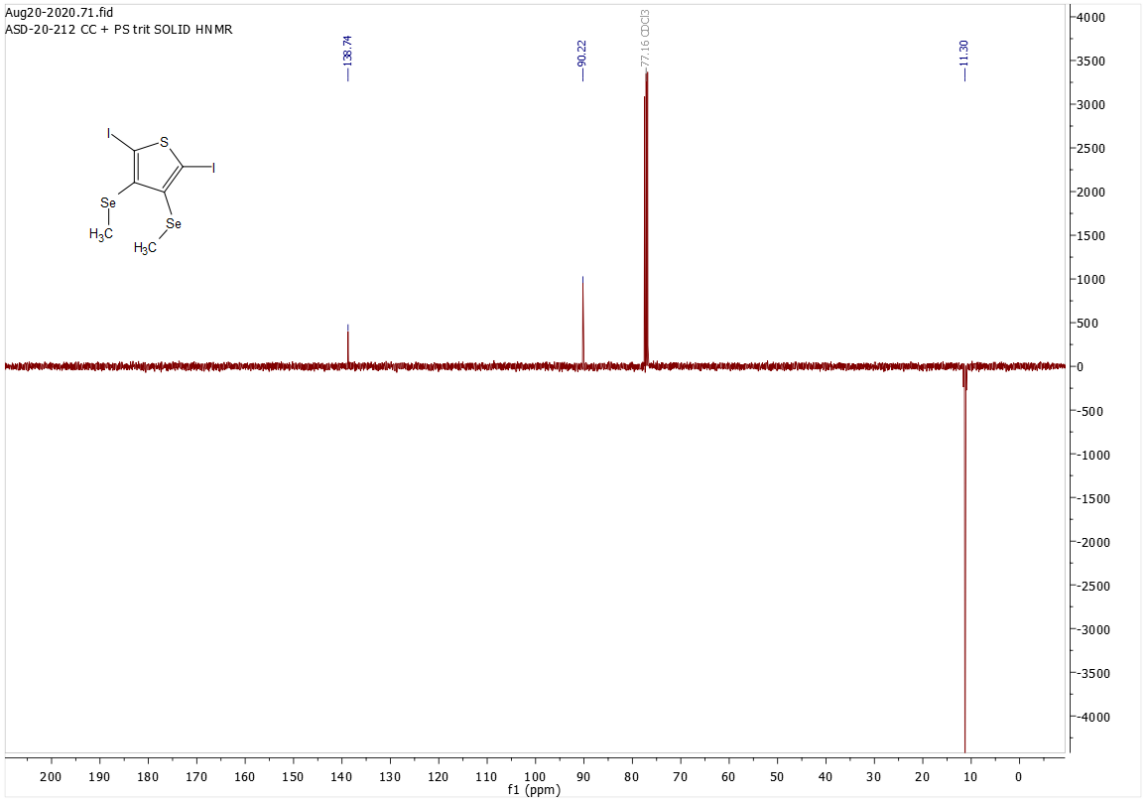
^{13}C NMR



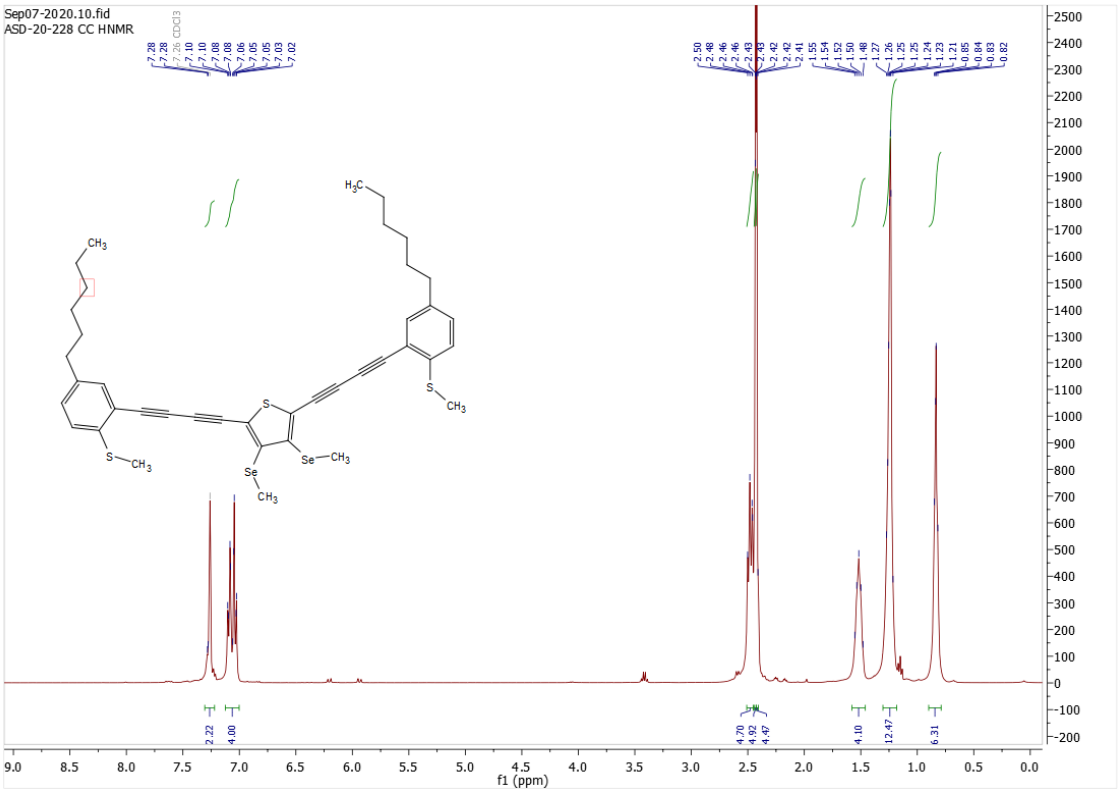
2,5-Diiodo-3,4-bis(methylselanyl)thiophene (375): ^{1}H NMR



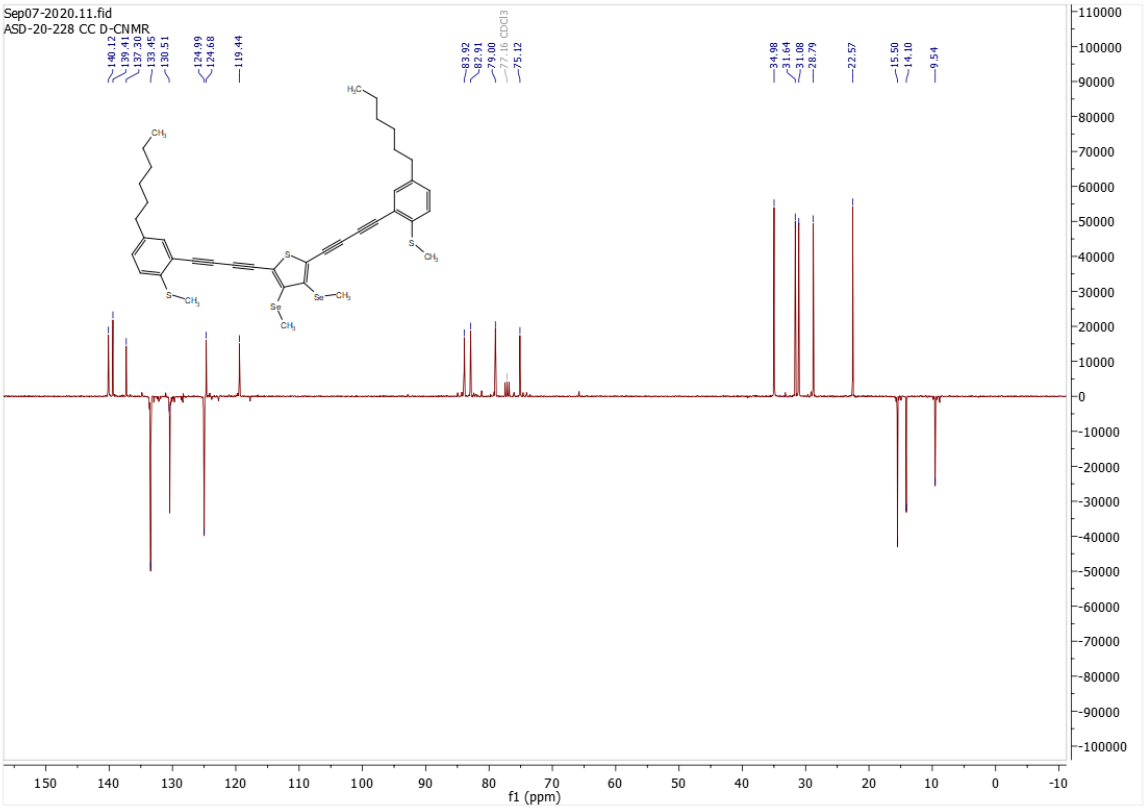
^{13}C NMR



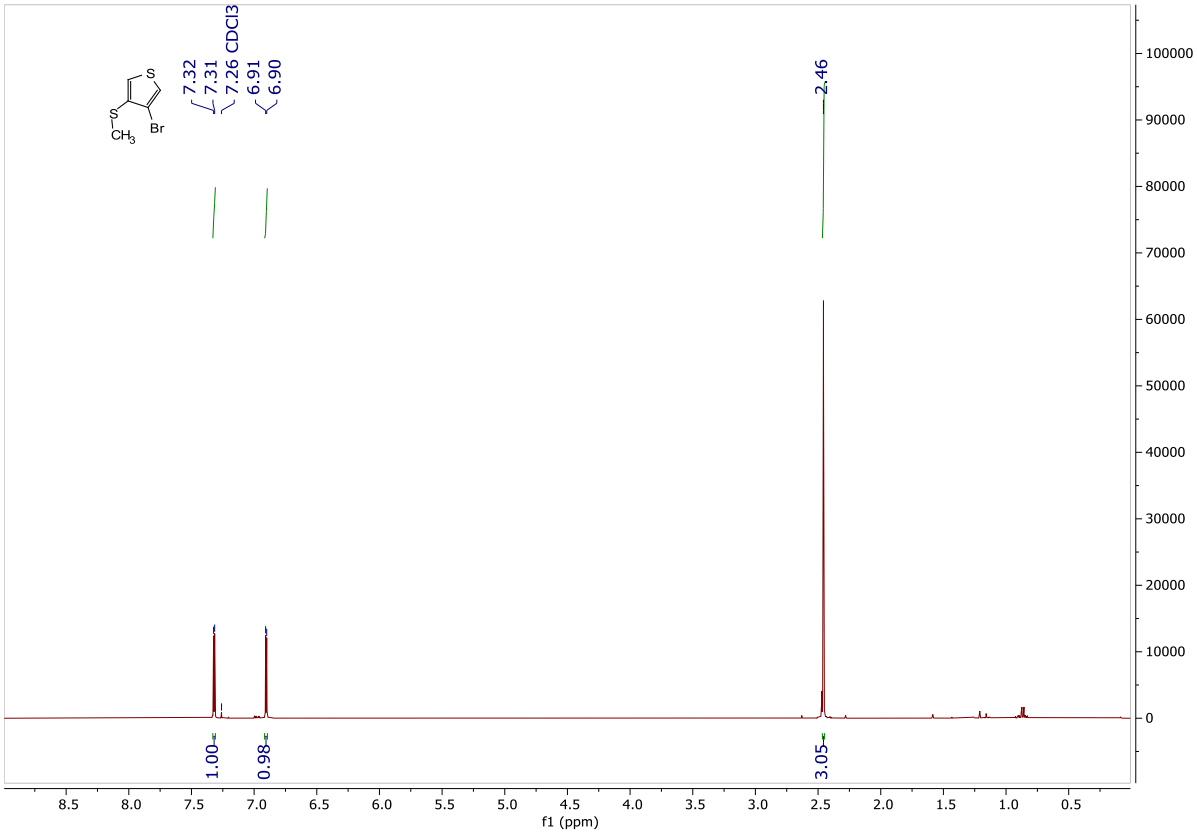
2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-3,4-bis(methylselanyl)thiophene (344): ^{1}H NMR



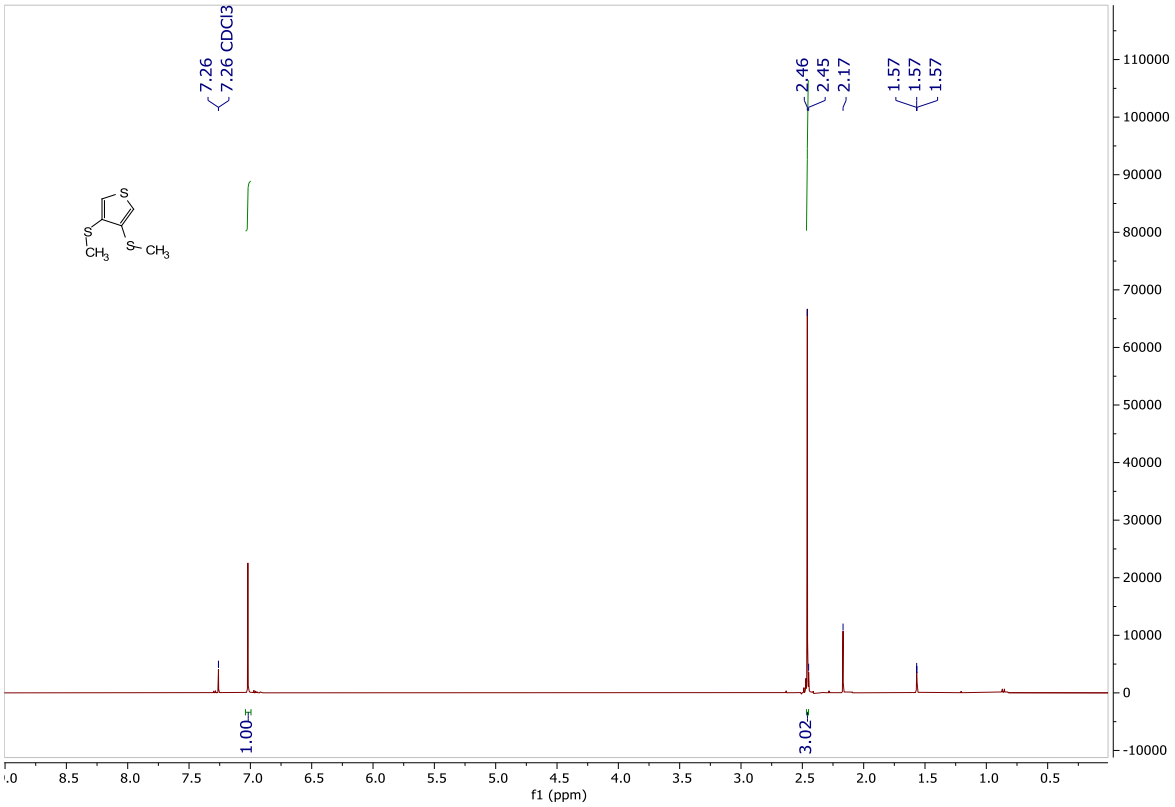
^{13}C NMR



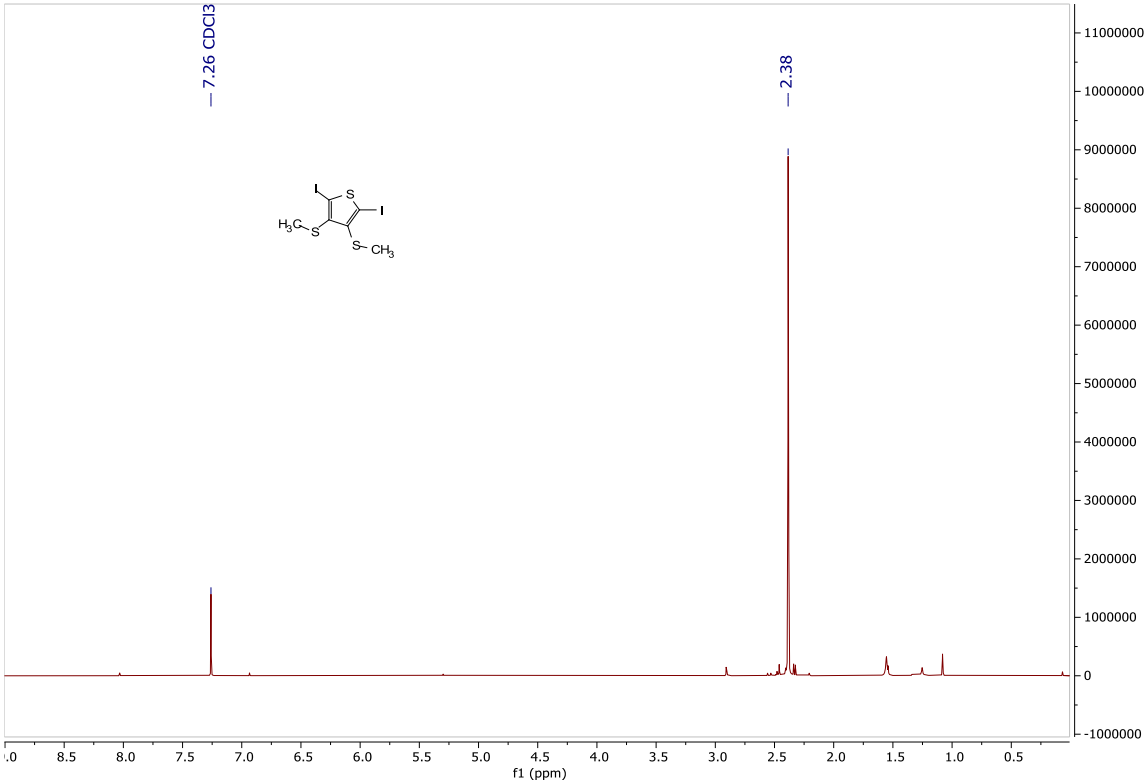
3-Bromo-4-(methylthio)thiophene (382): ^{1}H NMR



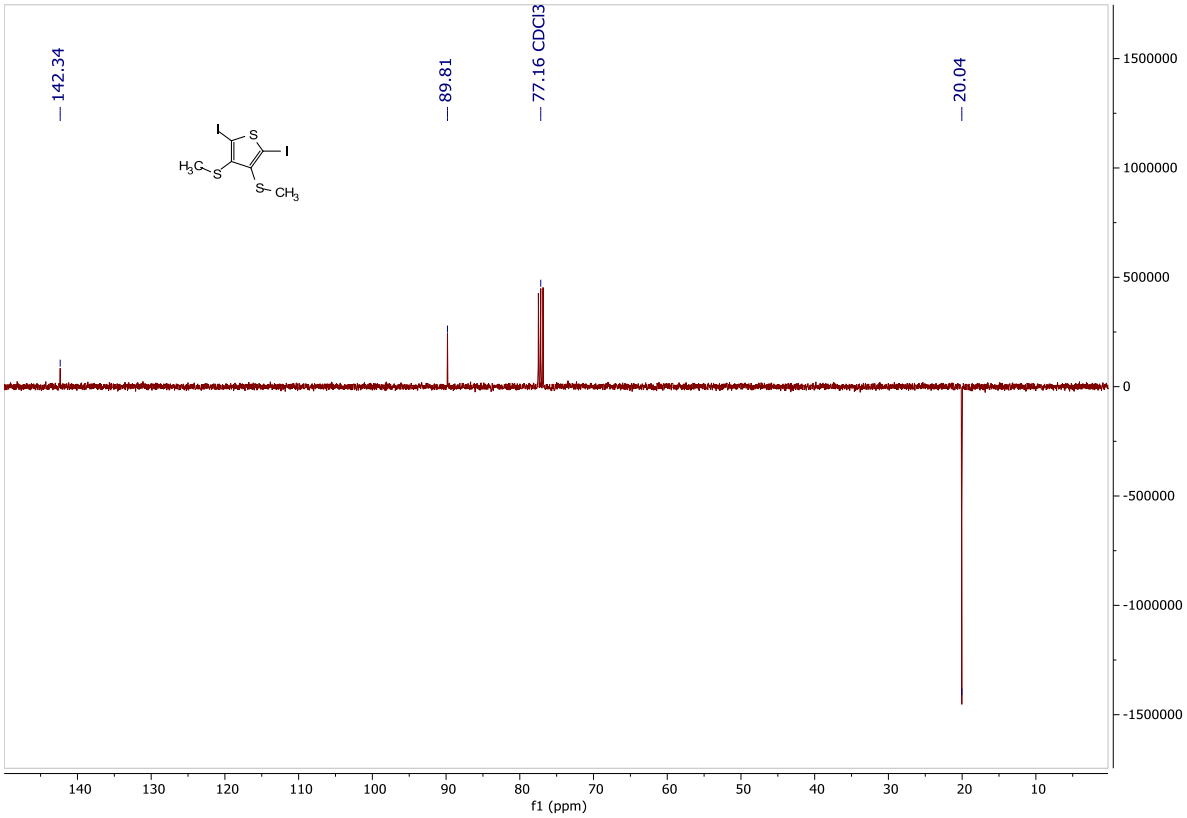
3,4-Bis(methylthio)thiophene (384): ^{1}H NMR



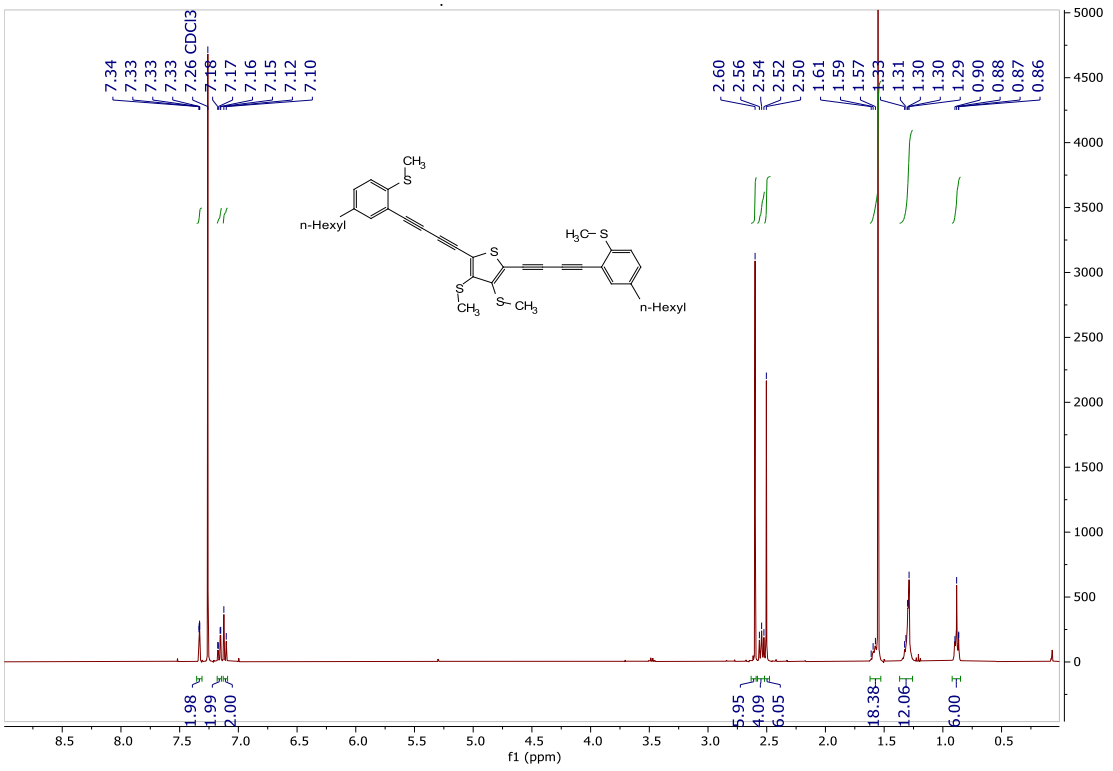
2,5-Diiodo-3,4-bis(methylthio)thiophene (385): ^{1}H NMR



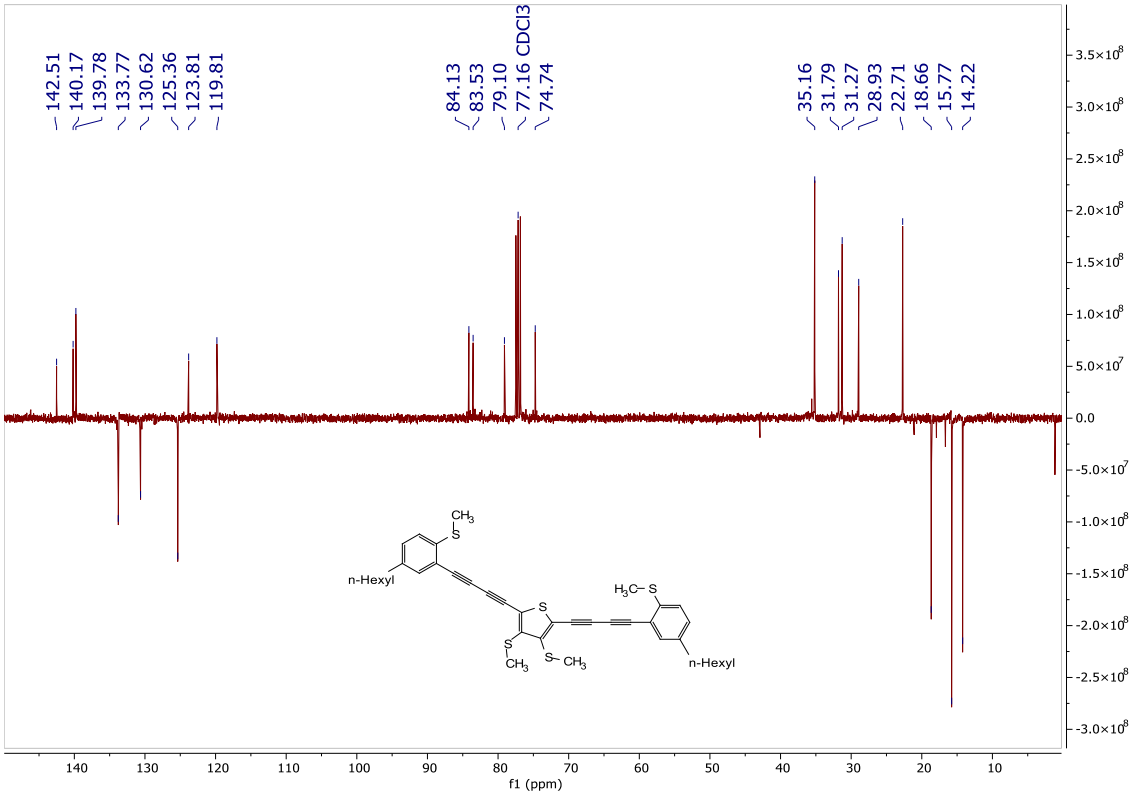
^{13}C NMR



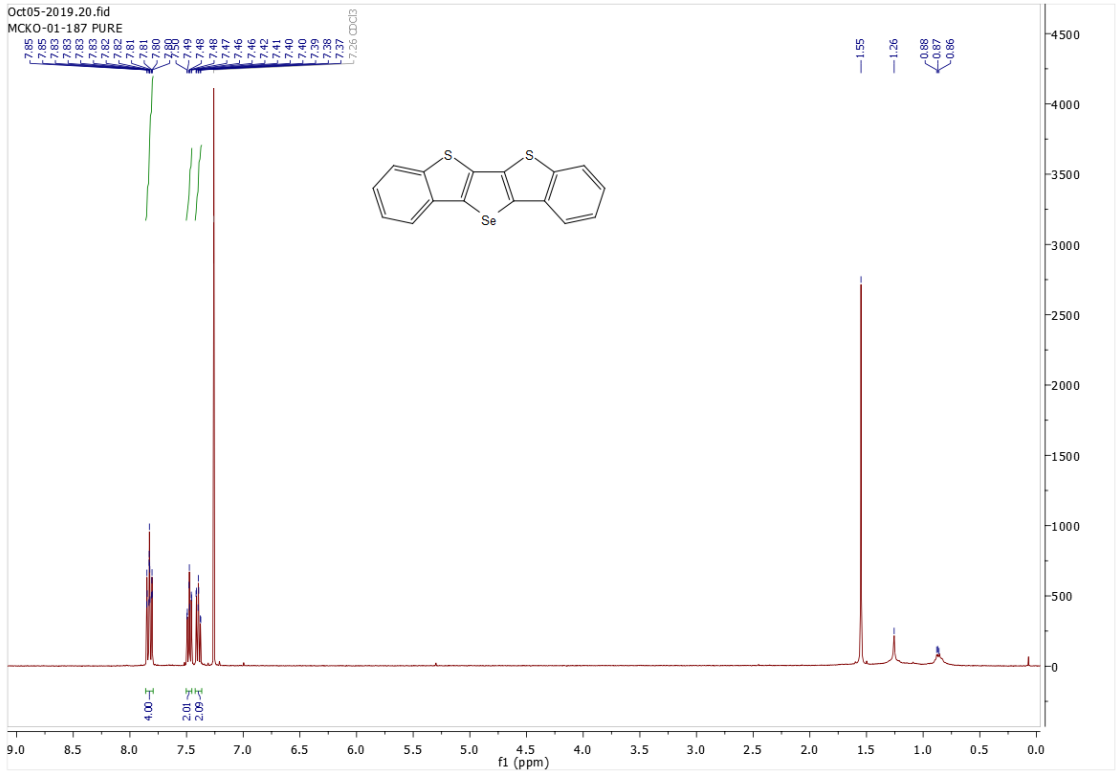
2,5-Bis((5-hexyl-2-(methylthio)phenyl)buta-1,3-diyn-1-yl)-3,4-bis(methylthio)thiophene (346): ^{1}H NMR



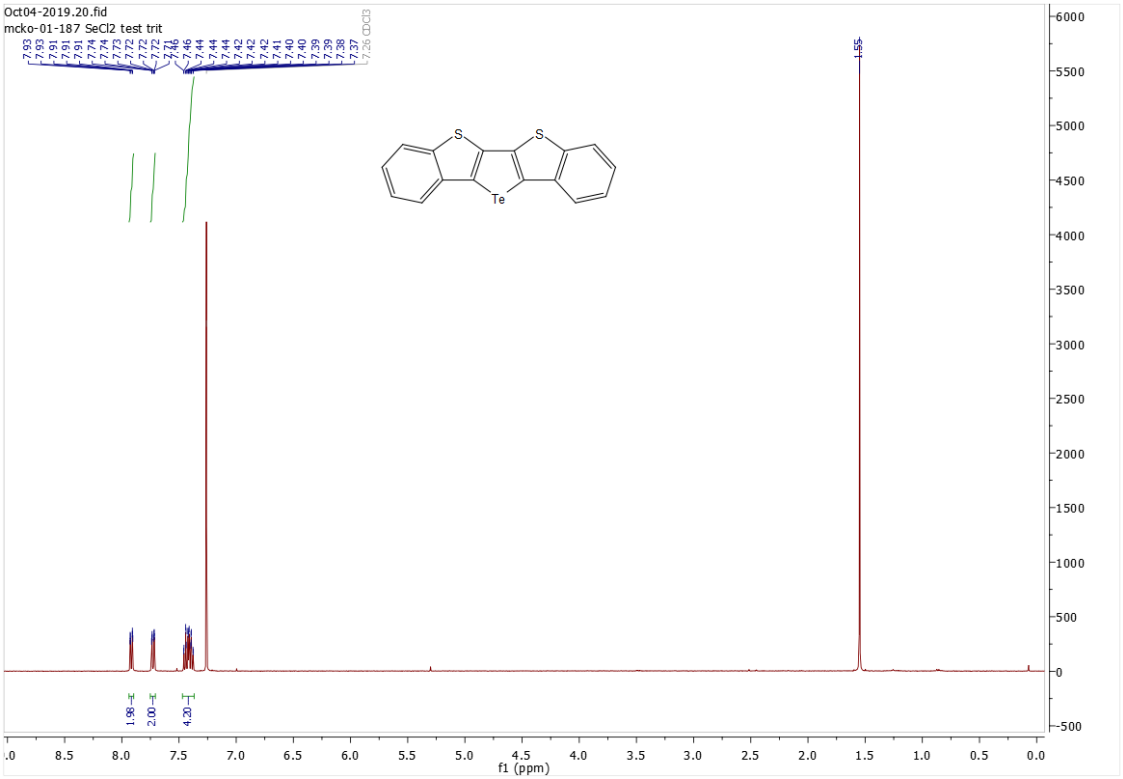
^{13}C NMR



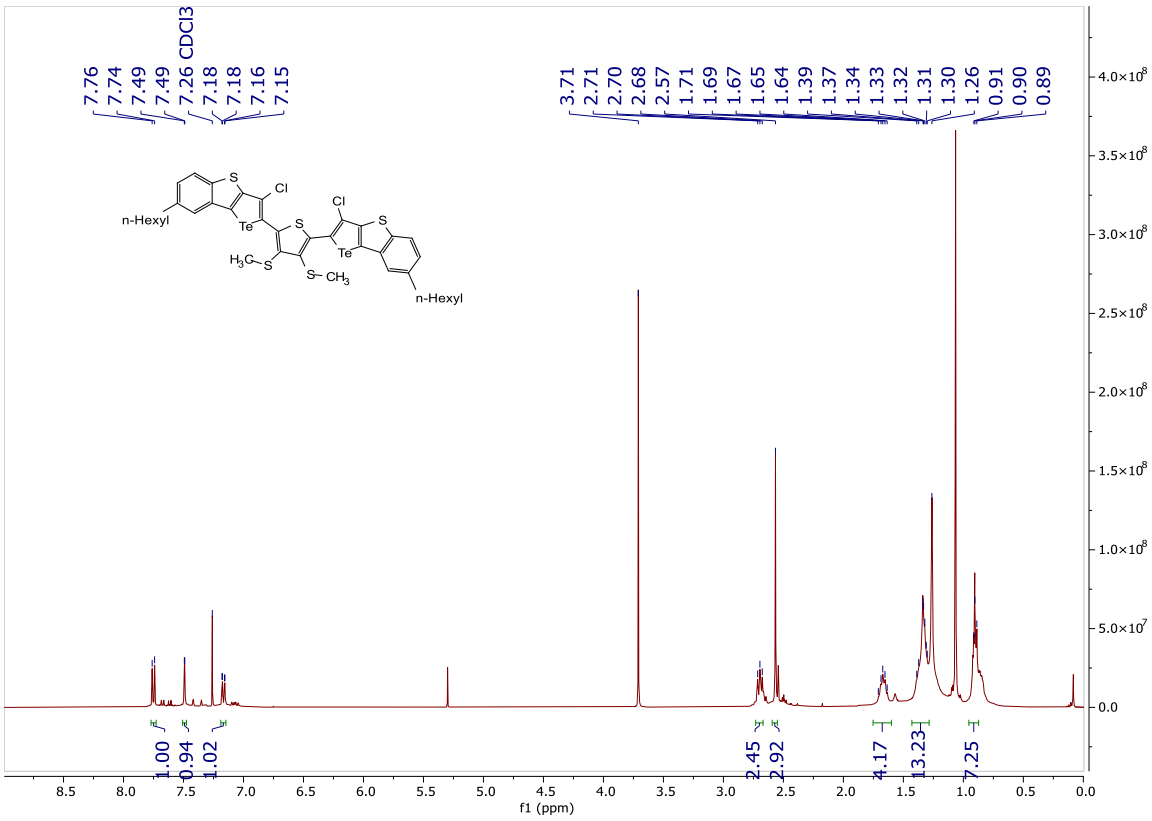
Selenocycle (387): ^{1}H NMR



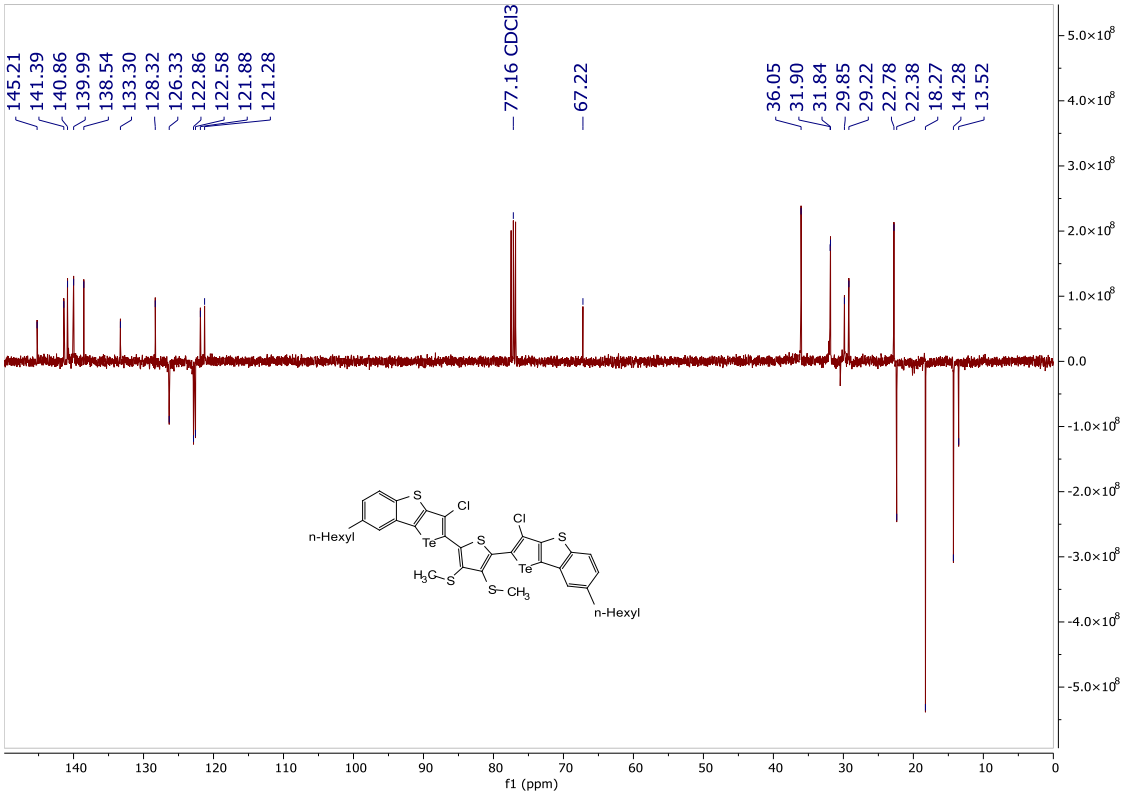
Tellurocycle (389): ^{1}H NMR



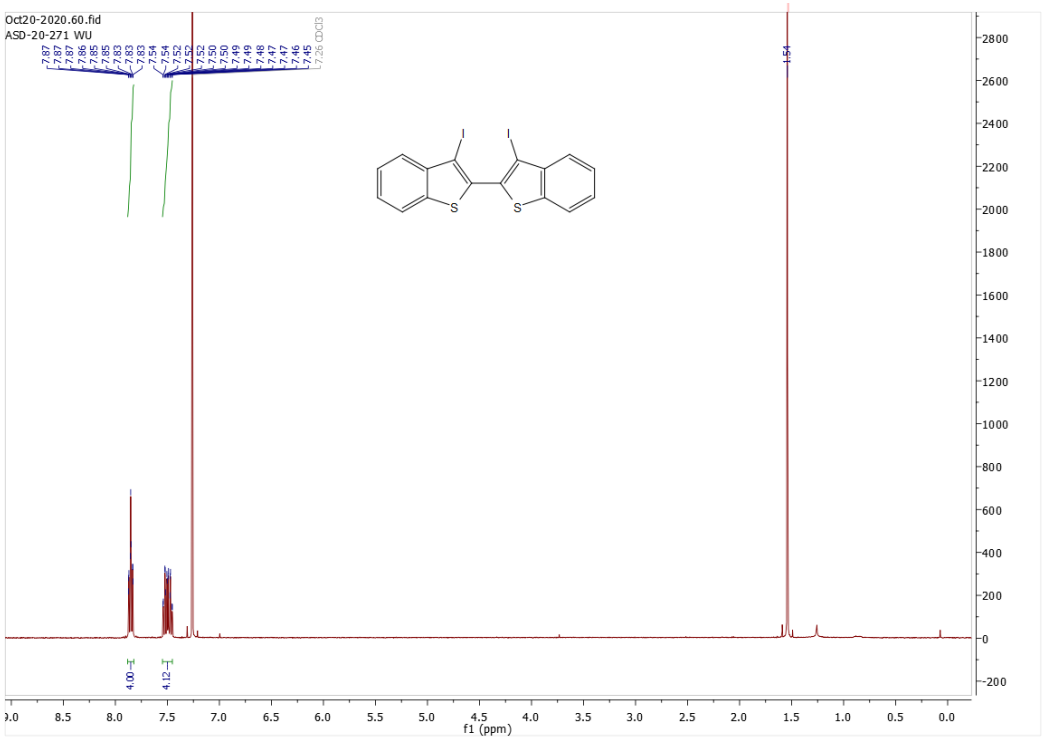
2,2'-(3,4-Bis(methylthio)thiophene-2,5-diyl)bis(3-chloro-7-hexylbenzo[*b*]telluropheno[2,3-*d*]thiophene) (393): ^{1}H NMR



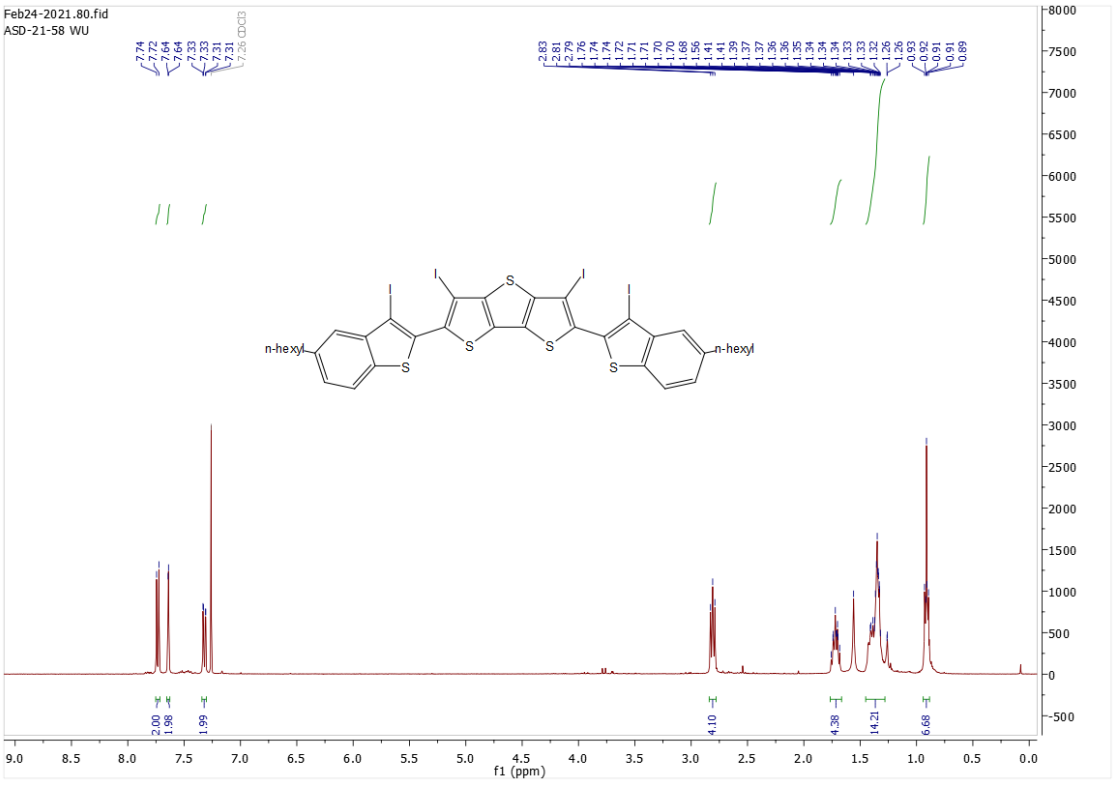
^{13}C NMR



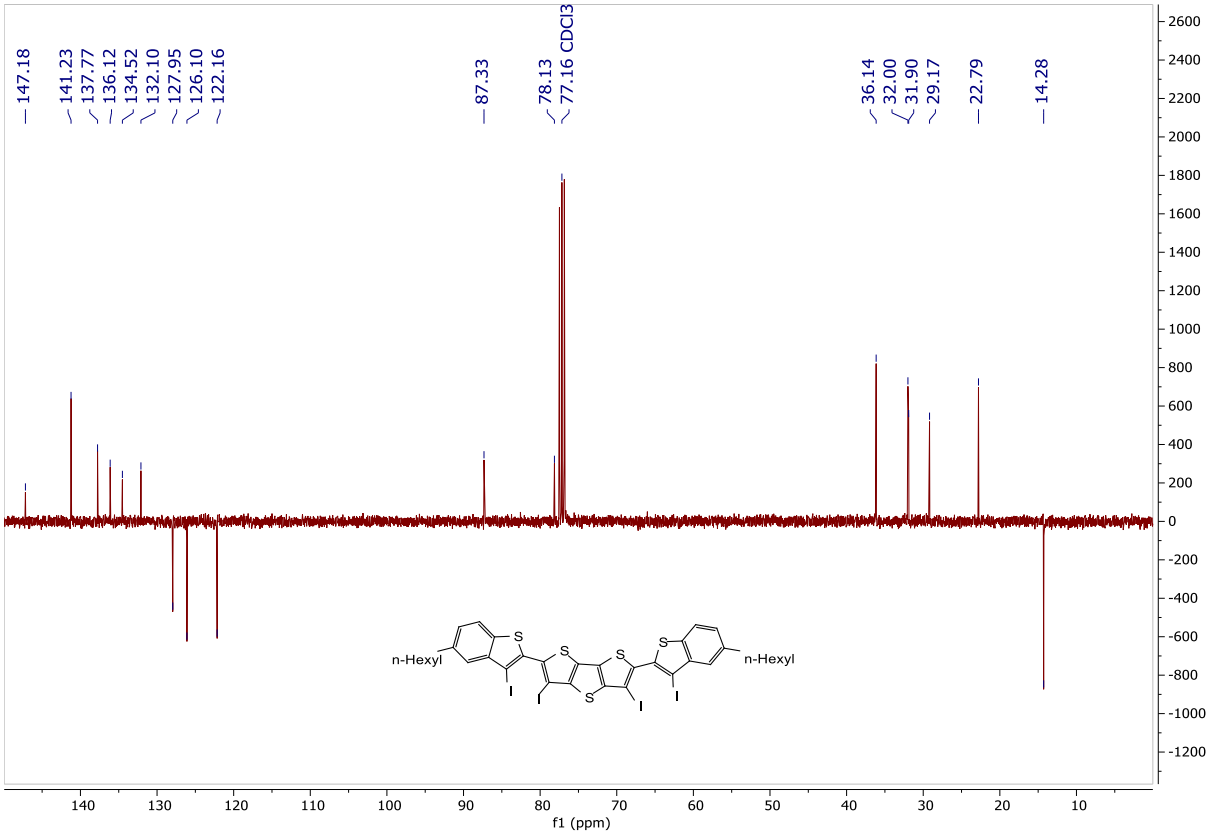
3,3'-Diiodo-2,2'-bibenzo[b]thiophene (407): ^{1}H NMR



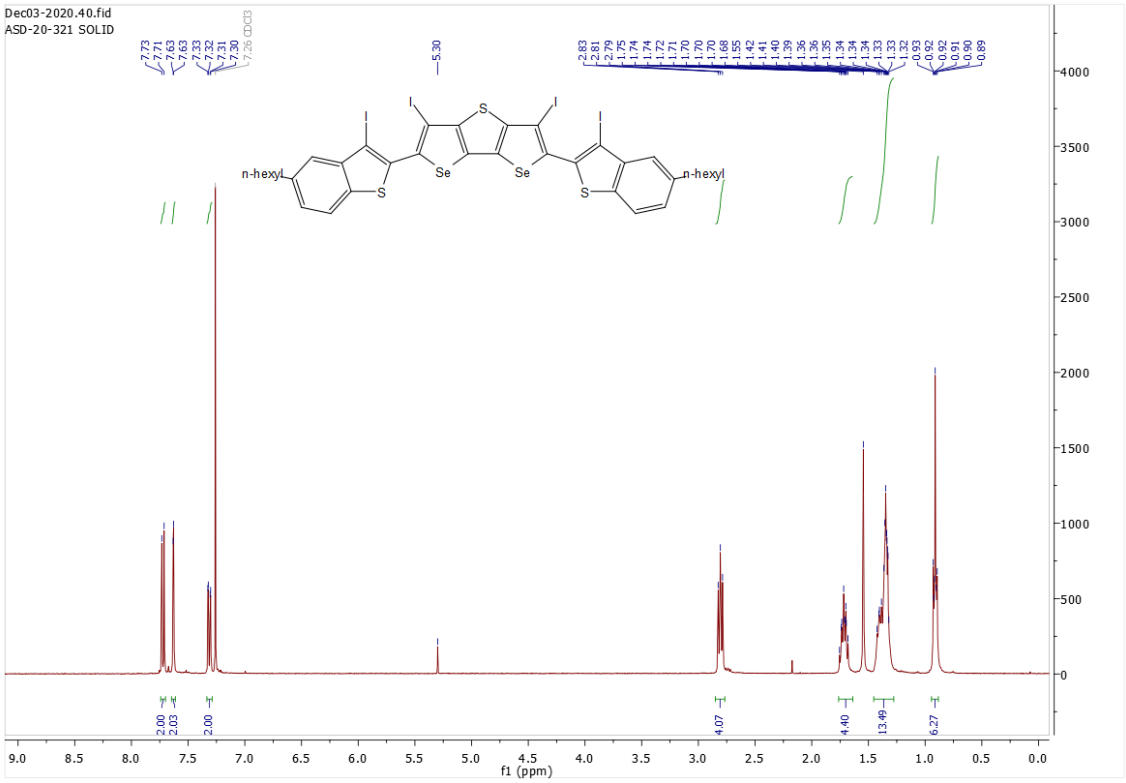
2,6-Bis(5-hexyl-3-iodobenzo[*b*]thiophen-2-yl)-3,5-diiododithieno[3,2-*b*:2',3'-d]thiophene (408): ^{1}H NMR



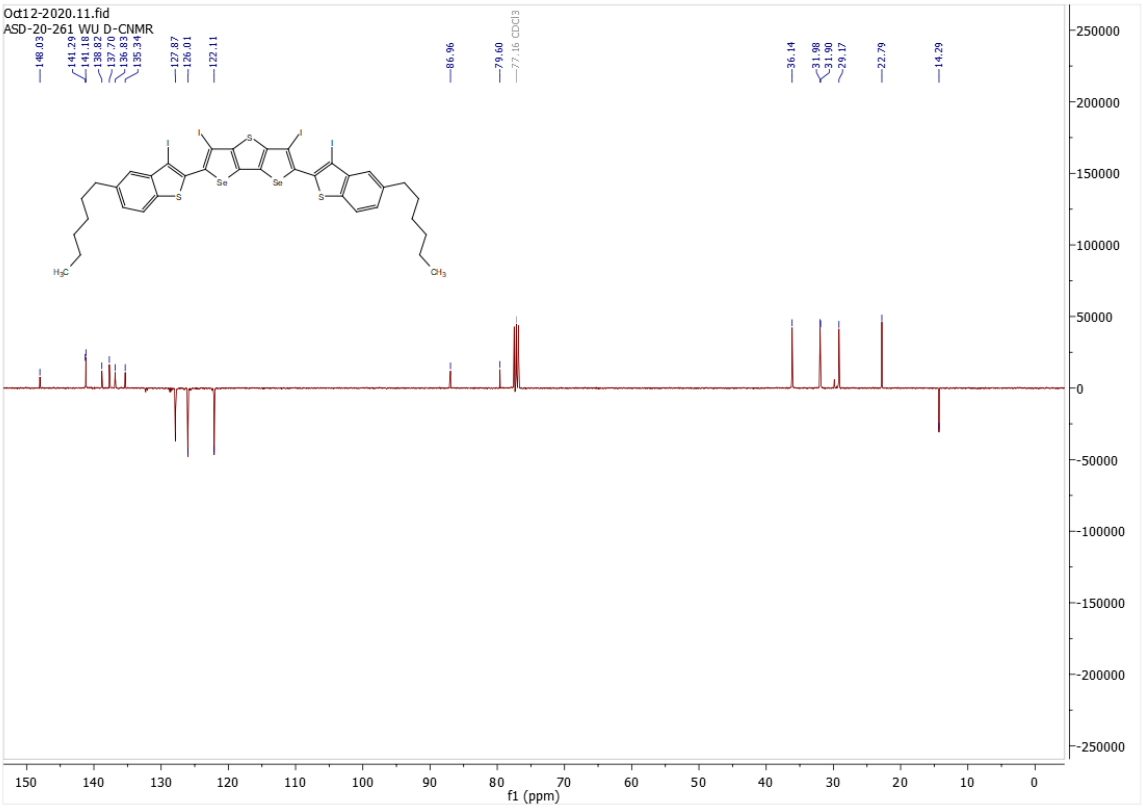
^{13}C NMR



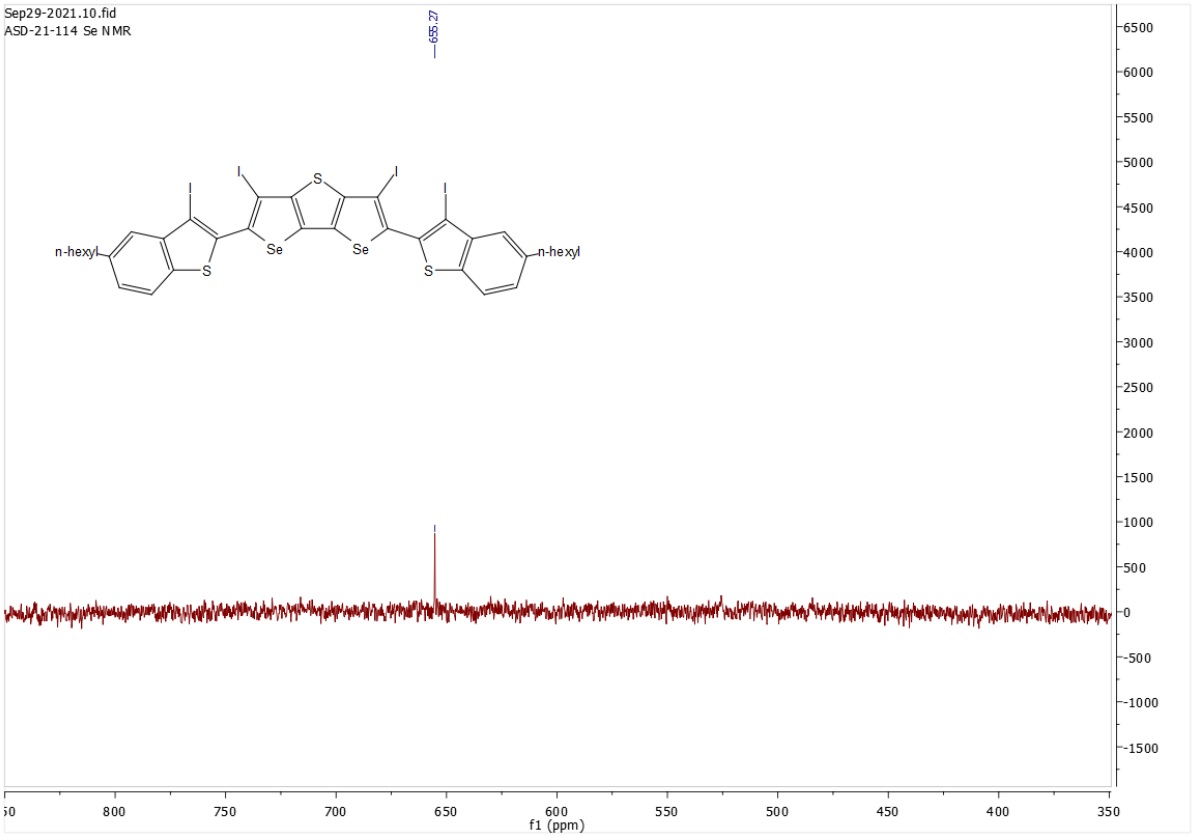
2,6-Bis(5-hexyl-3-iodobenzo[b]thiophen-2-yl)-3,5-diiododiselenopheno[3,2-b:2',3'-d]thiophene (409): ^{1}H NMR



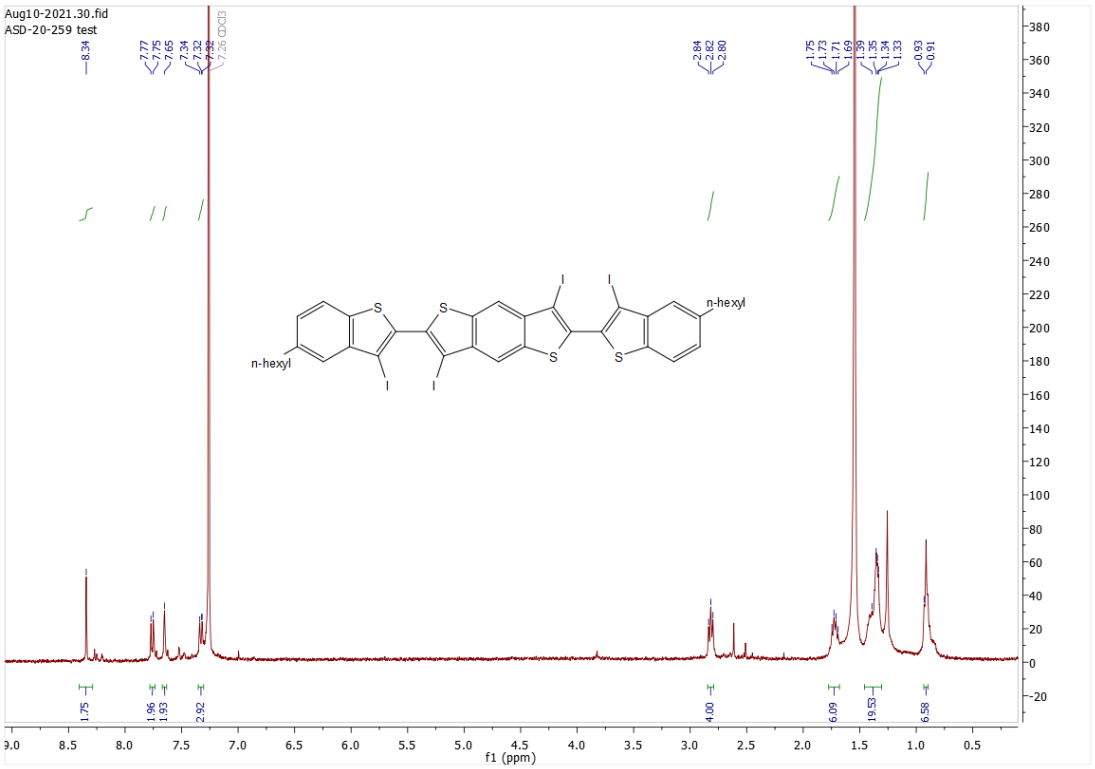
^{13}C NMR



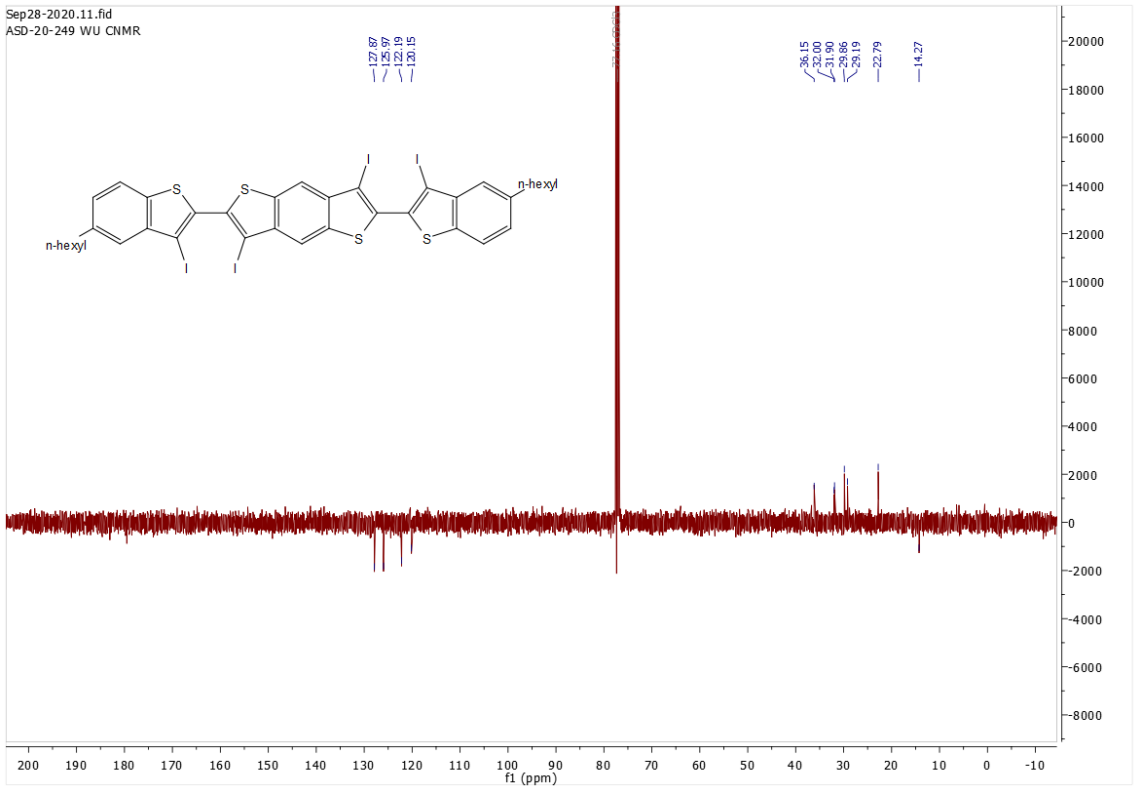
^{77}Se NMR:



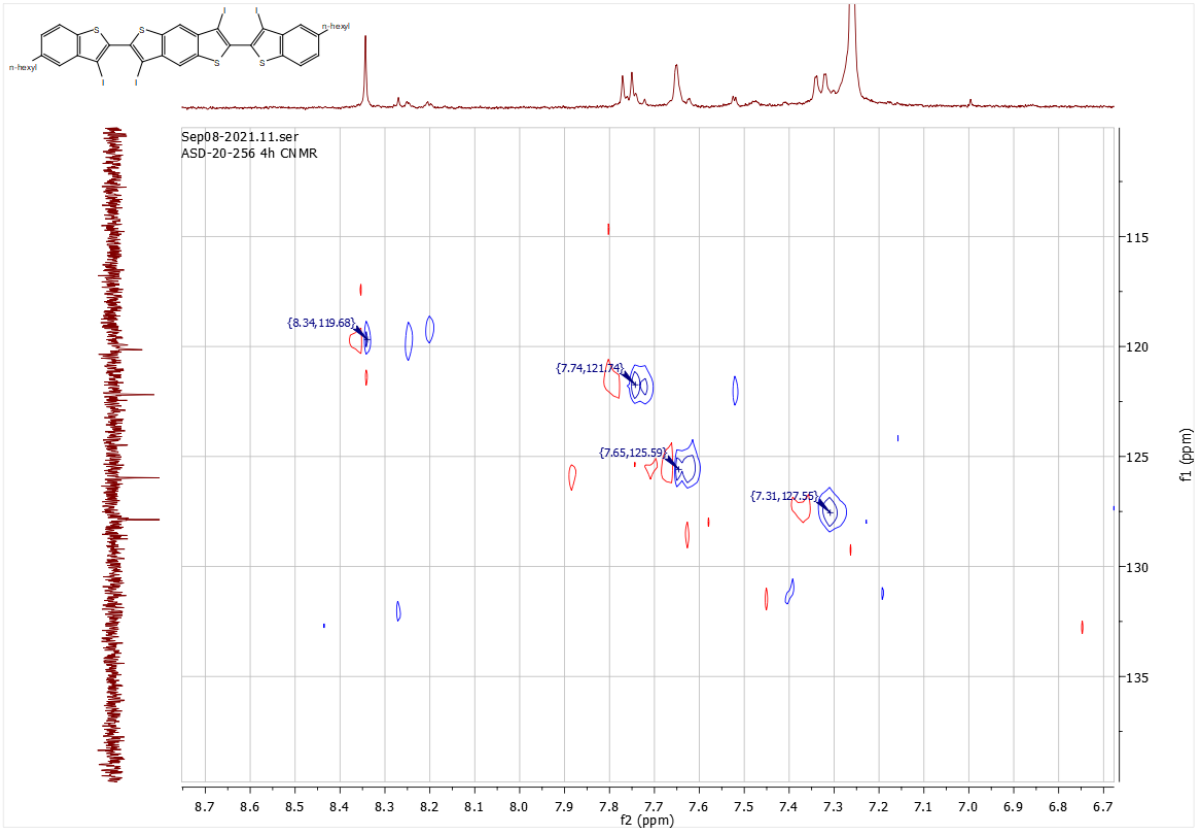
2,6-Bis(5-hexyl-3-iodobenzo[b]thiophen-2-yl)-3,7-diiodobenzo[1,2-b:4,5-b']dithiophene (410): ^{1}H NMR



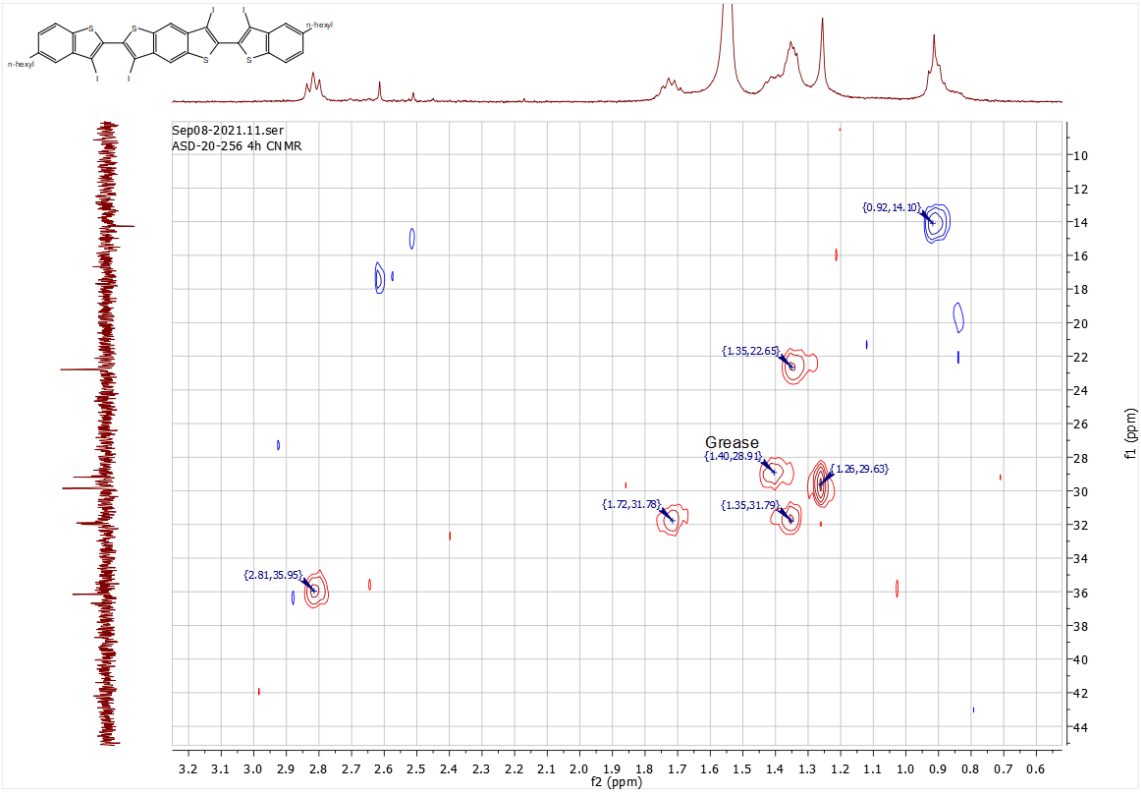
^{13}C NMR



HSQC aryl region

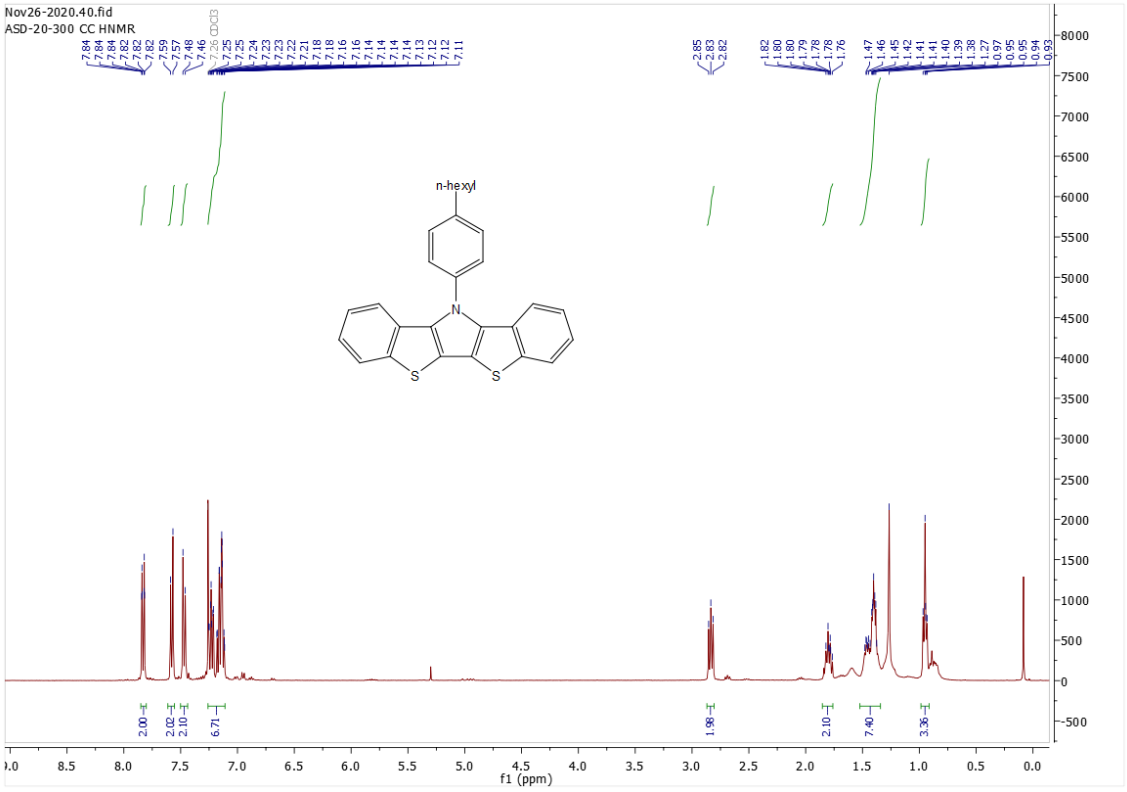


HSQC alkyl region

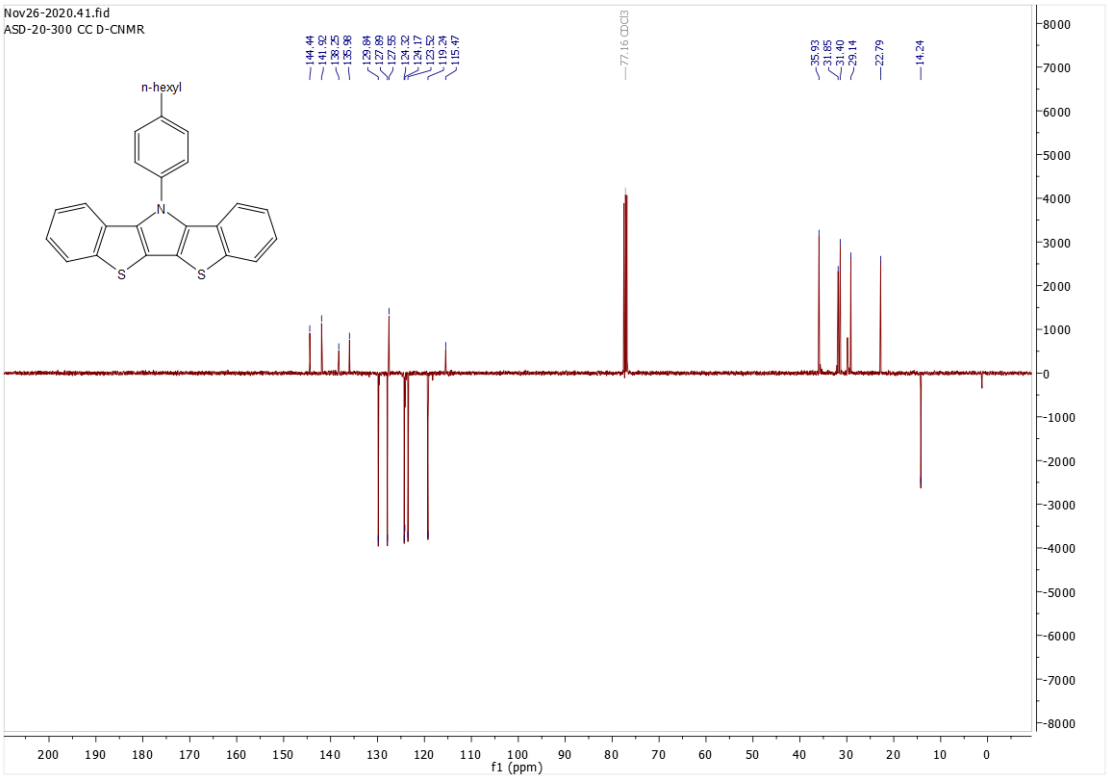


11-(4-Hexylphenyl)-11H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-d]pyrrole (414):

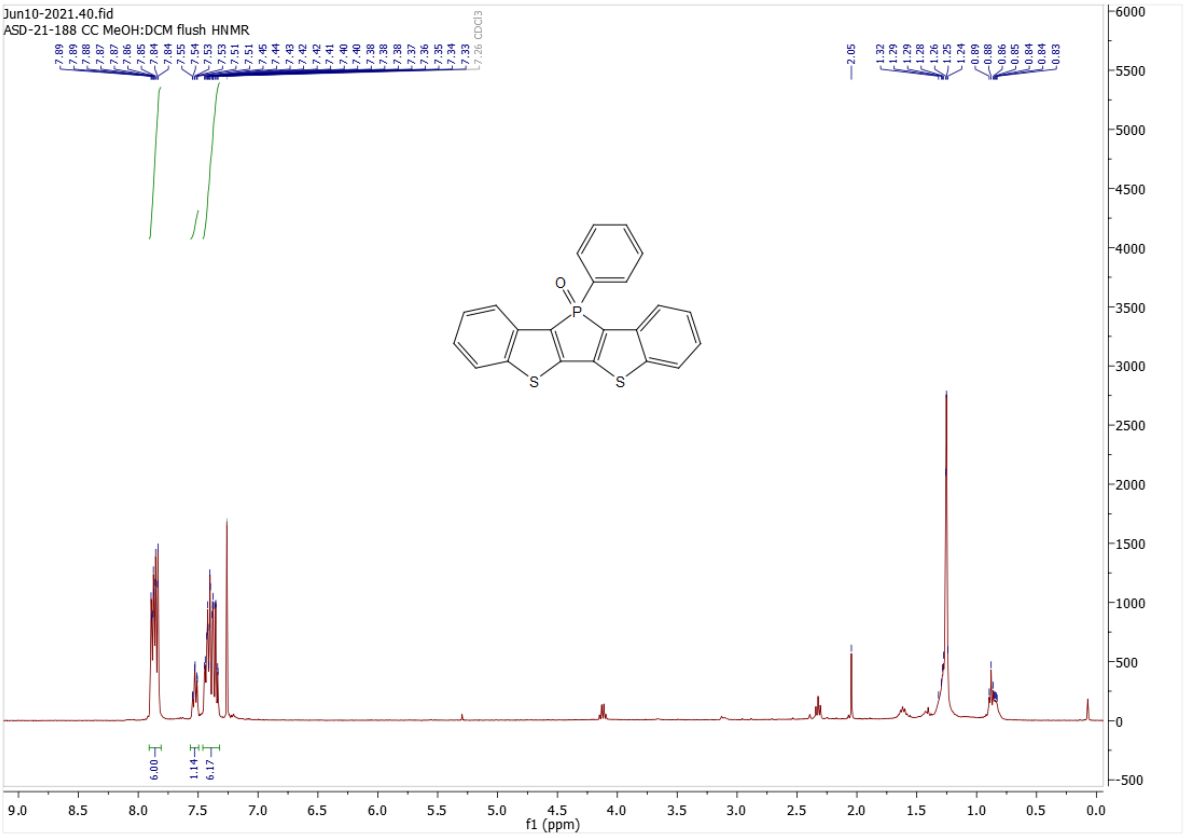
^{1}H NMR



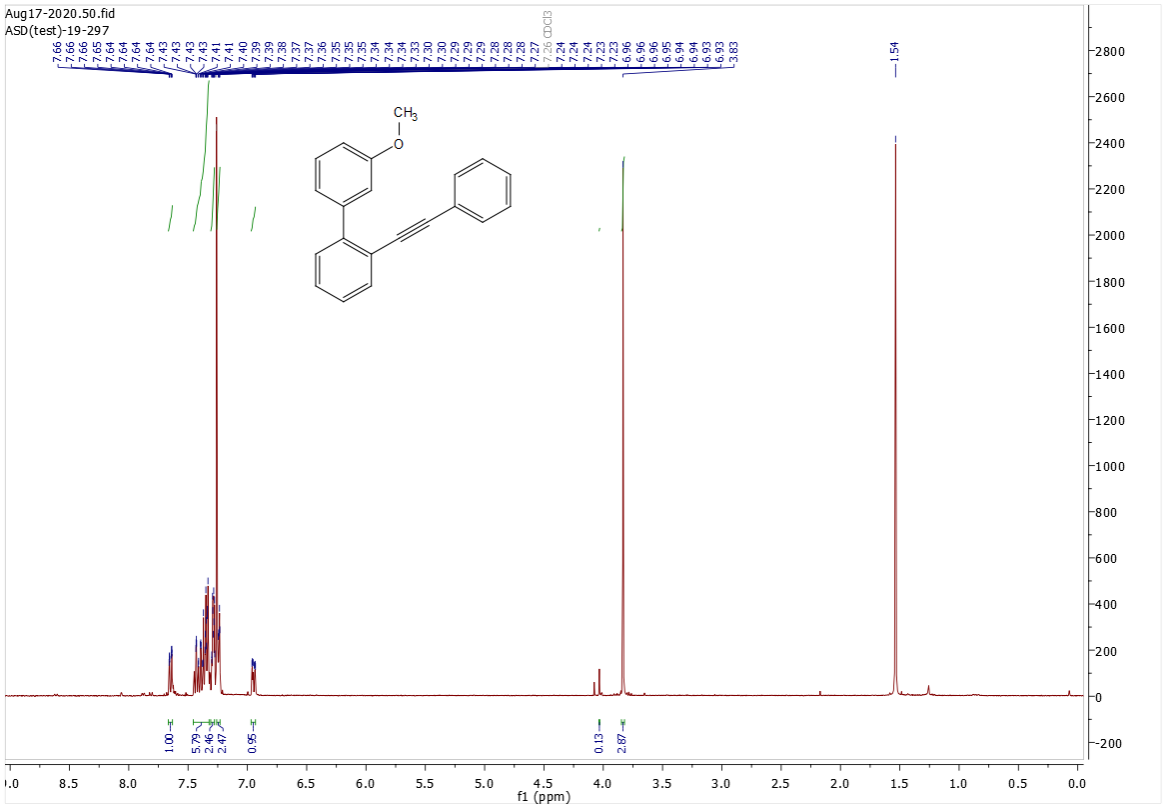
^{13}C NMR



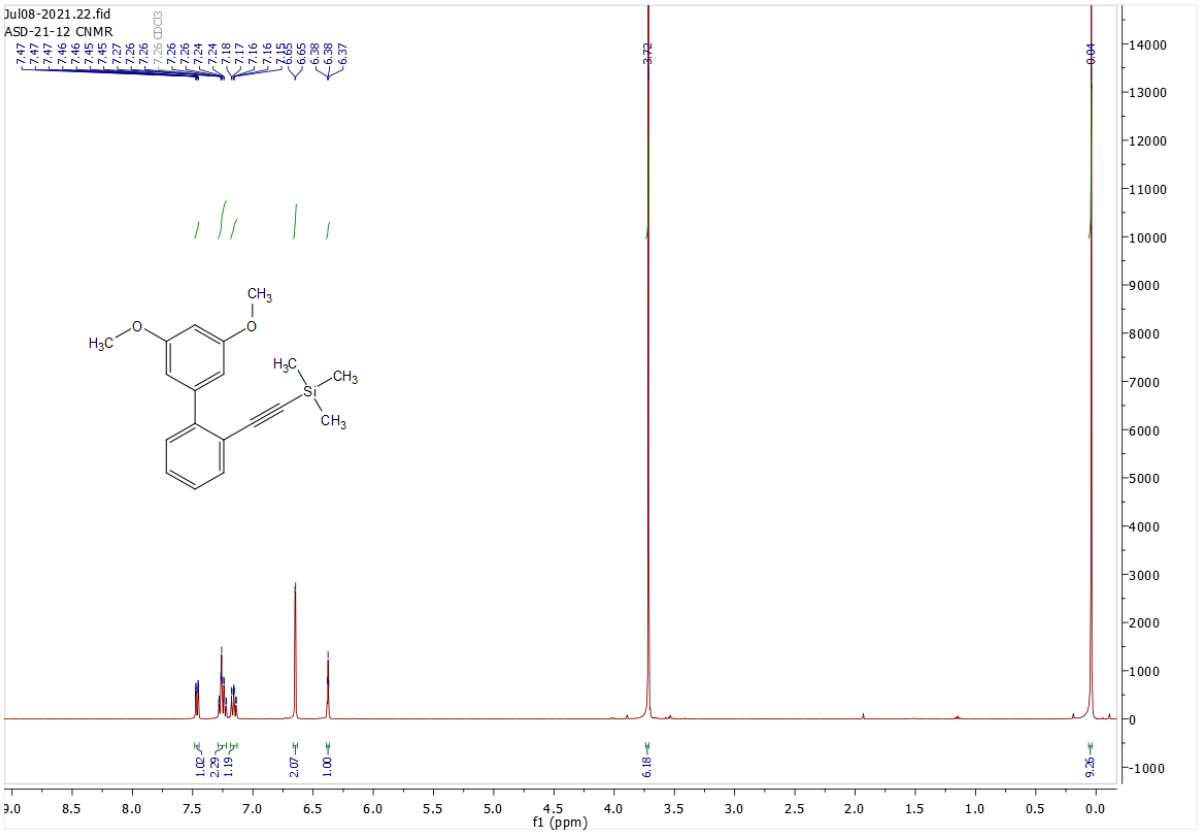
(423): ^{1}H NMR



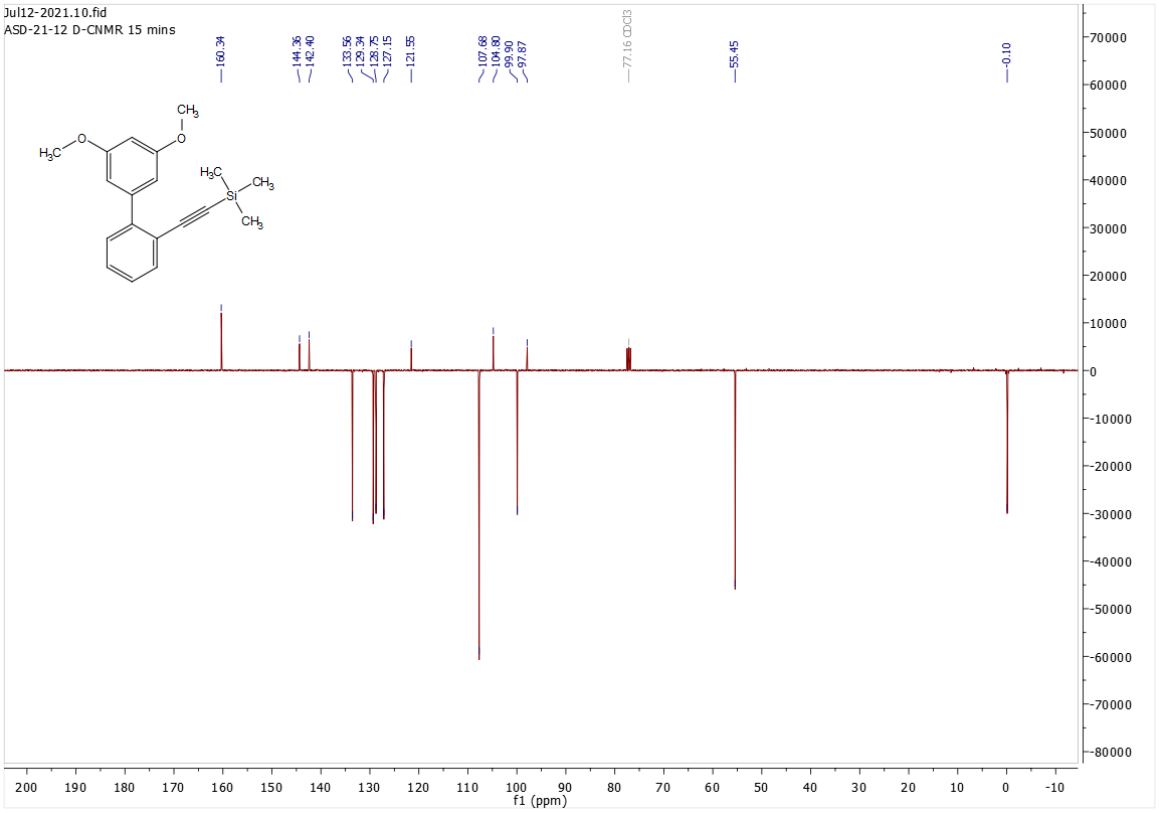
3'-Methoxy-2-(phenylethynyl)-1,1'-biphenyl (460): ^{1}H NMR



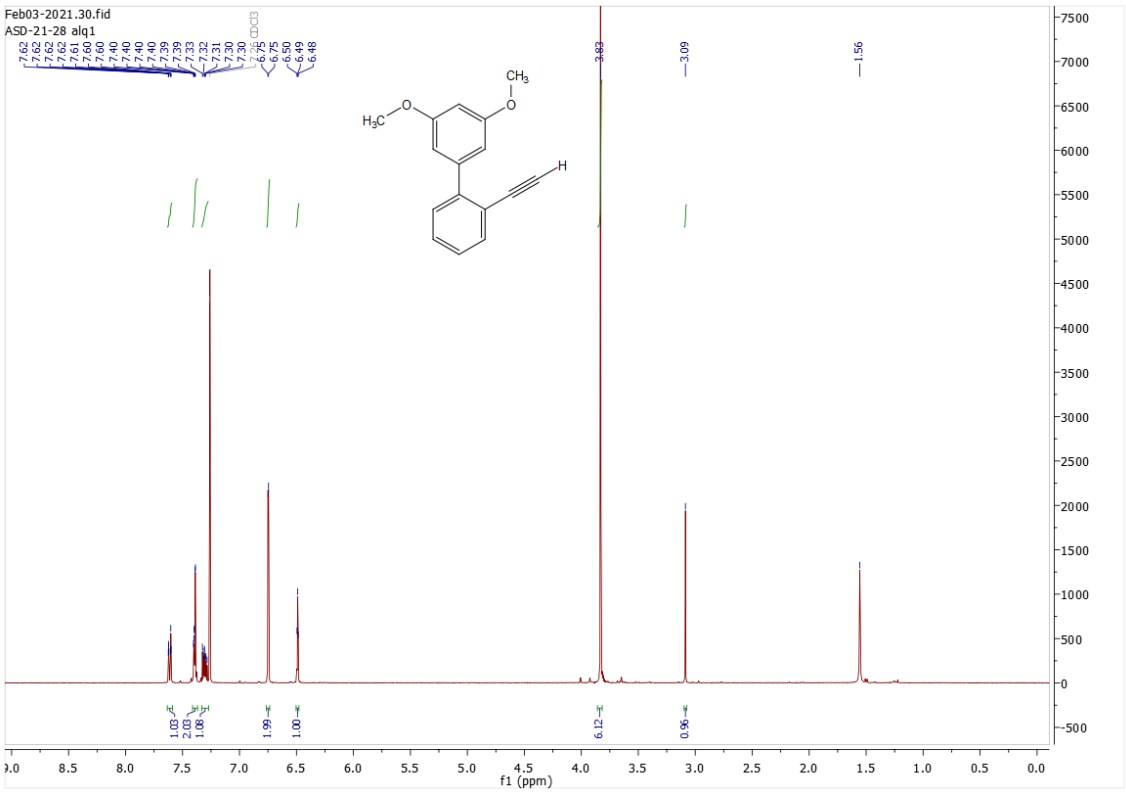
((3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)ethynyl)trimethylsilane (473): ^{1}H NMR



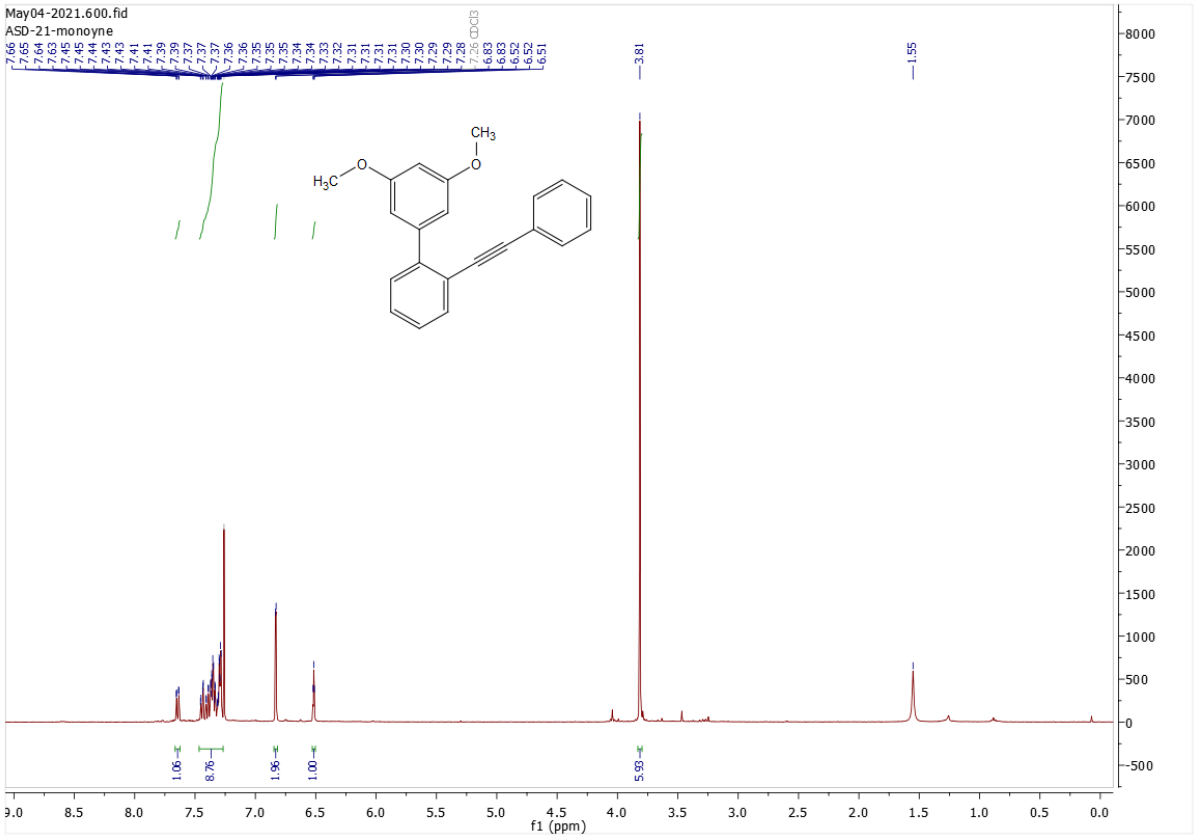
^{13}C NMR



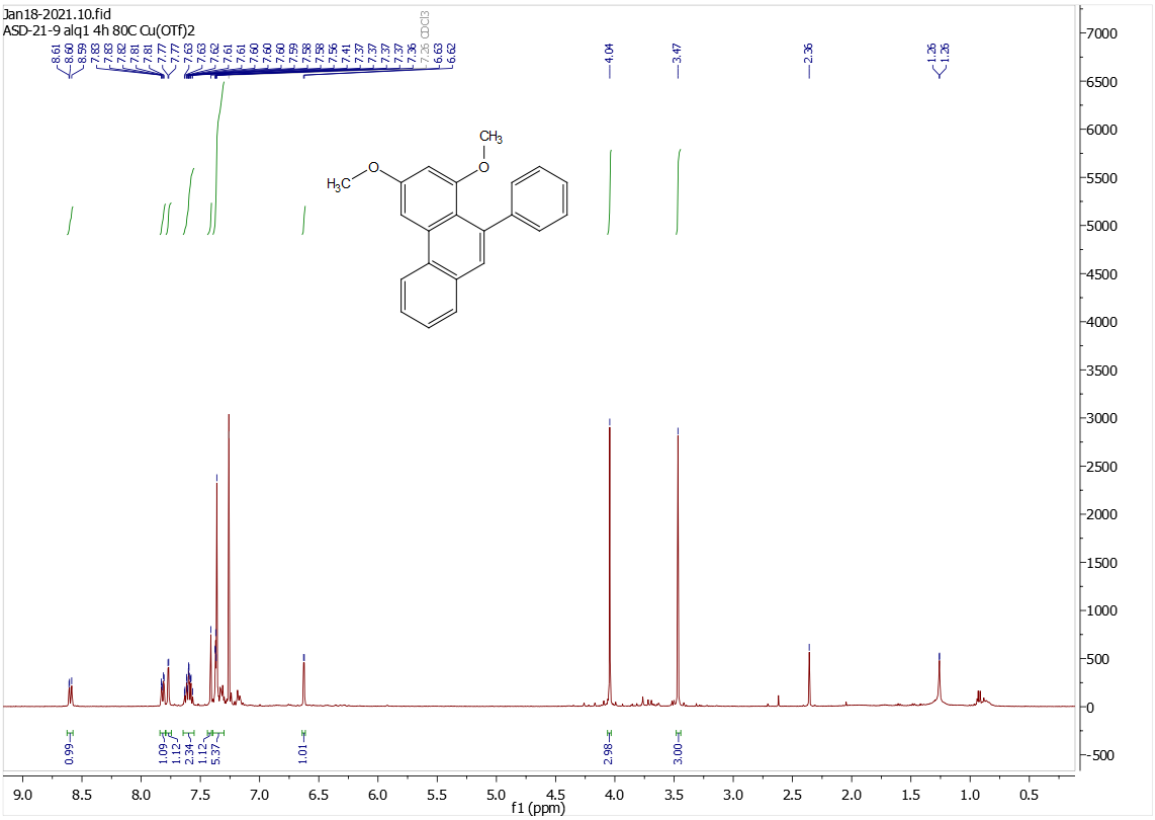
2-Ethynyl-3',5'-dimethoxy-1,1'-biphenyl (474): ^{1}H NMR



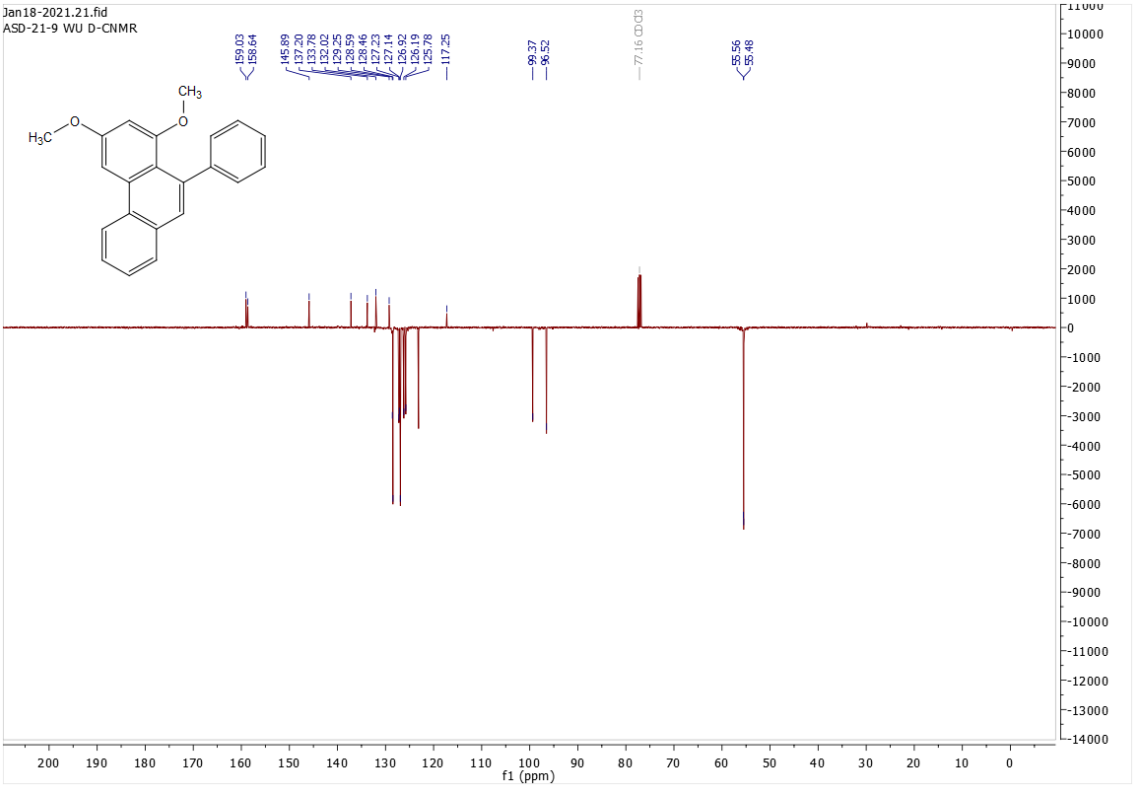
3',5'-Dimethoxy-2-(phenylethynyl)-1,1'-biphenyl (462): ^{1}H NMR



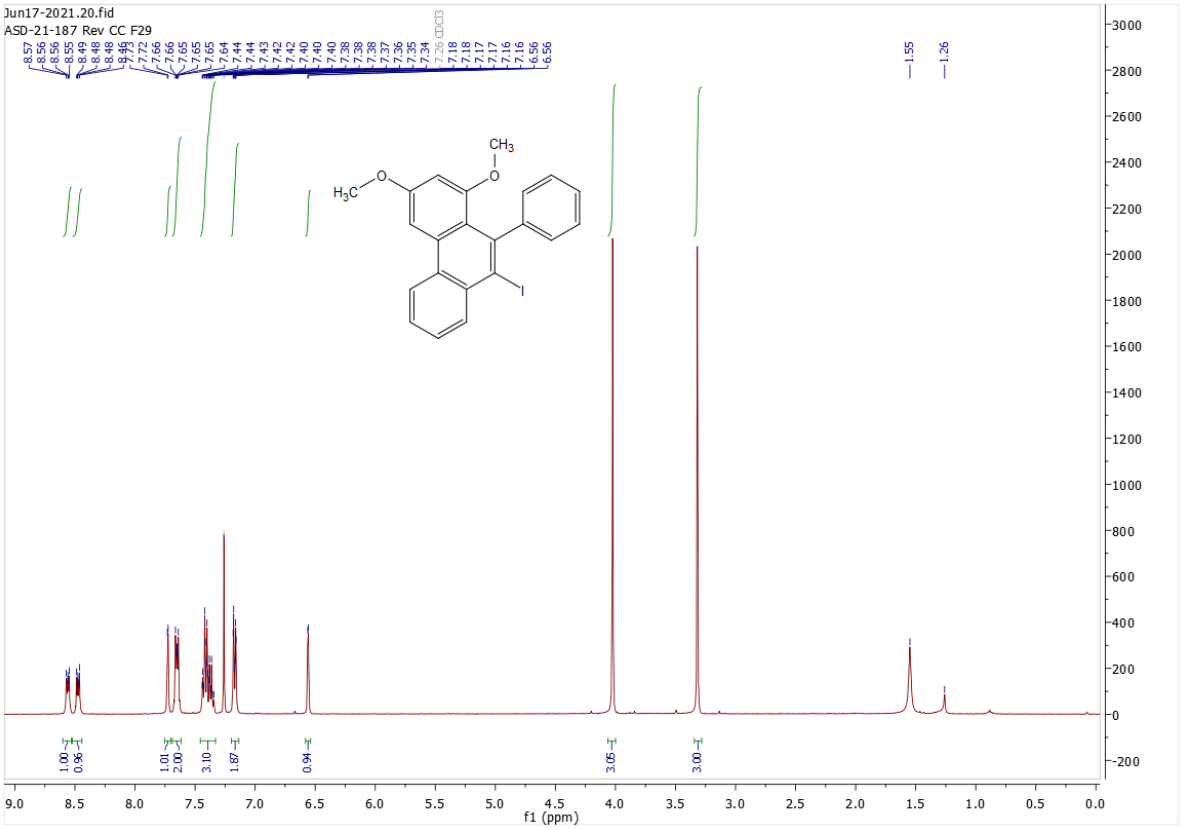
1,3-Dimethoxy-10-phenylphenanthrene (463): ^{1}H NMR



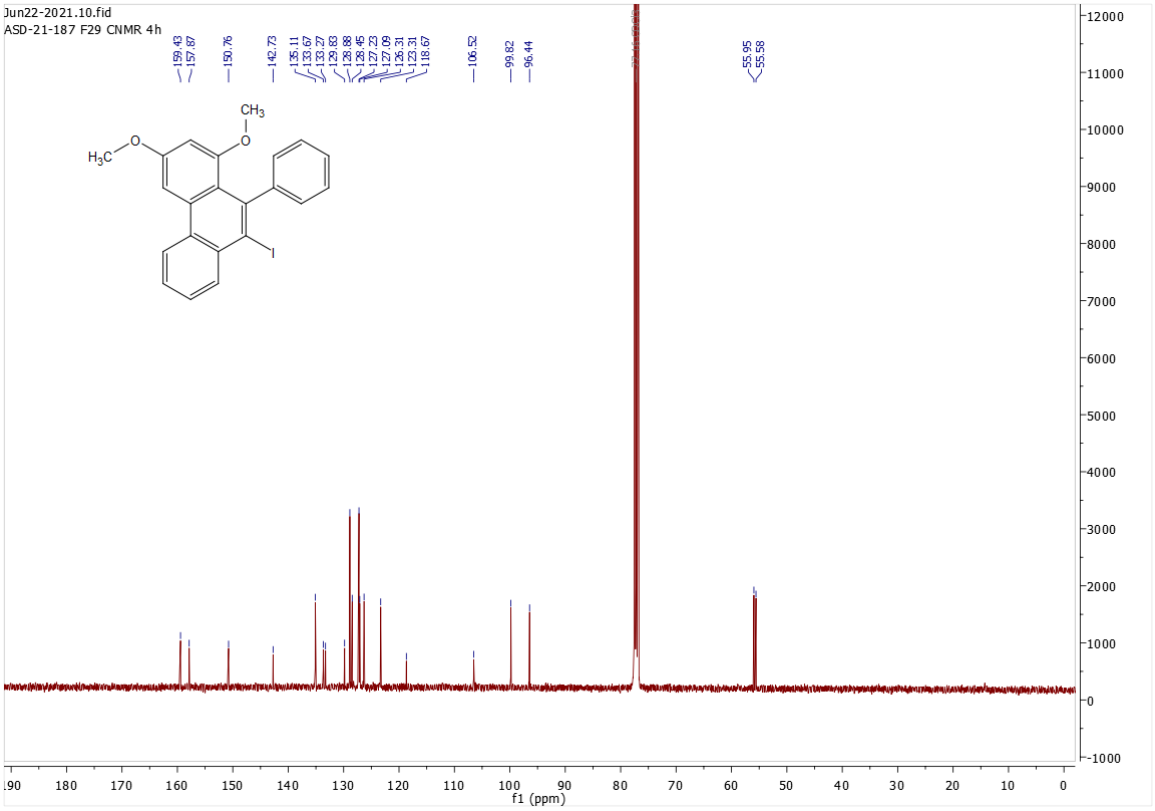
^{13}C NMR



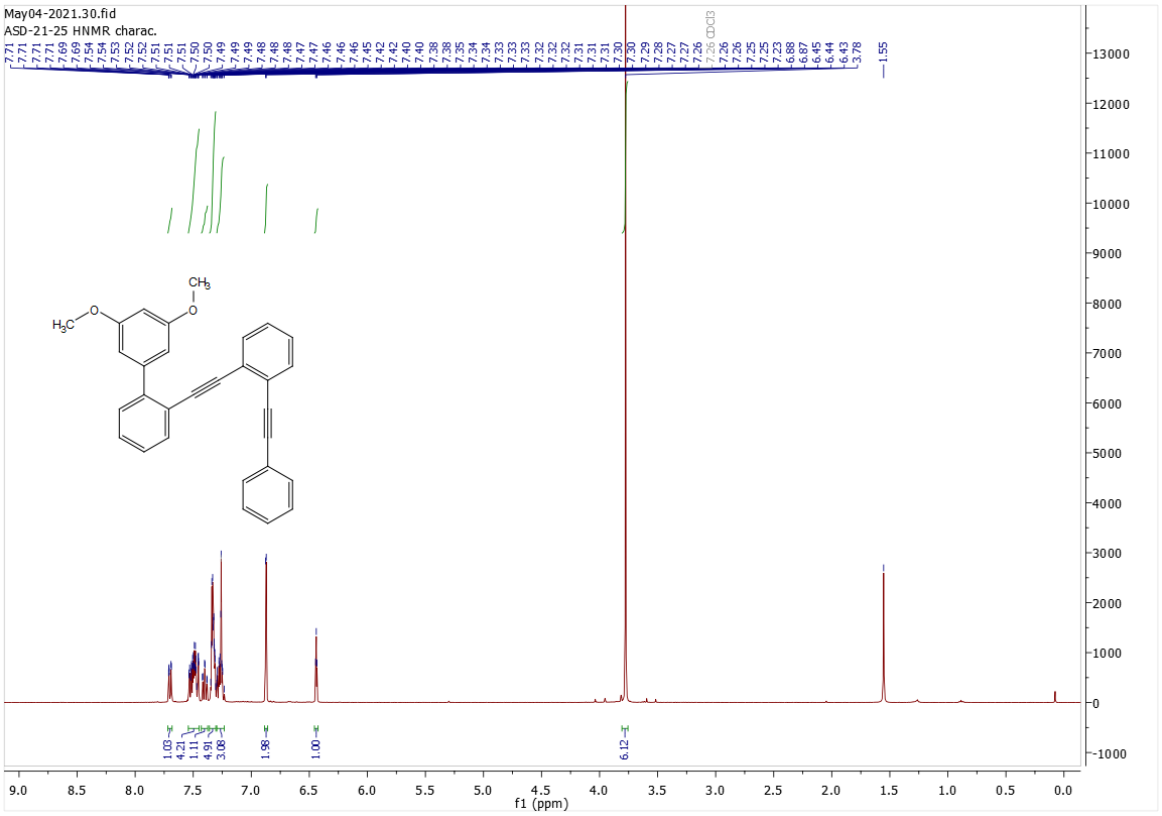
9-Iodo-1,3-dimethoxy-10-phenylphenanthrene (464): ^{1}H NMR



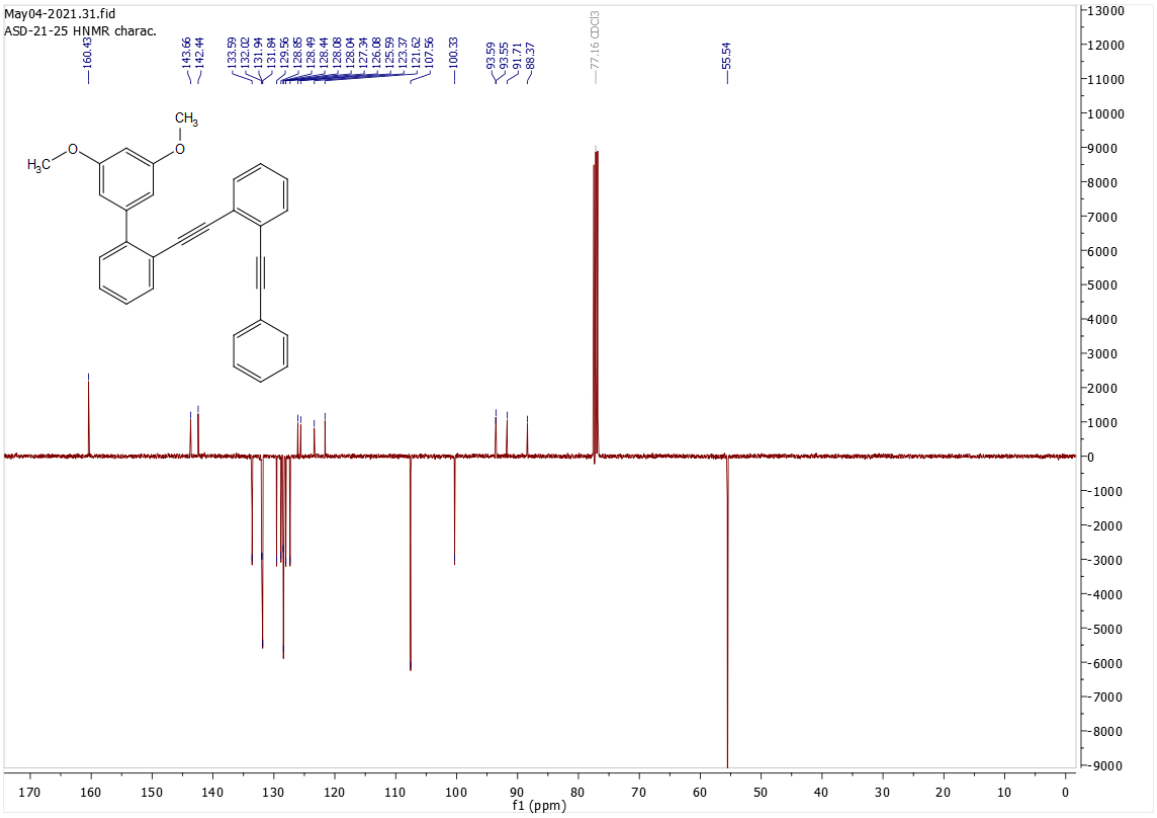
^{13}C NMR



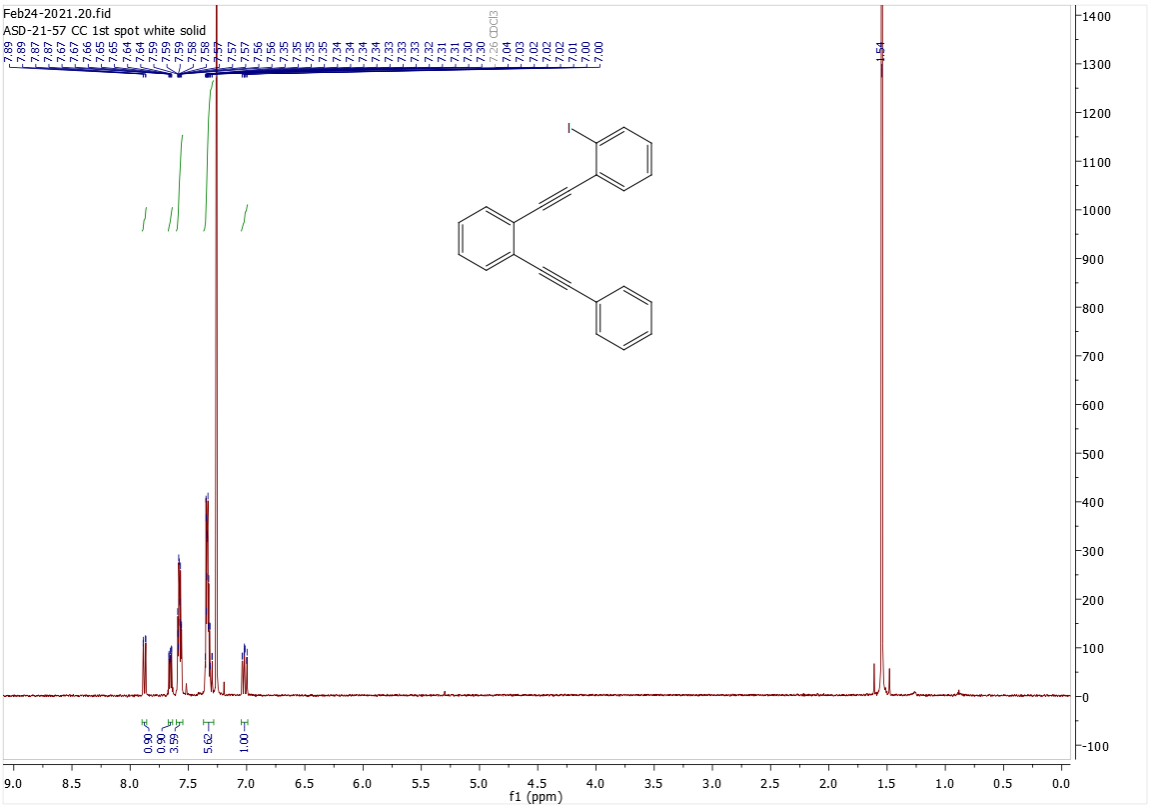
3',5'-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-1,1'-biphenyl (476): ^{1}H NMR



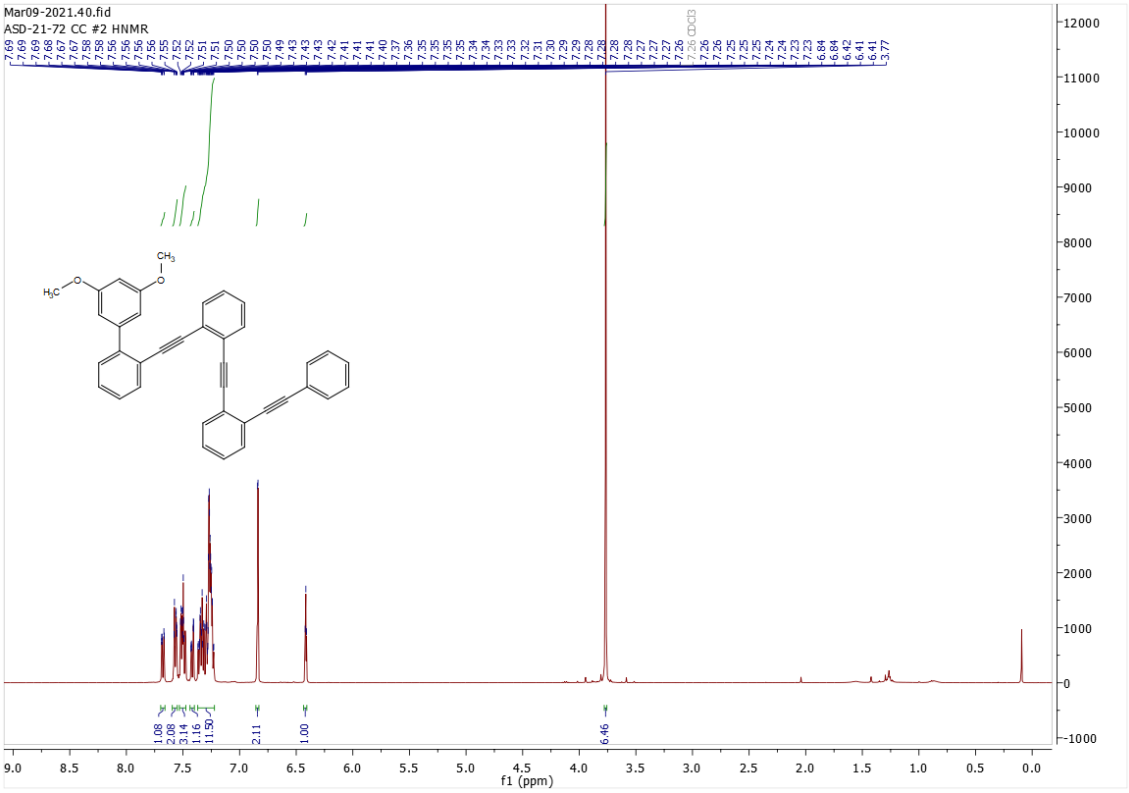
^{13}C NMR



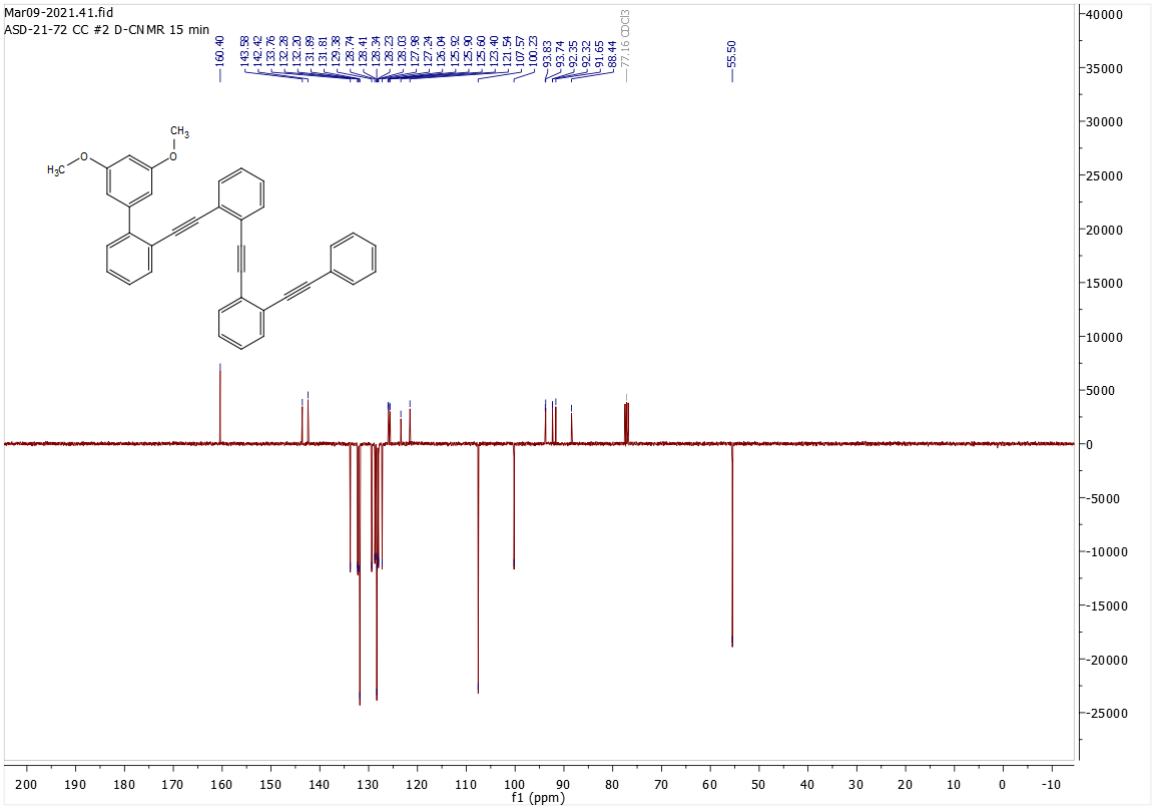
1-Iodo-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (483): ^{1}H NMR



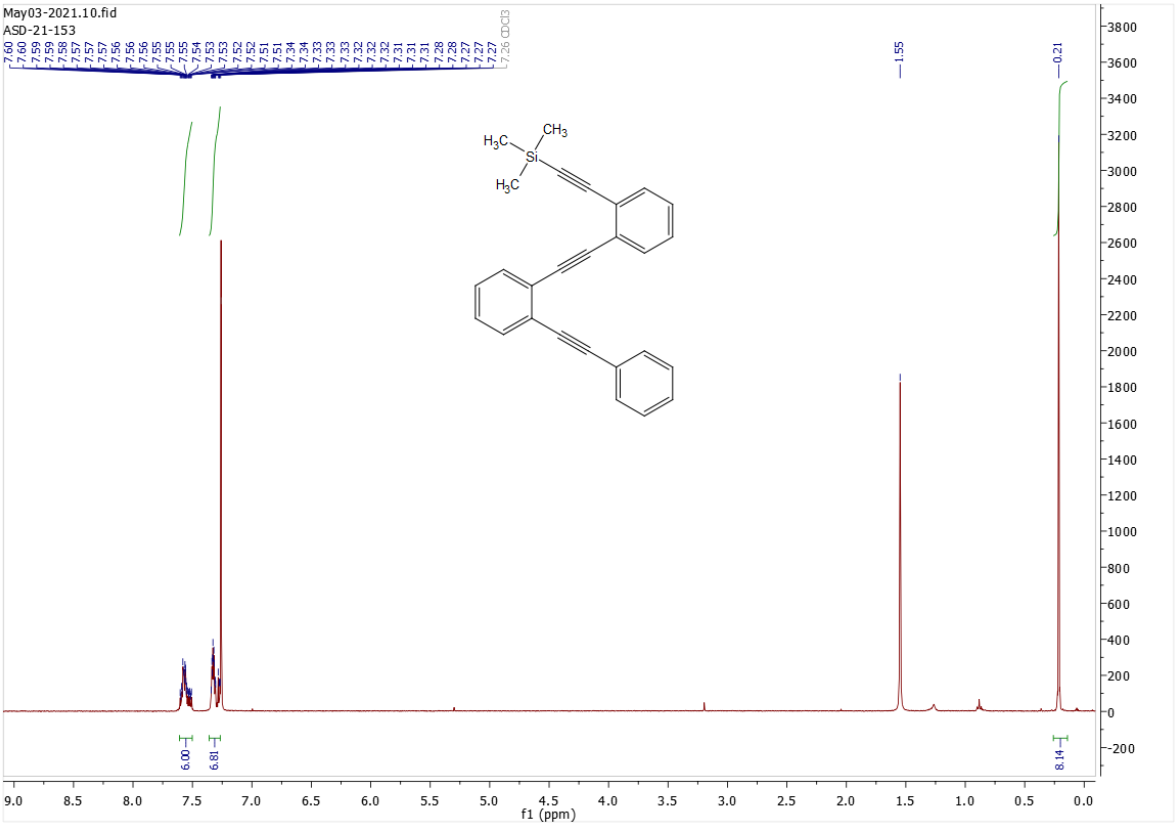
3',5'-Dimethoxy-2-((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,1'-biphenyl (477): ^{1}H NMR



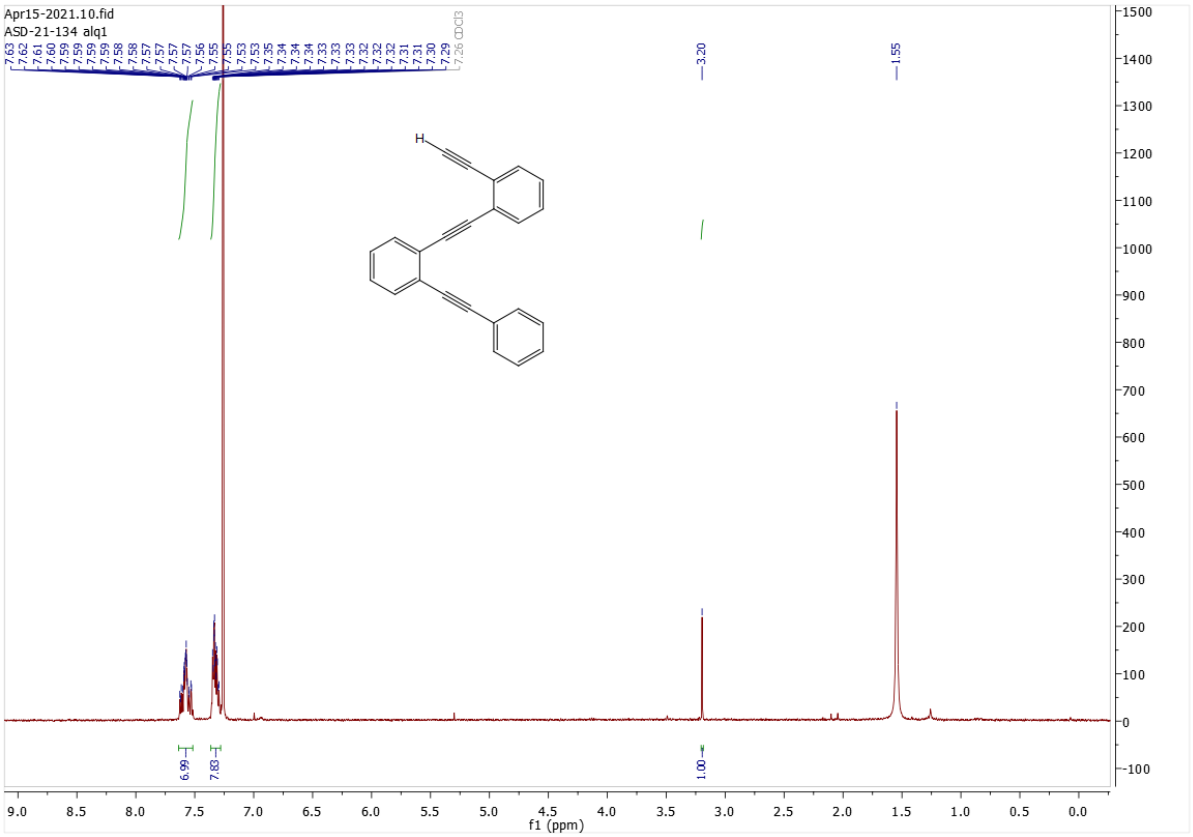
^{13}C NMR



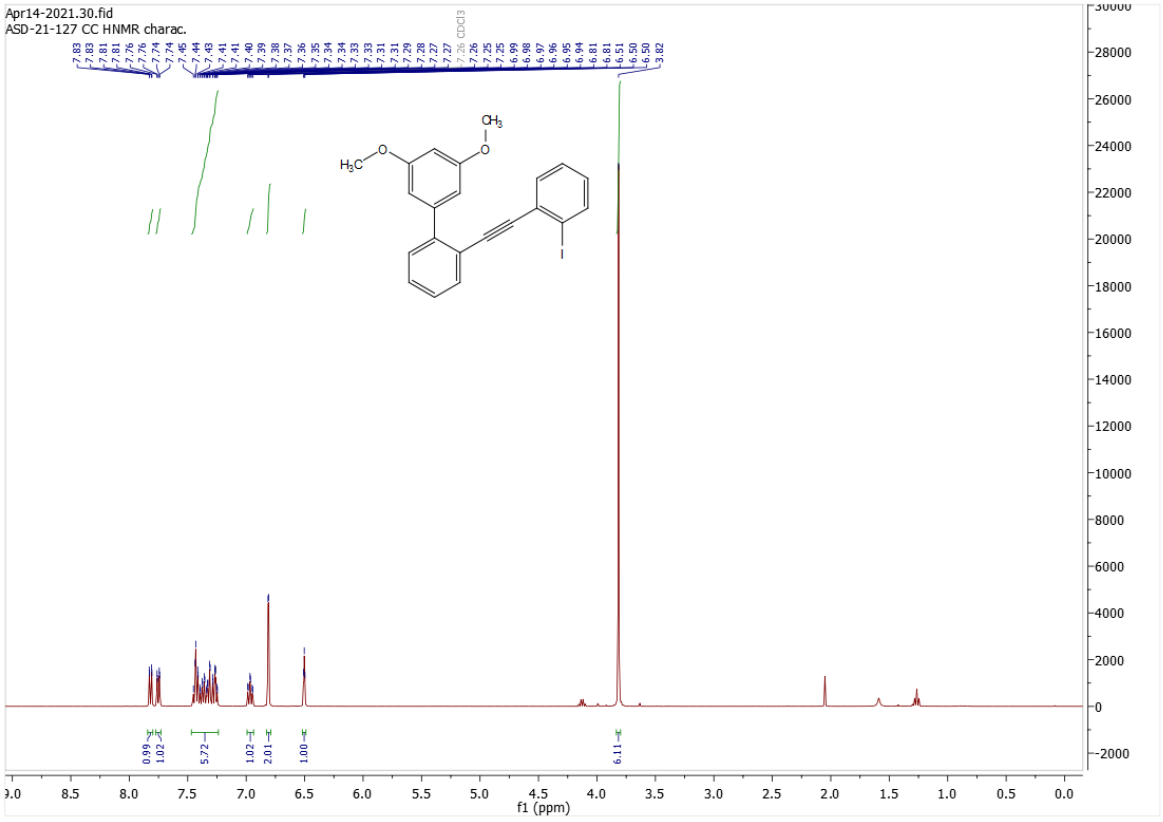
Trimethyl((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)silane (484): ^{1}H NMR



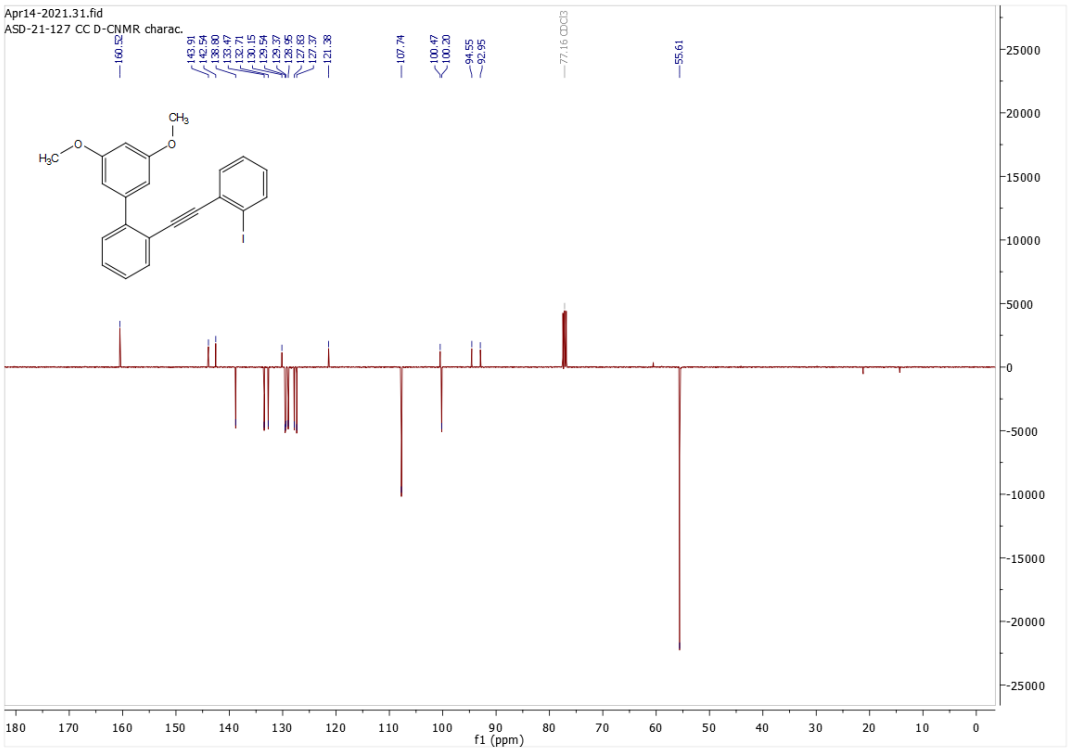
1-Ethynyl-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (485): ^{1}H NMR



2-((2-Iodophenyl)ethynyl)-3',5'-dimethoxy-1,1'-biphenyl (486): ^{1}H NMR

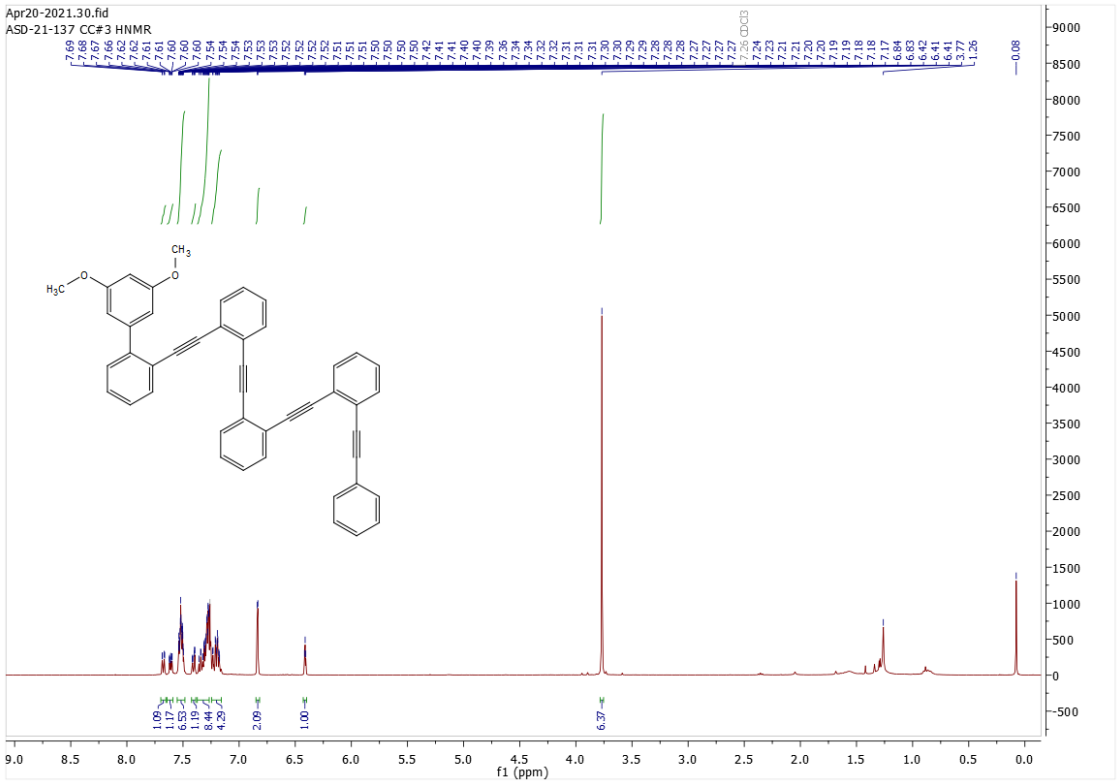


^{13}C NMR



3',5'-Dimethoxy-2-((2-((2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,1'-biphenyl (478):

^{1}H NMR



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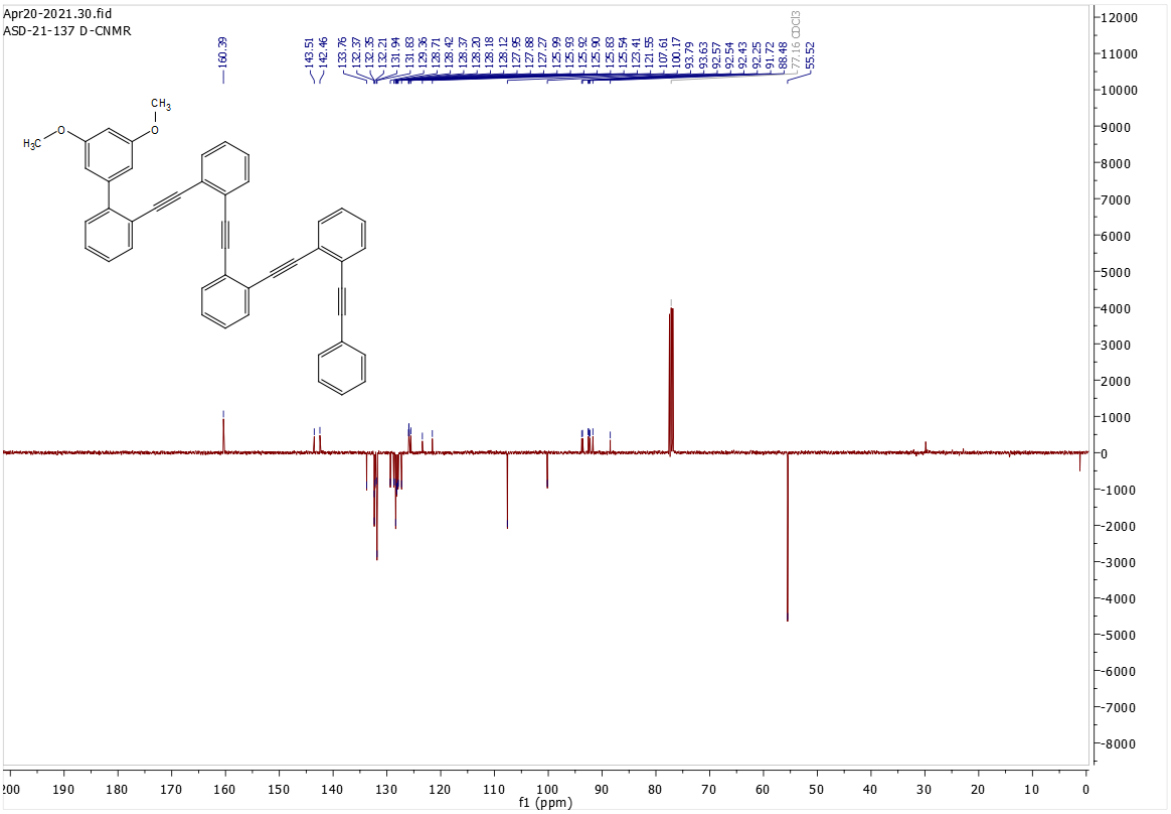
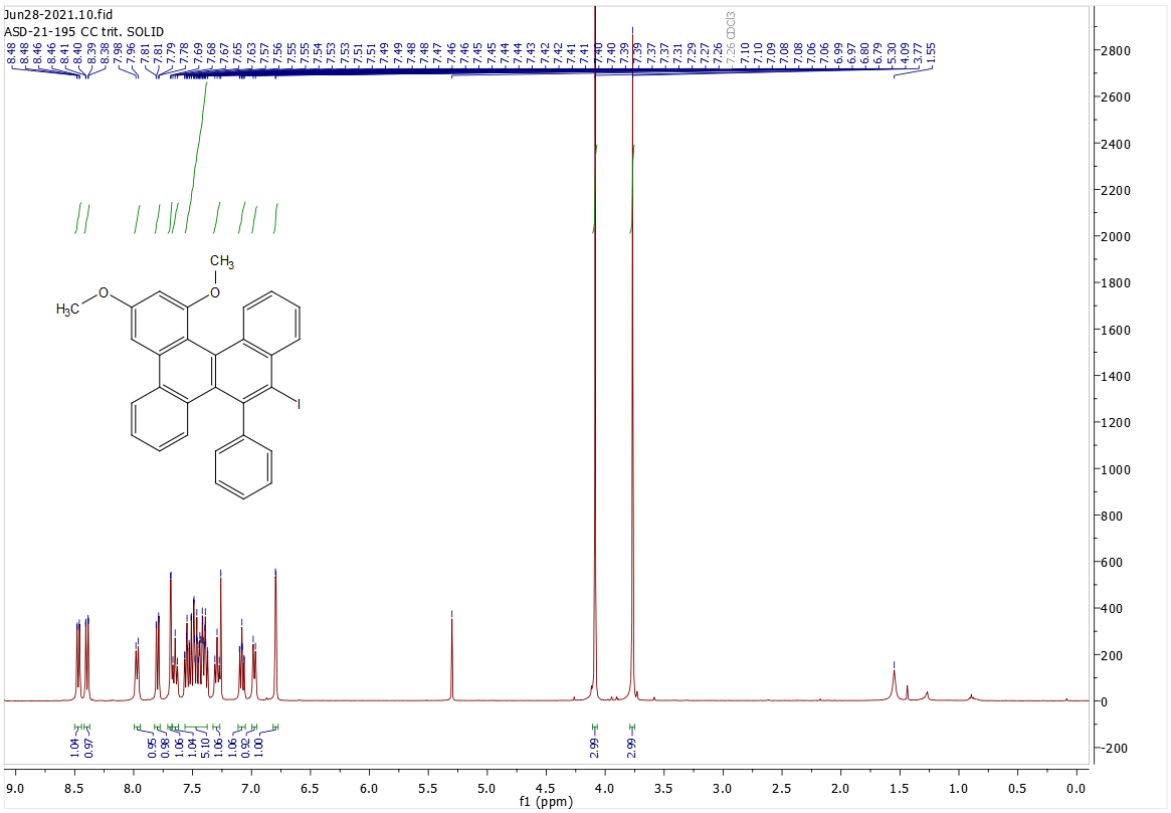


6-Iodo-11,13-dimethoxy-5-phenylbenzo[g]chrysene (488): ^{1}H NMR



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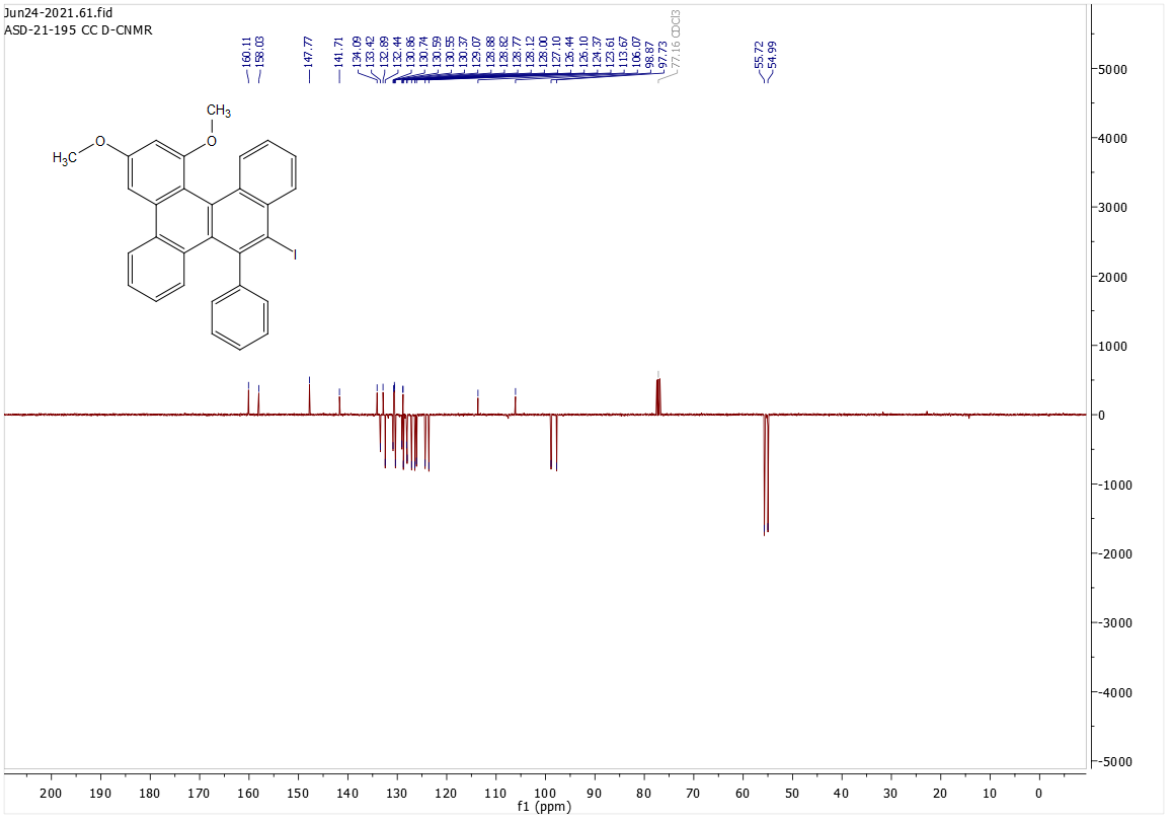
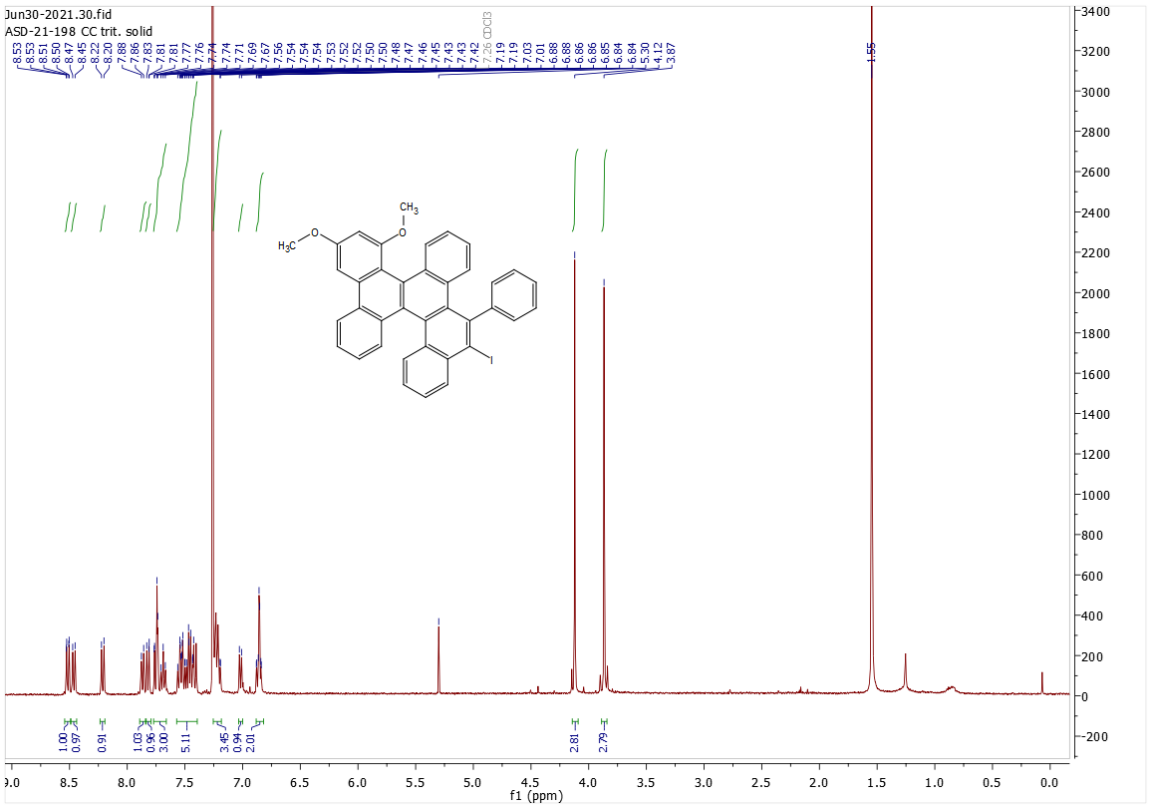
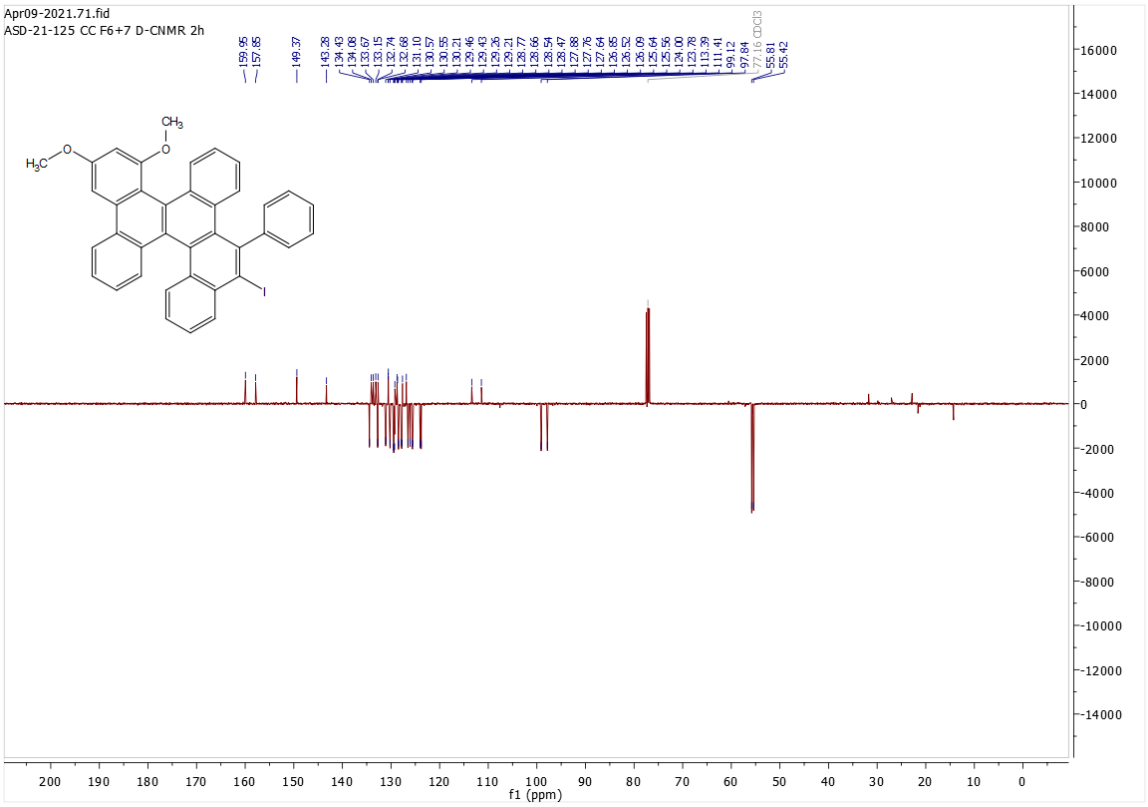


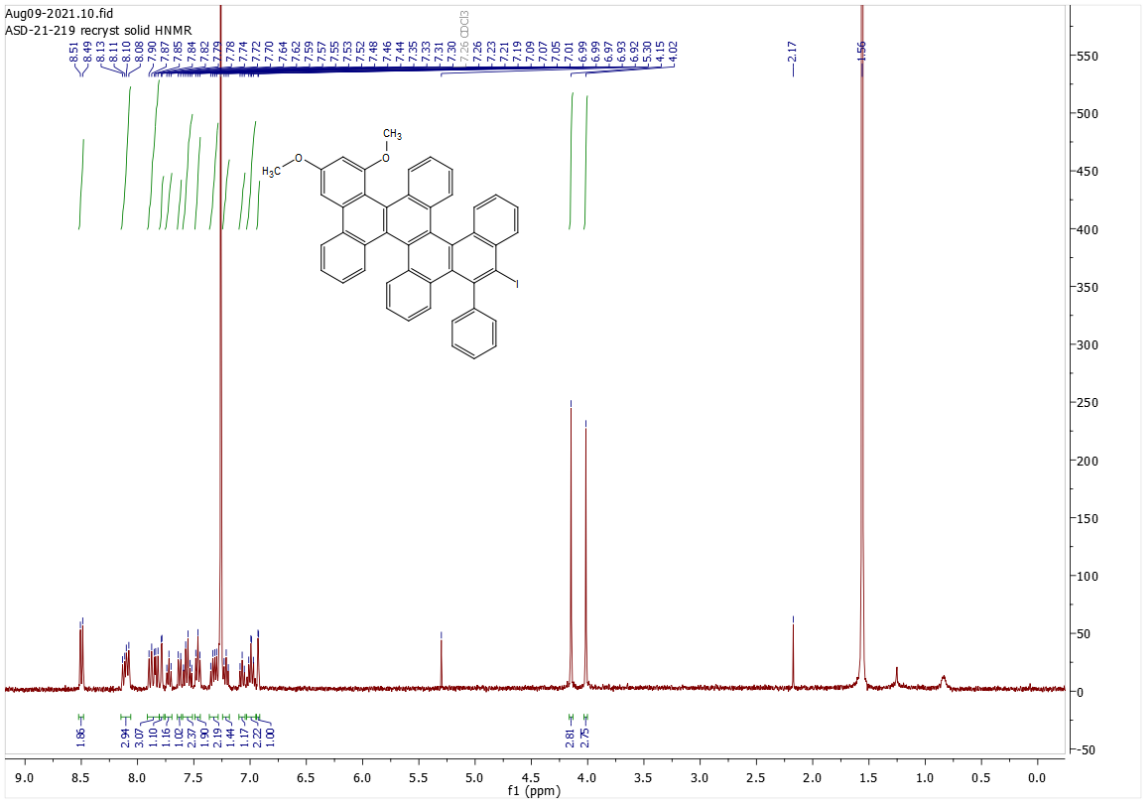
10-Iodo-2,4-dimethoxy-9-phenyltribenzo[c,g,p]chrysene (489): ^{1}H NMR



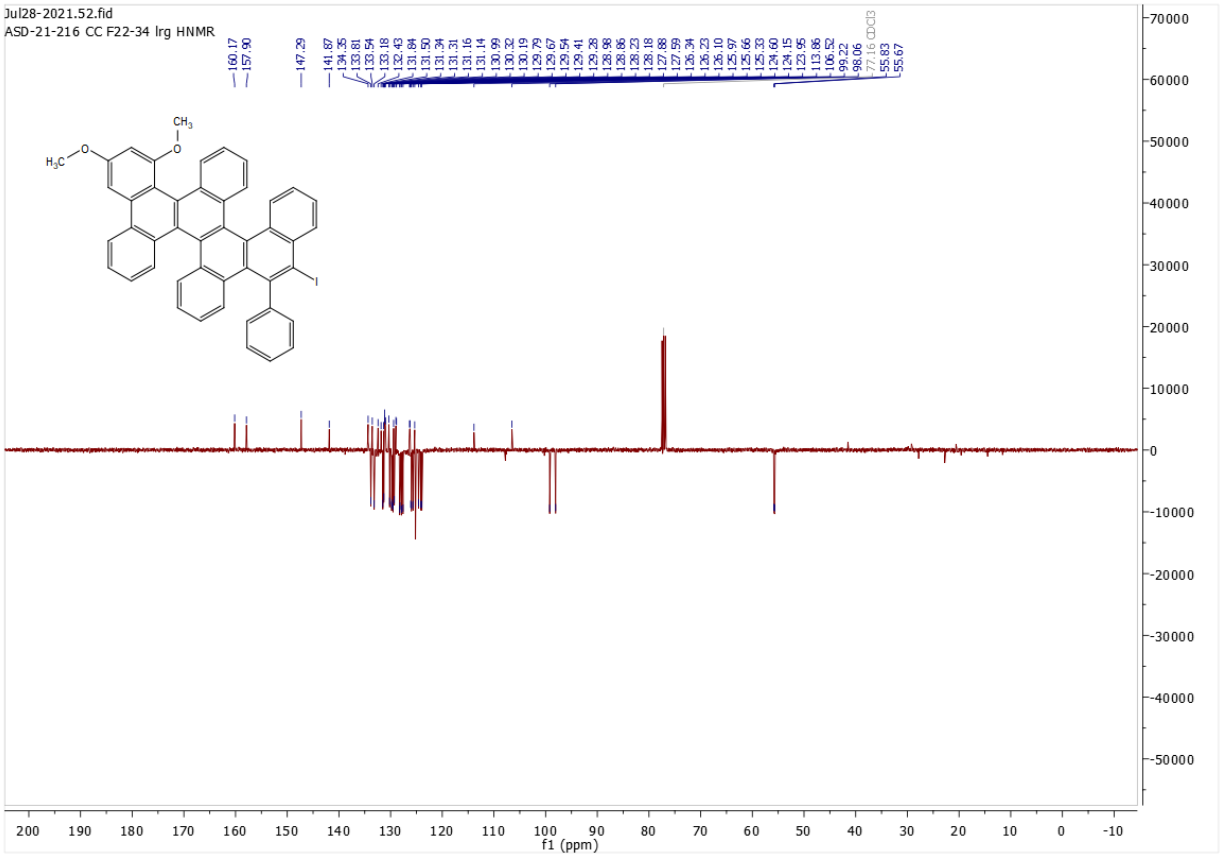
^{13}C NMR



10-Iodo-19,21-dimethoxy-9-phenyltetrabenzo[a,f,j,s]picene (490): ^{1}H NMR



^{13}C NMR


Jul28-2021.52.fid
ASD-21-216 CC F22-34 lrg HNMR
160.17
157.90
147.29
141.87
134.35
133.81
133.54
133.18
132.43
131.84
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131.34
131.31
131.16
131.14
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130.32
130.19
129.79
129.67
129.54
129.41
129.28
128.98
128.86
128.23
128.18
127.88
127.59
126.34
126.23
126.10
125.97
125.66
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124.60
124.15
123.95
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99.22
98.06
77.16 CDCl3
55.83
55.67
CH3
O
H3C
O
I
70000
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40000
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20000
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0
-10000
-20000
-30000
-40000
-50000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7.2 Appendices B: Published journal article

OL | Organic Letters

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Polyynes to Polycycles: Domino Reactions Forming Polyfused Chalcogenophenes

Annaliese S. Dillon and Bernard L. Flynn*

Cite This: *Org. Lett.* 2020, 22, 2987−2990 Read Online

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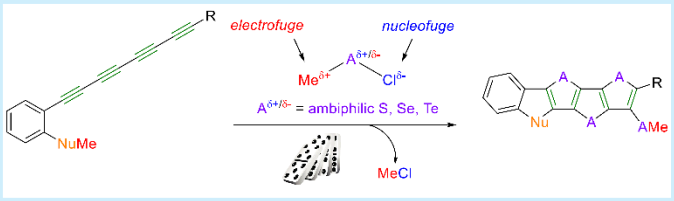
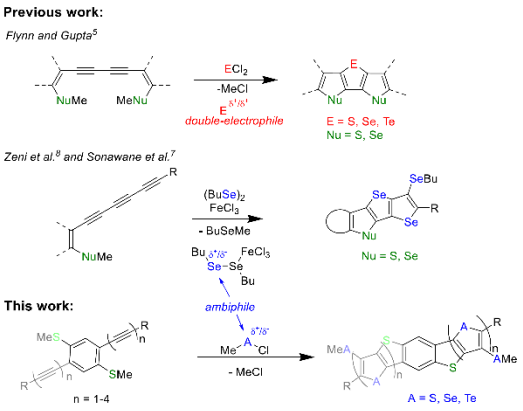


ABSTRACT: Polyfused chalcogenophenes are prepared in one step through polyelectrophilic cyclization of polyynes using the ambiphilic reagent MeACl (A = S, Se, or Te). Up to four new rings have been generated under mild conditions, including thiophenes, selenophenes, and tellurophenes.

Linearly (3,2-b) fused chalcogenophenes have emerged as extremely valuable functional π-systems in exciton science, finding applications in organic solar cells, organic light-emitting diodes, and semiconductors.[1] To date, the exploration of chalcogenophenes in materials science has been dominated by thiophenes; however, considerable interest lies in exploiting the superior properties of the heavier and more metallic chalcogens, Se and Te, and their associated heterocycles, selenophenes and tellurophenes.[2] While synthetic approaches to polyfused thiophenes are reasonably well developed,[1] these do not always translate well to selenophenes and even less so to tellurophenes. Indeed, despite the significant interest in tellurophenes in materials science, there are no previous reports of three or more contiguously fused tellurophenes.[3]

An attractive strategy for gaining direct access to polyfused chalcogenophenes is the conversion of polyynes to polycycles in a single step.[4−8] Recent advances in this approach have been achieved through exploiting the capacity of chalcogens to operate as either double electrophiles in double-electrophilic cyclization (DEC) in the form of ACl_2 (A = chalcogen) or ambiphiles (possessing both electrophilic and nucleophilic reactivity) in Fe-promoted cascade cyclization (Scheme 1, previous work).[5−8] In the case of the cascade cyclization, $FeCl_3$ increases the electrophilicity of dibutyldiselenide conferring ambiphilic reactivity. Herein, we report the use of simple chloro methyl chalcogens (MeACl, where A = S, Se, or Te) as highly effective ambiphiles in polyelectrophilic cyclization (PEC) reactions, with excellent atom economy requiring no other reagents to gain efficient access to up to four new chalcogen-containing rings, including examples of contiguously fused tellurophenes.

Scheme 1. Electrophilic Cyclization of Diynes and Polyynes



For this study, we prepared a series of alkyne and polyyne substrates **1** from 2-iodothioanisole (Scheme 2). These syntheses were accomplished in one or three steps and involved Sonogashira couplings, silyl deprotections, and Cadiot−Chodkiewicz couplings using terminal and bromo alkynes

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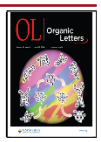
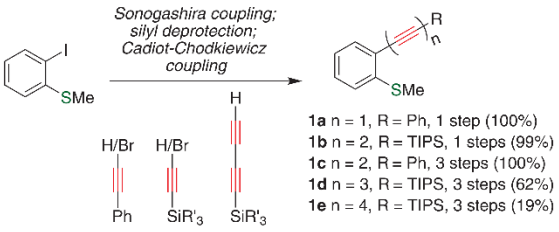


https://dx.doi.org/10.1021/acs.orglett.0c00733
Org. Lett. 2020, 22, 2987−2990

Scheme 2. Synthesis of Alkynyl Substrates 1

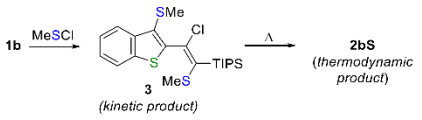


bearing phenyl or silyl (SiR'_3 = TMS or TIPS) substituents (see the Supporting Information for details). In this way, a series of mono-, di-, tri-, and tetraynes were efficiently prepared for use in our PEC studies with ambiphilic MeACl (A = S, Se, or Te) reagents.

The chalcogen reagents (MeACl) are most atom economically formed by addition of $Cl_{2(g)}$ to the associated dimethyl dichalcogen (MeA-AMe). However, for our lab-scale studies, SO_2Cl_2 has been employed as a more convenient chlorinating agent on a small scale. Thus, SO_2Cl_2 was added to MeA-AMe in dichloromethane (DCM) to generate MeACl [with loss of $SO_{2(g)}$] for direct use. These DCM solutions of MeACl were first evaluated as suitable electrophiles by reaction with simple 2-(phenylethynyl)-thioanisole **1a** (n = 1; R = Ph). Efficient formation of benzochalcogenophenes **2aS** (88%), **2aSe** (70%), and **2aTe** (81%) reflected effective formation of each respective reagent MeACl (Scheme 3). This efficient initial installation of a Me-A group also opened up the possibility of consecutive cyclizations (PEC reactions) for polyynes **1b–e**. These PEC reactions with MeACl were generally successful and were most successful for A = Se and Te (Scheme 3).

Despite performing well in the monocyclization of **1a** to give **2aS**, PEC of diyne **1c** (R = Ph) with MeSCl gave a complex mixture (not shown). By contrast, reaction of MeSCl with diyne **1b** (R = TIPS) at 0 °C initially gave a monocyclized product containing a MeS/Cl adduct **3** (kinetic product) (Scheme 4). This material was successfully converted into the fully cyclized benzothienothiophene **2bs** (thermodynamic product, 49%) upon heating. The mechanism of this reaction is discussed below.

Scheme 4. Formation of 2bS



This issue of competing addition of MeACl was much less apparent in PEC reactions involving MeSeCl and MeTeCl. These reactions generally went to completion between −20 and 0 °C for MeSeCl and at rt for MeTeCl, giving the respective chalcogen-containing heteroacenes in good yield (50−100%). Only in the case of tetracyclization to form **2eSe** was the fully annulated product formed in a complex mixture of other byproducts (suspected MeSe/Cl addition products). Heating this reaction mixture to reflux in DCE for 48 h led to a significant increase in the level of formation of **2eSe** at the expense of byproducts giving semipure **2eSe** in 50% yield by ^{1}H NMR. Chromatographic separation of **2eSe** from these byproducts proved to be difficult, and recrystallization afforded pure **2eSe** in 10% yield only.

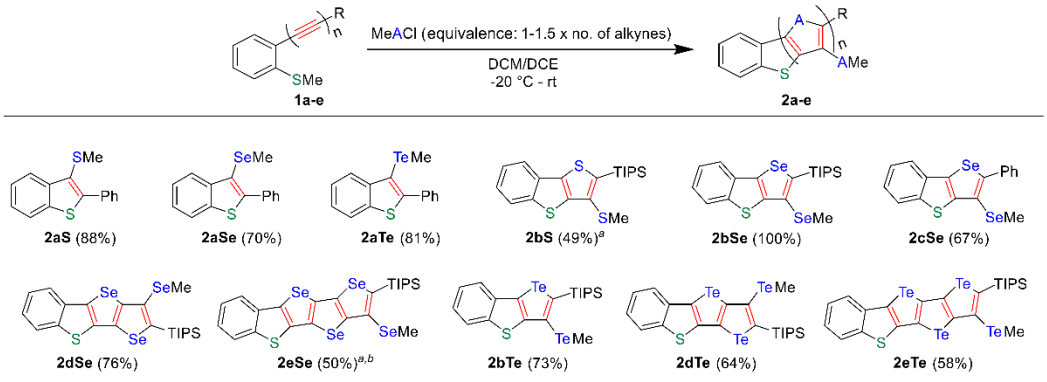
We next considered the possibility of generating extended heteroacenes through bidirectional PEC (biPEC). For this purpose, we generated two substrates, tetraynes **6** and **9** (Scheme 5). Tetrayne **6** was prepared from 1,4-dibromo-2,5-diiodobenzene **5** by initial Sonogashira coupling of TIPS-diyne (TIPS-CC-CC-H), followed by lithiation and thiomethylation to give **6** in an overall 90% yield (from **5**). Preparation of tetrayne **9** commenced with Sonogashira coupling of **8**[9] to TIPS-diyne, followed by desilylation and homocoupling, giving **9** in 67% yield (from **8**).

Both the diverging biPEC, **6** + MeSeCl → **7Se** (30%), and the converging biPEC, **9** + MeACl → **10S** (61%) and **10Se** (81%), were successful. The modest yield of **7Se** was attributed to the poor solubility of the product.

Attempts to perform the diverging and converging biPEC with MeTeCl were complicated by poor solubility, in the case of the reaction of **6**, and the formation of complex mixtures, in the case of the reaction of **9**.

The structural characterization of these heteroacenes is reflected mostly in the ^{13}C NMR, where the alkyne carbons are replaced with diagnostic chalcogenophene carbon reso-

Scheme 3. Polyelectrophilic Cyclization (PEC) of Polyynes 1 to Chalcogenophenes 2



[a]Reaction required heating of an intermediate chlorochalcogen addition product to bring the cyclization to completion (see the main text). [b]The yield shown is based on conversion in the ^{1}H NMR; the isolated yield from recrystallization was 10% (all other yields are isolated yields).

https://dx.doi.org/10.1021/acs.orglett.0c00733
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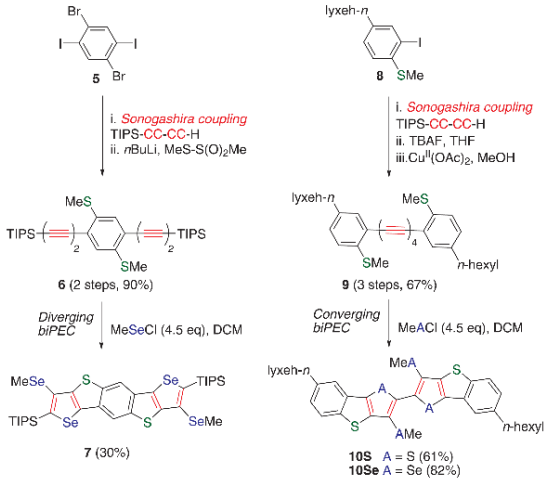
Scheme 5. Bidirectional Application of PEC



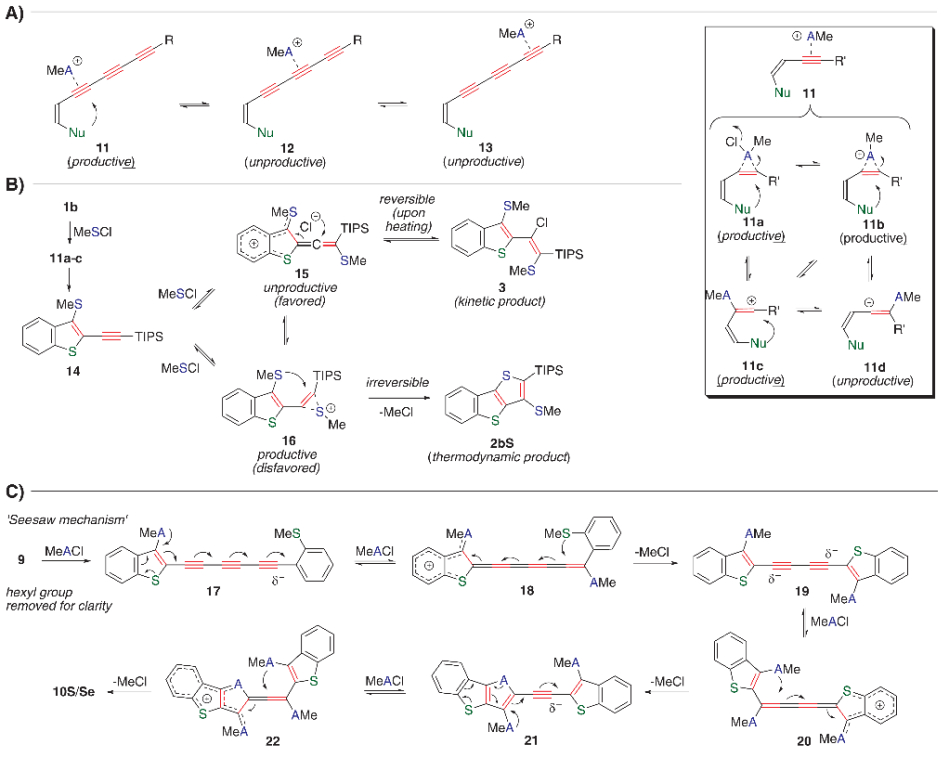
nances in the product. Also, MS gave diagnostic isotopic patterns for Se and Te compounds (correct HRMS also obtained). UV spectra of selected products show a general right shift in the absorption maxima with an increasing number of heterocyclic rings, in particular tellurophenes such as **2eTe**.[9]

Mechanistically for PEC, we envisage electrophilic MeACl (or MeA^+) may form an activation complex with any of the alkynes in the polyyne substrate (**11**−**13**), but only **11** is productive in a 5-*endo*-digonal cyclization (Scheme 6A).

The precise nature of the electrophile−alkyne complex **11** may fluctuate among **11a**−**d** (Scheme 6, box) and depends on the nature of the substituents on the alkyne and the nature of the chalcogen, A.[10] In circumstances where either or both of the alkyne substituents are capable of stabilizing a positive charge (electron-donating groups), vinyl cations **11c** and **11d** may dominate.[10] Of these two vinyl cations, only **11c** is capable of cyclization (productive), though unproductive **11d** may partake in reversible addition [Cl^- attack (not shown)]. The capacity of the different chalcogens A to form cyclic activation complexes **11a** and **11b** may also vary, possibly in the order A = Te > Se > S.

Nucleophilic Cl^- attack on an unproductive vinyl cation of the type **11d** was apparent in the reaction of dyne **1b** with MeSCl (Schemes 4 and 6B). As described above, this reaction initially yields a product of sequential monocylization and MeSCl addition to give **3**, which upon heating gave **2bS** (Scheme 4). It is proposed that initial cyclization of **1b** proceeds through any one of the "productive" intermediates **11a**−**c** (Scheme 6, box) to give benzothiophene **14** (Scheme 6B). However, the 3-(methylthio)-benzothiophenyl group in **14** acts as a strong donor, favoring the "unproductive" vinyl cation **15** (akin to **11d**). Intermediate **15** is stabilized by delocalization of the positive charge into the ring and onto the two S atoms. It is incapable of cyclization but can undergo Cl^- attack to give **3** (kinetic product). Heating, promotes reversible expulsion of Cl^- from **3** back to **15** and sustained access to the less favored yet productive thiirenium cation **16** (akin to **11b**, likely to dominate over the corresponding vinyl cation **11c**, due to R′ = TIPS

Scheme 6. Mechanistic Consideration in PEC of Polyynes



https://dx.doi.org/10.1021/acs.orglett.0c00733
Org. Lett. 2020, 22, 2987−2990

electronics), which undergoes irreversible cyclization to give **2bs** (thermodynamic product).[11]

The more facile access to PEC products **2b-eSe/Te** may be due to a stronger preference for the "productive" cyclic activation complexes **11a** and **11b** (A = Se and Te) that reduce the influence of unfavorable electronic bias.[10b] Alternatively, the competing addition reactions are much more reversible, and the thermodynamic PEC products form at lower temperatures.

In stark contrast to the complications arising from the PECs involving MeSCl and polyynes **1b** and **1c** (**1b** gives addition products **3** and **1c** as a complex mixture), reaction of tetrayne **9** with MeSCl proceeded smoothly to give the symmetrical tetracyclized product **10S**, under kinetic conditions. We propose that this arises from a seesawing mechanism involving alternating shifts in electron density from one end of the polyyne to the other with each cyclization step (Scheme 6C). After the initial cyclization of symmetrical **9** with MeSCl to give monocyclized product **17** (A = S), the resultant electron-rich 3-(methylthio)-benzothiophenyl group (more electron rich than the phenyl group) drives the electron density to distal alkynyl carbon (indicated by δ^-), favoring cyclization via stabilized cation intermediate **18** to give diyne **19**. Monocylization of symmetrical **19**, via **20**, gives **21**. In the final cyclization of unsymmetrical **21**, again, the more electron-dense 3-(methylthio)-benzothiophenothiophenyl group directs attack of MeSCl to the remote carbon, favoring cyclization via the most stabilized cation **22** to give **10S**. A similar scenario is likely for MeSeCl.

Attempts to observe or selectively form **17**, **19**, or **22** (A = S or Se) by reducing the stoichiometry of MeACl returned only **10S/Se** and unreacted **9**. Presumably, the accumulating electron density in the polyyne with each incorporation of MeACl (electron density in **21** > **19** > **17** > **9**) increases the rate of each subsequent cyclization, giving an accelerating domino reaction terminating in **10S/Se**.

Again, in stark contrast to the successful unidirectional PEC reactions involving MeTeCl and substrates **1**, reaction of **9** with MeTeCl gave complex mixtures. Possibly, MeTeCl generates predominantly the cyclic activation complexes **11a** and **11b** (A = Te) that help overcome unfavorable electronic bias associated with the unidirectional PEC, i.e., which avoids unproductive complex **11d**. However, in the converging biPEC, where similar vinyl cation intermediates are favorably disposed to the seesaw mechanism, the preference for **11a** and **11b** (A = Te) may lead to a mixture of different unsymmetrical and symmetrical cyclization products (to be confirmed).

In conclusion, MeACl (A = S, Se, or Te) reacts with suitable polyynes to provide atom economical access to chalcogen-based heteroacenes through PEC. This method generally requires no purification as volatile MeCl is the sole byproduct. It can be used to access thiophenes, selenophenes, and tellurophenes under mild conditions. Both uni- and bidirectional (diverging and converging) PEC reactions have been demonstrated to afford efficient access to structural classes of significant interest to emerging areas of photonic and electronic materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00733.

Description of synthesis and characterization (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Bernard L. Flynn − *Monash Institute of Pharmaceutical Sciences, Monash University, Parkville 3052, Victoria, Australia;* Email: Bernard.flynn@monash.edu

Author

Annaliese S. Dillon − *Monash Institute of Pharmaceutical Sciences, Monash University, Parkville 3052, Victoria, Australia;* orcid.org/0000-0003-4410-2423

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00733

Notes

The authors declare no competing financial interest.

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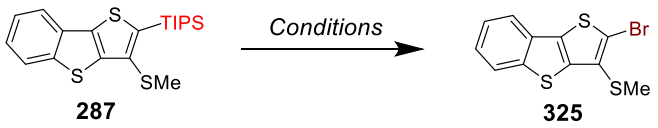
7.3 Appendices C: Additional data and Schemes

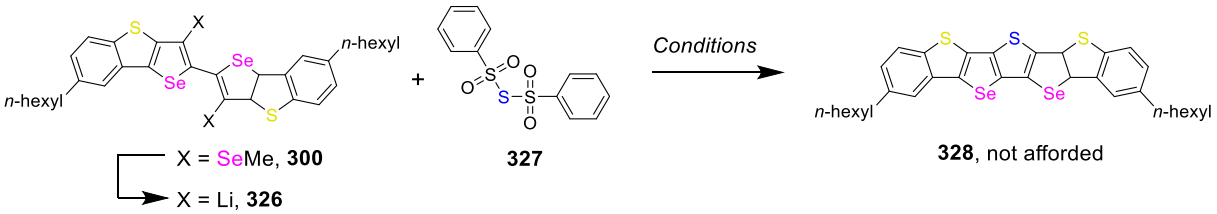
Detailed attempts at exchanging TIPS group of **287** for a bromo group to afford **325**.



287 **325**

Entry	Reaction Conditions	Outcome
1	Br_2 (1 eq), DCE, 10 min, 22 °C	Complex mixture
2	NBS (1 eq), HFIP*:DCM (1:4), 10 min, 22 °C *Hexafluoroisopropanol	Negligible presence of **325** + complex spectrum
3	NBS (1.5 eq), HFIP:DCM (1:4), 10 min, 22 °C	<5% yield of **325**
4	NBS (1.5 eq), DCM, 10 min, 22 °C	Negligible presence of **325** + complex spectrum

Detailed attempts at the ring closing reaction to afford **328** from **300**.



X = SeMe, **300**

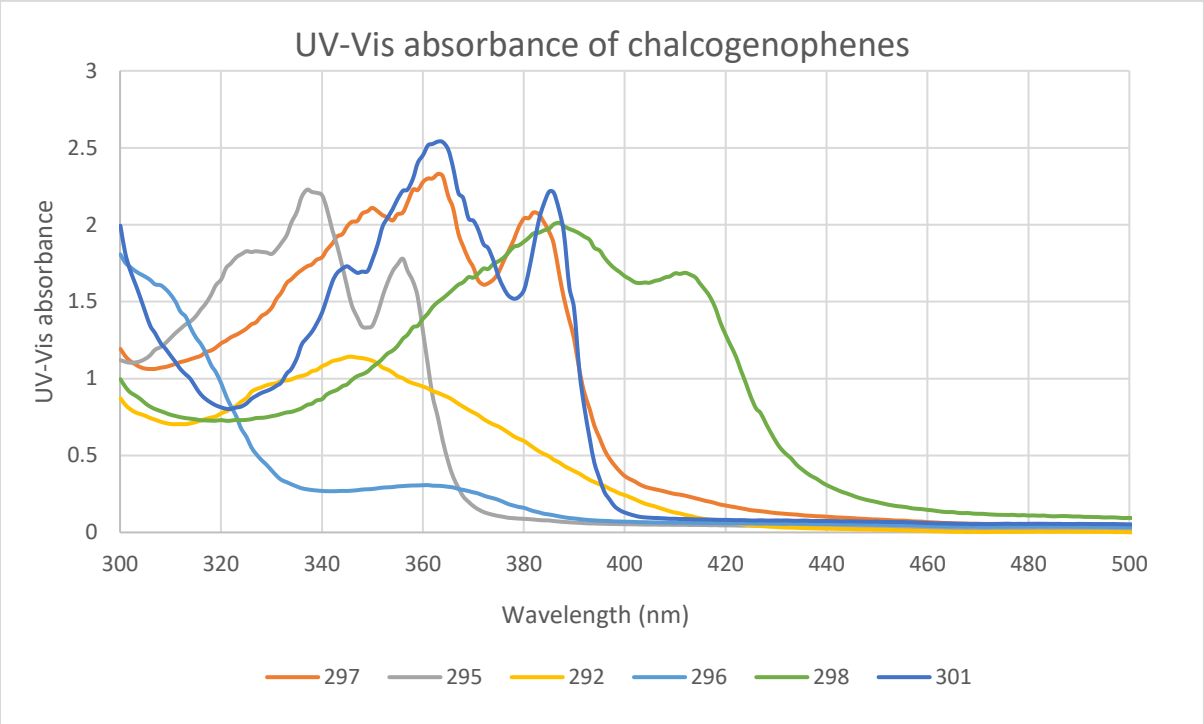
X = Li, **326**

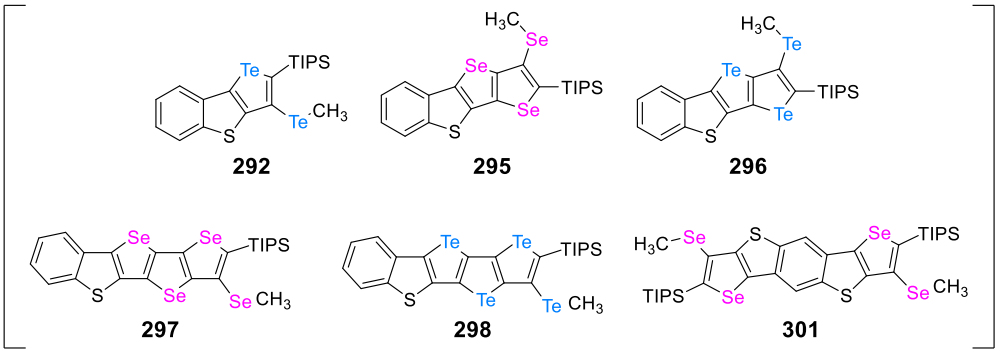
327

328, not afforded

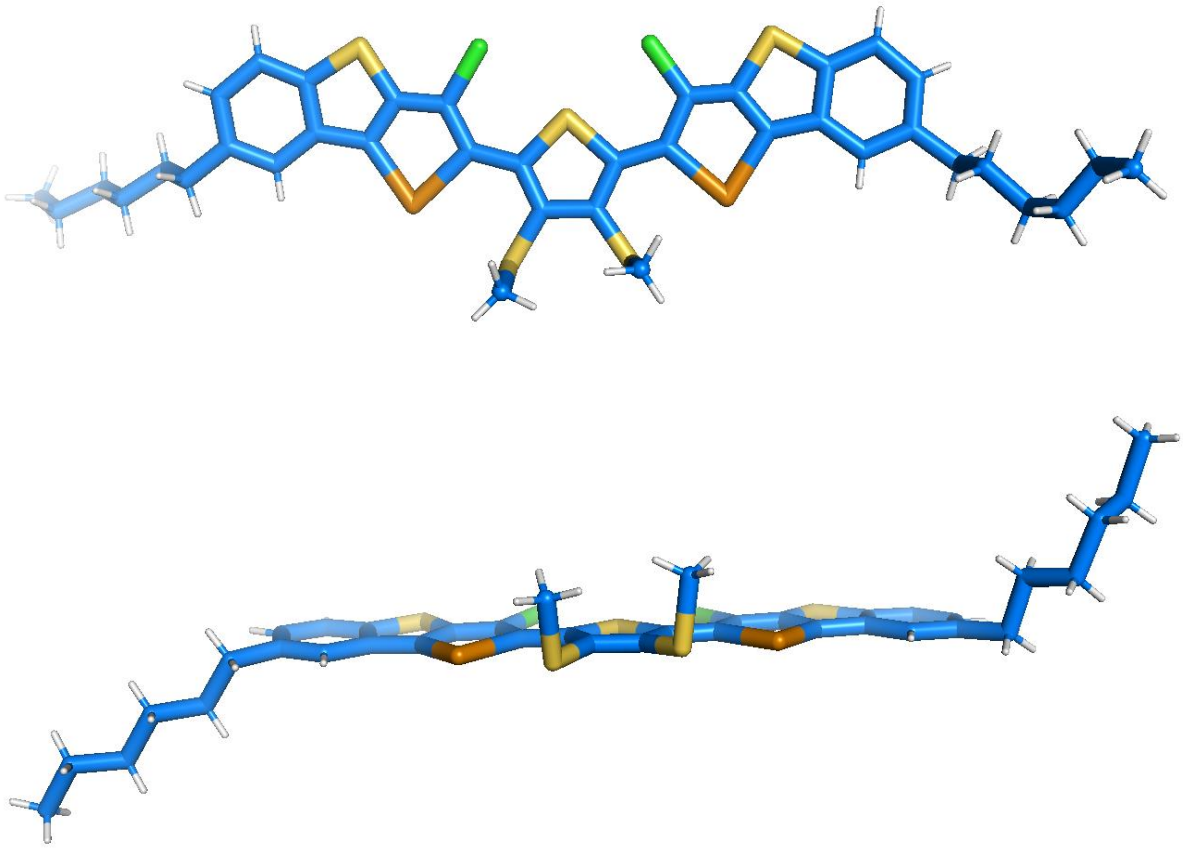
Entry	Reaction Conditions	Outcome
1	1. *n*-BuLi (2.1 eq), dry THF, -78 °C, 15 min -20 °C 2. **327** (1.1 eq), 1 h, 22 °C	Degraded starting materials
2	1. *n*-BuLi (2.1 eq), dry THF, -78 °C, 15 min 0 °C 2. **327** (1.1 eq), 1 h, 22 °C	Unreacted starting material + benzenesulfonic thioanhydride
3	1. *n*-BuLi (2.1 eq), dry THF, -78 °C, 15 min 22 °C 2. **327** (1.1 eq), 1 h, 22 °C	Unreacted starting material + benzenesulfonic thioanhydride
4	1. *s*-BuLi (2.1 eq), dry THF, -78 °C, 15 min 0 °C 2. **327** (1.1 eq), 1 h, 22 °C	Lithiation of **300** successful, addition of electrophile lead to degradation
5	1. *s*-BuLi (2.1 eq), dry THF, -78 °C, 15 min 0 °C 2. **327** (1.1 eq), 1 h, -78-0 °C	No electrophilic addition
6	1. *s*-BuLi (2.1 eq), dry THF, -78 °C 1 h 2. Iodine in THF, 1h -78 °C	Lithiation successful no electrophilic addition

UV-Vis absorbance spectra (100 μM in $CHCl_3$) of heteroacenes **292**, **295**, **296**, **297**, **298** and **301**:

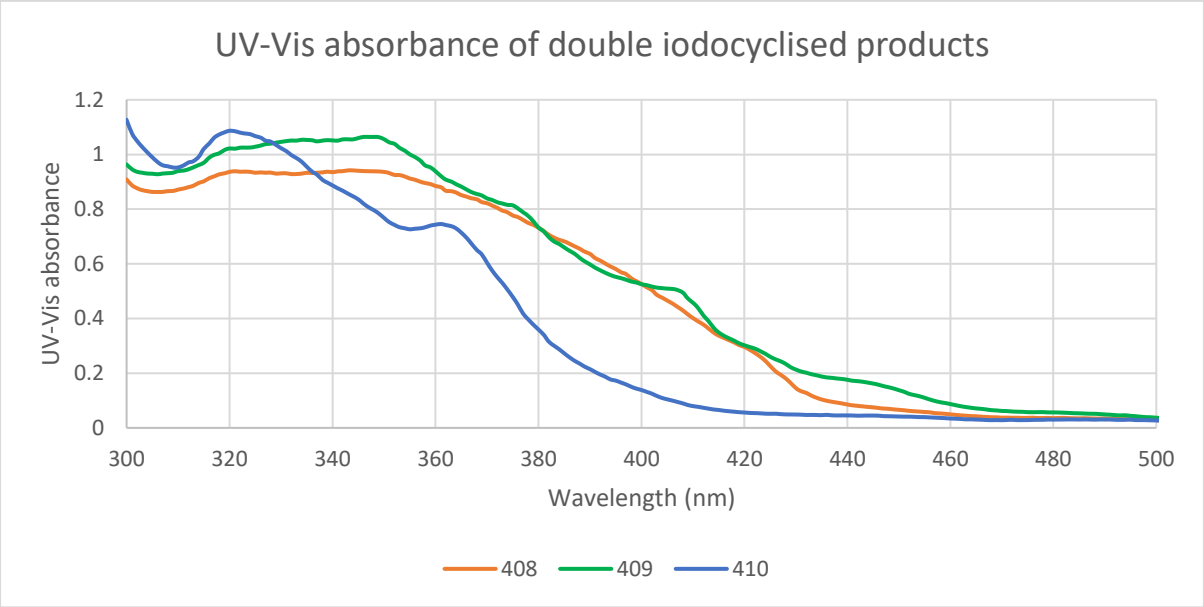


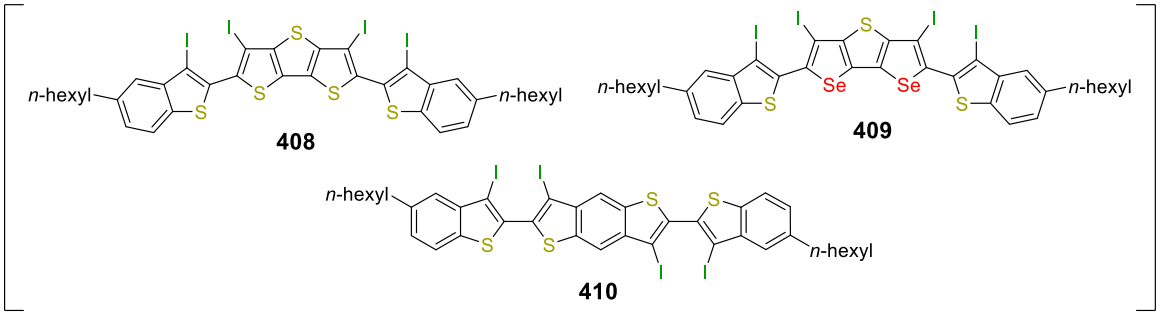


X-ray crystal structure of **2,2'-(3,4-Bis(methylthio)thiophene-2,5-diyl)bis(3-chloro-7-hexylbenzo[*b*]telluropheno[2,3-*d*]thiophene) (393):**



UV-Vis absorbance spectra (50 μM in DCM) of double iodocyclised heteroacenes **408**, **409** and **410**:





UV-Vis absorbance spectra (50 μM in DCM) of iodocyclised acenes **464**, **488**, **489** and **490**: