UNIVERSITY OF SOUTHAMPTON

FACULTY OF NATURAL AND ENVIRONMENT SCIENCES

Department of Chemistry

Synthesis of Novel Polyaromatic Hydrocarbons for Electronic Applications

by

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Thesis for the degree of Master of Philosophy

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ABSTRACT

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This report describes research towards the project ‘Synthesis of novel polyaromatic hydrocarbons for electronic applications’. Being an initial piece of research, there are a small number of PAHs that have been synthesised. However a lot of optimisation have been carried out in order to devise a good route for synthesising more. The synthesis mainly consisted of three reactions; A Sonogashira coupling which was unchanged from the literature, a Suzuki coupling which in some cases worked well using a known procedure but in others required optimising, and a base catalysed cyclisation of which there are only a small number of known examples, and required a great deal of optimisation which is described.

Contents

Author's Declaration

I, Jason Mark Howe, declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

Synthesis of Novel Polyaromatic Hydrocarbons for Electronic Applications.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;

2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;

3. Where I have consulted the published work of others, this is always clearly attributed;

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7. None of this work has been published before submission.

Academic Thesis: Declaration Of Authorship

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I would like to express thanks to all the people who made my research possible; the Chemistry Department of the University of Southampton, in particular the mass spectrometry and NMR teams, the Whitby research group; David, Cyril and Bogdan for their help with flow chemistry and the UV machine, and big thanks to Alan for his expertise of all things related to working in and out of the lab, all other researchers around the floor and department for any assistance, my sponsors Interreg and DTA for the funding, my Southampton adviser David Harrowven and Interreg supervisor Bernhard Witulski for their support, and finally huge thanks to my supervisor Richard Whitby for the opportunity to work on his project and all the support and expertise I was given. With the oversight of my main supervisor, editorial advice has been sought. No changes of intellectual content were made as a result of this advice. I would like to thank Sam for this advise and David for his assistance in getting the final pieces of data.

Abbreviations

AcOH	acetic acid
Ar	aromatic ring
Bu	butyl
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
dba	dibenzylideneacetone
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMA	dimethylacetamide
DME	dimethoxyethane
DMF	dimethylformamide
DMSO-d_6	deuterated dimethyl sulfoxide
E^+	electrophile
Et	ethyl
GC	gas chromatography
Hp	heptyl
HPLC	high performance liquid chromatography
Hr	hour
Hx	hexyl
IR	infrared
-br	broad
-m	medium
-s	strong
-w	weak
LDA	lithium diisopropylamide
Me	methyl
Mins	minutes
NBS	N-bromosuccinimide
n-BuLi	*n*-butyllithium
NOE	nuclear Overhauser effect
NMP	*N*-methyl-2-pyrrolidone

NMR		nuclear magnetic resonance
	-s	singlet
	-d	doublet
	-t	triplet
	-q	quartet
	-m	multiplet
	-br	broad
Oct		octyl
PAH		polycyclic aromatic hydrocarbon
PhMe		toluene
Pn		pentyl
Pr		propyl
RT		room temperature
SM		starting material
TBD		1,5,7-triazabicyclo[4.4.0]dec-5-ene
TEA		triethylamine
THF		tetrahydrofuran
TLC		thin layer chromatography
UV		ultraviolet
	-λ	wavelength
	-ε	extinction coefficient

1.0 Introduction

1.1 Project Aim

The aim of this project is to develop the synthesis of novel polyaromatic hydrocarbons for use in electronic applications. There are four primary target 'skeletons' which will be described later. Other targets of interest are heterocyclic systems. Before definite targets and synthetic routes to the compounds can be devised, a number of key reactions will have to be investigated. Cyclisations and other aryl-aryl bond formations are an integral part of this project. The use of palladium catalysed aromatic couplings, such as the Suzuki and Sonogashira reactions, will be frequently utilised to produce the precursors to the final PAH compounds. The final step is likely to be some kind of cyclisation reaction that effectively 'zips-up' the precursor. This will be the key step of the synthesis and will require a lot of optimisation. This report will discuss the investigation into cyclisation reactions, showing the pros and cons of the different methods which will then depict the structures of the final PAHs.

1.2 Background to Organic and Molecular Electronics

Since the 1970s chemists have been investigating π-conjugated hydrocarbon systems for applications in the field of organic and molecular electronics with such uses as light-emitting diodes, field-effect transistors, solar cells, and optoelectronic devices.[1] Organic electronics refer to the use of bulk organic materials in electronic devices, for example as semi-conducting layers. Molecular electronics refer to the use of single molecules, or defined arrangement of molecules, as components of electronic circuits (such as wires, diodes and transistors). Organic electronic materials already have a substantial commercial presence, for example as liquid crystals, organic light emitting diodes (OLEDs), capacitors and organic field effect transistors (OFETs). Molecular electronics is still undeveloped, principally because of the difficulty in arranging and measuring the properties of single molecules, but it does offer the prospect of dramatically smaller devices than silicon electronics are capable of. The most common organic electronic materials are conducting polymers such as polyacetylene, polypyrrole, polythiophene and polyphenylene vinylene (PPV) and the most reported molecular wires are oligomers of arylalkynes, shown in figure 1.2.1.

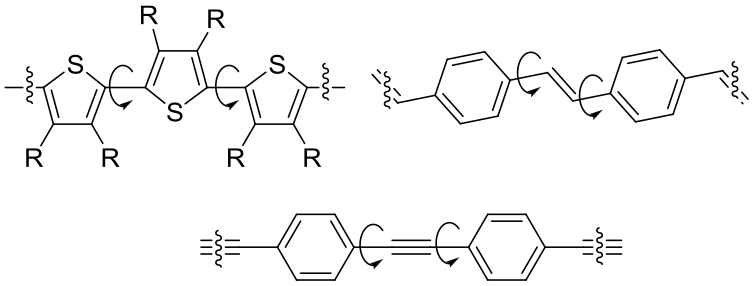
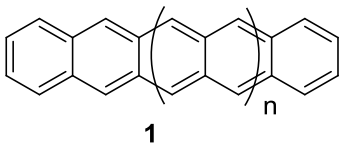


Figure 1.2.1. Conducting polymers and molecular wires.

All these materials, although they are fully conjugated, and can display good conductivity when doped, have no extended π-molecular orbital due to rotation about the single bonds as indicated in figure 1.2.1. and so have a low charge mobility. Carbon nanotubes and graphene have extended π-systems and show length independent (ballistic) conductivity and resistance. However, they have limitations such as processability and are not suitable for molecular electronic applications. Few other components with extended π-systems have been developed. Polyaromatic hydrocarbons (PAHs) should be ideal organic conductors due to having rigid planar structures that eliminate the problem of bond rotation and may have some of the exceptional properties of graphene and carbon nanotubes. The lack of development of PAHs may be due to the fact that stability of the obvious candidates, the linear acenes **1** rapidly decreases with length. Heptacene (**1**, n = 3) is the longest to have been made and is very unstable.[2] Pentacene (**1**, n = 1) is a widely used charge transport layer in a variety of electronic devices including OLEDs and OFETs.



1

Figure 1.2.2. n-Acenes. Pentacene (n=1)**,** Heptacene (n =3).

The reason for the instability is that the energy gap between the HOMO and the LUMO decreases with the length of the π-system, to the point where it is comparable to the thermal energy at room temperature. This allows the molecule to form a bi-radical species which is highly reactive.

Calculations[3] of the HOMO-LUMO gap for polyaromatic hydrocarbons have shown dependence on the precise structure, and for many structures predict a substantial (and selectable) gap even at infinite length, figure 1.2.3. It is interesting that it was recently reported that picene (**2**, n = 0) a staggered isomer of pentacene, is an excellent material for OFETs which, unlike those based on pentacene, are stable in the presence of oxygen and water.[4] The PAH systems that will be investigated can be viewed as 1-dimensional analogues of graphene, where the molecular orbitals

span the entire molecule. The energies of the HOMO and LUMO can be changed with different electron withdrawing/donating substituents, however the gap is predicted to remain relatively unaffected. It has also been predicted that heterocyclic analogues of the PAHs show similar HOMO-LUMO gaps but may, by analogy to polythiophenes, show much better inter-molecular charge transfer. Experimentally the HOMO-LUMO gap and energies can be measured by a combination of UV and electrochemical methods. In the UV spectra the highest wavelength absorption peak (λ_{max}) gives the energy gap between the ground and 1st excited electronic state, and provides a good estimate for the HOMO-LUMO separation.[5] Electrochemical methods will be investigated with Prof. Bernhard Witulski at the University of Caen.

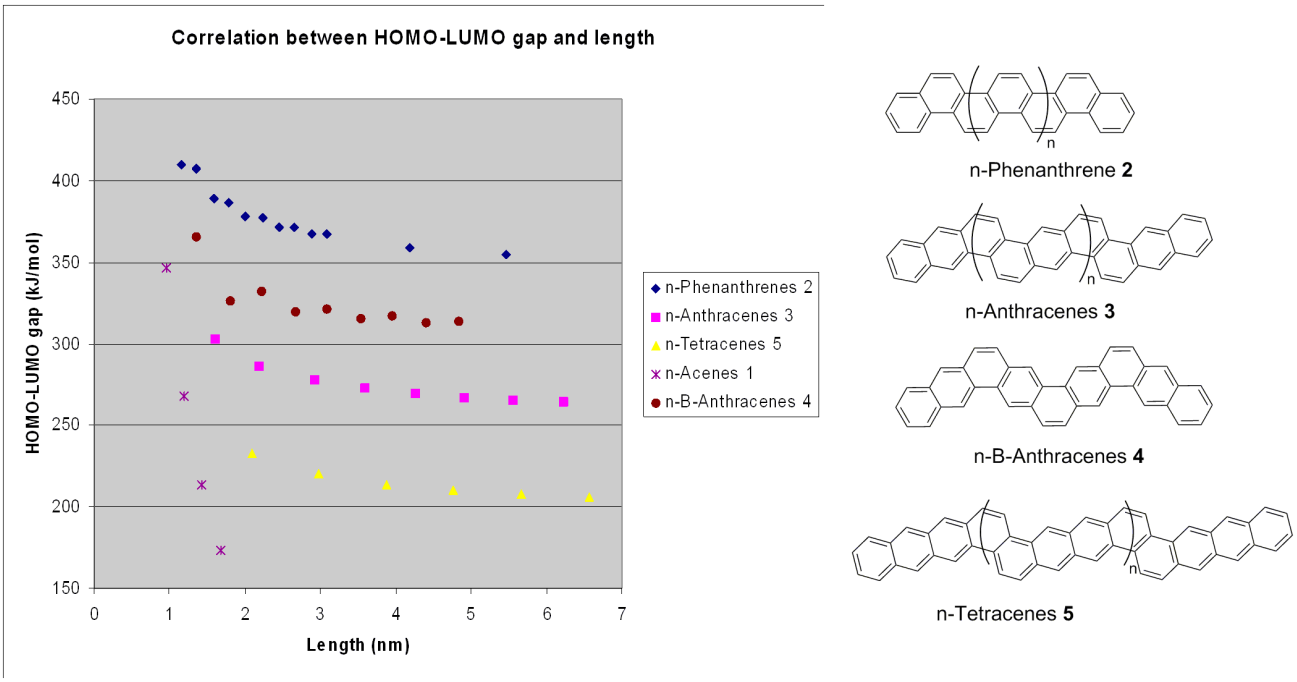


Figure 1.2.3. Correlation between HOMO-LUMO gap and length of polyaromatic hydrocarbons.

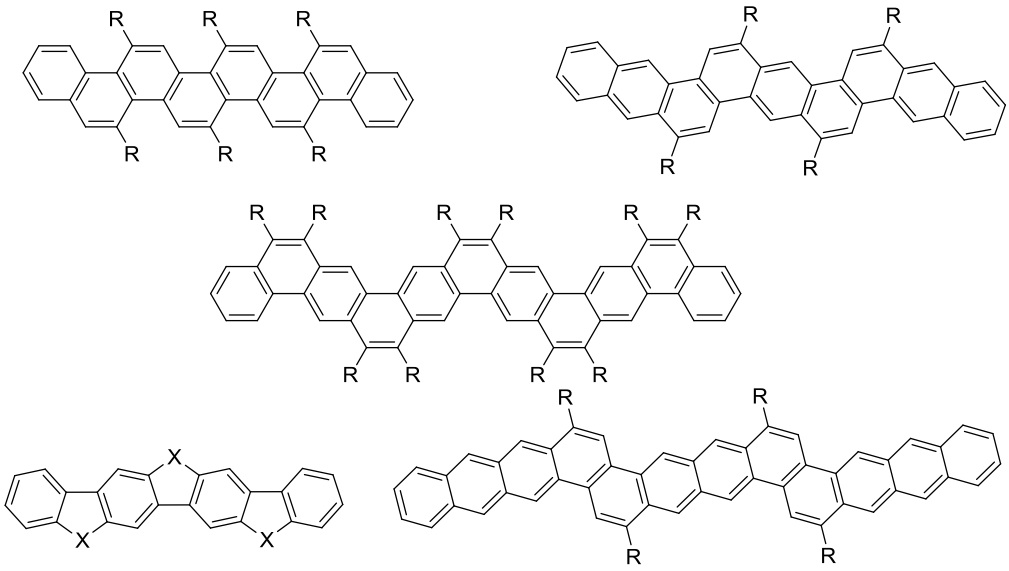


Figure 1.2.4. Primary target 'skeletons'.

Shown above, figure 1.2.4, are the initial target 'skeletons' **2-4** for this project, where R will be long alkyl or alkoxy groups for solubility.

1.3 Current synthetic routes to, and examples of extended PAHs

There are a number of synthetic methods that can be utilised to produce PAHs. A few of these will be investigated further and discussed in this report.

1.3.1 The Scholl oxidation

The Scholl oxidation is a reaction that forms a carbon-carbon bond between two C-H aryl substituents[6], shown in figure 1.3.1, and has been known to form 126 bonds in a single step.[7] A wide variety of oxidants have been used including $FeCl_3$[8], $MoCl_5$[9], DDQ[10], PIFA with $BF_3.Et_2O$[11]. Yields vary, but are generally higher with larger molecules and ones that have bulky groups attached to avoid the formation of side products. The use of $FeCl_3$ and DDQ and the reaction itself will be discussed further in the results and discussion section of this report.

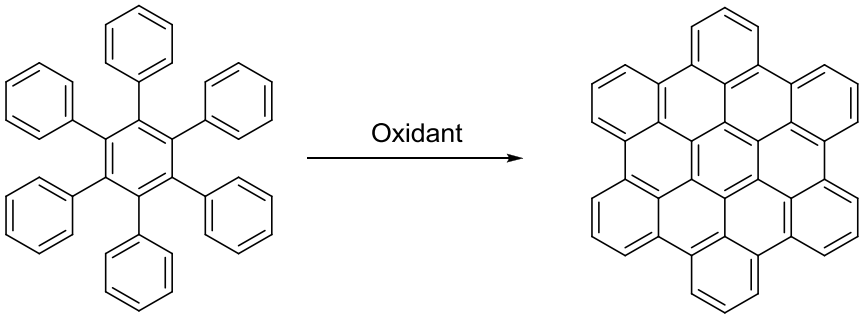


Figure 1.3.1. Scholl oxidation.

1.3.2 Photocyclisation

Oxidative photocyclisations have been extensively used to make small aromatic systems, though yields are generally poor. Mallory[12] has used photocyclisations of 1,2-diarylethylene systems to form phenanthrene-like PAHs. The aryl-ethylene precursors are synthesised from Wittig reactions, and various substituents, usually *t*-Bu, are placed around the aromatic rings to prevent side products from forming.

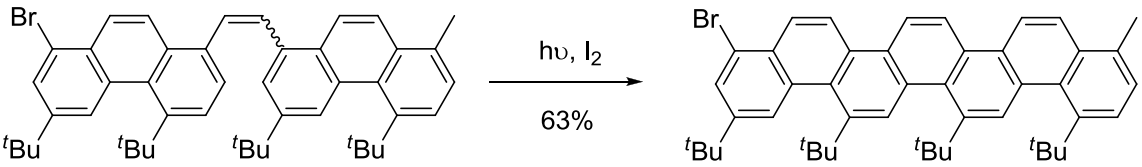


Figure 1.3.2. Photocyclisation.

1.3.3 The Swager reaction

The Swager reaction is an electrophile-induced cyclisation[13], shown in figure 1.3.3, and has been shown to work in yields greater than 95%. Commonly electrophilic iodine is used but also acids such as TFA. A severe limitation is the competitive cyclisation to form a 5 member ring. In the example shown, the strongly electron donating p-alkoxyphenyl group is used to direct initial protonation to the correct end of the alkyne.

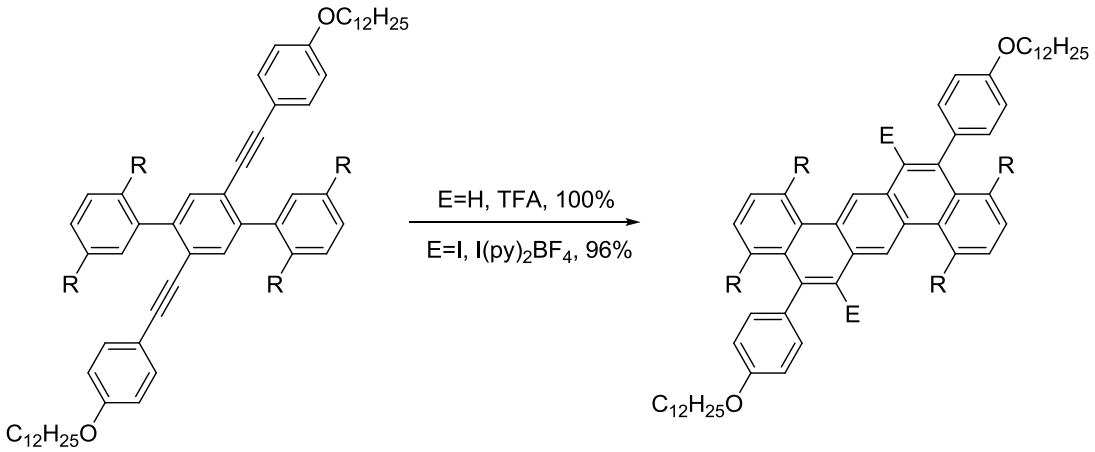


Figure 1.3.3. Swager reaction.

1.3.4 Metal catalysed version of the Swager cyclisation

A variation of the Swagger cyclisation is to use a metal as the electrophile. In the particular case of $PtCl_2$ as the catalyst, good selectivity for cyclisation to form 6- rather than 5- member rings is achieved, and during the course of our work this method has been used to make the same extended phenanthrene skeletons which are one of our targets. [14]

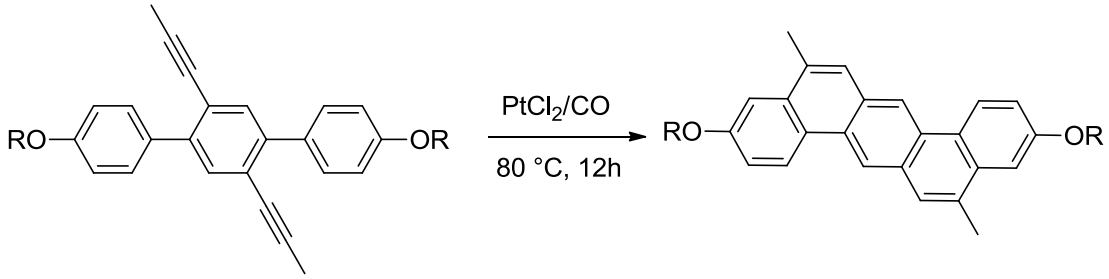


Figure 1.3.4. Metal catalysed cyclisations.

1.3.5 Ruthenium catalysed cyclisation of terminal alkynes

A ruthenium catalyst is effective in cyclising terminal alkynes, the mechanism presumably occurring via cyclisation of an intermediate ruthenium alkenylidene complex. As the mechanism should give excellent selectivity for 6 ring formation, the inability to include solubilising groups on the alkyne is a severe drawback for long PAH synthesis.[14]

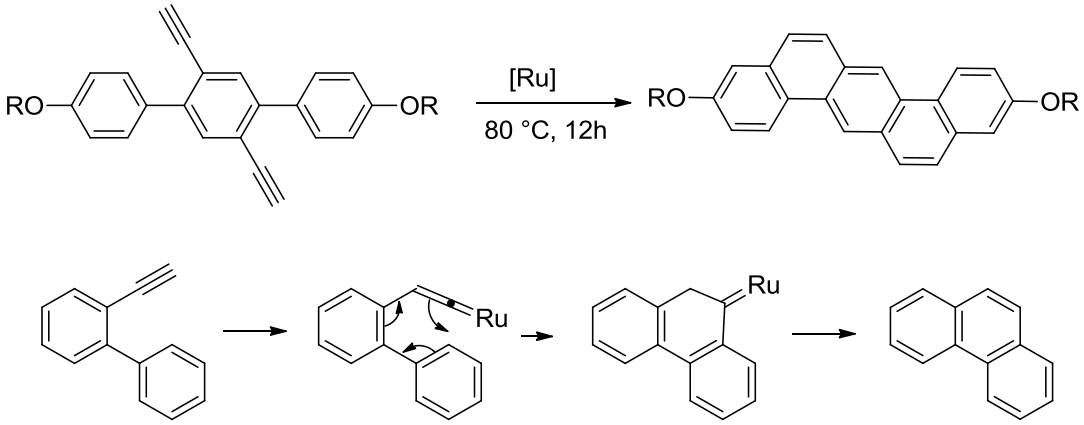


Figure 1.3.5. Ruthenium catalysed cyclisations.

1.3.6 Base catalysed cyclisations of aryl-acetylenes

Using the same arylalkyne precursors as the Swager reaction the base catalysed cyclisation to form a new aromatic ring was first reported by Müllen in the special case of corrylene formation from perylene[15], figure 1.3.6. The reaction was rediscovered by Burton[16] who showed for phenanthrene formation that the mechanism involved base catalysed isomerisation of the alkyne to an allene followed by 6e-cyclisation, figure 1.3.7. This reaction and its mechanism is a key one of the project and will be discussed further in the results and discussion. This cyclisation method has the advantage over the metal catalysed cyclisations above that only a 6-member ring can form in the pericyclic step, and the product is not contaminated with trace metals. It remains to be determined how the yields for extended systems compare.

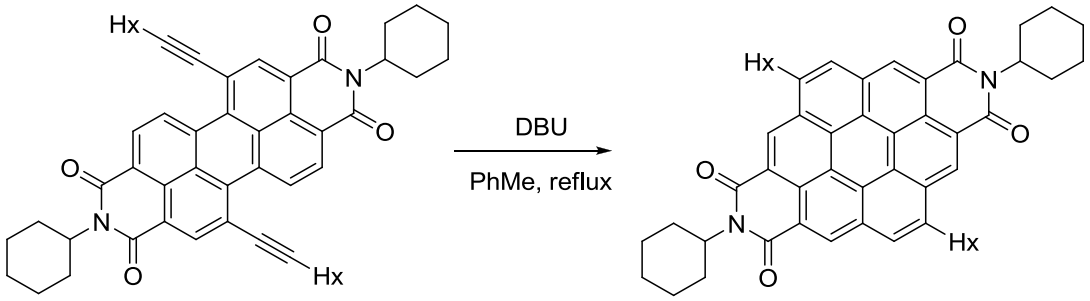


Figure 1.3.6. Base catalysed cyclisation, of a perylene to give a corrylene.

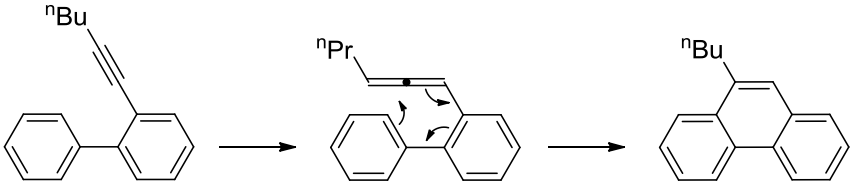


Figure 1.3.7. Base catalysed cyclisation.

1.3.7 Cyclisation of carbonyls

Müllen, has shown cyclisations of carbonyls to give phenanthrenes in good yields, followed by a nickel polycondensation to produce the PAH.[17]

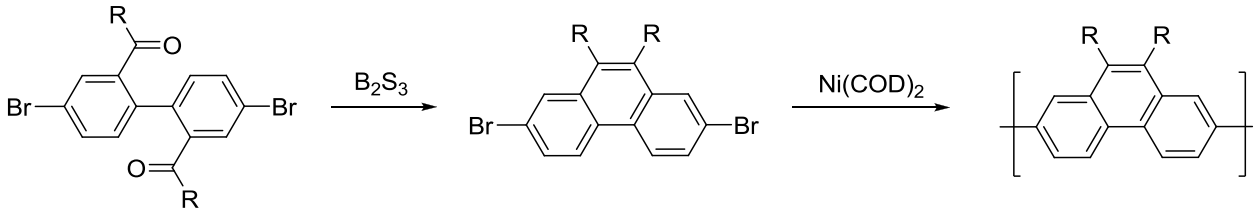


Figure 1.3.8. Müllen's cyclisation of carbonyls and polycondensation.

1.3.8 Ring-closing metathesis

Ring-closing metathesis is another way to produce PAHs in a high yielding step[18], however the precursors are complex to synthesise.

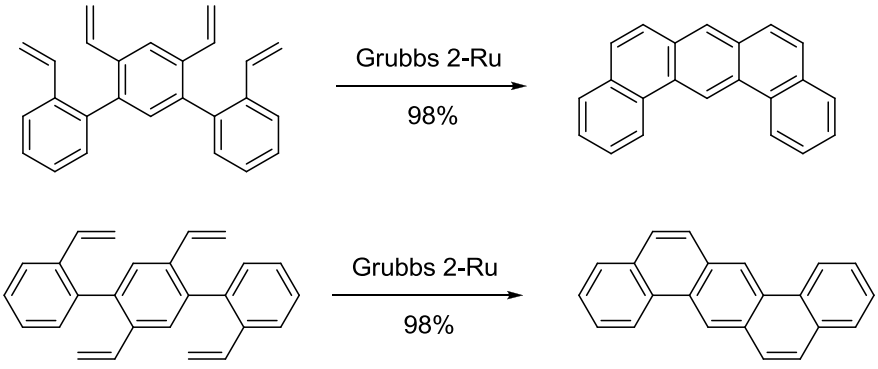


Figure 1.3.9. RCM

As shown there are many methods to synthesise PAHs. The reactions that will be investigated further in this report are the Scholl reaction (figure 1.3.1) and the base catalysed cyclisation (figure 1.3.7) which has not been used to great extent and will be the main focus of this project.

1.4 Polycyclic Aromatic Hydrocarbon Carcinogenesis

Polycyclic Aromatic Hydrocarbons and their carcinogenic properties have been investigated since the early 1900's, as it was observed that workers in professions such as coal tar industry and chimney sweepers were developing cancers due to their exposure to soot.[19] In brief, the structural feature that contributes to the carcinogenicity is what is known as the K-region, figure 1.4.1. Flat and small PAHs can intercalate with DNA and epoxides can easily form at the K-region which then react with DNA. The carcinogenic potency of a PAH is found to be lowered if the structure includes a bay-region, which if hindered by a methyl group or extra ring increases the potency.[20]

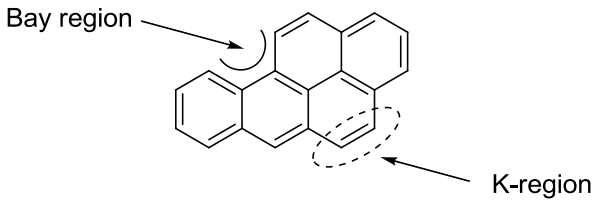


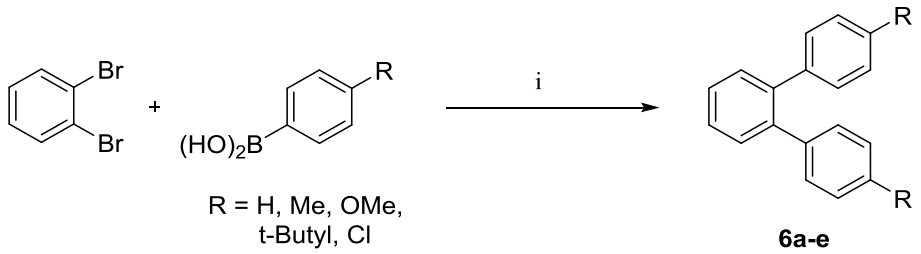
Figure 1.4.1. Benzo[α]pyrene, a known carcinogen.

It would be believed that substituents on either carbon of the K-region would lower potency however that has been found not be the case.[21] With this health issue in mind, great care will be taken when synthesising and analysing the final PAHs in this project. However as the project progresses and the PAHs synthesised become longer it would be expected that water solubility and the risk of DNA intercalation, due to the size, would decrease.

2.0 Results and Discussion

2.1 ortho-Terphenyls: Synthesis and oxidative cyclisations

The first objective of this project was to investigate the Scholl oxidative cyclisation reaction. This was first trialled on five ortho-terphenyl model systems using two different oxidants. The five o-terphenyls **6a-e** were synthesised using a palladium catalysed Suzuki reaction[8] coupling o-dibromobenzene with various phenyl boronic acids as shown in scheme 2.1.1.

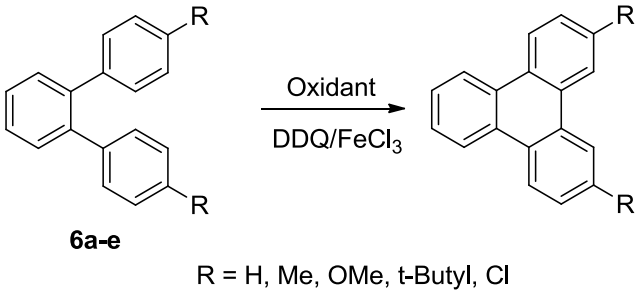


	R	Yield
6a	H	44
6b	Me	39
6c	MeO	70[a]
6d	t-Bu	79
6e	Cl	83

Scheme 2.1.1. Suzuki reactions to o-terphenyls. Reagents and conditions: (i) $PdCl_2$, PPh_3, Na_2CO_3, PhMe/EtOH/H_2O, reflux, 18-45 hrs, 39-83%. [a] Reagents (i) yielded 0%, $Pd(PPh_3)_4$ in NaOH and DME used instead.

o-Terphenyls **6a** and **b** were synthesised in modest yields of 39 and 44%, although these could have been improved by a longer reaction time. The p-methoxy-o-terphenyl **6c** was synthesised using a different Suzuki method of $Pd(PPh_3)_4$ and 2.5 M NaOH in DME[6] in a high yield of 70%.

The five o-terphenyls then underwent oxidative cyclisation reactions. Two different reagents were used following literature procedures, iron (III) chloride[8] and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[10].



Scheme 2.1.2. Scholl reaction.

Unfortunately these cyclisations were not successful. DDQ failed to cyclise o-terphenyls **6a**, **b** and **d** with no reaction occurring at all, and the methoxy-substituted **6c** gave many products. For this reaction to occur, the two aromatic rings that are to be coupled need to have a lower oxidation

potential than the oxidant, which is only the case for the methoxy o-terphenyl when using DDQ which has been shown in the literature to work well for similar models that have methyl and methoxy groups placed around the o-terphenyl. This would block any undesired dimers or polymers, which are formed due to the cyclised product having a lower oxidation potential than the starting material, i.e. is more reactive. A similar result was observed when using $FeCl_3$ which gave reaction on all the models, showing likely product formation but proved very difficult to purify and analyse. Purification of two reactions on the simple o-terphenyl model **6a**, could separate the impurities from the product but not the starting material. Analysis by GC and NMR showed very little product, table 2.1.3.

Entry	$FeCl_3$ equiv.	Mass[a]	Product by GC	Product by ^{1}H-NMR
1	2	49%	12%	18%
2	3	47%	28%	36%

Table 2.1.3. Cyclisations on o-terphenyl **6a**. [a]Post-column fractions containing only SM and product.

Two thermolysis experiments were attempted on o-terphenyl **6a**. Both involved simply loading the starting material onto 5% Pd/C and applying a high temperature; one with a heating block at 235 °C, the other with a blow torch. Neither resulted in product formation and the blow torch appeared to vaporise the starting material before it was able to react.

Conclusion

The investigation of the oxidative cyclisation reactions did not yield any desired products. The reaction was not found to be useful when using small molecular systems, such as the o-terphenyls, as many side products and di/polymers are formed that could not be separated. Published work has shown that $FeCl_3$ can be very useful for large molecular systems and could therefore be useful later on in this project when the systems are bigger. The DDQ reactions require very electron rich aromatic rings such as substituted methoxy groups, but also give many products, so again this may be useful later on in the project when using bigger molecular systems.

2.2 Phenyl-acetylenes: Synthesis

As the oxidative chemistry came to a close, work focused on the phenyl-acetylene systems which would undergo base induced cyclisations. Initially there were two main targets shown in figure 2.2.1.

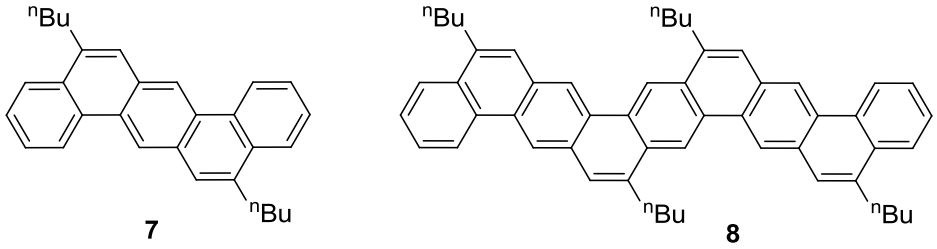
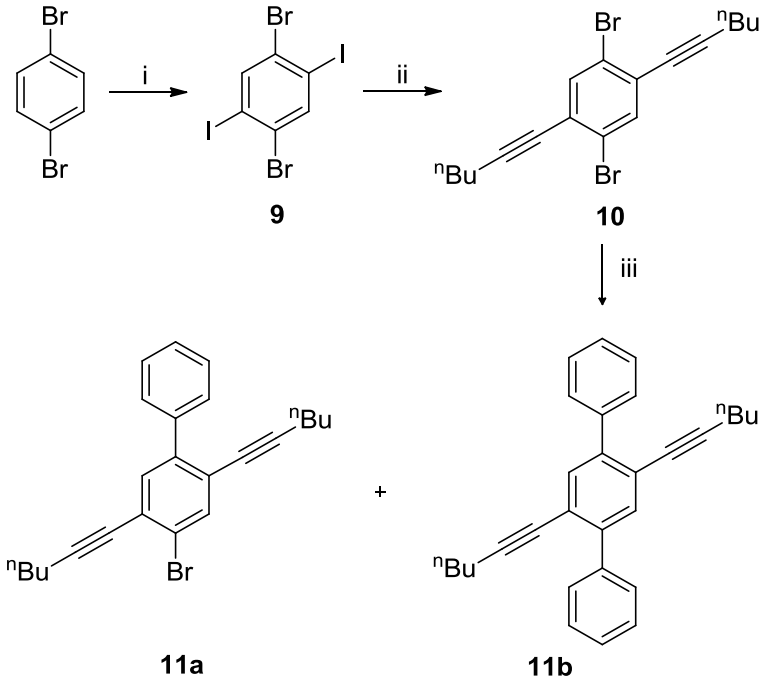


Figure 2.2.1. Cyclised targets.

The aryl-alkyne precursors to these compounds were synthesised following the scheme below 2.2.2.



Scheme 2.2.2. Reagents and conditions: (i) I_2, H_2SO_4, 125 °C, 5 days, Quant. (ii) 1-Hexyne, Et_3N, $PdCl_2(PPh_3)_2$, CuI, toluene, reflux, 2 hrs, 78%. (iii) Phenylboronic acid, $Pd(PPh_3)_4$, 2.5 M NaOH, DME.

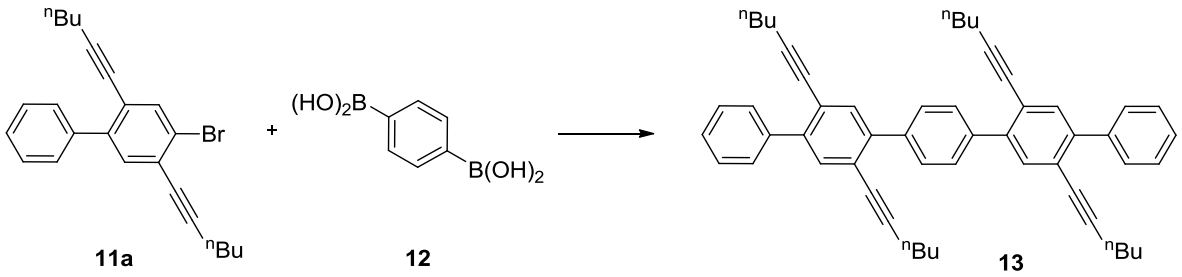
The first two steps of the sequence are relatively straight forward, the iodination gave clean product in quantitative yield.[22] The Sonogashira reaction proceeded very slowly with just triethylamine as the solvent, however using a mixture of triethylamine and toluene with heating gave higher yielding reactions but required careful purification. The Suzuki reaction[6, 8] was performed to give the mono-phenylbromide **11a** as the major product, and the p-terphenyl **11b** as a desired side product that was used in cyclisation experiments to give PAH **7**. However the reaction for the mono product proved to be low yielding as the following table shows.

Entry	Reaction Time	**11a** %	**11b** %	Mass recovery	Ratio mono:di
1	24 hrs	35	47[a]	82	43:57
2	5 hrs	17	12	29	58:42
3	3 hrs	44	27	71	62:38
4	2.5 hrs	26	57[a]	83	31:69
5	2 hrs	25	13	38[b]	65:35
6[c]	17 hrs	0	66	66	0:1

Table 2.2.3. Suzuki reactions. [a]product contained many impurities, [b]reaction not driven to completion, starting material also recovered, [c]phenyl Grignard used instead of boronic acid.

During entries 1 and 2, phenylboronic acid was added throughout the reaction to consume all of the starting material, and that total amount was used for the other reactions. Entry 4 was carried out at a lower concentration and resulted in more p-terphenyl product forming. Entry 5 used a different Suzuki method[8] and was stopped once the formation of mono product had peaked, however not in high yield.

The diphenylbromide **11a**, two equivalents, was then coupled to phenyl-diboronic acid **12** to make the pentaphenyl precursor **13**, which will then be cyclised to give compound **8**.



Scheme 2.2.4. Suzuki coupling to give pentaphenyl 13.

This double Suzuki coupling using a bis-boronic acid has proved problematic to optimise, and is still being improved upon. There are a vast range of coupling conditions in the literature, but unfortunately very few that contain ortho substitutents, especially alkynes. The conditions used in this project; palladium tetrakis(triphenylphosphine)/DME/aqueous potassium carbonate, reflux for no more than 5 hrs, gave high yields for monocouplings and modest, ~60%, for double onto a dibromobenzene moiety. However when using a diboronicbenzene ‘centre’ the yield does not exceed 30%.

A problem with this reaction is there is no good way of monitoring its progress. The product has too high molecular mass for standard GC, and TLC gives many spots on the plate with no way to quantify. Crude NMR is also not useful due to the spectra of the starting material and product being exactly the same, bar the integrals which cannot be calculated with crude material. The starting arylbromide **11a** can be seen on GC, so disappearance could be monitored relative to an internal standard, however this cannot confirm the formation of product. Optimisation, therefore, has taken time due to purification needed before a yield can be determined. Nearly 40 reaction conditions have been screened with various palladium catalysts, ligands, bases, and solvents. All reactions were heated to reflux and generally left overnight, however is it sometimes observed low mass recovery with longer reaction times. Reactions were monitored by TLC and the most promising were purified by column chromatography, while the rest were combined and starting material recovered. Conditions were based on similar substrates from the literature. Table 2.2.5 summarises the most successful reactions, all heated to 80 °C and performed on a 0.32 mmol scale.

Entry	Catalyst, %mol	Ligands	Base	Solvent	Time	Product[a]
1	$Pd(PPh_3)_4$ 1.5%	none	2 M K_2CO_3	DME	24 hrs	44%[b]
2	$Pd(PPh_3)_4$ 1.5%	none	1 eq. K_2CO_3	MePh/EtOH/H_2O	18 hrs	50%[b]
3	$Pd_2(dba)_3$ 2%	4 x PPh_3	2 M K_2CO_3	THF	18 hrs	18%
4	$Pd_2(dba)_3$ 2%	4 x PPh_3	2 M K_2CO_3	THF	3 hrs	34%
5	$Pd_2(dba)_3$ 2%	4 x P(2-MeOPh)$_3$	2 M K_2CO_3	THF	3 hrs	38%
6	$Pd_2(dba)_3$ 2%	4 x P(2-furyl)$_3$	2 M K_2CO_3	THF	21 hrs	50%[a]
7	$Pd(PPh_3)_4$ 2%	none	1 eq. K_2CO_3	DME	24 hrs	24%
8	$Pd(PPh_3)_4$ 2%	none	2 M Na_2CO_3	Dioxane	18 hrs	16%

Table 2.2.5. Suzuki coupling reactions to give pentaphenyl 13. [a]determined by NMR, [b]70-80% purity by NMR.

As well as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$, $Pd(OAc)_2$ was also tried but gave no reaction. Ligand-free $Pd_2(dba)_3$ gave poor reaction, which was slightly improved by two equivalents of PPh_3, then even more with four equivalents. Potassium carbonate was the most used base, 2 M sodium hydroxide gave very poor reactions, while caesium carbonate was only used once in the only dry reaction in toluene which yielded no product. As seen by the increase of yield in entry 4 from 3, long reaction times do appear to lower the yield of reaction, as discovered with the Suzuki coupling to

produce the starting material **11a**. However there are no examples in the literature using phenyl-1,4-diboronic acid for short reaction times. As for solvent, DME and THF appear to work best and dissolve the diboronic acid well. Toluene, a less polar solvent compared to DME and THF, yielded no reaction on its own, but a mix with EtOH does give better results.

As optimisation was taking quite some time it was necessary to develop a HPLC monitoring system. A 10% DCM/hexane solvent system was used along with diphenyl ether as an internal standard. Since then a further 12 reaction conditions have been investigated, unfortunately with no increase in yield. Conditions tried include using phase-transfer catalysts 18-crown-6 and tetrabutyl ammonium bromide, and varying the amount of base. Interestingly there was a dramatic difference between using 1 equivalent of potassium carbonate giving a yield of 24%, and a 2 M solution equalling 18 equivalents which gave very little product, both used 2% $Pd(PPh_3)_4$, in DME at 90 °C. However when using 1 equivalent of base was repeated, trace product was observed. Reactions using the diboronic ester of **12** were attempted but gave no better yield. Swapping around the organoboron and arylbromide groups was also tried, the boronic acid of the mono-phenyl-bis-hexyne **11a** could easily be made, however still the coupling gave no higher yield. Entry 8 was performed in darkness with the diboronic ester, which has been noted by a few examples in the literature[23] to give better yields.

It is apparent that oxygen must be thoroughly removed from the reaction mixture, as this destroys the palladium catalyst. Boronic acids, and esters, when left for a long time can decompose or form various non-reactive species.[24] Another problem with boronic acid/esters is that, either upon synthesis or during the Suzuki reaction, they can form boronic anhydrides which are less reactive mainly due to steric hindrance of the base molecule attacking the boron complex. Protodeborolation can also occur which halts the reaction after just one, or zero, couplings. Another concern is that the ortho-acetylene to the bromide which the palladium inserts into could further react with the triple bond. There is no literature precedent of similar ortho-acetylene couplings, but as mono couplings to the same moiety do not suggest it is a problem, it may not be of concern.

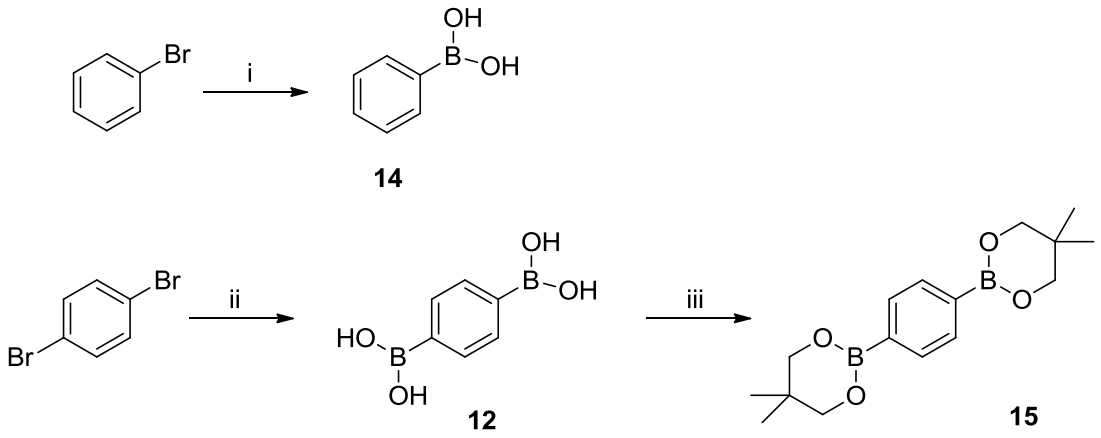
Conclusion

This Suzuki coupling is a very important reaction and needs to be high yielding, especially for making longer systems. The next step in the synthesis to the final compounds, the base catalysed cyclisation, is just as important. Work has focused on this reaction because if it were to prove unsuccessful, the efforts to optimise the Suzuki would not be required. This optimisation, although still not complete, has given some insight. Polar solvents such as DME or THF are required and $Pd(PPh_3)_4$ is the best catalyst. As for reaction time, short reactions tend to give better yields. Over

time the catalyst will decompose, and leave mono substituted coupled boronic product which can form a mix of dimers and trimers and lead to problems with purification. This double Suzuki onto a diboronicbenzene is further investigated with the naphthylene chemistry and will be discussed later in this report, and gives further insight into the reaction.

2.3 Boronic acids and esters

The efforts to make the pentaphenyl product **13** used commercially bought phenyl-1,4-diboronic acid **12**. Prior to this, synthesis of the diboronic acid **12** had also been attempted. There are two common ways to make boronic acids from an arylmonohalide, either by use of *n*-BuLi or magnesium to produce the aryllithium or Grignard reagent, followed by addition of a borate and an aqueous work up. Typically this is a high yielding reaction, however para-dibromobenzene to give the diboronic acid is not. Typical yields in the literature are around 30-40% and usually follow the Grignard route. An *n*-BuLi method[25] was used on bromobenzene and gave clean product in near quantitative yield. This method was applied, along with twice the equivalents of reagents, to dibromobenzene but yielded no product. There was no sign of butylated or unhydrolysed compound, however it is possible that boronic anhydrides had formed. The solid was converted to the ethylene glycol ester and supported this conclusion, as analysis showed a mixture of the boronic ester, and anhydrides. The Grignard method[26] was tried and gave clean product but in very low yield. Several attempts have been made to produce the diboronic via both methods, and various recrystallisation techniques, but yielded no analysable product. Other mono arylboronics have been produced in very high yields, and will be shown throughout the later sections of this report. This area of work will be investigated further once the need for a great amount of the diboronic acid **12** is required. Commercial diboronic acid was converted to the neopentyl glycol ester[23] **15** in quantitative yield and was used for the Suzuki optimisation, however made no change to the yield. Scheme 2.3.1 summarises this work.



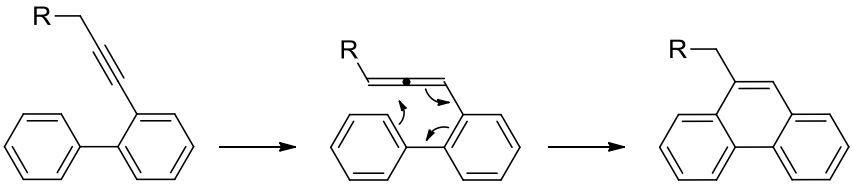
Scheme 2.3.1. Reagents and conditions: (i) n-BuLi, THF, $B(OPr^i)_3$, 96%. (ii) Mg, THF, $B(OPr^i)_3$, 3%. (iii) Neopentylglycol, toluene, reflux, 18 hrs, 96%.

Conclusion

This work ties in with the pentaphenyl optimisation, and is also prioritised by the actual need for the component; if the coupling cannot be optimised, there is no real need for it. There are other methods to make different diboronic species which can be attempted.

2.4 Phenyl-acetylenes: Base catalysed cyclisations

A major step in this aryl-acetylene field is the final base catalysed cyclisation to give the PAHs. Following the Wang/Burton method[16], using catalytic DBU in refluxing NMP, converts the alkyne to an allene, which then undergoes a 6 electron cyclisation to give the product as shown in figure 2.4.1.

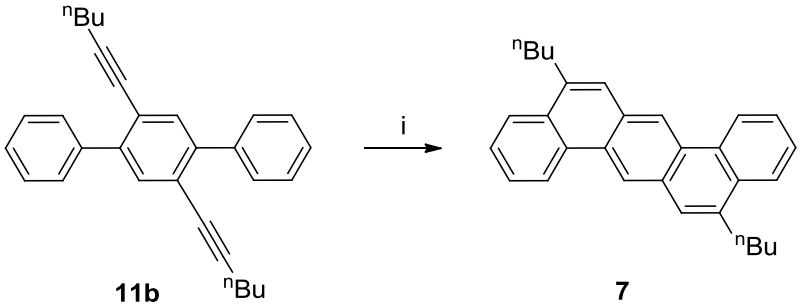


Scheme 2.4.1. Base catalysed cyclisation.

Unfortunately the literature does not state how long the reaction was left for, however initial studies carried out in the group showed it required 2-3 days at ~190 °C; the hottest the standard oil bath could heat to. Shorter reaction times, up to one hour, have to be performed using flow heating, but much higher amounts of DBU are required to push the reaction to near completion.

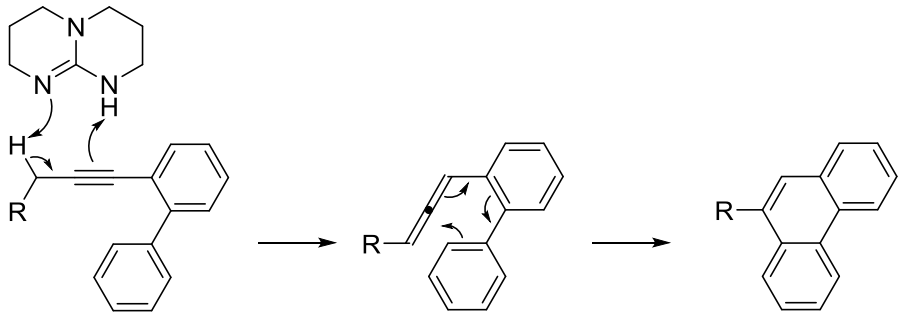
Investigation began on the o-terphenyl-bisacetylene **11b**, which involves two cyclisations to give the PAH **7**. Amounts of DBU, the use of other nitrogen containing bases, longer reaction times,

and different methods of heating were investigated. Firstly a reaction was carried out in the microwave with DBU, only yielded 23% of pure product **7** that was enough for analysis and give a reference for future reactions.



Scheme 2.4.2. Reagents and conditions: (i) DBU, NMP, 200 °C, 30 mins, 23%.

Three bases have been tried, DBU, DBN and TBD**.** TBD, shown in figure 2.4.3, was chosen with the theory of it being able to remove and deliver a proton at the same time, hence speeding up formation of the allene.



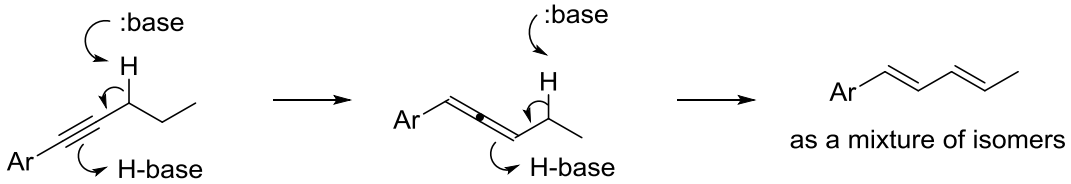
Scheme 2.4.3. Base catalysed cyclisation showing TBD as the base.

The first 11 reactions were preformed on the p-terphenyl **11b** using a flow reactor at 250 °C in NMP. The table below shows the results of these, where ‘mono’ is just one cyclisation occurring leaving one alkyne unreacted. Percentage of each product, starting material, mono and desired product, was determined by NMR of the crude reaction mixture with respect to each other.

Entry	Base, equivs	Time mins	SM %	Mono %	Product **7** %	Mass %
1	DBN, 1	30	38	56	6	86
2	DBN, 10	30	20	52	29	66
3	DBU, 10	30	9	39	52	32
4	DBU, 10	30	22	49	29	79
5	DBU, neat	30	-	-	-	61
6	DBU, neat	30	23	31	46	84
7	DBU, neat	10	20	61	19	94
8	TBD, 0.1	30	3	74	22	83
9	TBD, 1	30	-	-	-	82
10	TBD, 10	30	-	-	-	45[a]
11	DBU, 10, TBD, 0.1	30	3	48	49	89

Table 2.4.4. Flow reactions of p-terphenyl 11b. [a] Post column chromatography.

Unfortunately none of these were high yielding, and are not isolated yields. Entry 3 is seen as an anomaly with a low mass recovery, and the rerun was more consistent with the data trends. No real difference was seen between DBU and DBN, however the more basic TBD (entries 9 and 10) gave some interesting results. A 10% loading of the base consumed nearly all the starting material, but not a good yield of product, however in the NMR several peaks appeared between 5 and 6 ppm, indicating the presence of alkenes, most likely dienes. This side product(s) was major in the 10 equivalents reaction which produced trace desired product. TBD has been investigated further and discussed in the next section. These alkene peaks were also present when neat DBU (entry 5) was used, however in a much lower amount.



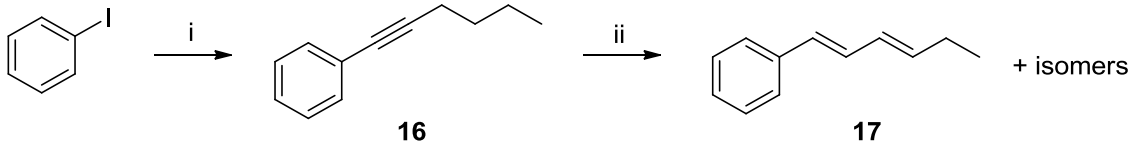
Scheme 2.4.5. Formation of dienes.

Conclusion

Unfortunately yields have not yet exceeded 50%. There are more bases that can be investigated, and chosen by strength and structure of the base. Time, temperature and equivalents of base, was investigated further and discussed later in the report.

2.5 Isomerisation of an alkyne to a diene: A brief aside

As observed in the base catalysed cyclisations, TBD is believed to isomerise the alkyne to a diene, as a likely mixture of cis- and trans- isomers. This isomerisation is extremely rare in the literature, with only two examples given but as side products to different methods. Therefore it was decided to investigate this further, starting with a simple phenyl-alkyne model as shown in figure 2.5.1.



Scheme 2.5.1. Reagents and conditions: (i) 1-Hexyne, Et_3N, $PdCl_2(PPh_3)_2$, CuI, RT, 1 hr, Quant. (ii) TBD/DBU, Flow, 10-60 mins, 200-250 °C.

A standard Sonogashira coupling gave the model **16** in high yield, which was then subjected to a range of flow chemistry reactions. The table below shows the preliminary results where the loss of starting material was measured by GC. Decane was present as an internal standard to observe mass recovery, which was consistently good.

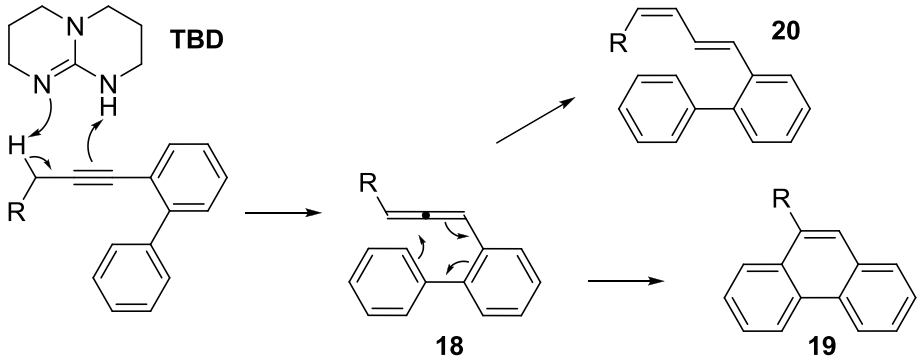
Entry	Base, equivs	Temp °C	Time mins	SM %
1	TBD, 1	200	10	100
2	TBD, 1	250	10	74
3	TBD, 1	250	30	9
4	TBD, 1	250	60	5
5	DBU, 1	250	10	100

Table 2.5.2. Initial flow isomerisation reactions.

These experiments gave a consistent set of data as seen by the trend in consumption of starting material with temperature and time, to give three 'product' peaks on the GC analysis, whose ratios to each other remained the same. The less basic DBU was tried but only starting material was observed. These reactions were performed on milligram scale; enough for an NMR which showed a mixture of isomers. Because this isomerisation required temperatures over 200 °C, i.e. not very convenient for most synthetic chemists, it was not investigated further.

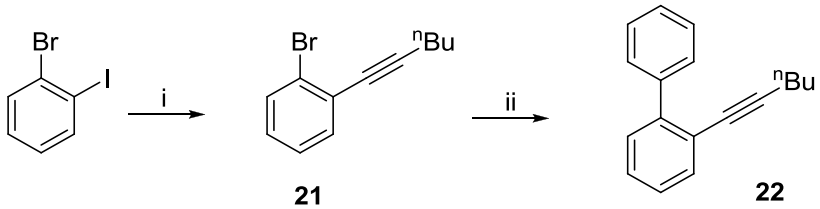
2.6 Back to the Phenyl-acetylenes

The base cyclisation still required optimising, yields of the p-terphenyl-bisacetylene compound did not exceed 50%, with a good proportion of mono-cyclised intermediate formed, and at high concentrations of base, a mixture of dienes was observed. TBD was chosen with the theory of speeding up formation of the allene **18**, shown in the scheme below. However this allene has two pathways; cyclise to the product **19**, or isomerise further, with the aid of TBD, to undesired phenyldienes **20**.



Scheme 2.6.1. Base catalysed cyclisation mechanism.

Several routes were taken to avoid this diene formation and these will be discussed in the following sections. First was to investigate the reaction further on a simple phenylacetylene model **22**.



Scheme 2.6.2. Reagents and conditions: (i) 1-Hexyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 60 °C, 1 hr, Quant. (ii) Phenylboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 2.5 hrs, Quant.

The model was synthesised in quantitative yield over two steps from the commercial dihalidebenzene, via ‘standard’ Sonogashira and Suzuki coupling methods. The table below shows the cyclisations carried out.

Entry	Base, equiv.	Temp °C	Method of heating	Solvent	Time	SM %	Diene %	Product **19** %
1	DBU, 1	~180	Hotplate	DMA	3 days	100	0	0
2	DBU, 1	~180	Hotplate	Mesitylene	3 days	100	0	0
3	TBD, 0.1	200	Microwave	NMP	30 mins	53	0	47
4	TBD, 1	250	Flow	NMP	30 mins	15	23	62
5	TBD, 0.5	~200	Hotplate	NMP	23 hrs	<5	22	78

Table 2.6.3. Base induced cyclisations on mono-model 22.

These results confirm the need for high temperatures to achieve product, but still requires tuning in terms of base used to avoid diene formation. All entries were analysed by NMR and crude mass recovery was good, but no products were isolated at this stage. It was concluded that flow was not an ideal reaction heater for these reactions. The flow reactor also has potential issues with solubility, whether that be of the starting material, or even worse the cyclised product which will be less soluble and block the flow equipment. The one advantage of flow is the high temperature capability compared to standard round-bottom flask chemistry. The microwave experiment showed a promising result with no diene observed, however 200 °C is the maximum temperature for the microwave. It was believed that longer times and less base would give the best results with less diene formed. Reactions were then carried out in a sealable J-Young tap vessel which can withstand the higher pressure produced at high temperatures. At 250 °C, heating in an aluminium block, the pressure should not exceed 2 Atmospheres. Monitoring is a slight issue, as it is necessary to let the vessel cool down, and then heat back up, so only one or two reaction points were taken, but this gave sufficient insight into the reaction profile. Conditions were experimented on the mono-model **22**, all in NMP.

Entry	Base, equiv.	Temp °C	Time	SM %	Diene %	Product %	Isolated yield %
1	TBD, 0.1	250	20 hrs	0	0	100	74
2	TBD, 0.05	250	20 hrs	13	0	87	58

Table 2.6.4. Base induced cyclisations on mono-model 22.

These two reactions showed very good results, with trace diene, even with catalytic TBD. The reactions were run together and NMR after 1 hour showed 72% product for entry 1, and 43% for entry 2 which then only increased to 87% after 20 times longer reaction time, likely due to

decomposition of the base. Two more reactions were run together to confirm this and the table below clearly shows the reaction halting then starting again once an extra quantity of TBD was added. The figures state amount of product observed by GC.

Entry	Base, equiv.	5 hrs	22 hrs	30 hrs[a]	46 hrs	Mass recovery %
1	TBD, 0.05	83	91	92	100	100
2	TBD, 0.02	50	73	75	97	87

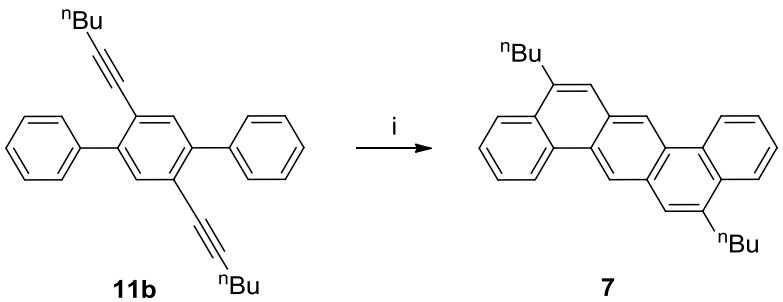
Table 2.6.5. Base induced cyclisations on mono-model 22. [a] Extra TBD added; 5% and 2% respectfully.

Catalytic TBD was giving good results and no diene, however decomposition of the TBD occurred before completion of the reaction. 10% loading fully converts the simple model, however as will be shown later, this is too much base for other systems and forms dienes. So reactions were tried using DBU, which is thermally stable at these high temperatures.

Entry	Base, equiv.	Temp °C	Time	SM %	Diene %	Product %	Mass recovery %
1	DBU, 1	250	23 hrs	6	0	94	89
2	DBU, 1	280	23 hrs	0	0	100	97
3	DBU, 0.1	280	23 hrs	43	0	57	98

Table 2.6.6. Base induced cyclisations on mono-model 22.

Entry 1 shows very near complete conversion at 250 °C, and the hotter entries 2 and 3 showed an increase with the reaction rate, and the 10% DBU was a little faster than a tenth of the stoichiometric base. And most importantly no diene was observed. With this promising result, the next test was to use the conditions on the bis-phenyl system, as shown below. 1 equivalent of DBU was used at 280 °C, and yielded a very high 78% of double cyclised product **7**.



Scheme 2.6.7. Reagents and conditions: (i) DBU, NMP, 280 °C, 20 hrs, 78%.

Conclusion

These reactions concluded that longer, high temperature reaction conditions gave best results, with a low loading of base. The simple mono phenyl model gave very good yields, and the bis-system a little lower, however other longer systems may require further optimisation, as the number of cyclisations to take place on one molecule would increase by 2 again.

2.7 Naphthyl-acetylenes: Synthesis and base catalysed cyclisations

Alongside the cyclisations of the simple phenyl model were the naphthylene systems. These should increase the reactivity of the cyclisation, hence giving the allene less time to isomerise to the diene. Calculations, performed by Prof. Richard Whitby, predicted that the 6-electron cyclisation onto a naphthyl group requires less energy than onto a phenyl. The extra bonus of using naphthyl groups is that it extends the length of the PAH. Some concerns of these systems include possible steric 1,5 hydrogen clashes on the final product **23**, and in some cases a chance of different isomers **24a** and **24b** formed, as shown in the generic examples below.

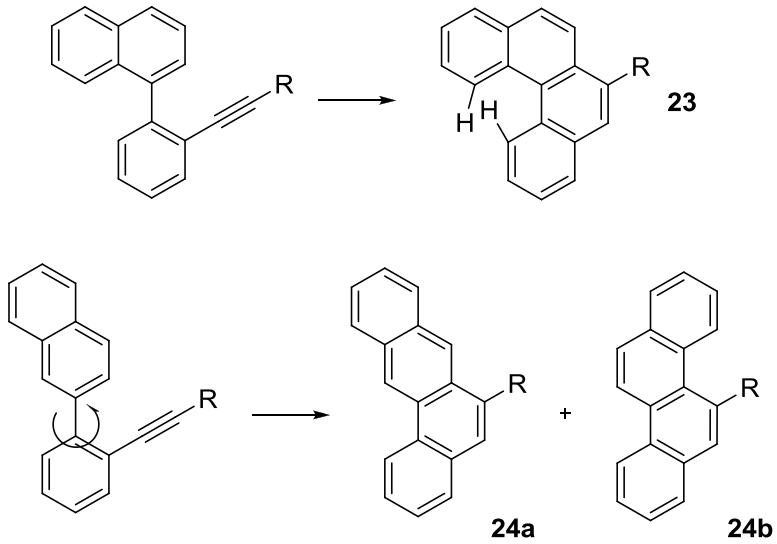


Figure 2.7.1. Possible problems with naphthyl cyclisations.

There were three initial precursor models to be made. Unfortunately compound **27** has not been synthesised yet, but **25** and **26** have been made in good yields.

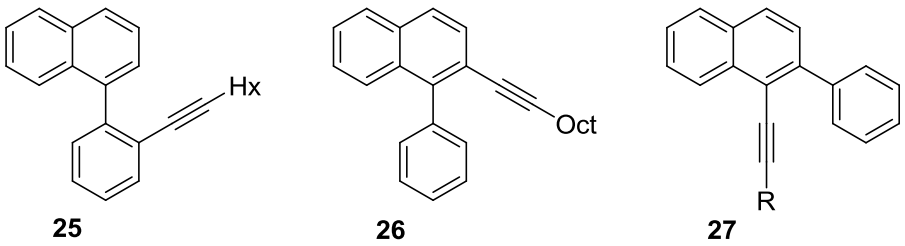
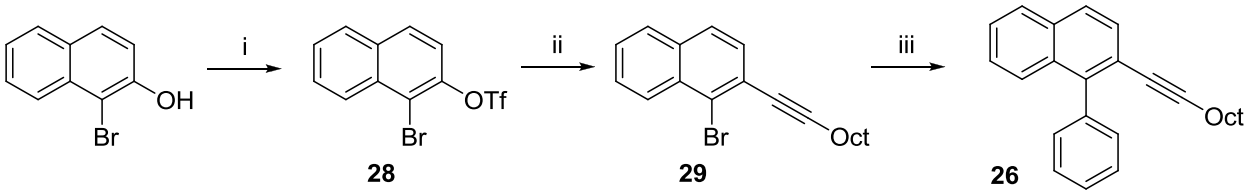


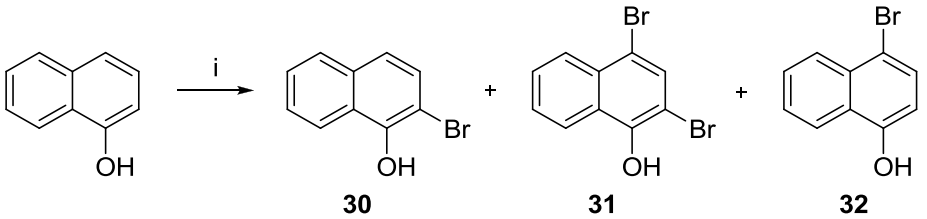
Figure 2.7.2. Initial naphthyl models.

Model **25** was made in very high yield over three steps; 1-naphthyl boronic acid was formed in quantitative yield from the standard aryl bromide using the, *n*-BuLi, $B(OMe)_3$ method, then taking commercial o-dihalidebenzene through the 'standard' Sonogashira and Suzkui coupling methods with yields of >95% and 63% respectfully. Model **26** was produced in slightly lower yields, but still a good result over three steps.



Scheme 2.7.3. Reagents and conditions: (i) TfO_2, py, 0 °C, 2.5 hrs, Quant. (ii) 1-Decyne, $PdCl_2(PPh_3)_2$, CuI, Bu_4NI, Et_3N, DMF, 80 °C, 2.5 hrs, 85%. (iii) Phenylboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 1 hr, 78%.

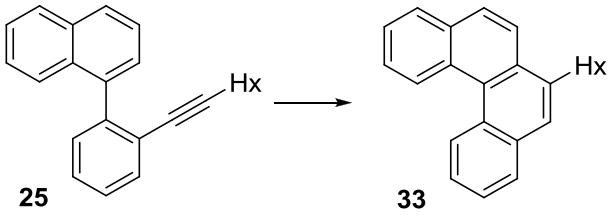
The commercial bromonaphthol was converted to the triflate[27] to allow for chemoselectivity of the Sonogashira coupling to the alkyne. The 'standard' coupling reaction to give **29** did not yield any product, however addition of tetrabutylammonium iodide in a mixture of TEA:DMF, gave compound **29** in high yield. Another 'standard' Suzuki coupling gave model **26** in high yield. Model **27** was due to be made in reverse style to **26**. Starting from commercial 1-naphthol and first inserting a halogen into the 2- position, then converting the alcohol to triflate, and following the coupling methods as before. Following a literature method[28] to insert a bromine, which boasted high selectivity and yield, a mixture of products was obtained.



Scheme 2.7.4. Reagents and conditions: (i) NBS, $(^iPr)_2NH$, DCM, 50 °C, 16 hrs.

After column chromatography, which at best gave two mixtures of SM + **32** and **30** + **31**, NMR and MS analysis showed only 9% of the desired product **30** had formed, along with **31** 19%, **32** 35% and the starting material 20%. Another literature method[29] using mild conditions to insert an iodide was attempted twice but gave unidentifiable compounds in both cases. The NBS reaction will be investigated further.

A series of cyclisation experiments were then carried out. NMR analysis was carried out, and products were not isolated at this stage. Below are the results for model **25** to give product **33**.



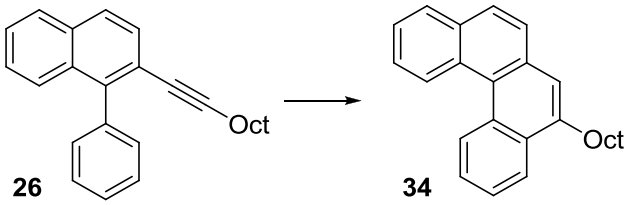
25 **33**

Entry	Base, equiv.	Temp °C	Method of heating	Time	SM %	Diene[a] %	Product %
1	TBD, 0.1	200	Microwave	30 mins	100	0	0
2	TBD, 1	250	Flow	30 mins	40	35	25
3	TBD, 0.1	250	Flow	30 mins	>95	<5	0
4	TBD, 0.1	~200	Hotplate	24 hrs	100	0	0
5	TBD, 0.5	~200	Hotplate	23 hrs	12	40	48
6	TBD, 0.1	250	J-Young	19 hrs	4	39	57
7	DBU, 1	280	J-Young	20 hrs	0	17	83

Table 2.7.5. Base cyclisations on naphthyl model 25. [a] Mixture of dienes and allene. % by NMR.

The conversions for this compound are quite poor, especially as it is believed that the cyclisation with a naphthyl, compared to a phenyl in compound **22**, should be faster. But comparing these results, the naphthyl has converted roughly half the amount of the phenyl system and more diene has been observed. The energy gained in cyclising to a naphthyl is clearly lost by the 1,5 hydrogen clash, thus lowering the yield. As these reactions were performed on a small scale, entries 1, 3 and 4 could be showing no conversion due to the small amount of base used, i.e. not easy to weigh out. Entries 6 and 7, performed in the sealed vessel, showed a better conversion to product, however still a significant amount of diene and allene formed, and unfortunately the desired product could not be isolated from these mixtures. These results do tell us that the cyclisation is favoured over the formation of diene at higher temperatures.

The other naphthyl model, to give compound **34**, to be tested shows an interesting, unexpected observation.



26 **34**

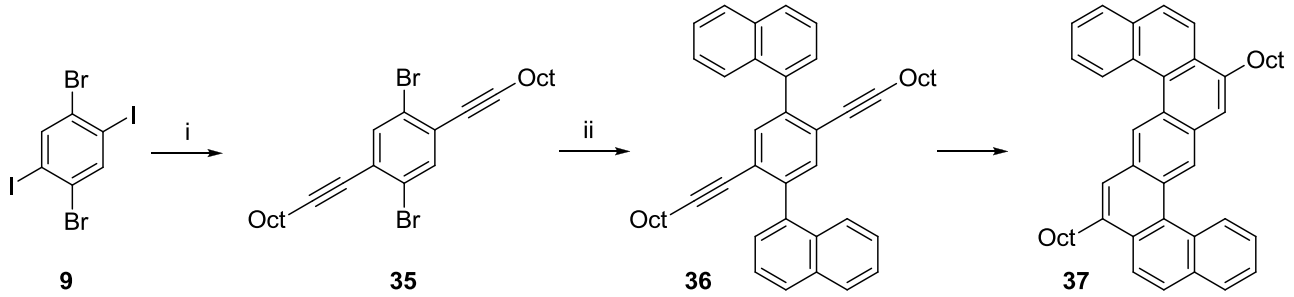
Entry	Base, equiv.	Temp °C	Method of heating	Time	SM %	Diene %	Product %
1	TBD, 0.1	200	Microwave	30 mins	89	0	11
2	TBD, 1	250	Flow	30 mins	<8	31	61
3	TBD, 0.5	~200	Hotplate	20 hrs	<5	31	69
4	TBD, 0.1	~200	Hotplate	23 hrs	85	0	15
5	DBU, 0.5	~200	Hotplate	23 hrs	79	0	21
6	TBD, 0.1	250	J-Young	19 hrs	64	0	36
7	DBU, 1	280	J-Young	20 hrs	0	0	100

Table 2.7.6. Base cyclisations on naphthyl model 21. % by NMR.

These reactions gave much better conversions, very good in entries 2 and 3, and does not show a linear trend with the previous naphthyl model and the simple phenyl. It would be expected that this product would have the same steric clash and similar results to the previous naphthyl model. Entry 7, performed in the sealed vessel, showed complete conversion to product with no diene observed. Entry 6 showed no diene or allene, however a low yield of product, in other words a slower but more selective reaction. The conditions of entry 7 were used for a scale-up reaction which isolated 84% of the desired cyclised product.

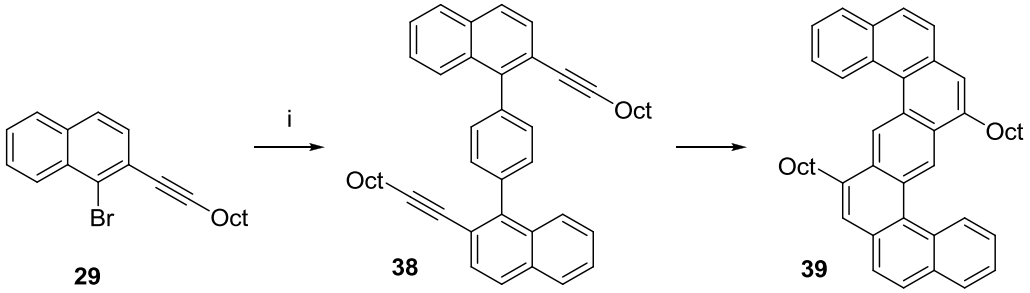
It was expected that the reactions of these two naphthyl compounds would have similar reactivity. However they don't, but with more investigation the results may be able to help to customise and optimise the synthesis of longer PAHs. Comparing the two model systems, two conclusions can be drawn: Either, the rate of allene formation in the first model **25** is faster than the second **26** which leads to more diene formation, or the rate of allene formation is the same for both models, but the cyclisation of the second model is faster/more favourable. As more starting material is consumed in the first case and some allene is observed in the NMR, it looks likely that the allene formation is faster, and as more diene is seen, the cyclisation slower. Unfortunately there is not enough evidence to support an explanation as to why this is the case.

With the difference in the two model naphthyl systems, both bis-forms were then synthesised and cyclisations attempted.



Scheme 2.7.7. Reagents and conditions: (i) 1-Decyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, toluene, reflux, 5 hrs, 56%. (ii) 1-naphthaleneboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 58%.

First bis-naphthyl-bis-acetylene **36** was synthesised using the 'standard' palladium coupling methods in modest yields. A flow cyclisation was performed using 1 equivalent of TBD, mass recovery was good, but the NMR gave weak/broad peaks and analysis could not be performed. However peaks in the high aromatic region (8-9 ppm) and alkene (5-6.5 ppm) suggested there was product **37** present and unfortunately diene and allene, as was observed with the model system. Two more reactions were performed in the sealed vessels, one with 10% TBD at 250 °C, the other with 1 equivalent of DBU at 280 °C. The latter appeared to work better, as expected, however some diene and allene was seen, and no product could be isolated from the small amounts of crude material. The second bis-naphthyl compound **38** was synthesised via the double Suzuki onto a diboronic component which as before caused some problems.



Scheme 2.7.8. Reagents and conditions: (i) Phenyl-1,4-diboronic neopentyl glycol ester, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 24 hrs, 20%.

The aryl bromide **29** was synthesised as with the model, then several attempts at the double Suzuki using the diboronic ester were made, in low yield. 1% Pd catalyst loading yielded only 17% isolated product after 3 hours, however only starting material made up the rest of the mass, suggesting the second coupling is a lot faster than the first. A second reaction left for 22 hours

showed 32% product on the NMR. On these small scale reactions it is likely that even when taking great care to avoid oxygen killing the catalyst, it is inevitable. An increase of palladium catalyst does not increase the yield of product but of a compound, most likely to be a mono-coupled starting material with some kind of boronic species. Boronic compounds are not easy to analyse with the possible formation of dimers, trimers, and anhydrides. The proton NMR suggests there is a mixture of these, and is consistent with the observation of very little product and starting material. With these points in mind, it is reasonable to suggest that the anhydrides are a lot less reactive. Sterics of the three molecules of the naphthyl-acetylene would certainly hinder the boron centre from attack of a base to form the borate complex, which then has to dock with another bulky arylbromide molecule, therefore stopping the reaction. Using cesium fluoride, to form the organotrifluoroborate, should confirm that the formation of anhydrides halts the reaction, as they should not form under the fluoride conditions. However this was attempted gave no increase in the yield.

Although the bis-naphthyl compound **38** has only been produced in low yield, an interesting observation was made. NMR showed that the product exists as two conformers in a 2:1 ratio, a ratio observed in all reactions performed, suggesting the sigma bonds to the centre benzene ring are not freely rotating. Calculations also predict roughly a 2:1 ratio of conformers. Varied temperature NMR was carried out, focusing on the CH_2 adjacent to the triple bond, and showed that the conformers interconvert at 60 °C.

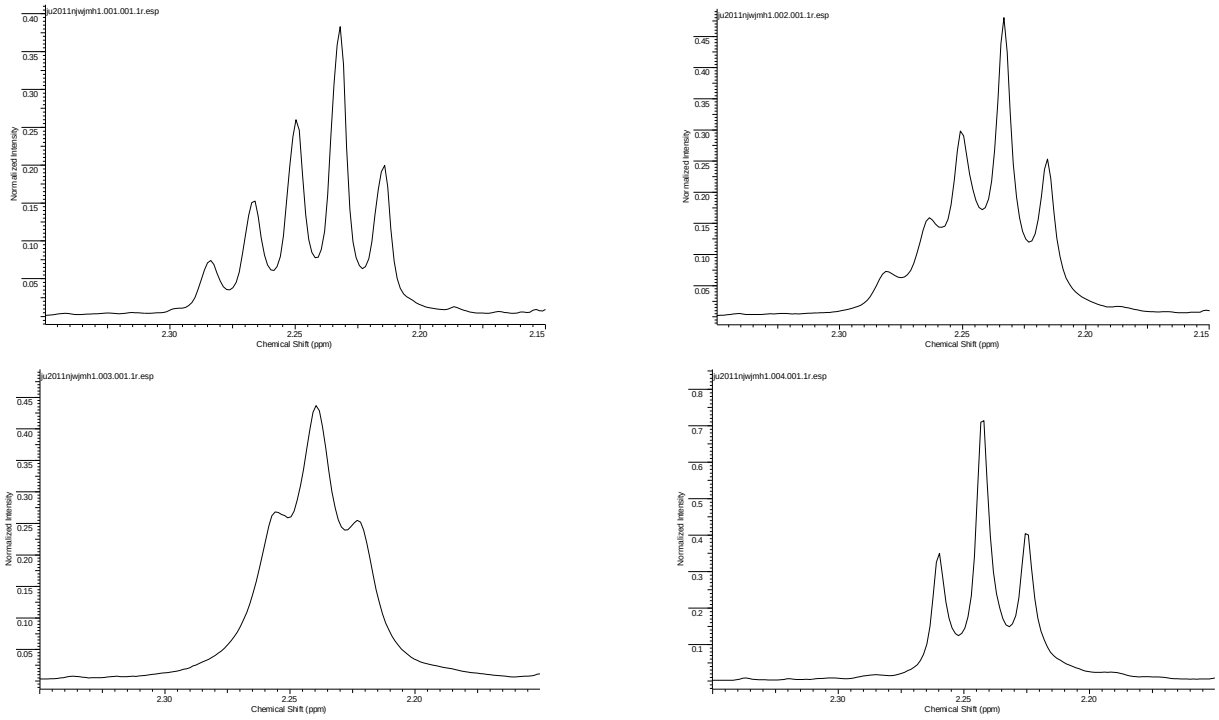


Figure 2.7.9. VT-NMR spectra recorded at 25, 40, 60 and 80 °C.

Since this penultimate reaction is currently low yielding, only two cyclisations had been performed using 1 equivalent of DBU at 280 °C, as with the bis-naphthyl **36**. As seen with the model systems, this one again gave a much better result, with majority one product **39** and trace amounts of dienes. However there was another expected side product, the mono-cyclised compound, in a 3:7 ratio with the desired double cyclised product. The two products could carefully be separated via recrystallisation, however with small amounts to begin with this resulted in 30% yield of product **39**.

Conclusion

The naphthyl-acetylene work is looking the most successful for producing long PAHs. The work on the two model systems, in particular the base cyclisation, has given a good insight into how best to design the precursor to the final PAH product, with the conclusions that the 1,5 hydrogen clash effectively cancels out the lower energy required to cyclise with a naphthyl ring, and the unexpected difference in rates of cyclisations between the two structural isomers **25** and **26.** Although both the bis-naphthylacetylene compounds are to be scaled up and synthesised, preliminary results have shown the trend to be consistent. Extending this structure to give longer PAHs, will introduce more 1,5 hydrogen clashes.

2.8 2-Naphthyl-acetylenes: Synthesis and base catalysed cyclisations

The majority of the work focused on 1-naphthyl systems, however 2-naphthyl systems were briefly investigated, which will give rise to start an array of new PAHs. One possible problem with the synthesis of these compounds, as stated in the previous section, is the chance of forming different isomers **41a** and **41b** formed, as shown in the example below.

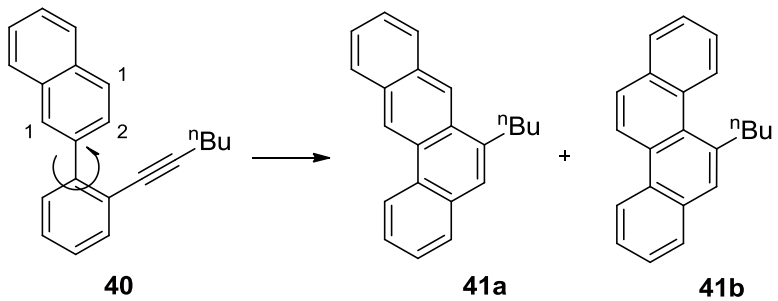
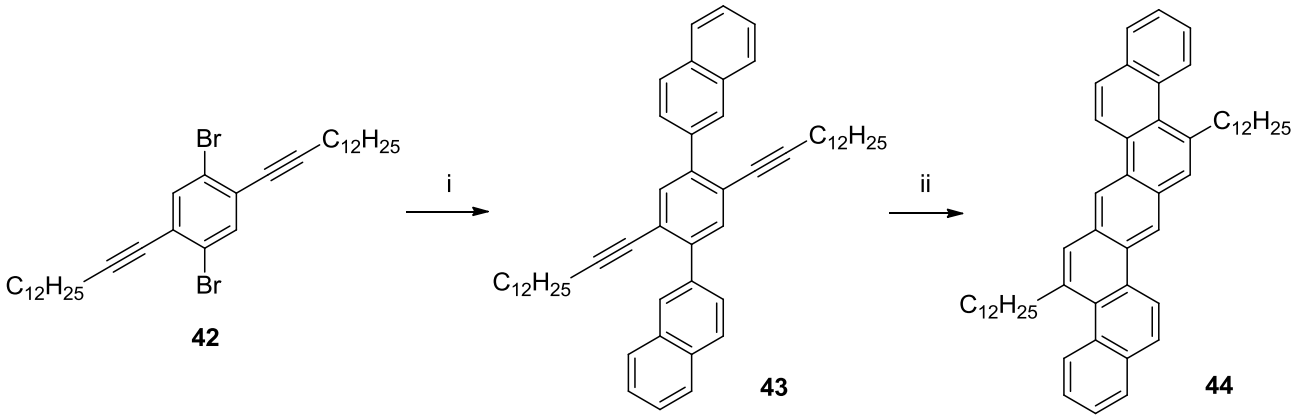


Figure 2.8.1. Possible problems with naphthyl cyclisations.

Calculations predicted that these naphthyl-acetylenes would cyclise onto the 1-position of the naphthyl ring. Initial studies in the Whitby group proved this to be the case with the model **40**

cyclising to give only product **41b**, confirmed by NOE NMR experiments. The model was then extended to give the bis-system following the route below.



42 **43** **44**

Scheme 2.8.2. Reagents and conditions: (i) 2-Naphthaleneboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 22 hrs, 70%. (ii) DBU, NMP, 280 °C, 19 hrs, 76%.

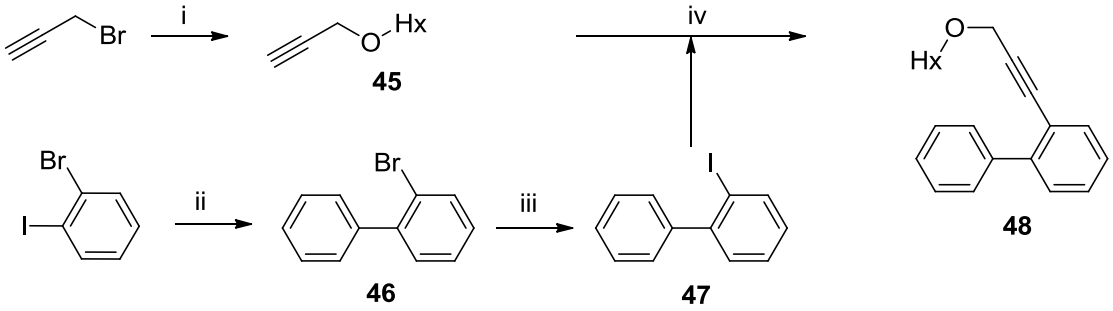
Previously prepared aryl bromide **42**, underwent a standard Suzuki coupling to give the precursor **43**, which was then cyclised under the optimised conditions to give the final PAH **44**, in a respectable yield of 76%. The only problem of the synthesis was the solubility of the final compound, even with two 12 carbon alkyl chains attached, the proton NMR had to be recorded at an elevated temperature whilst a carbon NMR could not be obtained.

Conclusion

The synthesis of the 2-naphthyl compounds worked as well as was expected. With no hydrogen clashes the cyclisation was a much cleaner reaction, and showed complete selectivity to the 1-position on the naphthyl ring. The issue with solubility could be overcome with the use of branched alkyl chains rather than linear.

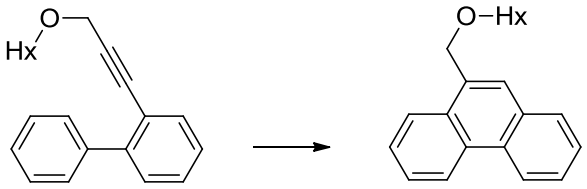
2.9 Phenyl-propargyl ethers: Avoiding the diene formation

A promising lead with the cyclisation reaction was the use of TBD with a fast consumption of starting material however this leads to another problem of further isomerisation from the allene to alkenes. So efforts were taken to overcome this problem by using a system where isomerisation to a diene is impossible. The first system tried was a propargyl ether acetylene, where allene formation is possible, but no further isomersation due to the oxygen atom present. A simple model **48** for this theory was made via the scheme 2.9.1 below.



Scheme 2.9.1. Reagents and conditions: (i) NaH, hex-1-anol, DMF, 0 °C → RT, 20 hrs, 75%. (ii) Phenylboronic acid, $PdCl_2$, PPh_3, K_2CO_3, MePh/EtOH/H_2O, reflux, 22 hrs, 82%. (iii) *n*-BuLi, I_2, THF, 3.5 hrs, 71%. (iv) $PdCl_2(PPh_3)_2$, CuI, Et_3N, 50 °C, 23 hrs, 64%.

Propargyl bromide was converted to the hexyl ether[30] in high yield. The other component was synthesised from 1-bromo-2-iodobenzene, which was coupled to phenyl boronic acid via Suzuki method[8] and unsurprisingly favoured iodide chemoselectivity leaving the arylbromide **46** which then had to be converted to the iodide **47** using *n*-BuLi and iodine[31], then coupled with the propargyl **45** using 'standard' Sonogashira conditions[32] yielding the model **48** in 64% yield. This mono-model **48** was then cyclised to give **49**.



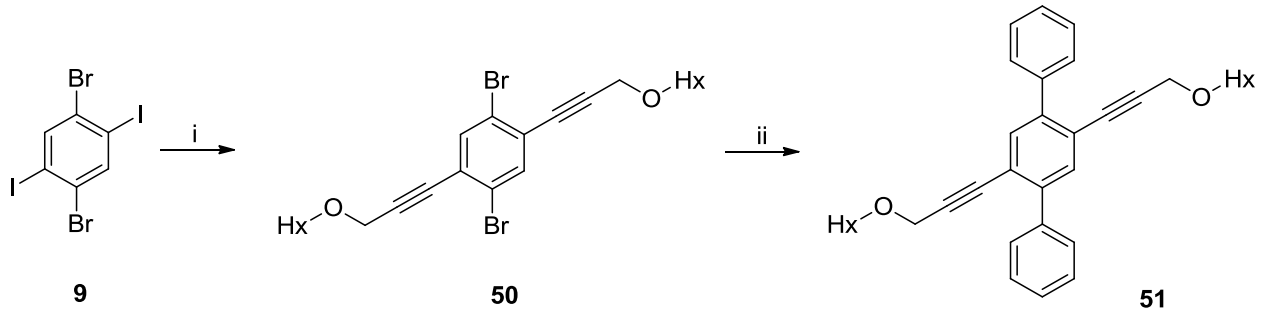
Entry	Base, equiv.	Temp °C	Solvent	Time	Product by NMR %	Mass recovery %
1	DBU, 1	110	Toluene	3 days	0	-
2	DBU, 20	250	NMP	30 mins	87	52
3	TBD, 1	250	NMP	30 mins	92	63
4	TBD, 1	250	NMP	30 mins	20	48

Scheme and table 2.9.2. Propargyl model cyclisations.

Entry 1 was performed in an NMR tube and showed no reaction. Another NMR tube reaction was performed, heating the already made allene in refluxing toluene, however again this did not yield any cyclised product, proving that high temperatures were required. Entries 2 and 3 performed in the flow reactor, gave very good conversions to product and starting material was the only

impurity, however with modest mass recovery performed on small scale. Entry 4, a scale-up of 3, gave an unusual result with 20% yield, and poor mass recovery.

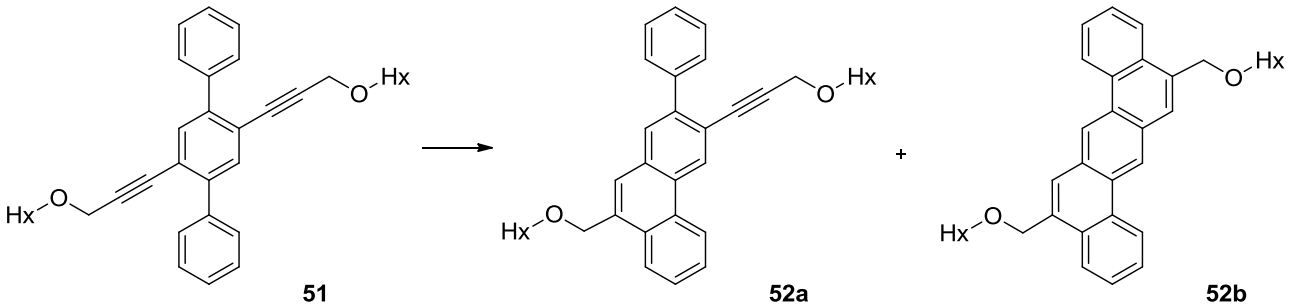
As the cyclisation was working, just with low mass recovery, the next size up bis-model **51** was synthesised.



9 **50** **51**

Scheme 2.9.3. Reagents and conditions: (i) Propargylhexyl ether, $PdCl_2(PPh_3)_2$, CuI, Et_3N, toluene, reflux, 2.5 hrs, 37%. (ii) Phenylboronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 43%.

The bispropargyl-model **51** was produced via 'standard' Sonogashira and Suzuki coupling reactions from the mass produced dibromodiiodobenzene **9**, however in low yields. Also recovered from the Suzuki reaction was the mono-coupled intermediate in 11%, which is a component that can be used to synthesise longer propargyl systems. The bis-model was then put through a short series of cyclisation reactions and summarised in the table below.



51 **52a** **52b**

Entry	Base, equiv.	Temp °C	Solvent	Time	SM **51** %	Mono **52a** %	Product **52b** %	Mass recovery %
1	TBD, 0.1	250	NMP	30 mins	18	67	15	77
2	TBD, 1	250	NMP	30 mins	<5	<5	>90	73
3	DBU, 20	250	NMP	30 mins	<5	<5	>90	67
4	TBD, 1	250	NMP	30 mins	<5	<5	>90	41

Table 2.9.4. Base cyclisations on bis-model. % by NMR.

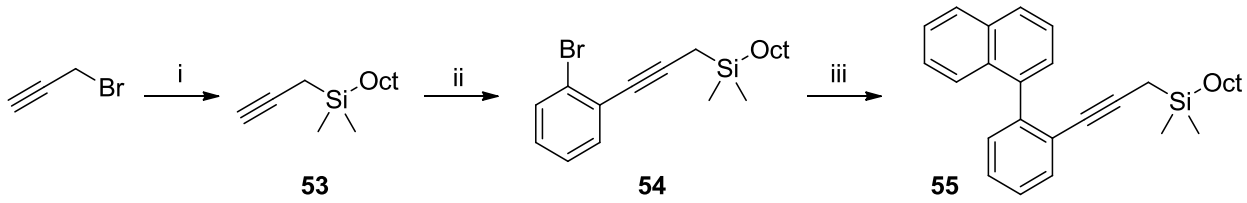
Once again excellent conversions were achieved. Catalytic, 0.1 equivalent, base is not enough to perform two cyclisations, however 1 equivalent is. All reactions were performed using the flow reactor, entries 1-3 being small scale, and 4 a scale up to isolate and fully analyse the final PAH **52b**. However the mass recovery was again very low, which was a concern because of the benzylic ether being put through high temperature basic conditions.

Conclusion

Although the cyclisation appeared to work very well, the mass recovery was consistently poor for the cyclisation and prior synthetic steps, meaning the propargyl ether route is unfortunately not a good one. There is the silyl propargyl moiety, much similar to the previous oxygen case, which should produce compounds that are more stable than propargyl ethers.

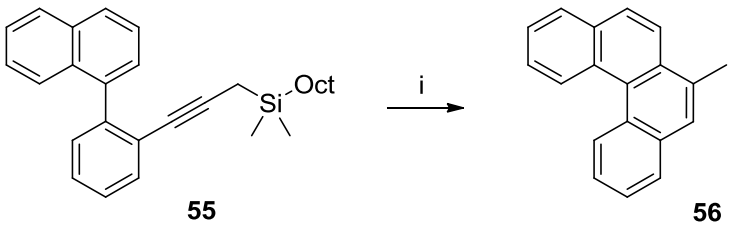
2.10 Propargylsilanes: Avoiding the diene formation

As mentioned in the previous section, propargyl ethers and silanes would make isomerisation to the diene impossible, however the ethers were very unstable and gave very low yields. The silanes were attempted as it would have been expected to give more stable compounds. A naphthyl silyl model **55** was synthesised. This model, with the acetylene attached to the phenyl rather than the naphthyl was chosen as it was the lowest yielding cyclisation reaction (compound **25** to **33**).



Scheme 2.10.1. Reagents and conditions: (i) Mg, $HgCl_2$, $OctSi(Me)_2Cl$, Et_2O, 0 °C → RT, 20 hrs, 58%. (ii) 1-Bromo-2-iodobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 50 °C, 1 hr, Quant. (iii) 1-Naphthyl boronic acid, $Pd(PPh_3)_4$, 2 M K_2CO_3, DME, reflux, 5 hrs, 26%.

The first step was a Grignard reaction[33] to give the propargylsilane **53**, which required very slow addition of the chlorosilane. The next two steps followed standard coupling reactions, the final Suzuki was very low yielding for unknown reasons. However gave enough of the model **55** to attempt the cyclisation. The reaction was carried out as with the optimal conditions, 1 equivalent of DBU at 280 °C, and gave a number of products. After purification it was analysed that 50% of the starting material had cyclised, but the with the silyl side chain removed. No desired cyclised product could be obtained.



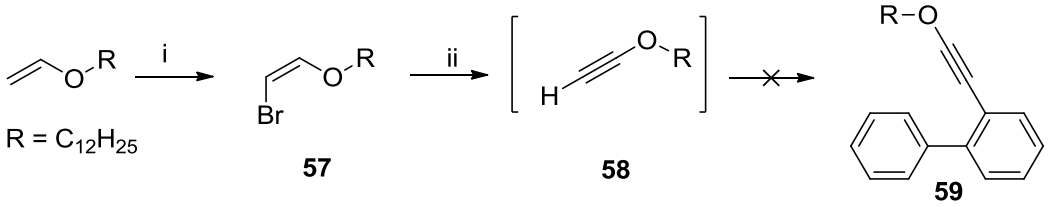
Scheme 2.10.2. Reagents and conditions: (i) DBU, NMP, 280 °C, 20 hrs, 50%.

Conclusion

Although the propargylsilanes had expected to be more stable than the ethers, the instability of the cyclised compounds was again too high. Avoiding the diene formation using propargyl system was not a viable option.

2.11 Phenyl-alkoxyalkynes: Avoiding the diene formation

Another method to obtain the zigzag polyaromatic hydrocarbons, similar to the base cyclisations, is acid cyclisations on similar phenyl-alkyne systems. This reaction would consist of direct protonation on the beta position to the oxygen, followed by cyclisation to form a 6 membered aromatic ring. This again began on a simple model **59**.



Scheme 2.11.1. Reagents and conditions: (i) Br_2, Et_3N, DCM, -78 °C → RT, 18 hrs, Quant., 73:26% Z:E. (ii) LDA, THF, -78 °C, 2 hrs, 33%.

Commercially available and very cheap dodecyl vinyl ether was brominated in a two step one-pot process[34] in high yield. Another one-pot synthesis to give the model **59**, using LDA to form the alkoxy-alkyne[35], trapped with $ZnCl_2$, then coupled to the aryl bromide **47** via a Negishi method[36], did not work with recovery of the aryl bromide. The model was attempted again by isolating the alkoxyalkyne **58**, then performing the Negishi coupling, however this failed a second time with a mixture of unidentifiable products. It was found in the literature that alkoxyalkynes would not couple to a 2-substituted benzene ring[37]. For this reason it was decided not to spend more time on this type of system.

2.12 Benzothiophenes: A side project

A short project to make three benzothiophenes was undertaken. This work is linked to the main project, as sulphur containing aromatic systems are another target group of molecules for the organic electronics. The targets for this mini project are shown in figure 2.12.1 and will be used by the Hursthouse group for crystallisation experiments.

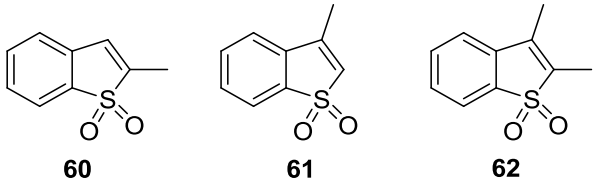
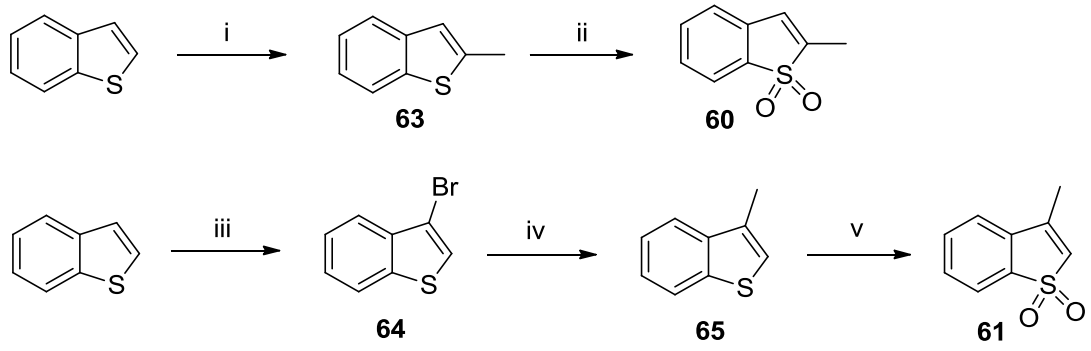
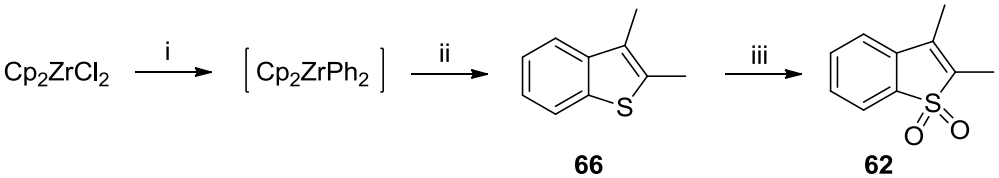


Figure 2.12.1. Benzothiophene targets.



Scheme 2.12.2. Reagents and conditions: (i) *n*-BuLi, MeI, THF, -78 °C, 2 hrs, 48%. (ii) AcOH, H_2O_2, reflux, 1 hr, 48%. (iii) AcOH, NBS, $CHCl_3$, 0 °C → RT, 20 hrs, 81%. (iv) *n*-BuLi, MeI, THF, -78 °C, 1hr, 66%. (v) AcOH, H_2O_2, reflux, 1 hr, 40%.

The synthesis to compounds **60** and **61** was relatively straight forward. Methylation on benzothiophene[38], followed by oxidation with hydrogen peroxide afforded clean product **60** after recrystallisation in good yield. Bromination on the 3- position using NBS[39], followed by methylation gave the 3-methylbenzothiophene **65** in high yield, and finally oxidation to give target thiophene **61**. Thiophene **62** was made via a different method using zirconium.



Scheme 2.12.3. Reagents and conditions: (i) PhLi, THF, -40 °C. (ii) 2-butyne, 80 °C, S_2Cl_2, -78 °C, THF, >95%. (iii) H_2O_2, AcOH, 80 °C, 25%.

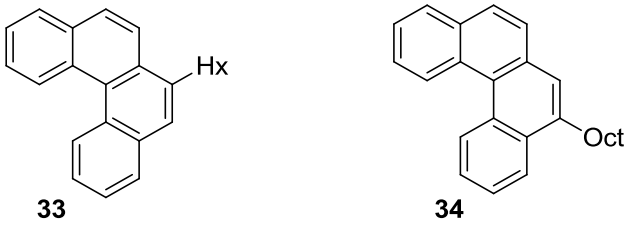
Diphenylzirconocene was first produced from zirconocene dichloride and phenyllithium[40], then reacted with 2-butyne and sulphur monochloride[41] in a one-pot synthesis to give dimethyl thiophene **66**. This was then oxidised as before to give the final compound **62**, in low yield but was enough material for the crystallography experiments.

3.0 Further Work

There are several reactions which require more optimisation/investigation. The double Suzuki coupling to a diboronicbenzene centre is clearly one that still needs optimising. There are a vast range of conditions that can be used, however from all the reactions run during this project so far, it appears that boronic anhydride formation stops the reaction from running to completion, so the boron component could be one to change, which to date it has not been. Otherwise the palladium coupling reactions are working quite well, although when it comes to making longer precursors, i.e. more couplings in one step, the yield may unfortunately decrease.

Aryl bromo to iodo conversions are quite likely to be an important tool for this project. A couple of efforts are shown in this report, the *n*-BuLi and Finkelstein methods, however they were not particularly high yielding and can be investigated further.

The base catalysed cyclisation has shown very good progress, with some of the systems cyclising in near quantitative yields. The difference in naphthyl systems is an interesting one, and efforts will be taken to optimise the 'poorer' one **33**, or only incorporate the 'better' one **34** in the longer systems.



33 **34**

Figure 3.0.1. 1-Naphthyl models **33** and **34**.

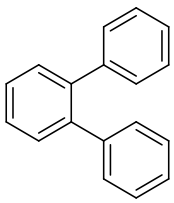
Efforts to produce the heteroatom polycyclic aromatic hydrocarbons have begun in the group with good results. This area will certainly be taken further to produce a range hetero-PAHs.

4.0 Experimental

4.1 General Experimental

All glassware was cleaned and oven dried before use. All reactions were carried out in either Schlenk flasks, round bottom flasks or sealable J-Young tap vessels and were magnetically stirred under an atmosphere of argon. Anhydrous reagents and solvents were added *via* needle, syringe and rubber 'subaseal'. Reactions were monitored by Gas Chromatography using Hewlett Packard 6890 Series GC system with a HP-5 crosslinked methyl siloxane column (30 m x 320 μm). All extractions were followed by drying the organic layer over magnesium sulphate, filtered and the solvent removed *in vacuo*. ^{1}H and ^{13}C NMRs were recorded on Bruker AV-300 at 75 and 300 MHz, Bruker DPX400 at 100 and 400 MHz, at room temperature unless otherwise stated. Chemical shifts are given in parts per million (ppm) and referenced to the NMR solvent. Electron impact ionisation mass spectra (EI) and chemical ionisation (CI) were recorded on a ThermoQuest TraceMS GCMS. Infra-red spectra were run as neat films on a Thermo Nicolet 380 FT-IR spectrometer with a Smart Orbit Goldengate attachment. Absorptions are given in wavenumbers (cm^{-1}). UV spectra was recorded on an Ocean Optics DH-2000-BAL at room temperature using Spectral suits interface and a silica cuvette with a 1 mm path length. Wavelengths are given in nm and the corresponding molar extinction coefficient with no units expressed.

1,1':2',1''-Terphenyl 6a



1,2 Dibromobenzene (0.75 mL, 6.25 mmol), phenylboronic acid (1.83 g, 15 mmol), sodium carbonate (2.12 g, 20 mmol), palladium chloride (16 mg, 0.09 mmol) and triphenylphosphine (47 mg, 0.18 mmol) were mixed together in a solution of toluene, ethanol and water (3:3:1) under an atmosphere of argon, then refluxed for 22 hours. Upon completion solvents were removed *in vacuo*, water added and product extracted with DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title terphenyl **6a** (0.64 g, 2.78 mmol, 44%) as a white crystalline solid. NMR data is consistent with the literature.[42]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47-7.41 (4H, m), 7.25-7.14 (10H, m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.51 (2C), 140.57 (2C), 130.58 (2CH), 129.88 (4CH), 127.83 (4CH), 127.46 (2CH), 126.42 (2CH).

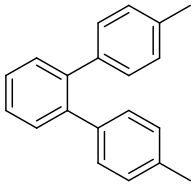
IR (neat) υ_{max} 3054 (w), 2922 (w), 1596 (w).

LRMS (GC/EI) *m/z* 230, 92% (M^+); 229, 100% (M^+-H); 226, 66%; 215, 82%; 202, 49%.

UV (hexane) λ_{max} 231 nm, ε_{max} 34055.

Melting point 54-56 °C, lit[43]: 56-57 °C.

4,4''-Dimethyl-1,1':2',1''-terphenyl 6b



1,2 Dibromobenzene (0.75 mL, 6.25 mmol), 4-methylbenzeneboronic acid (2.04 g, 15 mmol), sodium carbonate (2.12 g, 20 mmol), palladium chloride (16 mg, 0.09 mmol) and triphenylphosphine (47 mg, 0.18 mmol) were mixed together in a solution of toluene, ethanol and water (5:5:2) under an atmosphere of argon, then refluxed for 18 hours. Upon completion solvents were removed *in vacuo*, water added and product extracted with DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title terphenyl **6b** (0.63 g, 2.44 mmol, 39%) as a white solid. Analysis showed ~80% purity. NMR data is consistent to the literature.[42]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44-7.40 (4H, m), 7.08-7.03 (8H, m), 2.34 (6H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.43 (2C), 138.71 (2C), 135.94 (2C), 130.62 (2CH), 129.70 (4CH), 128.59 (4CH), 127.21 (2CH), 21.10 ($2CH_3$).

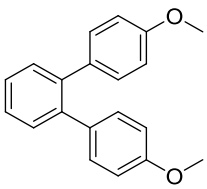
IR (neat) υ_{max} 3019 (w), 2914 (w), 1473 (w), 754 (s).

LRMS (GC/EI) *m/z* 258, 100% (M^+); 243, 92% (M^+-Me); 239, 54%; 228, 80% (M^+-2Me); 215, 31%.

UV (hexane) λ_{max} 237 nm, ε_{max} 59069.

Melting point 89-90 °C, lit[42]: 94-95 °C.

4,4''-Dimethoxy-1,1':2',1''-terphenyl 6c



1-Bromo-2-iodobenzene (0.52 mL, 4 mmol), 4-methoxybenzeneboronic acid (1.70 g, 11 mmol) and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) were mixed together in a solution of sodium hydroxide sol^{n} (2.5 M, 20 mL) and dimethoxyethane (20 mL) then refluxed for 20 hours. Upon completion product was extracted with hexane. Purification by column chromatography (silica gel, 0-10% ethyl acetate/hexane) gave the title terphenyl **6c** (0.31 g, 1.06 mmol, 26%) as a white solid. Further purification by recrystallisation from hot hexane gave the title product as one large crystal (0.52 g, 1.79 mmol, 44%). NMR and MS data is consistent to the literature.[6]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38 (4H, br s), 7.07 (4H, d, *J* = 8.8 Hz), 6.78 (4H, d, *J* = 8.8 Hz), 3.80 (6H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 158.20 (2C), 140.05 (2C), 134.08 (2C), 130.87 (4CH), 130.52 (2CH), 127.09 (2CH), 127.09 (2CH), 113.35 (4CH), 55.15 ($2OCH_3$).

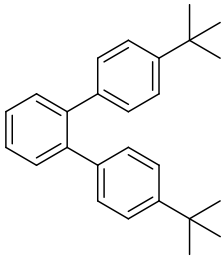
LRMS (GC/EI) *m/z* 290, 100% (M^+); 259 30% (M^+-OMe); 215, 54%; 203, 35%; 202, 47%.

IR (neat) υ_{max} 3012 (w), 2834 (w), 1609 (m), 1463 (m), 1236 (s), 1177 (m).

UV (hexane) λ_{max} 247 nm, ε_{max} 86686, λ 220 nm, ε 48488.

Melting point 109-111 °C, lit[6]: 107-108 °C.

4,4''-Di-tert-butyl-1,1':2',1''-terphenyl 6d



1,2 Dibromobenzene (0.72 mL, 6 mmol), 4-*t*-butylbenzeneboronic acid (2.67 g, 15 mmol), sodium carbonate (2.12 g, 20 mmol), palladium chloride (16 mg, 0.09 mmol) and triphenylphosphine (47 mg, 0.18 mmol) were mixed together in a solution of toluene, ethanol and water (5:5:2) under an atmosphere of argon, then refluxed for 30 hours. Upon completion solvents were removed *in vacuo*, water added and product extracted with DCM. Purification by column chromatography (silica gel, 0-5% ethyl acetate/hexane) gave the title terphenyl **6d** (1.65 g, 4.77 mmol, 79%) as a white crystalline solid. NMR data is consistent to the literature.[6]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.46-7.38 (4H, m), 7.23 (4H, d, *J* = 8.2 Hz), 7.08 (4H, d, *J* = 8.2 Hz), 1.31 (18H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 149.19 (2C), 140.53 (2C), 138.58 (2C), 130.51 (2CH), 129.45 (4CH), 127.15 (2CH), 124.60 (4CH), 34.38 (2C), 31.33 ($6CH_3$).

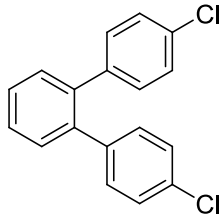
IR (neat) υ_{max} 2956 (w), 2902 (w), 1269 (w).

LRMS (GC/EI) *m/z* 342, 86% (M^+); 327, 100% (M^+-Me); 311, 9%; 271, 13% (M^+-*t*Bu-Me); 252, 13%; 229, 24% (M^+-2*t*Bu); 57, 84%.

UV (hexane) λ_{max} 238 nm, ε_{max} 26749, λ 212 nm, ε 24554, λ 269 nm, ε 22359.

Melting point 79-82 °C, lit[6]: 76-79 °C.

4,4''-Dichloro-1,1':2',1''-terphenyl 6e



1,2 Dibromobenzene (0.72 mL, 6.0 mmol), 4-chlorobenzeneboronic acid (2.34 g, 15.0 mmol), sodium carbonate (2.12 g, 20.0 mmol), palladium chloride (16 mg, 0.09 mmol) and triphenylphosphine (47 mg, 0.18 mmol) were mixed together in a solution of toluene, ethanol and water (5:5:2) under an atmosphere of argon, then refluxed for 45 hours. Upon completion solvents were removed *in vacuo*, water added and product extracted with DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title terphenyl **6e** (1.49 g, 4.97 mmol, 83%) as a white crystalline solid. ^{1}H data consistent with the literature.[44]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.46-7.38 (4H, m), 7.22 (4H, d, *J* = 8.4 Hz), 7.06 (4H, d, *J* = 8.4 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 139.61 (2C), 139.24 (2C), 132.78 (2C), 131.08 (4CH), 130.52 (2CH), 128.27 (4CH), 127.91 (2CH).

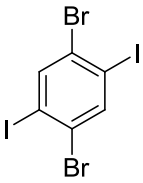
IR (neat) υ_{max} 2360 (w), 1908 (w), 1467 (m), 1084 (m), 757 (s).

LRMS (GC/EI) *m/z* 302, 15% (M^+, $Cl^{37/37}$); 300, 76% (M^+, $Cl^{35/37}$); 298, 96% (M^+, $Cl^{35/35}$); 263, 56% (M^+-Cl); 263, 56%; 228, 89% (M^+-2Cl); 113, 100%.

UV (hexane) λ_{max} 240 nm, ε_{max} 52395.

Melting point 133-136 °C, lit[44]: 136 °C.

1,4-Dibromo-2,5-diiodobenzene 9



p-Dibromobenzene (20 g, 84.8 mmol), iodine (86 g, 339.2 mmol) and conc. H_2SO_4 (100 mL) were mixed in a Schlenk tube then heated to 125 °C for 7 days. Reaction vessel outlet consisted of silica, empty flask, then water to trap released HBr. Upon completion the reaction mixture was cooled, then dissolved in DCM and washed with sat sodium metasulfide aq and sat sodium bicarbonate aq. The DCM phase was separated and solvent removed *in vacuo* to give title compound **9** (41.4 g, 84.8 mmol, 100%) as a pale yellow powdery solid. ^{1}H-NMR and MS data consistent with the literature.[22]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.06 (2H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.30 (2CH), 129.19 (2C), 101.31 (2C).

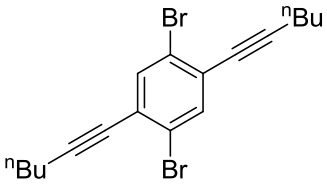
LRMS (GC/EI) *m/z* 489, 58% (M^+, $Br^{81/81}$); 487, 100% (M^+, $Br^{81/79}$); 485, 68% (M^+, $Br^{79/79}$); 360, 33% (M^+-I, $Br^{79/81}$); 234, 31% (M^+-I_2, $Br^{79/81}$).

IR (neat) υ_{max} 3057 (w), 2354 (w), 1407 (m), 1279 (m), 999 (s), 875 (s).

UV (hexane) λ_{max} 228 nm, ε_{max} 79323, λ 250 nm, ε 44436.

Melting point 143-146 °C, lit[22]: 163-165 °C.

1,4-Dibromo-2,5-di(hex-1-yn-1-yl)benzene 10



1,4-Dibromo-2,5-diiodobenzene **9** (4.87 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol), copper (I) iodide (0.08 g, 0.4 mmol) and 1-hexyne (2.5 mL, 22 mmol) were mixed in a 1:3 solution of triethylamine and toluene (50 mL) and heated to reflux for 2 hours. Upon completion product was extracted in DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **10** (3.13 g) as a dark orange oil; purity 80-95%. Further purification by recrystallisation from cold hexane gave >95% pure compound (1.07 g, 2.7 mmol, 27%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.60 (2H, s), 2.47 (4H, t, *J* = 7.0 Hz), 1.67 – 1.45 (10H, m), 0.96 (7H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.03 (2CH), 126.48 (2C), 123.46 (2C), 98.16 (2C), 78.26 (2C), 30.45 ($2CH_2$), 21.95 ($2CH_2$), 19.32 ($2CH_2$), 13.60 ($2CH_3$).

LRMS (GC/EI) *m/z* 398, 49% (M^+, $Br^{81/81}$); 396, 93% (M^+, $Br^{81/79}$); 394, 53% (M^+, $Br^{79/79}$); 381, 25% (M^+-Me, $Br^{79/81}$); 353, 40% (M^+-Pr, $Br^{79/81}$); 221, 95%; 193, 81%; 150, 100%.

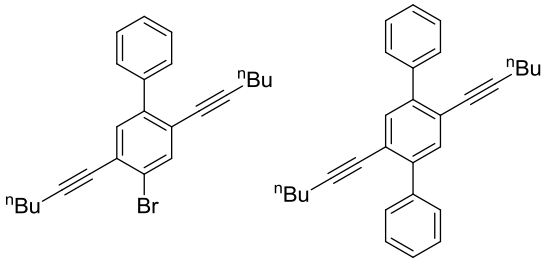
HRMS (GC/EI) Found 393.992775 ($M^+\cdot$), calculated 393.99263 for $C_{18}H_{20}Br_2$.

IR (neat) υ_{max} 2934 (s), 2871 (m), 2222 (m), 1463 (m), 1065 (s), 887 (s).

UV (hexane) λ_{max} 238 nm, ε_{max} 73413, λ 284 nm, ε 72857.

Melting point 45-48 °C.

4-Bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl 11a and 2',5'-Di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl 11b



1,4-Dibromo-2,5-di(hex-1-yn-1-yl)benzene **10** (0.28 g, 0.71 mmol), phenylboronic acid (0.17 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) were mixed with sodium hydroxide aq (2.5 M, 5 mL) and dimethoxyethane (5 mL) and heated to 80 °C for 3 hours. Upon completion HCl aq (2 M, ~15 mL) was added and the product extracted with DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title compounds **11a** (0.124 g, 0.32 mmol, 44%) as a yellow solid and **11b** (0.077 g, 0.19 mmol, 28%) as a pale yellow solid.

4-Bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl 11a:

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70 (1H, s), 7.55 – 7.53 (2H, m), 7.41 – 7.38 (4H, m), 2.49 (2H, t, *J* = 6.8 Hz), 2.30 (2H, t, *J* = 6.8 Hz), 1.68 – 1.25 (8H, m), 0.96 (3H, t, *J* = 7.1 Hz), 0.87 (3H, t, *J* = 7.1 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.39 (C), 139.14 (C), 136.13 (CH), 133.76 (CH), 128.98 (2CH), 127.86 (2CH), 127.56 (CH), 125.26 (C), 123.34 (C), 122.96 (C), 96.74 (C), 95.90 (C), 79.21 (C), 78.79 (C), 30.56 (CH_2), 30.28 (CH_2), 21.94 (CH_2), 21.79 (CH_2), 19.30 (CH_2), 19.17 (CH_2), 13.59 (CH_3), 13.54 (CH_3).

LRMS (GC/EI) *m/z* 394, 47% (M^+, Br^{81}); 392, 47% (M^+, Br^{79}); 351, 36% (M^+-Pr, Br^{81}); 349, 36% (M^+-Pr, Br^{79}); 271, 61%; 239, 74%; 226, 100% (M^+-Br-2Pr).

HRMS (GC/EI) Found 392.113325 ($M^+\cdot$), calculated 392.11341 for $C_{24}H_{25}Br$.

IR (neat) υ_{max} 2929 (m), 2870 (w), 2231 (w), 1473 (s), 1065 (m), 696 (s).

UV (hexane) λ_{max} 220 nm, ε_{max} 20848, λ 249 nm, ε 14769.

Melting point 89-91 °C.

2',5'-Di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl 11b:

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.64 (4H, d, *J* = 6.6 Hz), 7.53 (2H, s), 7.45 – 7.34 (6H, m), 2.31 (4H, t, *J* = 6.8 Hz), 1.51 – 1.27 (8H, m), 0.88 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.07 (2C), 139.81 (2C), 133.94 (2CH), 129.19 (2CH), 127.81 (2CH), 127.36 (2CH), 121.72 (2C), 94.68 (2C), 79.89 (2C), 30.42 ($2CH_2$), 21.82 ($2CH_2$), 19.23 ($2CH_2$), 13.59 ($2CH_3$).

IR (neat) υ_{max} 2951 (w), 2868 (w), 2225 (w), 1479 (m).

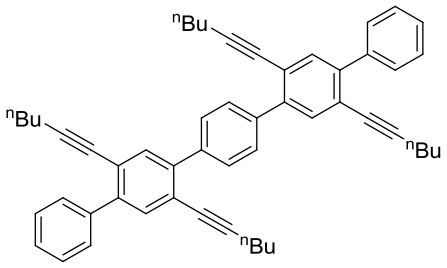
LRMS (GC/EI) *m/z* 390, 100% (M^+); 347, 63%, (M^+-Pr); 318, 14%; 302, 55%; 291, 71%; 289, 98%.

HRMS (GC/EI) Found 390.23402 ($M^+\cdot$), calculated 390.23475 for $C_{30}H_{30}$.

UV (DCM) λ_{max} 262 nm, ε_{max} 34137, λ 231 nm, ε_{max} 19739.

Melting point 176 °C.

2',2''',5',5'''-Tetra(hex-1-yn-1-yl)-1,1':4',1'':4'',1''':4''',1''''-quinquephenyl 13



4-Bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl **11a** (125 mg, 0.32 mmol), phenyl-1,4-diboronic acid **12** (26 mg, 0.16 mmol) and $Pd(PPh_3)_4$ (6 mg, 1.5% mol) were mixed with potassium carbonate aq (2 M, 3 mL) and DME (5 mL) and heated to 80 °C. Upon completion water was added and the product extracted with DCM. Purification by column chromatography (silica gel, 0-20% DCM/hexane) gave the title compound **13** (49 mg, 0.069 mmol, 44%) as a yellow/orange residue with ~80% purity. Combinations of crude products from several of these reactions were purified by recrystallisation from hot hexane to give fine orange needles and analysis obtained.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.55 (11H, m), 7.51 – 7.36 (7H, m), 2.35 (8H, q, *J* = 7.0 Hz), 1.57-1.30 (16H, m), 0.92 (6H, t, *J* = 7.0 Hz), 0.89 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.07 (2C), 141.72 (2C), 139.81 (2C), 138.84 (2C), 134.13 (2CH), 133.99 (2CH), 129.20 (4CH), 128.68 (4CH), 127.83 (4CH), 127.37 (2CH), 121.79 (2C), 121.67 (2C), 94.80 (2C), 94.71 (2C), 80.00 (2C), 79.92 (2C), 30.50 ($2CH_2$), 30.44 ($2CH_2$), 21.91 ($2CH_2$), 21.84 ($2CH_2$), 19.30 ($2CH_2$), 19.24 ($2CH_2$), 13.60 ($4CH_3$).

IR (neat) υ_{max} 3028 (w), 2955 (m), 2928 (m), 2360 (w), 2229 (w), 1601 (w), 1322 (w).

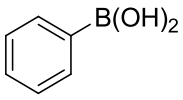
LRMS (GC/EI) *m/z* 702, 100% (M^+); 659, 16%, (M^+-Pr); 603, 12% (M^+-Hp); 489, 10%.

HRMS (GC/EI) Found 702.42472 ($M^+\cdot$), calculated 702.42255 for $C_{54}H_{54}$.

UV (DCM) λ_{max} 271 nm, ε_{max} 77953, λ 231 nm, ε 55565.

Melting point 112-115 °C.

Phenylboronic acid 14



Bromobenzene (0.34 mL, 3.18 mmol) was dissolved in THF (20 mL). n-BuLi (2.5 M, 1.44 mL, 3.60 mmol) was added slowly at -78 °C and left stirring for 1 hour. Triisopropyl borate (1.85 mL, 8 mmol) was added slowly left stirring for another hour then allowed to warm to room temperature. HCl (1M) was added and the product extracted with DCM to give the title boronic acid **14** (0.37 g, 3.04 mmol, 96%) as white crystals. NMR data is consistent with the literature.[45]

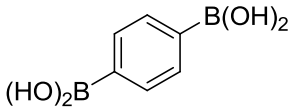
^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.27 (1H, d, *J* = 6.6 Hz,), 7.65 – 7.60 (1H, m), 7.53 (2H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 135.63 (CH), 132.69 (CH), 127.97 (CH).

IR (neat) υ_{max} 3077 (w), 1601 (m), 1440 (m), 1332 (br s).

Melting point 214-217 °C, lit[46]: 213-216 °C.

1,4-Phenylenediboronic acid 12



Dibromobenzene (5 g, 21.2 mmol) in THF (50 mL) was slowly added to a stirring solution of magnesium turnings (2 g, 84.8 mmol) in THF (5 mL) then refluxed for 18 hours. Reaction mixture was cooled to -78 °C and triisopropyl borate (12.2 mL, 53 mmol) was added slowly. Reaction left stirring for 2 hours then HCl (2M, ~40 mL) was added and product extracted with ether. Recrystallation in water gave the title boronic acid **12** (0.091 g, 0.55 mmol, 3%) as white crystals.

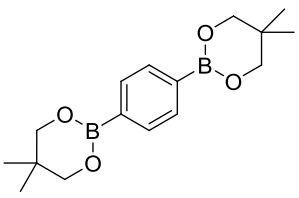
^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.00 (4H, s), 7.73 (4H, s).

^{13}C-NMR (75 MHz, DMSO-d_6) δ 133.03 (4CH).

IR (neat) υ_{max} 3278 (br m), 1514 (m), 1338 (br s).

Melting point >250 °C.

1,4-Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene 15



1,4-Phenylenediboronic acid (0.50 g, 3.02 mmol) and neopentylglycol (0.94 g, 9.06 mmol) was refluxed in benzene (40 mL) under a Dean-Stark apparatus for 18 hours. Benzene was removed, then the product was extracted into DCM and washed with water, to give the title boronic ester **15** (0.873 g, 2.90 mmol, 96%) as a white crystalline solid. Data consistent with the literature.[23]

^{1}H-NMR ($CDCl_3$) δ 7.79 (4H, s), 3.78 (8H, s), 1.03 (12H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 132.91 (4CH), 72.30 ($4CH_2$), 31.87 (2C), 21.91 ($4CH_3$).

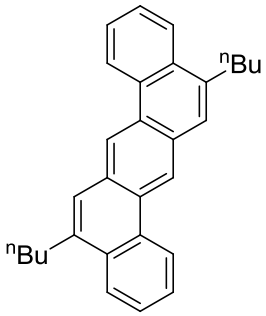
IR (neat) υ_{max} 2960 (w), 2871 (w), 1480 (m), 1289 (br s), 1132 (br m), 653 (s).

LRMS (GC/EI) *m/z* 302, 79% (M^+); 259, 25%; 217, 100%; 173, 18%.

UV (DCM) λ_{max} 233 nm, ε_{max} 13082.

Melting point 224-226 °C, lit[23]: 221-222 °C.

5,12-Dibutylbenzo[k]tetraphene 7



2',5'-Di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl **11b** (127 mg, 0.33 mmol) and DBU (48 µL, 0.33 mmol) were mixed in NMP (10 mL) in a sealed J-Young tap vessel and heated to 280 °C for 20 hours. Product was extracted into ether and washed with 2M HCl once and water twice. Purification by recrystallisation in hot hexane/toluene gave title product **7** (99 mg, 0.25 mmol, 78%) as light green crystals.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.92 (2H, s), 8.77 – 8.74 (2H, m), 8.05 – 8.02 (2H, m), 7.67 (2H, s), 7.54 – 7.52 (4H, m), 3.02 (4H, t, *J* = 7.7 Hz), 1.84 – 1.74 (4H, m), 1.53 – 1.41 (4H, m), 0.99 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.63 (2C), 131.59 (2C), 130.65 (2C), 130.35 (2C), 128.73 (2C), 126.77 (2CH), 126.36 (2CH), 126.21 (2CH), 124.56 (2CH), 123.37 (2CH), 121.22 (2CH), 33.28 ($2CH_2$), 32.24 ($2CH_2$), 22.97 ($2CH_2$), 14.09 ($2CH_3$).

IR (neat) υ_{max} 2951 (m), 2857 (w), 2360 (w), 2161 (w), 1622 (w), 1438 (w).

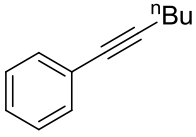
LRMS (GC/EI) *m/z* 390, 100% (M^+); 347, 70% (M^+-Pr); 304, 45% (M^+-Hx).

HRMS (GC/EI) Found 390.23409 ($M^+\cdot$), calculated 390.23475 for $C_{30}H_{30}$.

UV (DCM) λ_{max} 304 nm, ε_{max} 49844, λ 232 nm, ε 41758, λ 295 nm, ε_{max} 50352.

Melting point 181 °C.

Hex-1-yn-1-ylbenzene 16



Iodobenzene (1.12 mL, 10 mmol) was mixed with 1-hexyne (1.37 mL, 12 mmol), $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol), CuI (0.019 g, 0.1 mmol) in TEA (20 mL). After 1 hour stirring at room temperature, saturated NH_4Cl solution (~50 mL) was added, and the product extracted with DCM. DCM layer was washed with water, brine, and filtered through a short silica gel column to give compound **16** (1.58 g, Quant.) as a pale yellow oil. NMR data is consistent with the literature.[47]

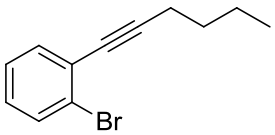
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.38 (2H, m), 7.30 – 7.27 (3H, m), 2.42 (2H, t, *J* = 7.0 Hz), 1.65 – 1.46 (4H, m), 0.96 (3H, t, *J* = 7.1 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 131.52 (C), 128.15 (C), 127.42 (C), 124.09 (C), 90.38 (C), 80.53 (C), 30.83 (CH_2), 22.00 (CH_2), 19.08 (CH_2), 13.63 (CH_2).

IR (neat) υ_{max} 2957 (m), 2930 (m), 2250 (w), 1326 (w).

LRMS (GC/EI) *m/z* 158, 67% (M^+); 143, 83% (M^+-Me); 115, 100% (M^+-Pr); 102, 47% (M^+-Bu).

1-Bromo-2-(hex-1-ynyl)benzene 21



1-Bromo-2-iodobenzene (1.28 mL, 10 mmol) was mixed with 1-hexyne (1.37 mL, 12 mmol), $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol), CuI (0.01 g, 0.1 mmol) in TEA (50 mL) and heated to 60 °C. After 1 hour saturated NH_4Cl solution (~50 mL) was added, and the product extracted with ether. Ether layer was washed with water and filtered through a short silica gel column to give compound **21** (3.21 g, Quant.) as an orange oil. Material was used in next step without further purification. NMR, MS and IR data consistent with the literature[48].

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.56 (1H, dd, *J* = 8.1, 1.1 Hz), 7.43 (1H, dd, *J* = 7.7, 1.5 Hz), 7.23 (1H, td, *J* = 7.6, 7.6, 1.3 Hz), 7.12 (1H, td, *J* = 7.6, 7.6, 1.3 Hz), 2.48 (2H, t, *J* = 6.6 Hz), 1.69 – 1.47 (4H, m), 0.97 (3H, t, *J* = 7.1 Hz).

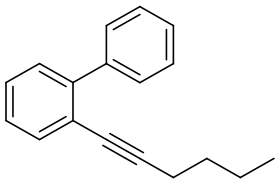
^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.28 (CH), 132.24 (CH), 128.60 (CH), 126.86 (CH), 126.08 (C), 125.42 (C), 95.58 (C), 79.31 (C), 30.61 (CH_2), 21.97 (CH_2), 19.26 (CH_2), 13.62 (CH_3).

IR (neat) υ_{max} 3062 (w), 2956 (m), 2929 (m), 2360 (w), 2232 (w), 1468 (m), 1025 (m), 752 (s).

LRMS (GC/EI) *m/z* 238, 61% (M^+, Br^{81}); 236, 68% (M^+, Br^{79}); 223, 67% (M^+-Me); 221, 69%; 195, 80% (M^+-Pr); 193, 82%; 157, 47% (M^+-Br); 142, 100% (M^+-Br-Me).

UV (hexane) λ_{max} 220 nm, ε_{max} 13791.

2-(Hex-1-yn-1-yl)-1,1'-biphenyl 22



1-Bromo-2-(hex-1-ynyl)benzene **21** (2.371 g, 10 mmol), phenylboronic acid (1.829 g, 15 mmol) and $Pd(PPh_3)_4$ (0.231 g, 0.2 mmol) were mixed in potassium carbonate (20 mL, 2 M) and DME (20 mL) and heated to 80 °C. After 2.5 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **22** (2.469 g, Quant.) as a yellow viscous oil. NMR and MS data is consistent with the literature.[16]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.60 (2H, dd, *J* = 7.7, 1.8 Hz), 7.52 (1H, d, *J* = 7.7 Hz), 7.45 – 7.24 (6H, m), 2.30 (2H, t, *J* = 6.8 Hz), 1.51 – 1.28 (4H, m), 0.88 (3H, t, *J* = 7.3 Hz).

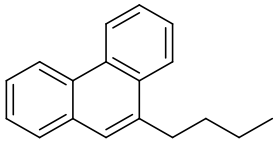
^{13}C-NMR (75 MHz, $CDCl_3$) δ 143.61 (C), 140.81 (C), 132.95 (CH), 129.35 (CH), 129.25 (2CH), 127.72 (2CH), 127.62 (CH), 127.12 (CH), 126.86 (CH), 122.38 (C), 93.38 (C), 80.08 (C), 30.45 (CH_2), 21.79 (CH_2), 19.14 (CH_2), 13.57 (CH_3).

IR (neat) υ_{max} 3059 (w), 2956 (m), 2930 (m), 2359 (w), 2228 (w).

LRMS (GC/EI) *m/z* 234, 45% (M^+); 219, 31% (M^+-Me); 202, 32%; 189, 100% (M^+-Pr); 165, 86% (M^+-Pn).

UV (DCM) λ_{max} 232 nm, ε_{max} 21027.

9-Butylphenanthrene 19



2-(Hex-1-yn-1-yl)-1,1'-biphenyl **22** (100 mg, 0.427 mmol) and TBD (5 mg, 0.042 mmol) were mixed in NMP (10 mL) in a sealed J-Young tap vessel and heated to 250 °C for 20 hours. Product was extracted into ether and washed with 2M HCl once and water twice. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **19** (70 mg, 0.298 mmol, 74%) as a pale yellow solid. NMR and MS data is consistent with the literature.[16]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.76 (1H, dd, *J* = 7.5, 2.0 Hz), 8.67 (1H, d, *J* = 7.6 Hz), 8.14 (1H, dd, *J* = 7.5, 2.0 Hz), 7.84 ((1H, dd, *J* = 7.1, 2.5 Hz), 7.70 – 7.56 (4H, m), 7.60 (1H, s), 3.14 (2H, t, *J* = 7.6 Hz), 1.83 (2H, quin, *J* = 7.7 Hz), 1.54 (2H, sxt, *J* = 7.1 Hz), 1.02 (3H, t, *J* = 7.6 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.95 (C), 131.96 (C), 131.35 (C), 130.70 (C), 129.59 (C), 127.99 (CH), 126.53 (CH), 126.42 (CH), 126.04 (CH), 125.94 (CH), 125.81 (CH), 124.48 (CH), 123.19 (CH), 122.42 (CH), 33.17 (CH_2), 32.40 (CH_2), 22.91 (CH_2), 14.04 (CH_3).

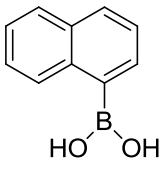
IR (neat) υ_{max} 2952 (w), 2924 (w), 2359 (w), 1602 (w).

LRMS (GC/EI) *m/z* 234, 99% (M^+); 191, 96% (M^+-Pr); 165, 80% (M^+-Pn).

UV (DCM) λ_{max} 244 nm, ε_{max} 17109.

Melting point 82-84 °C, lit[16]: 76-77 °C.

Naphthalen-1-ylboronic acid



1-Bromonaphthalene (0.56 mL, 4.00 mmol) was dissolved in THF (30 mL). n-BuLi (2.5 M, 1.76 mL, 4.40 mmol) was added slowly at -78 °C and left stirring for 1 hour. Methyl borate (1.11 mL, 10 mmol) was added slowly left stirring for another hour then allowed to warm to room temperature. HCl (1M) was added and the product extracted with eher to give the title boronic acid (0.856 g, Quant.) as white crystals. NMR data is consistent with the literature.[49]

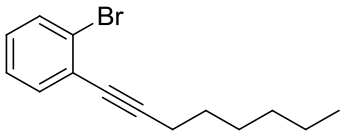
^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.38 – 8.35 (1H, m), 8.53 (2H, s), 7.92 – 7.87 (2H, m), 7.73 (1H, dd, *J* = 6.8, 0.9 Hz), 7.52 – 7.44 (3H, m).

^{13}C-NMR (100 MHz, DMSO-d_6) δ 135.65 (C), 132.92 (C), 132.12 (CH), 129.24 (CH), 128.76 (CH), 128.28 (CH), 125.70 (CH), 125.44 (CH), 125.15 (CH).

IR (neat) υ_{max} 3273 (br m), 1347 (s), 1317 (s).

Melting point 196-199 °C, lit[50]: 199-200 °C.

1-Bromo-2-(oct-1-yn-1-yl)benzene



1-Bromo-2-iodobenzene (0.38 mL, 3 mmol) was mixed with 1-octyne (0.53 mL, 3.6 mmol), $PdCl_2(PPh_3)_2$ (0.042 g, 0.06 mmol), CuI (0.005 g, 0.03 mmol) in TEA (20 mL) and heated to 60 °C. After 2.5 hours saturated NH_4Cl solution was added, and the product extracted with ether. Ether layer was washed with water and filtered through a short silica gel column to give title compound (0.864 g, Quant.) as a yellow oil. Material was used in next step without further purification. NMR data is consistent with the literature.[51]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.56 (1H, d, *J* = 8.1 Hz), 7.43 (1H, dd, *J* = 7.7, 1.5 Hz), 7.23 (1H, t, *J* = 7.5 Hz), 7.12 (1H, td, *J* = 7.7, 7.7, 1.1 Hz), 2.47 (2H, t, *J* = 7.0 Hz), 1.70 – 1.31 (8H, m), 0.92 (3H, t, *J* = 6.2 Hz).

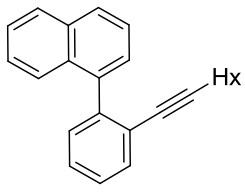
^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.28 (CH), 132.24 (CH), 128.59 (CH), 128.07 (C), 126.84 (CH), 125.44 (C), 95.64 (C), 79.33 (C), 31.35 (CH_2), 28.53 (CH_2), 22.57 (CH_2), 19.57 (CH_2), 14.06 (CH_3).

IR (neat) υ_{max} 2954 (m), 2928 (m), 2360 (w), 2339 (w), 1260 (w), 752 (s).

LRMS (GC/EI) *m/z* 266, 48% (M^+, Br^{81}); 264, 68% (M^+, Br^{79}); 237, 32% (M^+-Et); 235, 33% (M^+-Et); 223, 61% (M^+-Pr); 221, 63% (M^+-Pr); 142, 100% (M^+-Pn-Br).

UV (hexane) λ_{max} 220 nm, ε_{max} 11990.

1-(2-(Oct-1-yn-1-yl)phenyl)naphthalene 25



1-Bromo-2-(oct-1-yn-1-yl)benzene (0.796 g, 3 mmol), 1-naphthaleneboronic acid (0.773 g, 4.5 mmol) and $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol) were mixed in potassium carbonate (10 mL, 2 M) and DME (10 mL) and heated to 90 °C. After 1 hour water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **25** (0.586 g, 63%) as a yellow/orange viscous oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88 (2H, t, *J* = 7.9 Hz), 7.64 – 7.34 (9H, m), 1.98 (2H, t, *J* = 6.2 Hz), 1.17 – 0.91 (8H, m), 0.84 (3H, t, *J* = 7.0 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.96 (C), 139.20 (C), 133.47 (C), 132.00 (CH), 131.93 (C), 130.46 (CH), 127.97 (CH), 127.64 (CH), 127.23 (CH), 127.14 (CH), 126.48 (CH), 125.61 (CH), 125.48 (CH), 125.06 (CH), 124.41 (C), 94.11 (C), 79.83 (C), 31.24 (CH_2), 28.03 (CH_2), 27.96 (CH_2), 22.36 (CH_2), 19.14 (CH_2), 14.07 (CH_3).

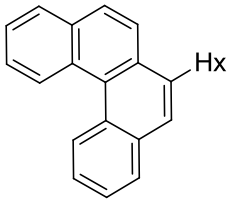
IR (neat) υ_{max} 3057 (w), 2927 (m), 2855 (w), 2360 (w), 2340 (w), 1332 (w).

LRMS (GC/EI) *m/z* 312, 74% (M^+); 252, 33%; 241, 83% (M^+-Pn); 239, 93%; 215, 100%.

HRMS (GC/EI) Found 312.18731 ($M^+\cdot$), calculated 312.18780 for $C_{24}H_{24}$.

UV (DCM) λ_{max} 232 nm, ε_{max} 48654.

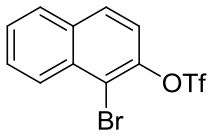
6-Hexylbenzo[c]phenanthrene 33



1-(2-(Oct-1-yn-1-yl)phenyl)naphthalene **25** (50mg, 0.16 mmol) and DBU (24 µL, 0.16 mmol) were mixed in NMP (5 mL) in a sealed J-Young tap vessel and heated to 280 °C for 20 hours. Product was extracted into ether and washed with 2M HCl once and water twice. The crude material (44 mg) was analysed by NMR, as 83% product, 17% diene impurity, unable to purify.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.12 (1H, d, *J* = 8.1 Hz), 9.08 – 9.05 (1H, m), 8.12 – 7.94 (4H, m), 7.76 (1H, s), 7.69 – 7.61 (4H, m), 3.20 (2H, t, *J* = 7.3 Hz), 1.91 – 1.81 (2H, m), 1.56 – 1.30 (8H, m), 0.95 (3H, t, *J* = 7.1 Hz).

1-Bromonaphthalen-2-yl trifluoromethanesulfonate 28



1-Bromo-2-naphthol (1.115 g, 5 mmol) was mixed with pyridine (20 mL) at 0 °C. Triflic anhydride (1.00 mL, 6 mmol) was slowly added to the mixture at 0 °C. After 2.5 hours HCl (2 M) was added and the product extracted with ether. Ether was washed with HCl (2 M) and water and filtered through a short silica gel column to give compound **28** (1.723 g, 97%) as a red oil. NMR and MS data is consistent with the literature.[52]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.34 (1H, d, *J* = 8.4 Hz), 7.91 (2H, d, *J* = 8.4 Hz), 7.71 (1H, t, *J* = 7.0 Hz), 7.63 (1H, t, *J* = 7.3 Hz), 7.45 (1H, d, *J* = 8.4 Hz).

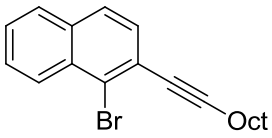
^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.00 (C), 132.95 (C), 132.60 (C), 129.69 (CH), 128.75 (CH), 128.31 (CH), 127.74 (CH), 127.65 (CH), 119.86 (CH), 116.15 (C).

IR (neat) υ_{max} 2929 (w), 2857 (w), 1423 (s), 1204 (brs), 1134 (s), 932 (s), 825 (s).

LRMS (GC/EI) *m/z* 356, 46% (M^+, Br^{81}); 354, 42% (M^+, Br^{79}); 223, 72% (M^+-Tf); 221, 69% (M^+-Tf); 193, 100%; 195, 99%.

UV (hexane) λ_{max} 223 nm, ε_{max} 15382.

1-Bromo-2-(dec-1-yn-1-yl)naphthalene 29



1-Bromonaphthalen-2-yl trifluoromethanesulfonate **28** (0.66 g, 1.86 mmol) was mixed with 1-decyne (0.40 mL, 2.23 mmol), $PdCl_2(PPh_3)_2$ (0.052 g, 0.074 mmol), CuI (0.007 g, 0.037 mmol), tetrabutylammonium iodide (0.687 g, 1.86 mmol) in TEA (5 mL) and DMF (15 mL) and heated to 80 °C. After 2.5 hours saturated NH_4Cl solution (20 mL) was added, and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **29** (0.455 g, 72%) as a orange oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.29 (1H, d, *J* = 8.4 Hz), 7.79 (1H, d, *J* = 8.1 Hz), 7.72 (1H, d, *J* = 8.4 Hz), 7.60 (1H, td, *J* = 7.8, 7.8, 1.3 Hz), 7.53 – 7.46 (2H, m), 2.54 (2H, t, *J* = 7.0 Hz), 1.75 – 1.32 (12H, m), 0.91 (3H, t, *J* = 6.2 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.31 (C), 132.22 (C), 129.35 (CH), 128.09 (CH), 127.68 (CH), 127.25 (CH), 126.70 (CH), 125.89 (C), 124.19 (C), 96.62 (C), 80.69 (C), 31.86 (CH_2), 29.24 (CH_2), 29.13 (CH_2), 28.93 (CH_2), 28.59 (CH_2), 22.67 (CH_2), 19.76 (CH_2), 14.12 (CH_3).

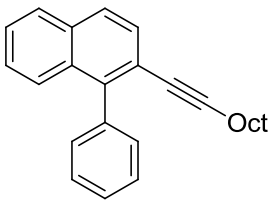
IR (neat) υ_{max} 3058 (w), 2924 (s), 2853 (m), 2360 (m), 2339 (m), 1238 (w), 813 (s).

LRMS (GC/EI) *m/z* 344, 16% (M^+, Br^{81}); 342, 15% (M^+, Br^{79}); 273, 10% (M^+-Pn); 271, 10% (M^+-Hp); 245, 19% (M^+-Hp); 243, 16% (M^+-Hp); 166, 100%.

HRMS (GC/EI) Found 342.09876 ($M^+\cdot$), calculated 342.09831 for $C_{20}H_{23}Br$.

UV (hexane) λ_{max} 221 nm, ε_{max} 23299, λ 243 nm, ε 26594.

2-(Dec-1-yn-1-yl)-1-phenylnaphthalene 26



1-Bromo-2-(dec-1-yn-1-yl)naphthalene **29** (0.45 g, 1.31 mmol), phenylboronic acid (0.23 g, 1.97 mmol) and $Pd(PPh_3)_4$ (0.03 g, 0.026 mmol) were mixed in potassium carbonate (10 mL, 2 M) and DME (10 mL) and heated to 90 °C. After 1 hour water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **26** (0.347 g, 78%) as a dark yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.85 (1H, d, *J* = 7.7 Hz), 7.78 (1H, d, *J* = 8.4 Hz), 7.60 – 7.35 (9H, m), 2.23 (2H, t, *J* = 6.8 Hz), 1.37 – 1.19 (12H, m), 0.92 (3H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.38 (C), 139.18 (C), 132.70 (C), 132.25 (C), 130.49 (CH), 128.91 (CH), 127.86 (CH), 127.22 (CH), 126.52 (CH), 126.23 (CH), 125.87 (CH), 120.86 (C), 94.43 (C), 80.68 (C), 31.89 (CH_2), 29.14 (CH_2), 28.59 (CH_2), 28.47 (CH_2), 22.68 (CH_2), 19.45 (CH_2), 14.11 (CH_3).

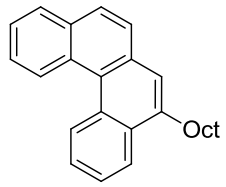
IR (neat) υ_{max} 3056 (w), 2924 (s), 2853 (m), 2225 (w).

LRMS (GC/EI) *m/z* 340, 36% (M^+); 253, 29% (M^+-Hx); 241, 88% (M^+-Hp); 239, 100%.

HRMS (GC/EI) Found 340.21885 ($M^+\cdot$), calculated 340.21910 for $C_{26}H_{28}$.

UV (DCM) λ_{max} 232 nm, ε_{max} 36667, λ 253 nm, ε 21497.

5-Octylbenzo[c]phenanthrene 34



2-(Dec-1-yn-1-yl)-1-phenylnaphthalene **26** (200mg, 0.58 mmol) and DBU (88 µL, 0.58 mmol) were mixed in NMP (12 mL) in a sealed J-Young tap vessel and heated to 280 °C for 20 hours. Product was extracted into ether and washed with 2 M HCl once and water twice. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **34** (168 mg, 84%) as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.20 – 9.17 (1H, m), 9.11 (1H, d, *J* = 8.4 Hz), 8.28 – 8.25 (1H, m), 8.04 (1H, dd, *J* = 7.9, 1.3 Hz), 7.91 (1H, d, *J* = 8.4 Hz), 7.81 (1H, d, *J* = 8.4 Hz), 7.74 – 7.60 (4H, m), 7.70 (1H, s), 3.22 (2H, t, *J* = 7.7 Hz), 1.94 – 1.84 (2H, m), 1.58 – 1.32 (8H, m), 0.94 (3H, t, *J* = 7.0 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.63 (C), 133.24 (C), 132.32 (C), 130.74 (C), 130.68 (C), 130.17 (C), 128.57 (CH), 128.50 (CH), 127.87 (CH), 127.42 (CH), 126.56 (CH), 126.30 (C), 126.24 (CH), 126.03 (CH), 125.71 (CH), 125.41 (2CH), 124.21 (CH), 33.26 (CH_2), 31.90 (CH_2), 30.40 (CH_2), 29.92 (CH_2), 29.55 (CH_2), 29.31 (CH_2), 22.66 (CH_2), 14.10 (CH_3).

IR (neat) υ_{max} 2926 (m), 2848 (m), 1463 (w).

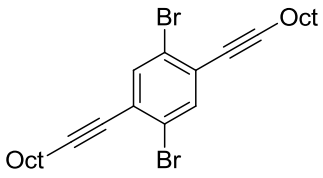
LRMS Submitted.

HRMS (GC/EI) Found 340.218793 ($M^+\cdot$), calculated 340.21855 for $C_{26}H_{28}$.

UV (DCM) λ_{max} 287 nm, ε_{max} 17820, λ 277 nm, ε 13052.

Melting point 43-44 °C.

1,4-Dibromo-2,5-di(dec-1-ynyl)benzene 35



1,4-Dibromo-2,5-diiodobenzene **9** (0.487 g, 1 mmol) was mixed with 1-decyne (0.40 mL, 2.2 mmol), $PdCl_2(PPh_3)_2$ (0.014 g, 0.02 mmol), CuI (0.007 g, 0.04 mmol) in TEA (5 mL) and toluene (15 mL) and heated to 80 °C. After 5 hours saturated NH_4Cl solution was added, and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) followed by recrystallisation in hexane gave the title compound **35** (0.284 g, 56%) as yellow crystals.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59 (2H, s), 2.46 (4H, t, *J* = 7.0 Hz), 1.68 – 1.31 (24H, m), 0.89 (6H, t, *J* = 6.6 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.03 (2CH), 126.49 (2C), 123.46 (2C), 98.24 (2C), 78.29 (2C), 31.84 ($2CH_2$), 29.19 ($2CH_2$), 29.08 ($2CH_2$), 28.86 ($2CH_2$), 28.39 ($2CH_2$), 22.66 ($2CH_2$), 19.64 ($2CH_2$), 14.12 ($2CH_3$).

IR (neat) υ_{max} 2925 (m), 2854 (m), 2361 (w), 2231 (w), 1469 (m), 888 (w).

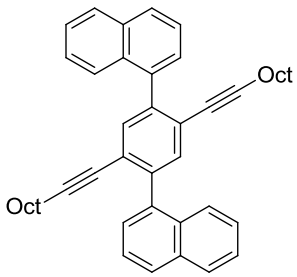
LRMS (GC/EI) *m/z* 438, 2% (M^+-Pn); 437, 7% (M^+-Pn).

HRMS (GC/EI) Found 506.117686 ($M^+\cdot$), calculated 506.11783 for $C_{26}H_{36}Br_2$.

UV (hexane) λ_{max} 220 nm, ε_{max} 23329.

Melting point 52-53 °C.

1,1'-(2,5-Di(dec-1-ynyl)-1,4-phenylene)dinaphthalene 36



1,4-Dibromo-2,5-di(dec-1-ynyl)benzene **35** (0.284 g, 0.55 mmol), 1-naphthylboronic acid (0.237 g, 1.38 mmol) and $Pd(PPh_3)_4$ (0.025 g, 0.022 mmol) were mixed in potassium carbonate (10 mL, 2 M) and DME (10 mL) and heated to 90 °C. After 2 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 0-20% DCM/hexane) gave the title compound **36** (0.19 g, 58%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.80 (6H, m), 7.62 – 7.45 (10H, m), 2.00 (4H, t, *J* = 6.6 Hz), 1.35 – 0.84 (30H, m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.88 (2C), 138.35 (2C), 134.01 (2CH), 133.50 (2C), 131.91 (2C), 128.03 (2CH), 127.87 (2CH), 127.31 (2CH), 127.25 (2CH), 126.57 (2CH), 125.73 (2CH), 125.60 (2CH), 125.12 (2CH), 123.43 (2C), 95.49 (2C), 79.65 (2C), 31.87 ($2CH_2$), 29.00 ($4CH_2$), 28.28 ($2CH_2$), 28.03 ($2CH_2$), 22.67 ($2CH_2$), 19.21 ($2CH_2$), 14.13 ($2CH_3$).

IR (neat) υ_{max} 2909 (m), 2850 (m), 2360 (w), 2228 (w), 1491 (m).

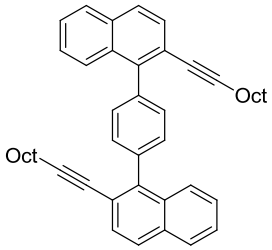
LRMS (GC/EI) *m/z* 602, 100% (M^+); 503, 35% (M^+-Hp); 447, 43% (M^+-Hp-Et); 398, 32% (M^+-Hp-Hp).

HRMS (GC/EI) Found 602.39071 ($M^+\cdot$), calculated 602.39125 for $C_{46}H_{50}$.

UV (hexane) λ_{max} 222 nm, ε_{max} 56129.

Melting point 61-63 °C.

1,4-Bis(2-(dec-1-ynyl)naphthalen-1-yl)benzene 38



1-Bromo-2-(dec-1-yn-1-yl)naphthalene **29** (172 mg, 0.5 mmol), 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene **15** (76 mg, 0.25 mmol), and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) were mixed in potassium carbonate (2 M, 10 mL) and DME (10 mL) and heated to 80 °C. After 3 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 0-10% DCM/hexane) gave the title compound **38** (25 mg, 0.041 mmol, 17%) as a pale yellow oil.

^{1}H-NMR (300 MHz, toluene-D_8, 363K) δ 7.87 – 7.84 (2H, m), 7.63 – 7.53 (10H, m), 7.25 – 7.21 (4H, m), 2.24 (4H, t, *J* = 6.8 Hz), 1.50 – 1.16 (24H, m), 0.80 (6H, t, *J* = 6.6 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.42 (2C), 138.10 (2C), 132.82 (2C), 132.37 (2C), 130.13 (4CH), 128.96 (2CH), 127.96 (2CH), 127.26 (2CH), 126.59 (2CH), 126.17 (2CH), 125.89 (2CH), 120.92 (2C), 94.44 (2C), 80.81 (2C), 31.76 ($2CH_2$), 29.15 ($2CH_2$), 28.99 ($2CH_2$), 28.89 ($2CH_2$), 28.63 ($2CH_2$), 22.53 ($2CH_2$), 19.55 ($2CH_2$), 14.01 ($2CH_3$).

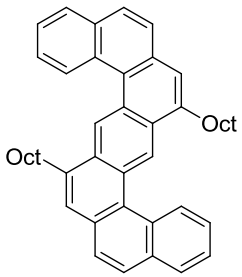
IR (neat) υ_{max} 2925 (w), 2854 (w), 2360 (m), 2339 (m), 905 (m), 728 (s).

LRMS Submitted.

HRMS (GC/EI) Found 602.390868 ($M^+\cdot$), calculated 602.39070 for $C_{46}H_{50}$.

UV (hexane) λ_{max} 220 nm, ε_{max} 25171, λ 252 nm, ε 18087.

8,17-dioctylbenzo[a]naphtho[1,2-k]tetraphene 39



1,4-bis(2-(dec-1-ynyl)naphthalen-1-yl)benzene **38** (71 mg, 0.11 mmol) and DBU (17.5 µL, 0.11 mmol) were mixed in NMP (10 mL) in a sealed J-Young tape vessel and heated to 280 °C for 19 hours. Product was extracted into ether and washed with 2M HCl once and water twice. Purification by column chromatography (silica gel, 0-20% DCM/hexane) followed by recrystallisation in toluene gave the title compound **39** (21 mg, 0.03 mmol, 30%) as fluorescent yellow/green crystals.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.83 (2H, s), 9.29 (2H, d, *J* = 8.1 Hz), 8.11 (2H, d, *J* = 7.1 Hz), 8.00 (2H, d, *J* = 8.6 Hz), 7.87 (2H, d, *J* = 8.1 Hz), 7.75 (2H, t, *J* = 7.1 Hz), 7.72 (2H, s), 7.68 (2H, t, *J* = 7.1 Hz), 3.29 (4H, t, *J* = 7.6 Hz), 2.08 (4H, quin, *J* = 7.7 Hz), 1.64 (4H, quin, *J* = 7.5 Hz), 1.53 - 1.34 (16H, m), 0.92 (6H, t, *J* = 6.6 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.97 (2C), 133.30 (2C), 130.84 (2C), 130.27 (2C), 129.82 (2C), 128.80 (2C), 128.73 (4CH), 127.76 (2CH), 127.39 (2CH), 126.61 (2CH), 126.43 (2C), 125.46

(2CH), 124.27 (2CH), 33.65 ($2CH_2$), 31.95 ($2CH_2$), 31.02 ($2CH_2$), 30.07 ($2CH_2$), 29.73 ($2CH_2$), 29.41 ($2CH_2$), 22.69 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max} 2924 (m), 2852 (m), 1464 (w), 1420 (w).

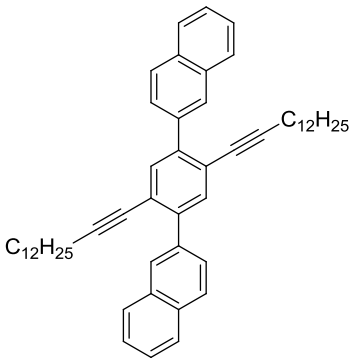
LRMS Submitted.

HRMS (GC/EI) Found 602.390826 ($M^+\cdot$), calculated 602.39070 for $C_{46}H_{50}$.

UV (DCM) λ_{max} 333 nm, ε_{max} 47961, λ 238 nm, ε 33301.

Melting point 102-104 °C.

2,2'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)dinaphthalene 43



1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **42** (633 mg, 1.02 mmol), 2-naphthyleneboronic acid (438 mg, 2.55 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) were mixed in potassium carbonate (2 M, 10 mL) and DME (10 mL) and heated to 80 °C. After 22 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 0-10% DCM/hexane) gave the title compound **42** (0.51 g, 0.71 mmol, 70%) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (2H, s), 7.90 (6H, d, *J* = 7.6 Hz), 7.82 (2H, dd, *J* = 8.1, 2.0 Hz), 7.68 (2H, s), 7.53 - 7.51 (4H, m), 2.29 (4H, t, *J* = 7.1 Hz), 1.44 (4H, quin, *J* = 7.2 Hz), 1.33 - 1.13 (36H, m), 0.90 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.13 (2C), 137.36 (2C), 134.24 (2CH), 133.21 (2C), 132.70 (2C), 128.21 (2CH), 128.13 (2CH), 127.61 (2CH), 127.55 (2CH), 127.22 (2CH), 126.00 (4CH), 95.10 (2C), 80.03 (2C), 31.92 ($2CH_2$), 29.63 ($6CH_2$), 29.43 ($2CH_2$), 29.36 ($2CH_2$), 29.14 ($2CH_2$), 28.83 ($2CH_2$), 28.43 ($2CH_2$), 22.68 ($2CH_2$), 19.61 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max} 2919 (m), 2849 (m), 2361 (w), 1465 (w).

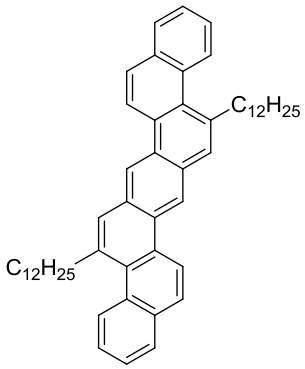
LRMS Submitted.

HRMS (GC/EI) Found 714.515811 ($M^+\cdot$), calculated 714.51590 for $C_{54}H_{66}$.

UV (DCM) λ_{max} 264 nm, ε_{max} 43262.

Melting point 70-71 °C.

5,14-didodecylbenzo[c]naphtho[2,1-k]tetraphene 44



2,2'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)dinaphthalene **43** (200 mg, 0.28 mmol) and DBU (41 µL, 0.28 mmol) were mixed in NMP (12 mL) in a sealed J-Young tape vessel and heated to 280 °C for 19 hours. Product was extracted into toluene and washed with 2M HCl once and water twice. Purification by recrystallisation in hot toluene gave the title compound **44** (156 mg, 0.21 mmol, 76%) as fluorescent yellow/green crystals.

^{1}H-NMR (400 MHz, toluene-D_8, 333K) δ 9.11 (2H, s), 8.89 (2H, d, *J* = 8.6 Hz), 8.84 (2H, d, *J* = 9.1 Hz), 8.04 (2H, s), 7.88 (4H, t, *J* = 8.6 Hz), 7.51 (2H, t, *J* = 7.6 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 3.57 (4H, t, *J* = 7.1 Hz), 2.03 – 1.95 (4H, m), 1.56 – 1.29 (40H, m), 0.89 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR Could not be obtained due to heating required.

IR (neat) υ_{max} 2915 (m), 2847 (m), 1464 (w), 1371 (w).

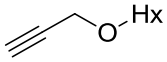
LRMS Submitted.

HRMS (GC/EI) Found 714.516184 ($M^+\cdot$), calculated 714.51590 for $C_{54}H_{66}$.

UV (DCM) λ_{max} 323 nm, ε_{max} 22597, λ 311 nm, ε 16023.

Melting point 157-158 °C.

1-(Prop-2-yn-1-yloxy)hexane 45



Sodium hydride (60% dispersion in oil, 0.60 g, 15 mmol), and hexanol (3.28 mL, 26 mmol) were mixed in DMF (40 mL) at 0 °C for 1 hour. Propargyl bromide (80% in toluene, 1.45 mL, 13 mmol) was then added and stirred for 2 hours. The mixture was allowed to warm to room temperature and stirred for 20 hours. The product was extracted into ether, then washed with water. Purification by column chromatography (silica gel, 0-50% ether/hexane) gave title product **45** (1.35 g, 9.56 mmol, 75%) as a pale yellow oil. NMR data is consistent with the literature.[53]

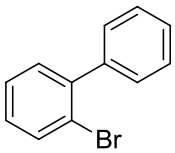
^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.14 (2H, d, *J* = 2.3 Hz), 3.52 (2H, t, *J* = 6.6 Hz), 2.42 (1H, t, *J* = 2.4 Hz), 1.64 – 1.55 (2H, m), 1.46 – 1.34 (6H, m), 0.94 (3H, t, *J* = 7.0 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 80.05 (C), 73.98 (CH), 70.30 (CH_2), 57.98 (CH_2), 31.62 (CH_2), 29.46 (CH_2), 25.75 (CH_2), 22.57 (CH_2), 14.01 (CH_3).

IR (neat) υ_{max} 3302 (w), 2930 (m), 2858 (m), 2360 (s), 1261 (w), 1101 (m).

LRMS (GC/EI) *m/z* 84, 34% (M^+-Bu); 79, 12%; 69, 97% (M^+-Pn); 67, 20%; 56, 88% (M^+-Hex).

2-Bromo-1,1'-biphenyl 46



1-Bromo-2-iodobenzene (1.28 mL, 10 mmol), phenylboronic acid (1.22 g, 10 mmol), potassium carbonate (2.76 g, 20 mmol), palladium chloride (35 mg, 0.2 mmol) and triphenylphosphine (105 mg, 0.4 mmol) were mixed together in a solution of toluene, ethanol and water (12 mL, 5:5:2) and refluxed for 22 hours. Water was added and the product extracted with DCM. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **46** (1.91 g, 8.17 mmol, 82%) as a colourless oil. NMR and MS literature.[42, 54]

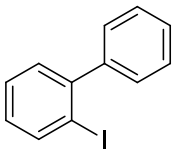
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.69 (1H, d, *J* = 8.3 Hz), 7.46 – 7.40 (5H, m), 7.38 – 7.34 (2H, m), 7.25 – 7.19 (2H, m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.57 (C), 141.09 (C), 133.09 (CH), 131.25 (CH), 129.35 (CH), 128.69 (CH), 127.94 (CH), 127.58 (CH), 127.34 (CH), 122.61 (C).

IR (neat) υ_{max} 3055 (w), 2360 (w), 1026 (m), 746 (s).

LRMS (GC/EI) *m/z* 234, 59% (M^+, Br^{81}); 232, 59% (M^+, Br^{79}); 152, 100% (M^+-Br); 126, 34%; 77, 44%.

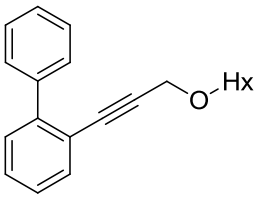
2-Iodo-1,1'-biphenyl 47



n-BuLi (2.5 M, 0.86 mL, 2.15 mmol) was added slowly to a solution of the aryl bromide **46** in THF (7 mL) at -78 °C and left to stir for 30 mins. Iodine (1.1 g, 4.30 mmol) in THF (3 mL) was added slowly, then stirred still at -78 °C for 2 hours then allowed to warm to RT over another hour. Saturated NH_4Cl solution was added and the product extracted into DCM, washed with saturated $Na_2S_2O_5$ solution and brine, and filtered through a short silica gel column to give the title compound **47** (0.66 g) as a mixture of product and biphenyl 71:29% analysed by GC-MS.

LRMS (GC/EI) *m/z* 280, 65% (M^+); 152, 100% (M^+-I); 126, 38%; 76, 36%.

2-(3-(Hexyloxy)prop-1-ynyl)biphenyl 48



2-Iodo-1,1'-biphenyl **47** (71% pure) (0.485 g, 1.73 mmol) was mixed with 1-(prop-2-ynyloxy)hexane (0.294 g, 2.08 mmol), $PdCl_2(PPh_3)_2$ (0.024 g, 0.034 mmol), CuI (0.003 g, 0.017 mmol) in TEA (20 mL) and heated to 50 °C. After 23 hours saturated NH_4Cl solution was added, and the product extracted with ether. Ether layer was washed with saturated NH_4Cl solution and water. Purification by column chromatography (silica gel, 0-10% ether/hexane) gave the title compound **48** (0.326 g, 1.11 mmol, 64%) as a yellow oil with a purity of 88% by GC.

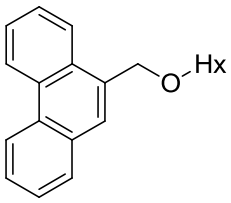
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.56 (3H, m), 7.44 – 7.30 (6H, m), 4.25 (2H, s), 3.38 (2H, t, *J* = 6.6 Hz), 1.59 – 1.20 (8H, m), 0.90 (3H, t, *J* = 6.4 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.51 (C), 133.22 (CH), 130.67 (C), 129.47 (CH), 129.20 (2CH), 128.51 (CH), 127.88 (2CH), 127.34 (CH), 126.95 (CH), 121.14 (C), 88.43 (C), 85.54 (C), 69.98 (CH_2), 58.67 (CH_2), 31.68 (CH_2), 29.50 (CH_2), 25.78 (CH_2), 22.61 (CH_2), 14.04 (CH_3).

IR (neat) υ_{max} 3059 (w), 2928 (m), 2855 (m), 2360 (w), 1261 (w), 1094 (s), 697 (s).

LRMS (GC/EI) *m/z* 292, 8% (M^+); 221, 16% (M^+-Pn), 207, 42% (M^+-Hx); 189, 89%; 178, 100% (M^+-CH_2OHx).

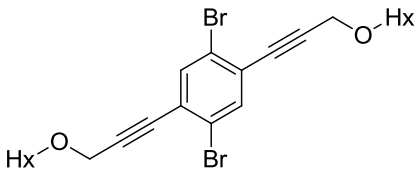
9-(Hexyloxymethyl)phenanthrene 49



2-(3-(Hexyloxy)prop-1-ynyl)biphenyl **48** (30 mg, 0.1 mmol) was mixed with TBD (14 mg, 0.1 mmol) in NMP (2 mL). This solution was injected into a flow reactor and heated to 250 °C for 30 mins. Upon collection the product was extracted into ether, and washed with water. The crude product (22 mg) was analysed by NMR.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.74 (1H, d *J* = 9.4 Hz), 8.68 (1H, d, *J* = 7.9 Hz), 8.20 (1H, d, *J* = 7.5 Hz), 7.89 (1H, d, *J* = 7.5 Hz), 7.78 (1H, s), 7.69 – 7.58 (4H, m), 5.01 (2H, s), 3.61 (2H, t, *J* = 6.6 Hz), 1.70 – 1.25 (8H, m), 0.89 (3H, t, *J* = 6.8 Hz).

1,4-Dibromo-2,5-bis(3-(hexyloxy)prop-1-yn-1-yl)benzene 50



1,4-Dibromo-2,5-diiodobenzene **9** (1.11 g, 2.27 mmol) was mixed with 1-(prop-2-ynyloxy)hexane (0.70 g, 5.00 mmol), $PdCl_2(PPh_3)_2$ (0.063 g, 0.09 mmol), CuI (0.008 g, 0.045 mmol) in TEA (5 mL) and toluene (15 mL) and heated to 90 °C. After 2.5 hours saturated NH_4Cl solution was added, and the product extracted with ether. Ether layer was washed with saturated NH_4Cl solution and water. Purification by column chromatography (silica gel, 0-20% ether/hexane) gave the title compound **50** (0.428 g, 37%) as a yellow oil.

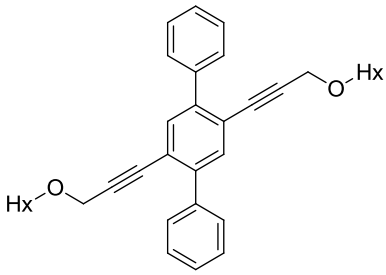
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.67 (2H, s), 4.41 (4H, s), 3.61 (4H, t, *J* = 6.6 Hz), 1.68 – 1.59 (4H, m), 1.41 – 1.29 (12H, m), 0.90 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.37 (CH), 126.17 (C), 123.57 (C), 93.18 (C), 83.04 (C), 70.51 (CH_2), 58.61 (CH_2), 31.66 (CH_2), 29.50 (CH_2), 25.81 (CH_2), 22.61 (CH_2), 14.04 (CH_3).

IR (neat) υ_{max} 2929 (m), 2857 (m), 2360 (m), 2340 (m), 1351 (m), 1215 (w), 1098 (s), 1071 (m).

LRMS (GC/EI) *m/z* Attempted but mass ion not observed.

2',5''-Bis(3-(hexyloxy)prop-1-yn-1-yl)-1,1':4',1''-terphenyl 51



1,4-Dibromo-2,5-bis(3-(hexyloxy)prop-1-yn-1-yl)benzene **50** (0.42 g, 0.82 mmol), phenylboronic acid (0.26 g, 2.13 mmol) and $Pd(PPh_3)_4$ (0.018 g, 0.016 mmol) were mixed in potassium carbonate (10 mL, 2 M) and DME (10 mL) and heated to 80 °C. After 3.5 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 0-10% ether/hexane) gave the title compound **51** (0.178 g, 43%) as a yellow viscous oil.

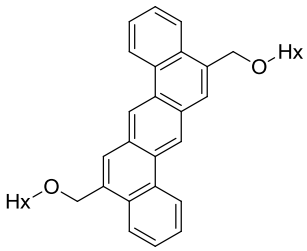
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.59 (6H, m), 7.46 – 7.35 (6H, m), 4.25 (4H, s), 3.39 (4H, t, *J* = 6.6 Hz), 1.53 – 1.49 (4H, m), 1.32 – 1.20 (12H, m), 0.89 (6H, t, *J* = 6.6 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.42 (C), 139.30 (C), 134.21 (CH), 129.12 (CH), 128.02 (CH), 127.68 (CH), 121.32 (C), 90.03 (C), 85.10 (C), 70.10 (CH_2), 58.67 (CH_2), 31.67 (CH_2), 29.50 (CH_2), 25.76 (CH_2), 22.60 (CH_2), 14.03 (CH_3).

IR (neat) υ_{max} 2929 (m), 2856 (m), 2360 (m), 2339 (m), 1098 (s).

LRMS (GC/EI) *m/z* Attempted but mass ion not observed.

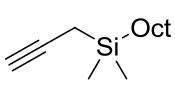
5,12-Bis(hexyloxymethyl)benzo[k]tetraphene 52b



2',5'-Bis(3-(hexyloxy)prop-1-yn-1-yl)-1,1':4',1''-terphenyl **51** (30 mg, 0.059 mmol) was mixed with DBU (0.176 mL, 1.18 mmol) in NMP (2 mL). This solution was injected into a flow reactor and heated to 250 °C for 30 mins. Upon collection the product was extracted into ether, and washed with water. The crude product (30 mg) was analysed by NMR.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.10 (2H, s), 8.89 (2H, d, *J* = 7.7 Hz), 8.19 (2H, d, *J* = 8.1 Hz), 7.98 (2H, s), 7.76 – 7.67 (4H, s), 5.04 (4H, s), 3.66 (4H, t, *J* = 6.6 Hz), 1.77 – 1.30 (16H, m), 0.90 (6H, t, *J* = 6.6 Hz).

Dimethyl(octyl)(prop-2-yn-1-yl)silane 53



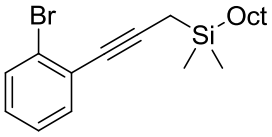
Propargyl bromide (80% in toluene, 2.79 mL, 21.5 mmol) was added slowly to a solution of magnesium turnings (0.88 g, 41 mmol), mercury (II) chloride (0.01 g, 0.04 mmol) in dry ether (2 mL) via cannula over 40 mins. Reaction mixture was then cooled to 0 °C, then chloro(dimethyl)octylsilane (5.6 mL, 23.8 mmol) in dry ether (18 mL) was slowly added over 30 mins. After 16 hrs saturated NH_4Cl solution was added and the product extracted with ether. Ether

layer was washed with water twice and brine twice. Purification by column chromatography (silica gel, 100% hexane) gave title product **53** (2.91 g, 13.8 mmol, 58%) as a clear colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.83 (1H, t, *J* = 2.9 Hz), 1.48 (2H, d, *J* = 2.9 Hz), 1.28 (12H, br s), 0.89 (3H, t, *J* = 6.6 Hz), 0.62 (2H, t, *J* = 7.1 Hz), 0.10 (6H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 82.70 (C), 66.71 (CH), 33.50 (CH_2), 31.93 (CH_2), 29.28 ($2CH_2$), 23.61 (CH_2), 22.67 (CH_2), 14.57 (CH_2), 14.11 (CH_3), 5.41 (CH_2), -3.79 ($2CH_3$).

(3-(2-Bromophenyl)prop-2-yn-1-yl)dimethyl(octyl)silane 54

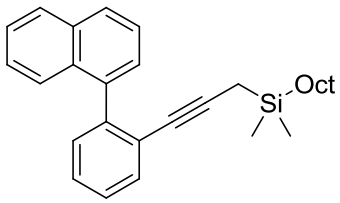


1-Bromo-2-iodobenzene (0.12 mL, 1.0 mmol) was mixed with dimethyl(octyl)(prop-2-yn-1-yl)silane **53** (0.25g, 1.2 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (2 mg, 0.01 mmol) in TEA (10 mL) and heated to 50 °C. After 1 hour saturated NH_4Cl solution (20 mL) was added, and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **54** (0.41 g, Quant.) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55 (1H, d, *J* = 7.6 Hz), 7.40 (1H, d, *J* = 7.6 Hz), 7.21 (1H, t, *J* = 7.6 Hz), 7.09 (1H, t, *J* = 7.6 Hz), 1.77 (2H, s), 1.37 - 1.28 (12H, m), 0.89 (3H, t, *J* = 6.6 Hz), 0.70 (2H, t, *J* = 7.1 Hz), 0.17 (6H, s).

LRMS (GC/EI) *m/z* 366, 1% (M^+, Br^{81}); 364, 1% (M^+, Br^{79}); 253, 33% (M^+-Oct, Br^{81}); 251, 32% (M^+-Oct, Br^{79}); 172, 48% (M^+-Oct-Br); 145, 24% (M^+-Oct-Br-Me_2); 59, 100%.

Dimethyl(3-(2-(naphthalen-1-yl)phenyl)prop-2-yn-1-yl)(octyl)silane 55



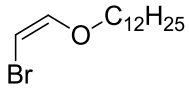
(3-(2-Bromophenyl)prop-2-yn-1-yl)dimethyl(octyl)silane **54** (0.365 g, 1.0 mmol), 1-naphthylboronic acid (0.258 g, 1.5 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) were mixed in potassium carbonate (10 mL, 2 M) and DME (10 mL) and heated to 80 °C. After 5 hours water was added and the product extracted with ether. Ether layer was washed with water. Purification by column chromatography (silica gel, 100% hexane) gave the title compound **55** (0.106 g, 0.25 mmol, 26%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (2H, dd, *J* = 12.1, 8.1 Hz), 7.59 – 7.29 (9H, m), 1.37 – 1.02 (12H, m), 0.90 (3H, t, *J* = 6.8 Hz), 0.17 (2H, t, *J* = 8.1 Hz), -0.37 (6H, s).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.49 (C), 139.51 (C), 133.59 (C), 132.47 (CH), 132.06 (C), 130.51 (CH), 128.00 (CH), 127.58 (CH), 127.16 (CH), 127.03 (CH), 126.71 (CH), 126.42 (CH), 125.17 (CH), 125.52 (CH), 125.17 (CH), 152.12 (C), 91.85 (C), 78.45 (C), 33.34 (CH_2), 31.95 (CH_2), 29.31 (CH_2), 29.25 (CH_2), 23.49 (CH_2), 22.68 (CH_2), 14.20 (CH_2), 14.13 (CH_3), 6.56 (CH_2), -4.16 ($2CH_3$).

LRMS (GC/EI) *m/z* 412, 11% (M^+); 313, 6% (M^+-Hp); 299, 24% (M^+-Oct); 242, 11% (M^+-$SiMe_2Oct$); 215, 17% (M^+-$CC_3H_2SiMe_2Oct$); 59, 100%.

1-((2-Bromovinyl)oxy)dodecane 57



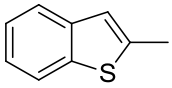
Bromine (1.54 mL, 30 mmol) in DCM (10 mL) was added to a solution of dodecyl vinyl ether (7.79 mL, 30 mmol) in DCM (10 mL) at -30 °C and stirred at this temperature for 2 hours. Triethylamine (7 mL) was added slowly and the reaction mixture stirred for another 2 hours at -30 °C. Reaction mixture was warmed to RT, and the product was washed with 2 M HCl solution, then saturated $NaHCO_3$. Concentrated to give the crude title product **57** (8.99 g, Quant.) as a brown liquid. ^{1}H-NMR showed a ratio of 73:27% Z:E isomers.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.59 (1H, d, *J* = 4.4 Hz), 5.09 (1H, d, *J* = 4.4 Hz), 3.90 (2H, t, *J* = 6.8 Hz), 1.27 (20H, br s), 0.89 (3H, t, *J* = 6.6 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 147.53 (CH), 81.83 (CH), 73.40 (CH_2), 31.86 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.57 (CH_2), 29.50 (CH_2), 29.44 (CH_2), 29.37 (CH_2), 29.28 (CH_2), 29.22 (CH_2), 25.54 (CH_2), 22.63 (CH_2), 14.03 (CH_3).

IR (neat) υ_{max} 2921 (m), 2852 (m), 1642 (w), 1103 (m), 738 (w).

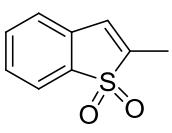
2-Methylbenzo[b]thiophene 63



Benzothiophene (1 g, 7.45 mmol) was dissolved in THF (50 mL) under an atmosphere of argon and cooled to -78 °C. *n*-butyllithium (2.5 M sol^n in hexanes, 3.88 mL, 9.69 mmol) was slowly added and the reaction mixture was left stirring at -78 °C for 20 minutes. Iodomethane (0.69 mL, 11.18 mmol) was added slowly keeping the temperature below -70 °C. Upon completion after 20 minutes the reaction mixture was allowed to warm to room temperature then sodium bicarbonate solution (~50 mL) was added and the product extracted with ethyl acetate. Recrystallisation in hexane and small amount of ethyl acetate gave the title thiophene **54** as light yellow crystals (0.53g, 3.55 mmol, 48 %). Crude product present in mother liquor. ^{1}H data consistent with the literature.[55]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.76 (1H, d, *J* = 7.5 Hz), 7.66 (1H, d, *J* = 7.2 Hz), 7.34-7.23 (2H, m), 6.99 (1H, brs), 2.60 (3H, d, *J* = 1.1 Hz).

2-Methylbenzo[b]thiophene 1,1-dioxide 60



2-Methylbenzo[b]thiophene **63** (0.52 g, 3.55 mmol) was dissolved in a solution of glacial acetic acid (5 mL) and hydrogen peroxide (30%, 2.25 mL, 22.40 mmol) and

heated to reflux. After 3 hours water (10 mL) was added and a solid formed which was filtered off. Purification by column chromatography (silica gel, 50% ethyl acetate/hexane) followed by recrystallation from hexane with a small amount of ethyl acetate gave title thiophene **60** as light green needles (0.306 g, 1.698 mmol, 48%). NMR data is consistent with the literature.[56]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.72 (1H, d, *J* = 7.3 Hz), 7.55-7.42 (2H, m), 7.28 (1H, d, *J* = 7.7 Hz), 6.78 (1H, brs), 2.23 (3H, d, *J* = 1.8 Hz).

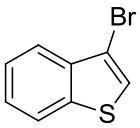
^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.98 (C), 136.51 (C), 133.57 (CH), 131.65 (C), 129.31 (CH), 125.86 (CH), 124.25 (CH), 121.55 (CH), 9.08 (CH_3).

LRMS (GC/EI) *m/z* 180, 80% (M^+); 137, 100%; 131, 66%; 115, 75%; 109, 75%.

IR (neat) υ_{max} 2359 (w), 2158 (w), 1448 (w), 1282 (m), 1141 (m).

Melting Point 105-107 °C, lit[57]: 104-105 °C.

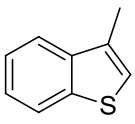
3-Bromobenzo[b]thiophene 64

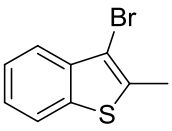


Benzothiophene (1 g, 7.45 mmol) was dissolved in a solution of glacial acetic acid (7.5 mL) and chloroform (7.5 mL) at 0 °C. N-bromosuccinimide (1.66 g, 9.31 mmol) was added over a period of 90 minutes. Reaction mixture allowed to warm to room temperature and stirred for 20 hours. Upon completion reaction mixture was washed with saturated sodium thiosulphate solution followed by saturated sodium carbonate solution. Product was then filtered through a short pad of silica to give title thiophene **64** as a brown oil (1.44 g, 6.76 mmol, 91%). ^{1}H data consistent with the literature.[39] Crude material was used in the next step.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88-7.84 (2H, m), 7.51-7.40 (3H, m).

3-Methylbenzo[b]thiophene 65 and 3-bromo-2-methylbenzo[b]thiophene





3-Bromobenzo[b]thiophene **55** (1.44 g, 6.76 mmol) was dissolved in THF (50 mL) under an atmosphere of argon and cooled to -78 °C. *n*-butyllithium (2.5 M sol^{n} in hexanes, 2.70 mL, 6.76 mmol) was slowly added and the reaction mixture was left stirring at -78 °C for 20 minutes. Iodomethane (0.51 mL, 8.11 mmol) was added slowly keeping the temperature below -70 °C. Upon completion after 20 minutes reaction mixture was allowed to warm to room temperature then sodium bicarbonate solution (~50 mL) was added and the product extracted with ethyl acetate. Purification by column chromatography (silica gel, 100% hexane) gave the title thiophene **65** as pale yellow oil (0.66 g, 4.44 mmol, 66%) (analysis showed ~80% purity) and 3-bromo-2-methylbenzo[b]thiophene (0.18g, 0.79 mmol, 12%). ^{1}H consistent with the literature.[55, 58]

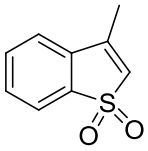
3-Methylbenzo[b]thiophene 65

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.87 (1H, dd, *J* = 7.3, 1.8 Hz), 7.74 (1H, dd, *J* = 7.1, 1.6 Hz), 7.44-7.33 (2H, m), 7.09 (1H, d, *J* = 0.7 Hz), 2.47 (3H, d, *J* = 1.5 Hz).

3-Bromo-2-methylbenzo[b]thiophene

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.74 (1H, d, *J* = 5.5 Hz), 7.72 (1H, d, *J* = 4.8 Hz), 7.42 (1H, t, *J* = 7.0 Hz), 7.34 (1H, t, *J* = 7.3 Hz), 2.57 (3H, s).

3-Methylbenzo[b]thiophene 1,1-dioxide 61



3-Methylbenzo[b]thiophene **65** (0.30 g, 2.00 mmol) was dissolved in a solution of glacial acetic acid (5 mL) and hydrogen peroxide (30%, 1.26 mL, 12.60 mmol) and heated to reflux. After 30 minutes water (10 mL) was added and a solid formed which was filtered off. Purification by column chromatography (silica gel, 0-30% ethyl acetate/hexane) gave title thiophene dioxide **61** as a white solid (0.145 g, 0.80 mmol, 40%). NMD data is consistent with the literature.[56, 57]

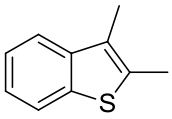
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.72 (1H, d, *J* = 7.3 Hz), 7.63-7.52 (2H, m), 7.42 (1H, d, *J* = 7.3 Hz), 6.48 (1H, brs), 2.28 (3H, d, *J* = 0.7 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.78 (C), 137.54 (C), 133.44 (CH), 133.09 (C), 130.39 (CH), 125.76 (CH), 122.23 (CH), 120.90 (CH), 13.81 (CH_3).

LRMS (GC/EI) *m/z* 180, 79% (M^+); 151, 100%; 131, 62%; 115, 53%.

IR (neat) υ_{max} 3091 (w), 2360 (w), 1377 (w), 1286 (m), 1181 (s), 1104 (m).

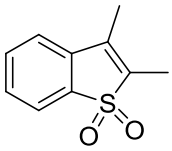
2,3-Dimethylbenzo[b]thiophene 66



Cp_2ZrCl_2 (0.5 g, 1.7 mmol) was dissolved in THF (8 mL) and kept at -40 °C. PhLi (1.8 M, 1.92 mL, 3.45 mmol) was added slowly then stirred for 1 hour at -40 °C. Reaction mixture was allowed to warm to room temperature then transferred to a sealable reaction vessel. 2-Butyne (0.26 mL, 3.4 mmol) and solution underwent 2 freeze-thaw cycles then heated to 80 °C for 24 hours. Reaction mixture cooled to -78 °C then S_2Cl_2 (0.2 mL, 2.5 mmol) was added then stirred for 10 minutes. HCl (1M, 0.5 mL) added to form a solid. THF removed and solid washed with hexane to give title thiophene **66** (0.294 g, Quant.) as a yellow oil. Crude mixture used directly in next reaction. ^{1}H-NMR data is consistent with the literature.[41]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.75 (1H, d, *J* = 7.7 Hz), 7.60 (1H, d, *J* = 7.7 Hz), 7.38-7.25 (2H, m), 2.50 (3H, s), 2.31 (3H, s).

2,3-Dimethylbenzo[b]thiophene 1,1-dioxide 62



2,3-Dimethylbenzo[b]thiophene **66** (0.29 g, 1.81 mmol) was dissolved in a solution of glacial acetic acid (10 mL) and hydrogen peroxide (30%, 0.98 mL, 10.86 mmol) and heated to reflux. After 1 1/2 hour water (10 mL) was added and a solid formed which was filtered off. Purification by column chromatography (silica gel, 0-30% ethyl acetate/hexane) gave title thiophene dioxide **62** (89 mg, 0.46 mmol, 25%) as a white solid. NMR data is consistent with the literature.[56, 57]

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.74 (1H, d, *J* = 7.3 Hz), 7.58 (1H, td, *J* = 7.7, 1.5 Hz), 7.47 (1H, td, *J* = 7.7, 1.1 Hz), 7.38 (1H, d, *J* = 7.3 Hz), 2.16 (6H, s).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.47 (CH), 129.14 (CH), 121.50 (CH), 120.95 (CH), 10.92 (CH_3), 6.85 (CH_3).

LRMS (GC/EI) *m/z* 194, 50% (M^+); 151, 100%; 128, 24%; 115, 30%.

IR (neat) υ_{max} 2921 (w), 1643 (w), 1442 (m), 1280 (s), 1151 (s).

Melting Point 144-148 °C, lit[59]: 150-151 °C.

5.0 References

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