Synthesis of substituted phenylene-ethynylene- based conjugated rods

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Synthesis of Substituted Phenylene-Ethynylene-Based Conjugated Rods

By

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A Thesis Submitted for the Degree of Master of Science

Department of Chemistry
University of Durham

2006

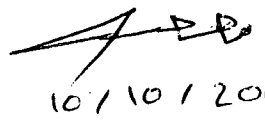
Dedication

To my parents, my husband Ibraheem and my son Ahmed for their love and support

Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between March 2005 and September 2006, under the supervision of Prof. Todd B. Marder. All the work is my own, unless otherwise stated, and has not been submitted previously for a degree at this or any other university.

Maha Al-Haddad



10/10/2006

Statement of Copyright

Acknowledgements

I would like to thank Professor Marder for giving me the opportunity to contribute to this area of research and for all the help, advice and insight he gave me throughout my project.

My special thanks to Dr. Jon Collings for his expert guidance in all aspects of my project as well as patience he afforded me during my time in the lab. Thanks to my dear husband, Dr. Ibraheem Mkhalid, for his support, patience and kindness, especially in the difficult time that we faced this year, and also my dear son, Ahmed.

I would like to thank all the members of the laboratory group. Many thanks to Richard Ward for all his help especially in UV-Vis spectroscopy, Kittia Wongkhan for her help in Raman spectrum and Jonathan Barnard for advice and help as well as making my stay in the lab more enjoyable. Thanks also to Brian Hall for all his technical help in the laboratory.

I would like to thank all of the departmental staff, particularly those from the NMR service (Ian Mckeag, Alan Kenwright and Catherine Heffernan), and X-ray diffraction service (Dr. Andrei Batsanov and Dr. David Albesa-Jove), and elemental analysis (Jaroslava Dostal), for their support and help. I thank the EPSRC National Mass Spectrometry Service Center, Swansea, for some of the MS data.

Also I give my special thanks and love to my mother and my father's soul. Also, my thanks and love to my sisters and brothers; Manal, Osama, Hassan, Laila and Hibah.

Lastly, I am grateful to the Saudi Arabian cultural attaché for the scholarship and their generous funding through one and a half years.

Abstract

A series of *p*-substituted-4-(4-trimethylsilanylethynyl-phenylethynyl)benzenes **(4a-e)** have been prepared via Pd^{II}/Cu^{I}-catalysed cross-coupling of 1-iodo- or bromo-*p*-substituted benzenes with 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**). Deprotection by removal of the TMS from compounds (**4a-e**) was used to obtain *p*-ethynyl tolans with different functional groups (**5a-e**) at the other *para* position. A number of new symmetrical conjugated diynes (**6a-e**) were formed by homocoupling of the terminal alkynes (**5a-e**).

A Hamett plot λ_{masx} (Abs) versus Hammet constants σ_p for compounds (**4a-e**), (**5a-e**) and (**6a-e**) showed that both donors and acceptors red shift absorption.

Also, diynes have been synthesised from esters containing a long chain aliphatic group to improve solubility. Thus, 4-bromobenzoic acid was reacted with octan-1-ol to obtain 4-bromobenzoic acid octyl ester, **7**, which has a C_8 chain and a Br group in the *para* position for subsequent coupling reactions. Then compound **7** was used in two pathways. In path A, compound **7** was coupled with TMSA to obtain the protected alkyne, **8**. Then the TMS protecting group was removed under mild condition to give the terminal alkyne, **9**, which was oxidatively homocoupled to give diyne, **10**.

In path B, compound **7** was coupled with compound **3** to give 4-(4-trimethylsilanylethynylphenylethynyl) benzoic acid octyl ester, **11**. The next step was deprotection of **11** to form the terminal alkyne **12**. Lastly, 2 equivalents of compound **12** was oxidatively homocoupled to give 4,4'-bis-(4''-carbooctyloxylphenylethynyl)diphenylbuta-1,3-diyne, **13**.

List of Abbreviations

Å	Angstrom	**Me**	methyl
Ar	aromatic group	**m.p.**	melting point
***t*-Bu**	*tert*-butyl	**mmol**	millimole
Cy	cyclohexyl	**MS**	mass spectrometry
DAMP	4-(dimethylamino)pyridine	**m/z**	mass to charge ratio
DABCO	1,4-diazabicyclo[2.2.2]-octane	**NMP**	*N*-methylpyrrolidinone
dppf	1,1-bis(diphenylphosphino)ferrocene	**NMR**	Nuclear Magnetic Resonance
DCM	dichloromethane	**Ph**	phenyl
DCCI	dicyclohexylcarbodiimide	**PPh_3**	triphenylphosphine
EI	electron impact	***i*-Pr**	iso-Propyl
Et_3N	triethylamine	**THF**	tetrahydrofuran
equiv.	equivalent	**TMS**	trimethylsilyl
Et	ethyl	**TMSA**	trimethylsilylacetylene
g	gram	**R**	alkyl
GC/MS	gas chromatography-mass spectrometry	**r.t.**	room temperature
h	hour	**UV**	ultra violet
IR	infrared	**X**	halogen
L	ligand	**υ**	Frequency (cm^{-1})
MALDI	matrix assisted laser desorption ionisation	**λ**	Wavelength (nm)

Abbreviations used for NMR

d	doublet	**q**	quartet
J	coupling constant	**s**	singlet
m	multiplet	**t**	triplet
MHz	megahertz		

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carbonate which gave compound **5d**

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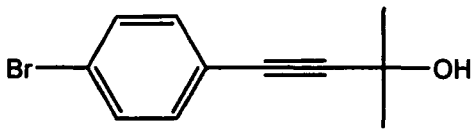
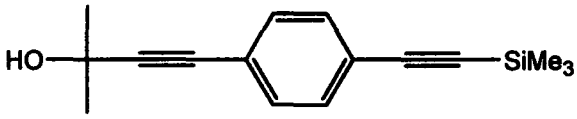
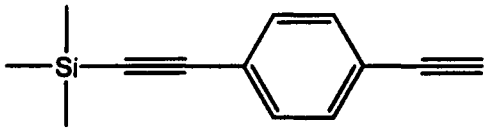
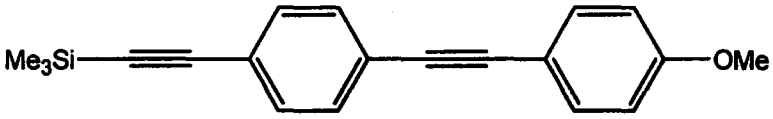
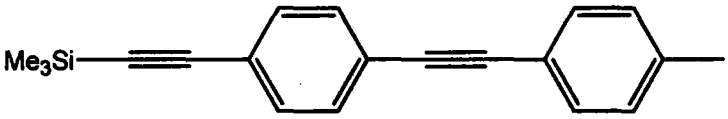
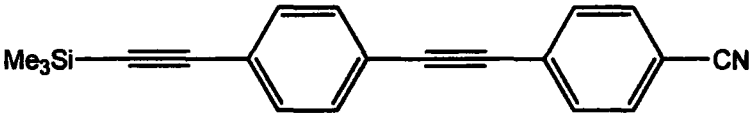
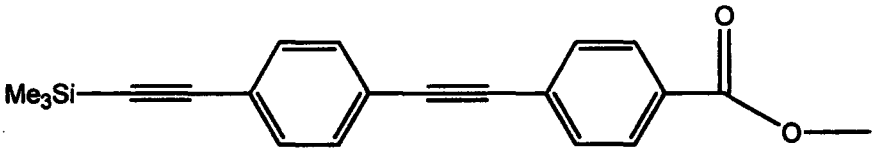
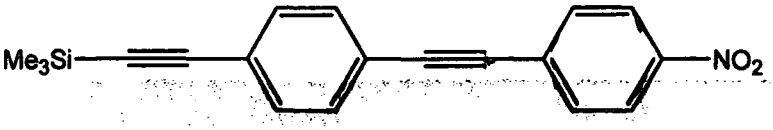
Compound Numbering Scheme

Structure	NO
	1
	2
	3
	4a
	4b
	4c
	4d
	4e

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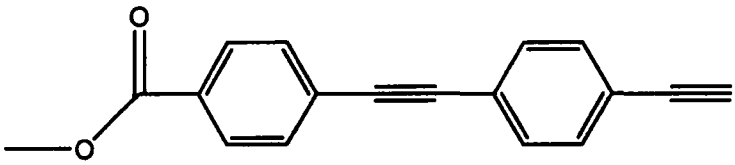

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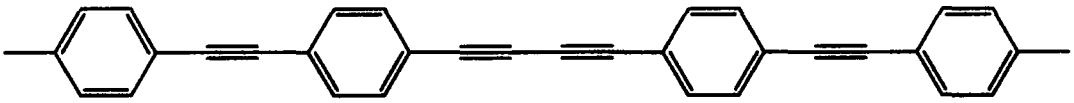

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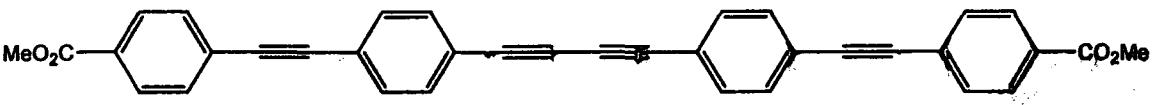

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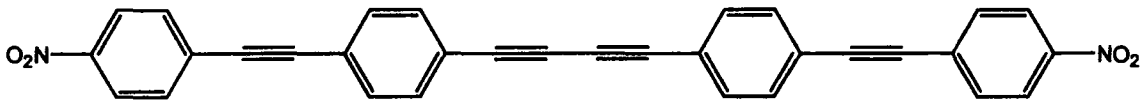

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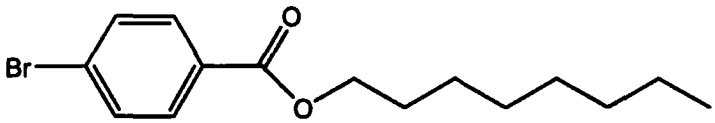

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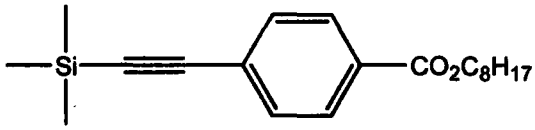

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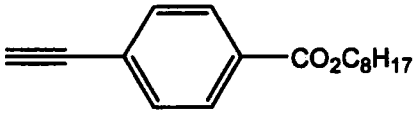

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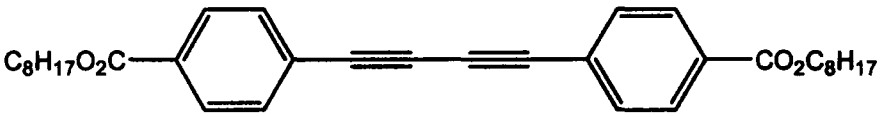

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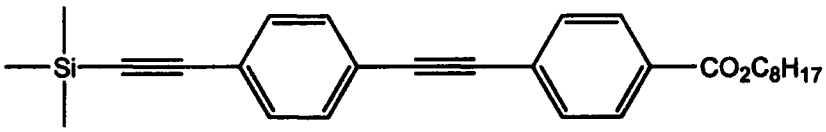

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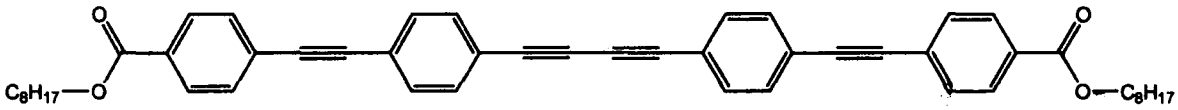

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Chapter 1

Introduction to the Sonogashira reaction

1.1 Introduction

Cross-coupling reactions of terminal alkynes with aryl or alkenyl halides or triflates in the presence of a palladium complex, copper iodide and an amine, are extensively used in organic chemistry and materials science for the preparation of alkynyl arenes and enynes. This reaction is known as the Sonogashira reaction.[1,2] Thus, the Sonogashira reaction is used in numerous syntheses of natural products, for instance, enediyne antibiotics, as well as in the preparation of liquid crystals, conducting polymers and other engineering materials.[3,4] The conditions and the mechanism of typical Sonogashira reactions will be discussed in this chapter.

1.2 General view

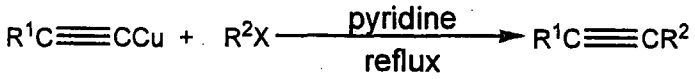
Sonogashira reactions involve the formation of C-C bonds between sp and sp^2 centres. The formation of these bonds is thermodynamically favourable, but in practice, the kinetic barriers to coupling are large in the absence of a suitable catalyst. Before 1975,[5] the scope of cross-couplings was largely limited to those involving Mg and Li reagents. In general, organometallics containing these metals undergo synthetically useful cross-coupling only with certain relatively unhindered alkyl halides, such as those containing groups such as methyl, primary alkyl, allyl, benzyl, and so on.[6] However, the cross-couplings between Grignard or organolithium reagents and alkyl halides are subject to various side reactions. The Kharasch reaction depends on various transition metal salts

being added as catalysts for the reaction of the Grignard reagent with organic halides,[7] but Pd was not employed. However, the Kharasch reaction was generally not well suited for cross-coupling with the notable exception of the Cu-catalysed variant.

The discovery in 1972, by Kumada and Tamao and their associates, represents the birth of the modern transition metal-catalysed cross-coupling.[8,9] Their reaction involved cross-coupling of Grignard reagents with aryl halides using a Ni catalyst and phosphine ligands. During the 1975-76 period, several groups of workers reported many studies of Pd-catalysed cross-coupling reactions.[10-15] The variation on the Castro-Stephens reaction,[16] using CuI salts and Pd complexes as catalysts, known as the Sonogashira reaction,[1] was also reported during the same period.

1.3 The Sonogashira reaction

In 1963, Stephens and Castro demonstrated the coupling of aryl halides with alkynyl copper(I) species to obtain arylacetylenes.[17]

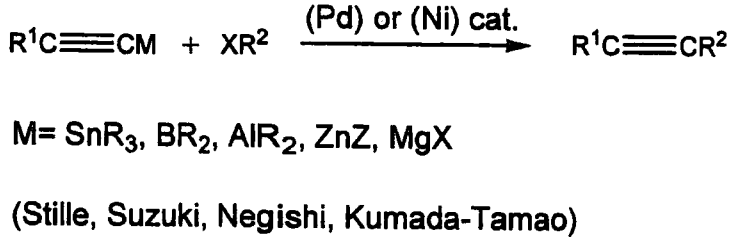


Scheme 1.1: Stephens-Castro reaction

Since then, much effort has been directed to elucidating the mechanism of the Stephens-Castro reaction, and to developing synthetic protocols that would not require stoichiometric copper. Sonogashira and co-workers found that combining catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI enabled the same coupling without the need for stoichiometric copper or for isolating the alkynyl copper intermediate.[1]

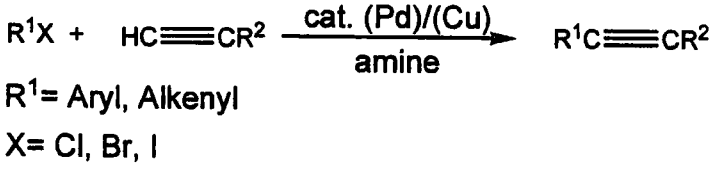
For the coupling of alkynes with organohalide compounds, there are two important metal-mediated reactions:

1- reaction of metallated alkynes with the organohalide compounds in the presence of Pd or Ni such as the Stille,[18] Suzuki,[19] Negishi[20-23] and Kumada-Tamao[8,9] couplings;



Scheme 1.2: Metal-catalysed cross-coupling reactions

2- reaction of a terminal alkyne with an organohalide in the presence of catalytic Pd/Cu and excess amine which is known as the Sonogashira reaction.



Scheme 1.3: Sonogashira cross-coupling reaction

The Sonogashira reaction was first reported in 1975,[1] and is one of the most important reactions for the preparation of arylalkynes and conjugated enynes. The reaction has been applied to vinyl halides, aryl iodides and bromides and recently, aryl chlorides.[1,24,25] The

reactivity of the aryl halides are in the order: Ar-I > Ar-Br >>Ar-Cl>>Ar-F. In the case of aryl iodides, the cross-coupling can sometimes be carried out under mild conditions such as at room temperature, but generally, the reaction times are relatively long. For aryl bromides, the reaction usually requires a reflux. Recently, Buchwald, Fu and co-workers[26] have developed a palladium system using a bulky, electron rich phosphine ligand, P(*t*-Bu)$_3$, to produce a highly active catalyst that can couple relatively inactive aryl bromides at room temperature. This study depended on using 0.5% $PdCl_2(PhCN)_2$/1.0% P(*t*-Bu)$_3$ to couple 4-bromoanisole with phenylacetylene, and the isolated yield was 99% after 22 h. Using similar conditions it has been shown that bromoarenes react with different alkynes to afford the coupled products in good to excellent yields 70-90%. Even very electron-rich 4-bromo-*N*,*N*-dimethylaniline reacts cleanly at room temperature in good yield (94%).

However, aryl chlorides, which show a much lower reactivity than bromo and iodo analogs, have been used only recently. This low reactivity is ascribed to their much lower tendency to undergo oxidative addition to palladium(0) in the catalytic cycle. Most recently, Peyrat and Alami *et al.*[27] have found that by using palladium catalysts with organozincate reagents, generated *in situ*, by reaction of Grignard compounds with less than molar amounts of zinc chloride, in the presence of conjugated organo chlorides gave, rapidly and cleanly, the corresponding coupling product in high yields. This suggests that the transmetallation step (vide infra) can also be important in influencing the rate of the reaction.

Usually, the Sonogashira coupling is carried out in the presence of a catalytic amount of palladium(II) complex as well as copper(I) iodide in an amine as solvent.

1.3.1 The Effect of the Palladium Catalyst

The most widely used catalysts are $PdCl_2(PPh_3)_2$ is pre-catalyst or $Pd(PPh_3)_4$ in conjunction with copper(I)iodide. For the synthesis of the $PdCl_2(PPh_3)_2$ catalyst, $PdCl_2(PhCN)_2$ was reacted with PPh_3 in DCM. The yellow precipitate, $PdCl_2(PPh_3)_2$, was obtained after washing with DCM.[28]

$$PdCl_2 \xrightarrow[120\ ^oC]{PhCN} PdCl_2(PhCN)_2 \xrightarrow[DCM]{2\ PPh_3} PdCl_2(PPh_3)_2$$

Scheme 1.4: Synthesis of $[PdCl_2(PPh_3)_2]$

d^8-Metal complexes often prefer square planar, 4-coordinate geometries which provide good ligand field stabilisation as the $d_{x^2-y^2}$ orbital remains empty.[29]

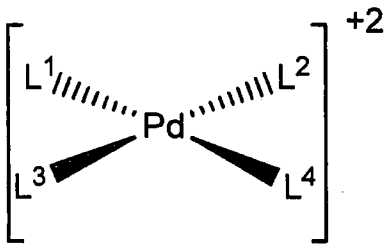


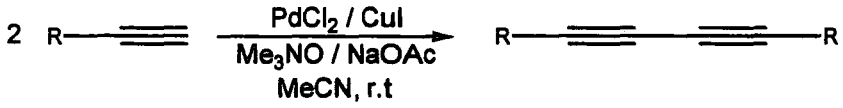
Figure 1.1: Pd(II)L_4 structure

Monodentate, bulky and electron-donating, tertiary phosphines are often employed as ancillary ligands in coupling systems.[30] The specific applications benefit from or require the use of sterically demanding phosphine ligands to stabilise unsaturated reactive intermediates.

In 1983, Sabourin *et al.*[31] studied the cross-coupling between m-bromonitrobenzene and 2-methyl-3-butyn-2-ol, using $PdCl_2$ in the absence of phosphines. The reaction showed extremely low catalytic activity. The activity was high when the PPh_3/Pd ratio was 2. When the ratio was increased from 2 to 110, the $t_{1/2}$ increased 5 times.

Some phosphine ligands are sensitive to air and are expensive, which puts significant limits on their synthetic applications. They often require air free handling to prevent ligand oxidation.

Li *et al.*[32] have developed an efficient amine and phosphine-free catalyst for homocoupling reactions. They used $PdCl_2$, CuI, Me_3NO and NaOAc instead of amines as the base. Mixtures of MeCN / H_2O were used as the most effective solvent for the homocoupling reaction. This has proven to be an extremely effective catalytic system for the homocoupling of various terminal alkynes.

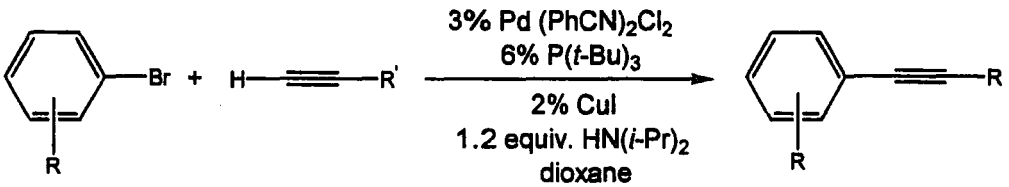


R= Me-C_6H_4, MeO-C_6H_4, F_3C-C_6H_4, *t*-Bu

Scheme 1.5: Synthesis of diynes by homocoupling

Recently, it has been demonstrated that palladium catalysts that incorporate bulky, and electron rich phosphines can display unusually high reactivity in a wide range of coupling processes.[33] Buchwald, Fu and co-workers[26] established that one such ligand, P(*t*-Bu)$_3$, does indeed furnish a highly active catalyst for Sonogashira coupling of aryl bromides at room temperature. For optimisation, they chose to focus on the Sonogashira coupling of

4-bromoanisole, an electron rich and therefore relatively unreactive aryl bromide, as their test substrate. They found that, among the five ligands, PPh_3, P(*o*-tolyl)$_3$, dppf, PCy_3, and P(*t*-Bu)$_3$, P(*t*-Bu)$_3$ is uniquely effective in accomplishing the palladium-catalysed Sonogashira reaction at room temperature. The best conditions established in this study were using 3 mol% $Pd(PhCN)_2Cl_2$, 6 mol% P(*t*-Bu)$_3$, 2 mol% CuI and 1.2 equiv. of HN(*i*-Pr)$_2$ in dioxane solvent.



Scheme 1.6: Room temperature Sonogashira coupling catalysed by $PdCl_2(PhCN)_2$/P(*t*-Bu)$_3$

The Sonogashira cross-coupling reaction usually proceeds with Pd^0/Cu^I catalysts and a base as the solvent, if necessary, starting from the more convenient Pd^{II}/Cu^I system. Active 14-electron Pd^0 species are generated *in situ* by bis(alkynylation) of the Pd complex followed by reductive elimination of the butadiyne. Recently, Heuze and Astruc have reported a series of chelating bis(*t*-Bu$_2$P) and bis(Cy$_2$P) functionalised Pd^{II} monomers and polyamino (DAB) dendritic catalysts which were synthesised and investigated for Sonogashira coupling reactions in a copper-free procedure. These catalysts exhibited tremendous differences in their reactivies and recoverabilities that were dependent on the phosphine substituents (*t*-Bu versus Cy).[34] The catalytic activity was much higher with *t*-Bu substituents on the phosphines than with Cy substituents.

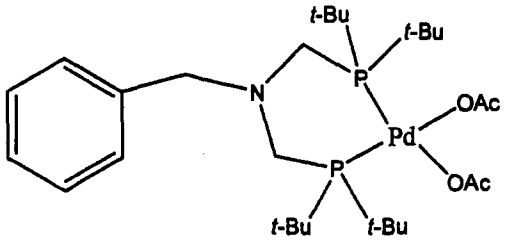
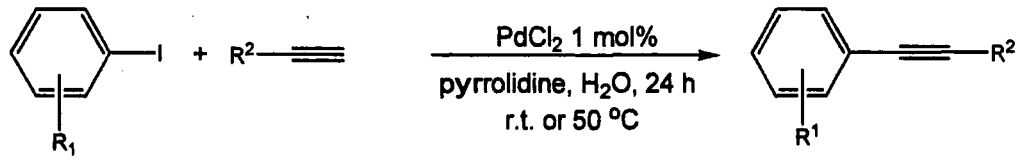


Figure 1.2: Pre-catalyst [Pd{*t*-Bu_2-$PCH_2N(CH_2C_6H_4)CH_2P$-*t*-Bu_2}$(OAc)_2$], for the Sonogashira reaction

1.3.2 The Effect of Copper Iodide

Generally, the Sonogashira reaction is carried out by using palladium catalysts with Cu(I) iodide as a co-catalyst, allowing the reaction to occur under mild conditions. The use of copper(I) iodide as co-catalyst requires elimination of air because it induces the homocoupling reaction (Glaser-type reactions) of terminal alkynes to diynes in the presence of oxygen.[35-37] This side reaction is problematic when: (1) the diyne has similar solubility to the desired alkyne; or (2) the coupling is carried out with a multi-terminal alkyne such as diethynyl benzene or a triethynyl arene, as this leads to incorporation of diyne in the growing chain. Alkynyl complexes of other metals such as zinc, tin, boron, aluminum, Ag_2O and AgOTf have been developed to address this issue; however, additional steps are required to make these reagents. Many of these reactions were carried out without a copper salt, which provides the opportunity to develop the Sonogashira reaction under aerobic conditions, because the copper (or Cu/Pd)-mediated oxidative homocoupling of acetylene is prevented.

In 1992, Genêt *et al.* [38] reported the first, effective copper-free cross-coupling of alkynes with aryl or vinyl iodides using a water soluble Pd-catalyst. Chen and co-workers[38] have developed a mild protocol for the phosphine- and copper-free Sonogashira coupling of aryl iodides with terminal acetylenes under aerobic conditions. The use of 1 mol% of $PdCl_2$ in the presence of pyrrolidine allows the coupling reaction to proceed at room temperature or 50 °C with good to excellent yields.[39]



R^1= CN, NO_2, Me, MeO, Ph
R^2= Me_2N-C_6H_4, MeO-C_6H_4, Br-C_6H_4, Ph, C_4H_9

Scheme 1.7: Copper-free Sonogashira coupling of aryl iodides

Leadbeater *et al.*[40] have also developed a copper-free methodology. They used 4 mol% of $PdCl_2(PPh_3)_2$ and 3 equiv. of piperidine as a base to couple aryl iodides or bromides with phenyl acetylene. The mixture was heated in an oil bath at 70 °C for 10 minutes, and the yield was 90% for coupling 1-bromo-4-nitro-benzene with phenyl acetylene, for example. Recently, Astruc and co-workers[41] employed the complex [Pd{*t*-$Bu_2PCH_2N(CH_2Ph)CH_2P$*t*-Bu_2}$(OAc)_2$], (Fig. 1.2), which efficiently catalyses the Sonogashira cross-coupling reaction of aryl halides with acetylenes at room temperature, without a co-catalyst.

1.3.3 The Effect of Amine

The Sonogashira reaction is sometimes carried out in an organic solvent such as benzene, toluene, THF, DMF, or dioxane. However, it also requires a base such as triethylamine, diethylamine or diisopropylamine to assist in deprotonation of the alkyne. Often the amine is not only used as a base but also as a solvent, to scavenge hydrogen halides which are generated during the reaction. The effect of the nature of the amine was studied by Alami and co-workers[42] who found that when the reaction was performed in the presence of copper iodide as co-catalyst, very short reaction times were observed using pyrrolidine, piperidine or diisopropylamine.

There have been many developments to allow the reaction to be conducted in an aqueous solvent, which is important for the environment and economics. Najera and co-workers[43] developed a copper and amine-free reaction using an oxime palladacycle, $[PdCl(2\text{-}CH{=}N(OH)(C_6H_4Cl)\text{-}5\text{-}ClC_6H_4)]_2$, for the cross-coupling of terminal acetylenes with aryl iodides and bromides (> 99% for the reaction of *p*-chloroiodobenzene with phenylacetylene under reflux in NMP/H_2O).

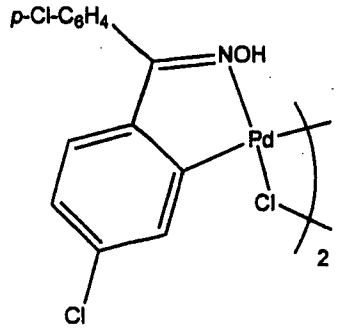


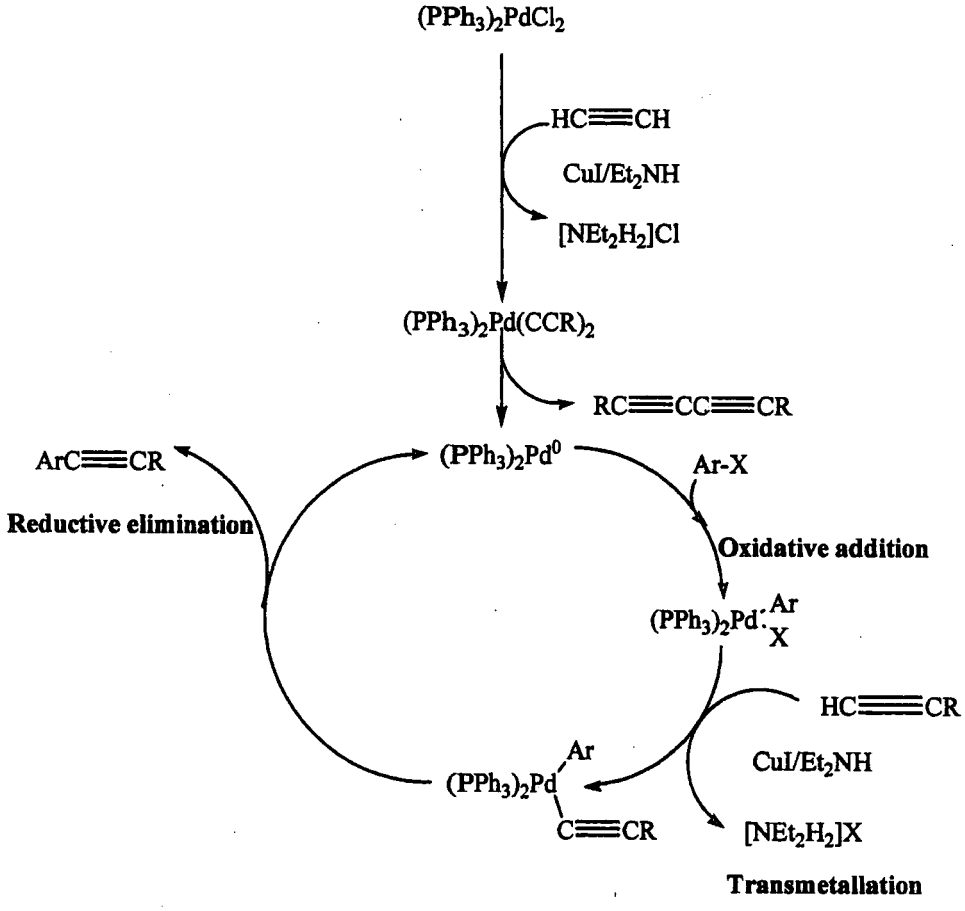
Figure 1.3: Oxime palladacycle $[PdCl(2\text{-}CH{=}N(OH)(C_6H_4Cl)\text{-}5\text{-}ClC_6H_4]_2$ for cross-coupling

1.4 The Mechanism of the Sonogashira Reaction

The standard three-step catalytic cycle consisting of (1) oxidative addition of an organic electrophile to a Pd(0) complex, (2) transmetallation to generate diorganopalladium derivatives, and (3) their reductive elimination to produce the desired alkynes with concomitant regeneration of the Pd(0) complex, had been proposed in the 1970s.[1,2]

As shown in Scheme 1.8, a reduction of Pd(II) to Pd(0) is believed to occur through the oxidative coupling of two equivalent of the alkyne to produce a diyne, HX and the reactive catalyst. This side reaction can increase, inducing excess homocoupling reactions (Glaser-type reaction) of terminal alkynes to diynes in the presence of oxygen, so oxygen must be rigorously excluded.[36,37]

If we compare Pd(0) and Pd(II) complexes for the reaction of alkynes with aryl halides, we found that when Pd(0) was used as the starting material, the amount of diyne produced was negligible. But, when Pd(II)was added, one equivalent of diyne was produced for each palladium. Thus, when it is required that little or no diyne is produced, Pd(0) should be used as the catalyst.[36]



Scheme 1.8: Catalytic cycle for the Sonogashira coupling reaction[1,2]

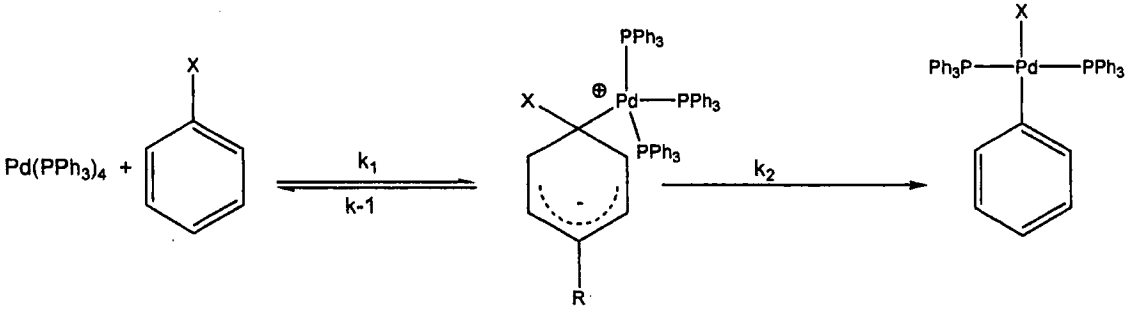
However, the detailed mechanism of the Sonogashira reaction has not yet been fully clarified. Each step of the mechanism can be summarised as described below.

1.4.1 The Oxidative Addition

The oxidative addition of aryl halides to Pd^0, forming an Pd^{II} aryl halide complex, is a fundamental reaction in organometallic chemistry.

Scheme 1.9: The oxidative addition at Pd^0 to give Pd^{II}

The oxidative addition step of the reaction has been proposed to proceed *via* different neutral or ionic transition states.[44,45] The comparative reactivity of the aryl halides towards addition to $Pd(PPh_3)_4$ suggests that this may be another example of aromatic nucleophilic substitution.

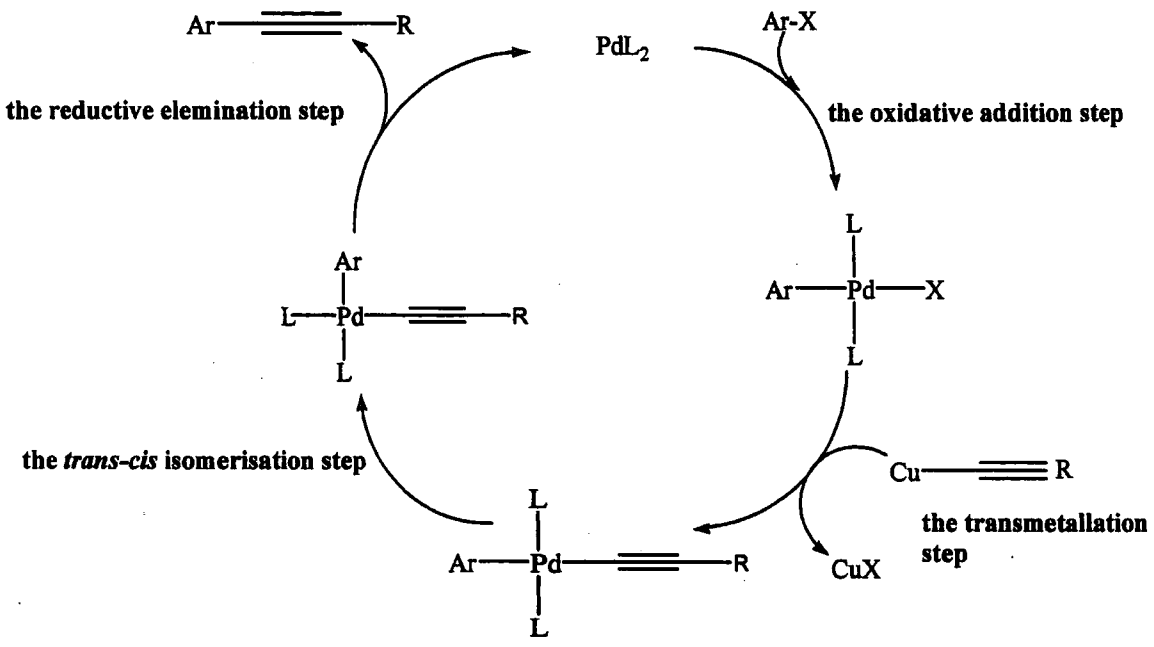


Scheme 1.10: Oxidative addition mechanism proposed *via* nucleophilic aromatic substitution

The nucleophilic aromatic substitution pathway was studied by Fitton and Rick.[44] Their research examined the comparative reactivity of halobenzenes towards oxidative addition to $Pd(PPh_3)_4$. Aryl chlorides substituted with electron-donating groups were unreactive, but aryl chlorides substituted with electron–withdrawing groups are reactive. This increased reactivity, and the order of reactivity ($4\text{-}NO_2C_6H_4Cl$ > $4\text{-}CN\text{-}C_6H_4Cl$ > $4\text{-}C_6H_4COC_6H_4Cl$ > PhCl) suggested that the mechanism of the oxidative addition is similar to that of bimolecular nucleophilic aromatic displacement reaction in which breaking of the bond to the leaving group is involved in the rate determining step. Also, as shown in Scheme 10, assuming that C-X bond breaking is important in the rate-determining step, one would predict that k_2 (and hence the overall rate constant, k_2k_1/k_{-1}) would increase as one went from C-Cl to C-Br to C-I. They observed that PhCl is less reactive than PhBr which in turn is less reactive than PhI. However, this mechanism cannot exclude the possibility that the reaction occurs by an electron transfer process wherein electrons are transferred from the metal to the ring to give a radical anion, or possibly a dianion.

1.4.2 The Transmetallation Step

This step is less well understood than the oxidative addition step. According to the proposed pathway, "Cu(C≡CR)", generated *in situ* from a mixture of CuI, terminal alkyne and amine, undergoes alkyne ligand transfer to $Pd(Ar)(X)L_n$ (X = halide), giving $Pd(Ar)(C{\equiv}CR)L_n$, which is responsible for the subsequent reductive elimination of the coupled product.



Scheme 1.11: The proposed cross-coupling mechanism

1.4.3 The *Trans-Cis* Isomerisation

Before reductive elimination can take place, *trans-cis* isomerisation must occur. The complex *trans*-[$Pd(PEt_3)_2(Ar)(C{\equiv}CR)$] had been isolated which confirms the mechanism.[46] The *trans*-complex must be isomerised to the *cis*-complex before the reductive elimination step can occur (Scheme 1.11). This may occur through dissociation of a phosphine ligand or by the association of halide to a form a 5-coordinate complex,[47] which could then rearrange to the necessary configuration.

1.4.4 The Reductive Elimination Step

The final step is the reductive elimination. This step can only take place if the ligands being eliminated are *cis* to each other.[47] In the catalyst activation step, the acetylides on the palladium then reductively eliminate to leave the palladium species in the zero oxidation state. [47] The aryl and acetylide ligands eliminate in the product forming final step.

1.5 Deprotections of Trimethylsilyl and CMe_2OH Protecting Groups

1.5.1 Protecting Groups

Sonogashira coupling reactions tolerate a wide variety of functional groups, and will couple any terminal alkynes present. There are many occasions when this is not desirable, so effective ways of protecting these have had to be found. Consequently, the synthesis of terminal alkynes by the Sonogashira reaction has required:

a- preparation of monoprotected ethynes, containing silane or alcohol protecting groups;

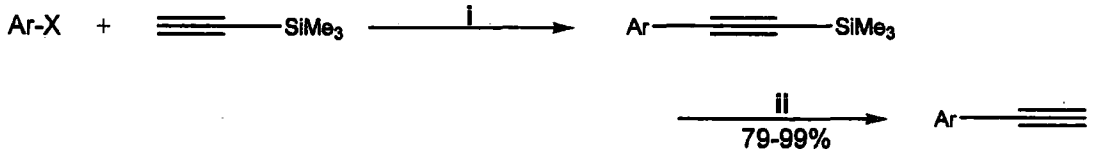
b- their Sonogashira coupling;

c- deprotection.

This three–step procedure is circuitous, and can lead to modest overall yields of the desired terminal alkynes in some cases.

1.5.2 Trimethylsilyl Protecting Group

The C(sp)-Si bond is generally not affected by the Sonogashira conditions. The silyl group can, therefore, if desired, subsequently be removed to furnish a structurally modified terminal alkyne. The most widely used silyl protecting group is the trimethylsilyl group, TMS,[48,49] which can be easily removed. The coupling reaction between an aromatic halide and TMSA in the presence of a palladium and copper(I)iodide, followed by treatment with dilute aqueous potassium hydroxide in methanol, provides simple access to various arylalkynes[49,50] (Scheme 1.12). The TMS group can also be removed by using $Bu_4N^+F^-$ or excess sodium carbonate.



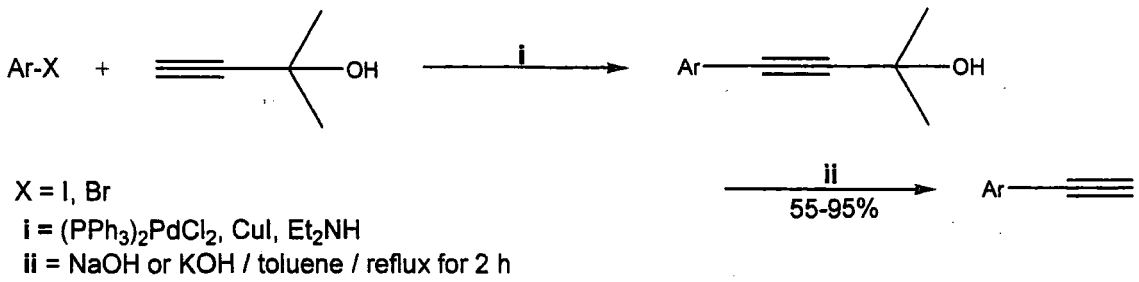
X = I, Br
i = $(PPh_3)_2PdCl_2$, CuI, Et_3N
ii = 1 N aq. KOH / MeOH, 1 h, r.t.

Scheme 1.12: Deprotection of the trimethylsilyl group

1.5.3 CMe_2OH Protecting Group

The most widely used protected alkyne other than TMSA is 2-methyl but-3-yn-2-ol. This alcohol has received considerable attention because it is much less expensive than TMSA and can react with base at elevated temperature to give terminal alkynes whilst liberating acetone. This easily available starting material can couple with an aryl halide followed by

treatment with sodium or potassium hydroxide in refluxing toluene to provide the correspondary terminal alkyne[51,52] (Scheme 1.13).

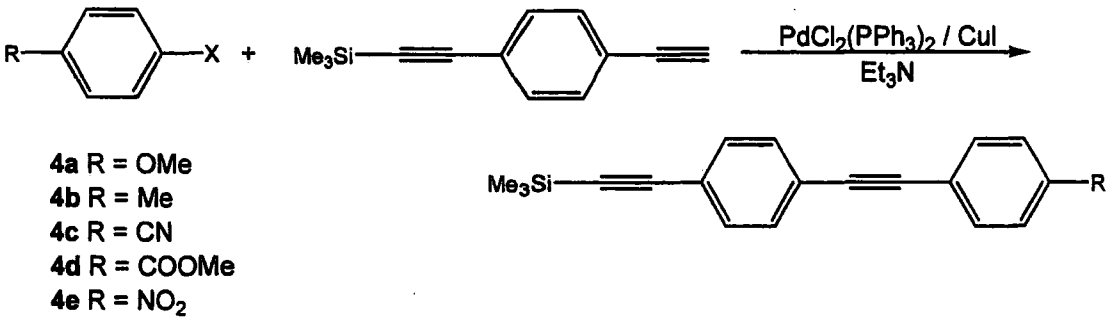


Scheme 1.13: Deprotection of the CMe_2OH group

1.6 Potential for Improvement in the Sonogashera Reaction

The Sonogashira reaction is one of the most widely used C-C bond forming reactions. Some improvements have been made by new methodologies. Looking into the future, however, one should note that there still is considerable room for improvement. Thus, the leaving group in the organic electrophiles has been mostly I, with Br and OTf accounting for a relatively small number of the remaining cases. In fact, Cl has been used in some cases, but the current scope of the Pd-catalysed alkynylation of organic chlorides is still rather limited. In this respect, (i) optimisation of ligands and Pd complexes, (ii) screening and development of superior additives including co-catalysts, and (iii) screening and improvement of solvent and other reaction parameters are highly desirable.[53]

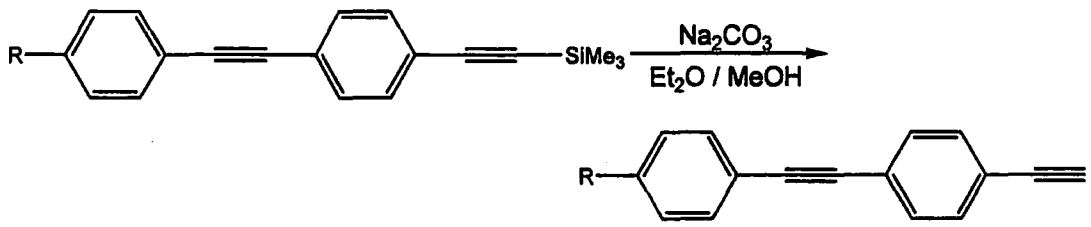
In the next chapter, the Sonogashira cross-coupling reaction will be used as the key step in the synthesis of *p*-substituted-4-(4trimethylsilanylethynylphenylethynyl) benzenes (**4a-e**).



4a R = OMe
4b R = Me
4c R = CN
4d R = COOMe
4e R = NO_2

Scheme 1.14: General reaction for the synthesis of TMS-protected ethynyl tolans (**4a-e**)

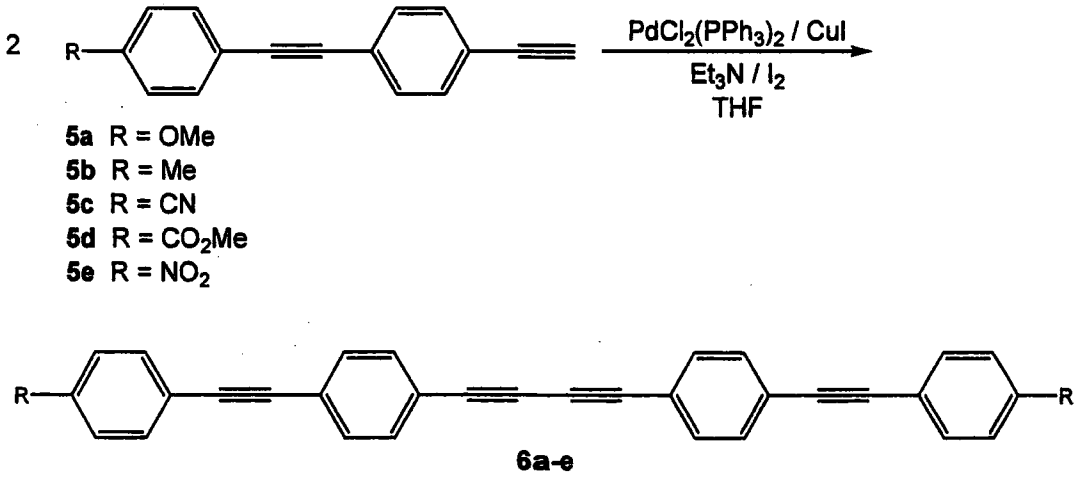
Deprotection by removal of the TMS group from compounds (**4a-e**) was used to obtain *p*-ethynyl tolans with different functional groups (**5a-e**) at the other *para* position.



5a R = OMe
5b R = Me
5c R = CN
5d R = COOMe
5e R = NO_2

Scheme1.15: General deprotection reaction to form terminal alkynes (**5a-e**)

The new symmetrical conjugated diynes (**6a-e**), the target compounds of the thesis, were formed by catalysed homocoupling of the *p*-ethynyl tolans (**5a-e**).



Scheme 1.16: Homocoupling reaction of terminal alkynes to prepare diynes (**6a-e**)

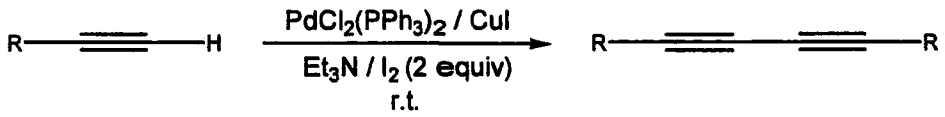
Chapter 2

Pd-Catalysed Sonogashira Reaction of Terminal Alkynes to Diynes

2.1 Introduction

Diynes are useful building blocks in organic synthesis and a recurring functional group in many natural products and bioactive compounds.[54-56] Also, diynes are important compounds in terms of the solid state properties of their homopolymers.[57] Diynes may be synthesised in a number of ways.[58,59]

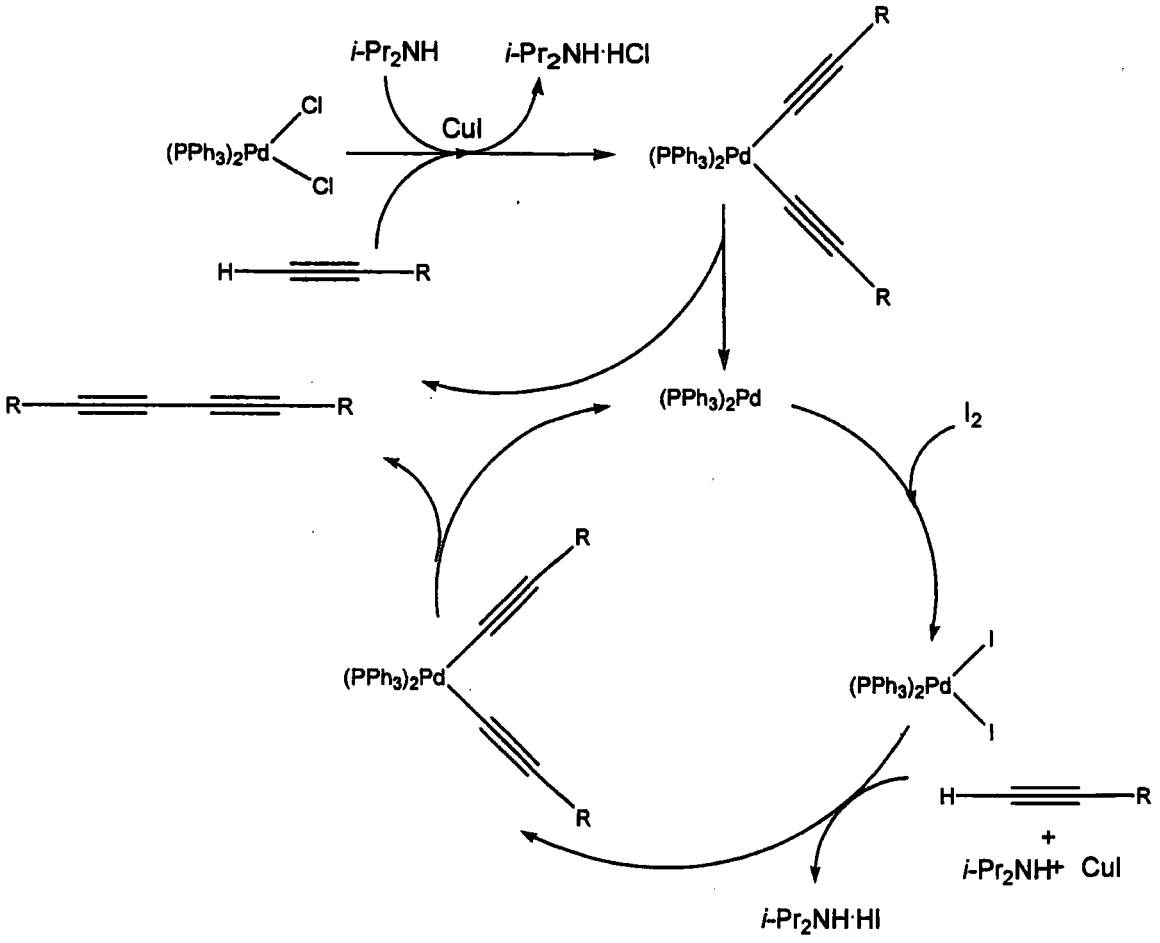
Burton and co-workers[60] have described a facile method for the synthesis of symmetrical conjugated diynes by reaction of 1-alkyne with 0.5 equiv. of iodine in diisopropylamine in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ (1.3 mol%) and CuI (5 mol%). In this project, we used the same method, but triethylamine has been used instead of diisopropylamine with 2 mol% of $PdCl_2(PPh_3)_2$, 5 mol% of CuI and 2 equiv. of iodine (Scheme 2.1).



Scheme 2.1: Synthesis of symmetrical 1,3-diynes

It had been suggested that diynes may be produced *via* a reductive elimination from the bis(triphenylphosphine) dialkynylpalladium, which resulted from reaction of 1-alkyne and $PdCl_2(PPh_3)_2$ in the presence of CuI and amine.[60] This reductive elimination also

generates the active palladium(0) catalyst, $Pd(PPh_3)_2$. I_2 can be used to regenerate the Pd(II) catalyst from the Pd(0) formed in the catalytic cycle upon diyne reductive elimination from bis(triphenylphosphine) dialkynylpalladium (Scheme 2.2).



Scheme 2.2: Catalytic cycle for the synthesis of symmetrical 1,3-diynes

2.2 Ethynylarenes and Diynes in Conjugated Materials

Aromatic conjugated polymers are a class of polymers receiving significant attention in academia as well as industry. Conjugated polymers such as poly-(*p*-phenylene) **PPP** and poly-(*p*-phenylenevinylene) **PPV** are important because of their thermal stability and electrical conductivity.[61]

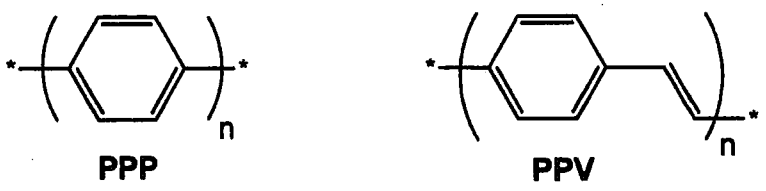


Fig 2.1: poly-(*p*-phenylene) **PPP** and poly-(*p*-phenylenevinylene) **PPV**

An another class of aromatic conjugated polymer is poly-(*p*-phenyleneethynylene) **PPE**, which is the alternating linkage of phenylene units in the 1,4-position with acetylene groups (Fig 2.2).

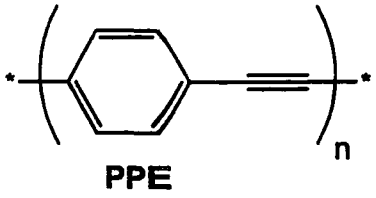


Fig 2.2: Conjugated polymer poly-(*p*-phenyleneethynylene) **PPE**

Aromatic conjugated polymers are organic semiconductors and are of importance for applications in electronic and photonic devices.[62] Aromatic conjugated polymers can be used in light-emitting diodes,[63] plastic lasers,[64] photovoltaic cells,[65] and in organic semiconductors.[66] They can be also used in sensory materials for water, organic vapors and in artificial nose devices.[62] Recently, Swager,[67] Müllen[68] and Wender[69] demonstrated

that PPEs can be used in widely varying applications, from explosives detection to molecular wires for bridging nanogaps.[67-69]

Rigid-rod materials have received attention because of their long-distance interaction, allowing electron and energy transfer and can be used as molecular rods and connectors for the building of supramolecular structures.[64]

Conjugated diyne systems, are the key component of a large numbers of natural[70] and unnatural products.[71] Other examples are the symmetric and unsymmetric diarylethynes, some of which have useful liquid crystal[72] and/or nonlinear optical properies.[73] An alternative application of conjugated materials systems is the synthesis of pseudohexagonal porous materials (Fig. 2.3).[74]

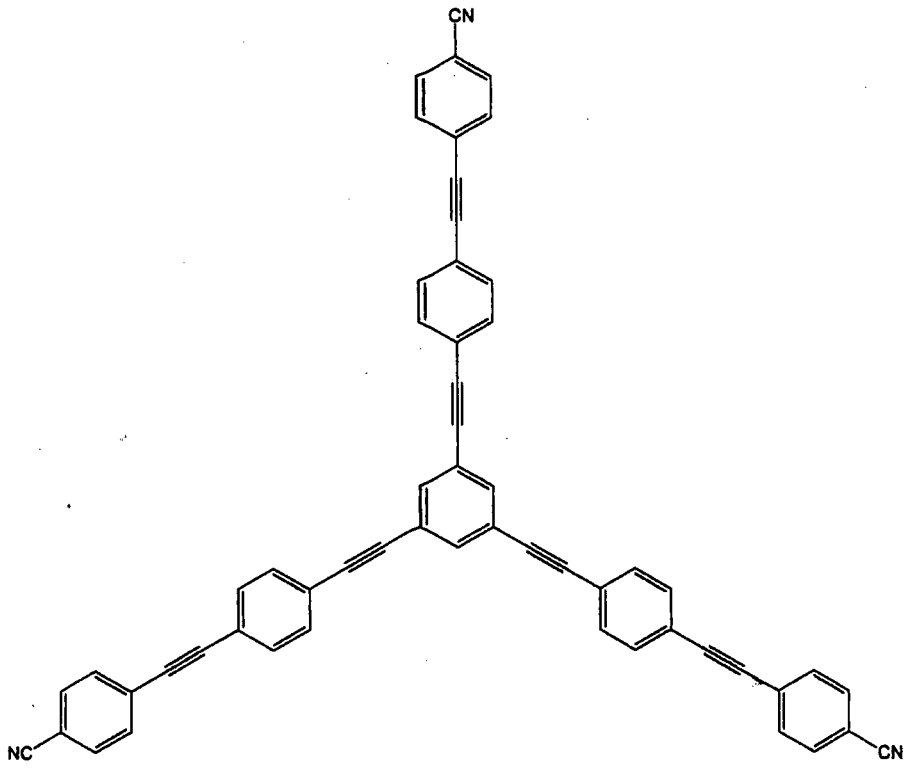
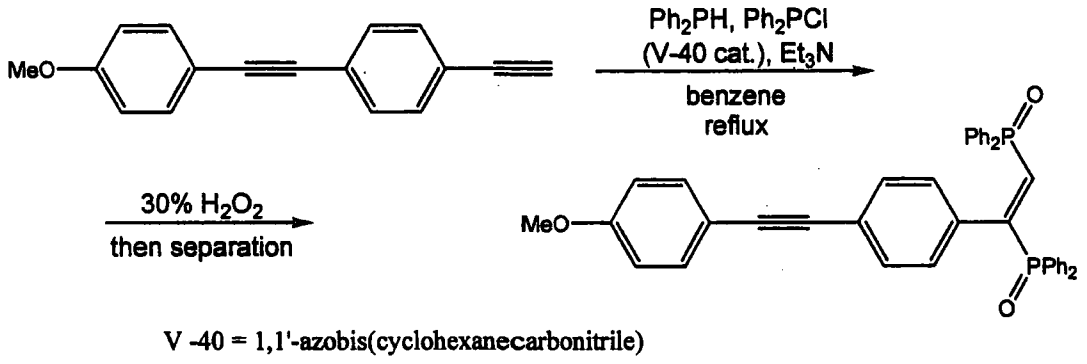


Fig 2.3: Synthesis of a trigonal conjugated compound for use in the preparation of pseudohexagonal porous material containing Ag

Conjugated materials can also be used in synthesis of (*E*)-1,2-diphosphinoethene[75] derivatives from alkynes (Scheme 2.3).

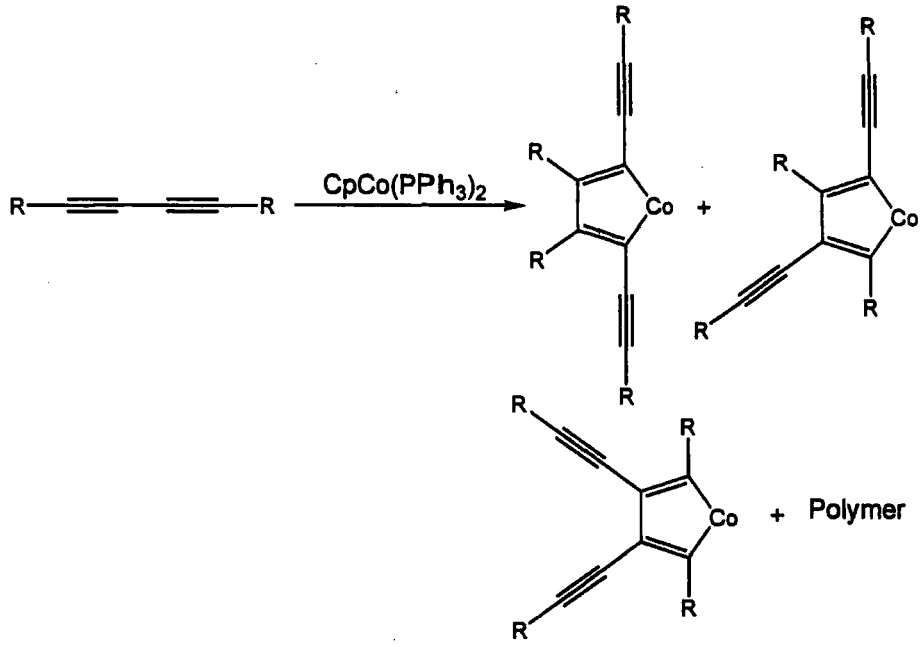


V -40 = 1,1'-azobis(cyclohexanecarbonitrile)

Scheme 2.3: Synthesis of (*E*)-1,2-diphosphinoethene derivatives from alkynes

Rigid-rod conjugated systems such as 1,4-bis(phenylethynyl)benzenes,[76] 9,10-bis(phenylethynyl)anthracenes[77] and 2,5-bis(phenylethynyl)thiophenes,[78] have shown interesting electronic, non-linear optical and luminescent properties.

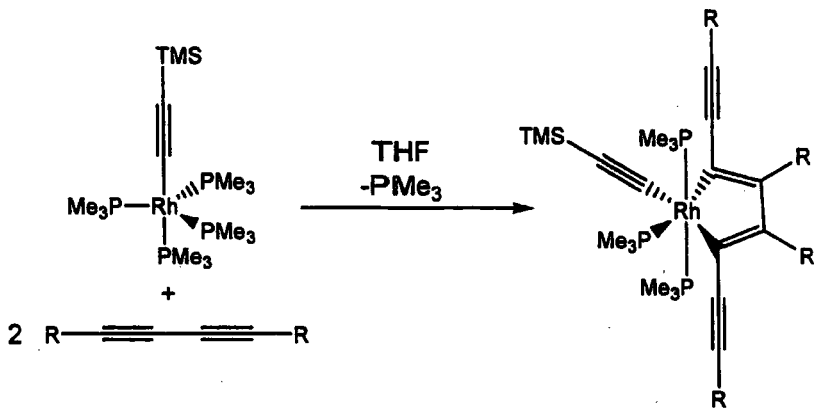
The reductive coupling of diarylbuta-1,3-diynes on transition metals leading to metalla-cyclo-pentadienes functionalised at the 2, 3, 4 and 5 positions on the MC_4 rings has been observed. The first example was reported by Nishihara and co-workers[79] who used cobalt to synthesise π-conjugated systems; however, the reaction of $CpCo(PPh_3)_2$ with PhC≡C-C≡CPh gave three isomers of the cobaltacyclopentadiene and some insoluble polymeric products (Scheme 2.4).



Scheme 2.4: Coupling of diynes on a transition metal (cobalt) by Nishihara[79]

Another example was demonstrated in the reaction of diphenylbutadiyne with $[Ru_3(CO)_{10}(NCMe)_2]$ in the presence of Me_3NO. The reaction gave 2,5-dialkynyl-ruthenacyclo-pentadiene complex, but the maximum yield was very low (4%).[80]

In 2001, Marder and co-workers[81] reported a high yield, one pot, regiospecific synthesis of luminescent rhodacyclopentadienes from 1,4-diarylbuta-1,3-diynes and Rh(C≡C-TMS)$(PMe_3)_4$, (Scheme 2.5). The 2,5-isomer was formed in quantitative yield and was characterised by single crystal X-ray diffraction.

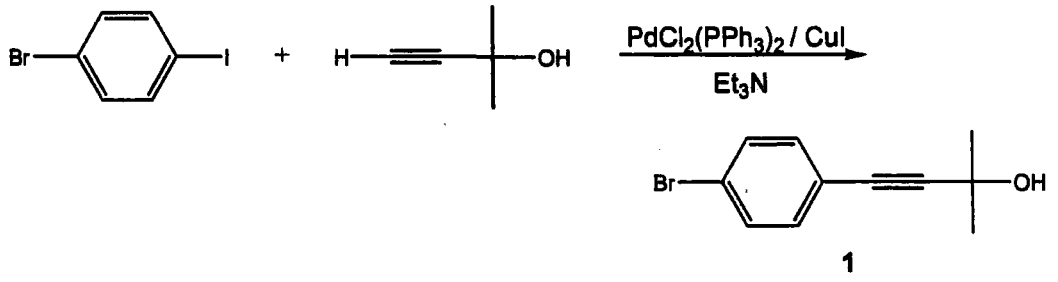


Scheme 2.5: Reaction of $Rh(C{\equiv}C\text{-}TMS)(PMe_3)_4$ with 1,4-diarylbuta-1,3-diynes

New diynes (**6a-e**) are required to prepare extended analogues of the above rhodacyclopentadienes. These should show red shifted emissions due to extended conjugation.

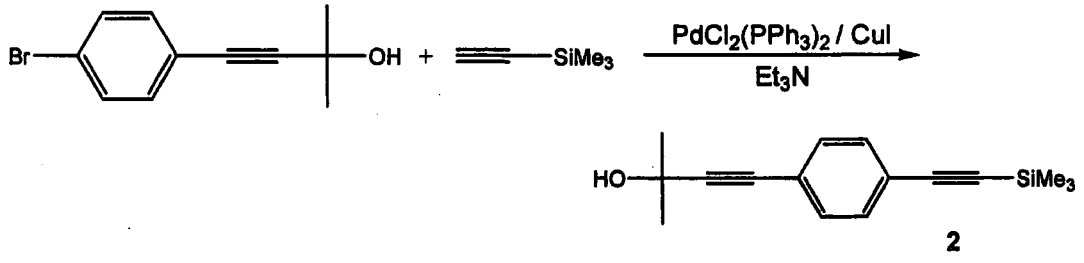
2.3 Results and Discussion

Several *para*-substituted 1,4-diaryl-1,3-butadiynes diynes have been prepared in multi-gram quantities using a variety of oxidative coupling methods suitable for terminal alkynes. The synthetic route to these diynes depends on using the Sonogashira coupling reaction of 1-bromo-4-iodo-benzene with 2-methyl-but-3-yn-2-ol to form the protected terminal alkyne with an alcohol group **1**, as shown in Scheme 2.6. The next step was the reaction of this protected alkyne **1** with TMSA. The reaction was heated to reflux under nitrogen for 24 hours at 80 °C, until it was complete, to obtain a terminal alkyne protected on both sides **2** (Scheme 2.7). Deprotection of the alcohol group was to obtain a protected terminal alkyne with TMS on the other alkyne, namely giving 1-(trimethylsilylethynyl)-4-ethynyl benzene, **3**, (Scheme 2.8).



Scheme 2.6: Preparation of protected alkynes with an alcohol group

Interestingly, in the synthesis of 4-(4-bromophenyl)-2-methyl-but-3-yn-2-ol, if 1,4-dibromo-benzene was used instead of 1-bromo-4-iodo-bezene, the reaction required heating at reflux for 24 hours and the yield of the mono-coupled product was low (only 14%). In contrast, when 1-bromo-4-iodo-benzene was used under the same conditions, with stirring under nitrogen at room temperature, the yield was 79%.



Scheme 2.7: Preparation of protected alkyne with alcohol and TMS groups

Single crystals of 2-methyl-4-(4-trimethylsilanylethynylphenyl)-but-3-yn-2-ol suitable for X-ray diffraction (Fig. 2.4), were grown by slow evaporation of solvent from a concentrated solution of 2-methyl-4-(4-trimethylsilanylethynylphenyl)-but-3-yn-2-ol in acetone. The compound crystallizes in the trigonal space group R-3.

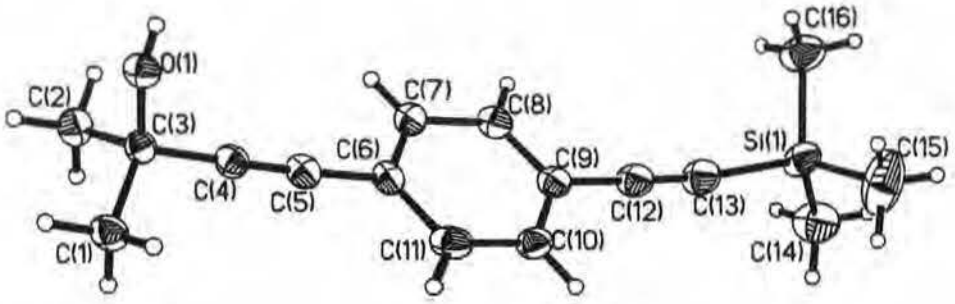


Fig. 2.4: Molecular structure of 2-methyl-4-(4-trimethylsilanylethynylphenyl)-but-3-yn-2-ol

The two triple bonds, $C^4 \equiv C^5$ and $C^{12} \equiv C^{13}$ are 1.1961(19) and 1.203(2) Å in length, respectively. The two alkyne units are slightly non-linear in the molecule with angles C^4-C^5-C^6 and C^9-C^{12}-C^{13} of 176.20(14)° and 177.51(17)°, respectively. Carbon-silicon bond lengths, Si^1-C^{13}, Si^1-C^{14}, Si^1-C^{15} and Si^1-C^{16}, are 1.8403(16), 1.849(2), 1.863(2) and 1.8507(18) Å, respectively. There is hydrogen bonding between H and O atoms. The distance between the H atom and the O atom of another molecule is 1.67 Å, which is a typical hydrogen bond distance. The angle O-H···O is 173.1°.[82] The OH groups form co-operative hydrogen bonds with molecules related by a 3-fold screw axis forming an infinite chain (Fig. 2.5).

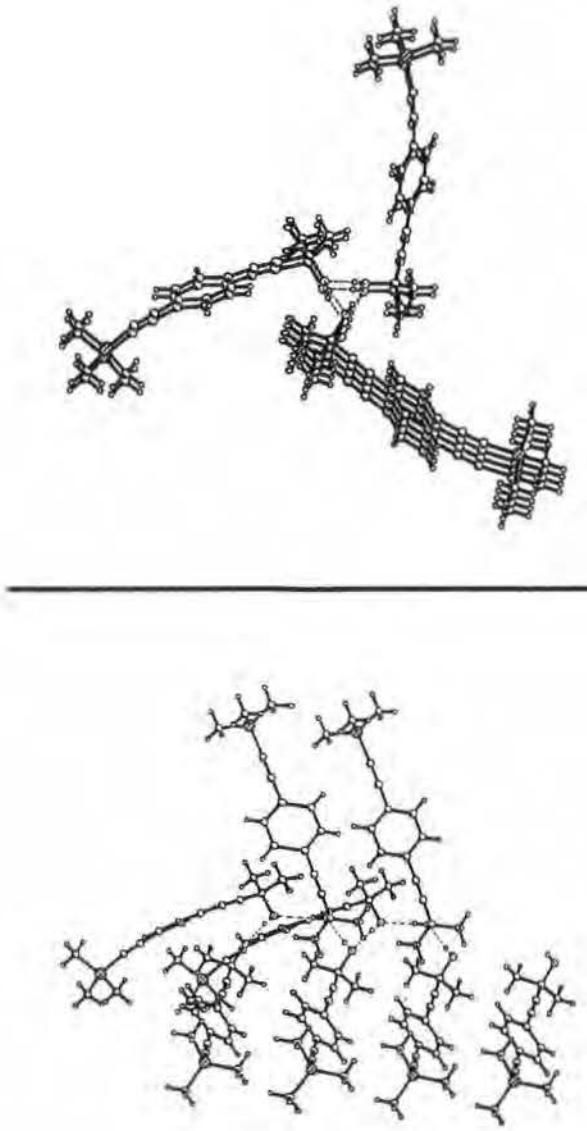
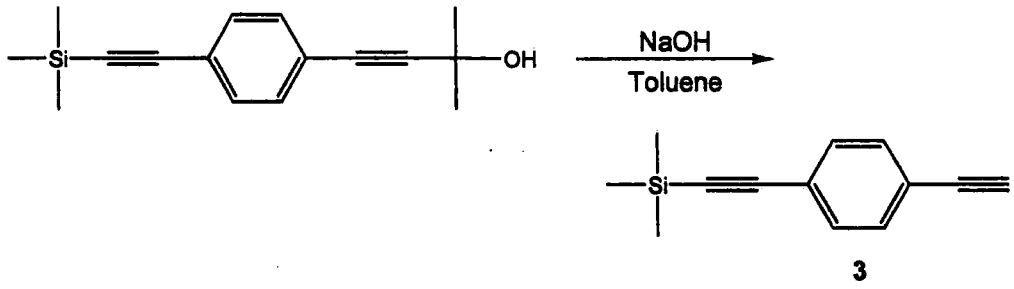


Fig. 2.5: Two views of the molecular packing of 2-methyl-4-(4-trimethyl-silanylethynylphenyl)-but-3-yn-2-ol. The hydrogen bond is shown with a dotted line

Deprotection of the alcohol group was achieved using powdered NaOH in toluene at reflux for 4 hours. The reaction mixture was filtered to remove NaOH, and the filtrate

was evaporated on a rotary evaporator. The oily residue was eluted through a silica pad with hexanes, and the solvent was removed on a rotary evaporator to give a yellow oily product which solidified over time to a crystalline material, providing crystals suitable for X-ray diffraction.



3

Scheme 2.8: Deprotection of the alcohol group to form the terminal alkyne with protected TMS group only

Monoclinic single crystals of 1-(trimethylsilylethynyl)-4-ethynyl benzene **3** (space group C2/c) were obtained by evaporation of hexanes, and these were suitable for X-ray diffraction (Fig. 2.6). The two triple bonds, $C^7 \equiv C^8$ and $C^9 \equiv C^{10}$ are 1.2038(15) and 1.1921(16) Å in length, respectively. The two alkyne units are slightly non-linear in the molecule with angles C^8-C^7-C^1, Si^1-C^8-C^7 and C^{10}-C^9-C^4 of 177.67(11), 178.49(10) and 177.74(12)° respectively. Carbon-silicon bond lengths, Si^1-C^8, Si^1-C^{11}, Si^1-C^{12} and Si^1-C^{13}, are 1.8465(11), 1.8581(13), 1.8597(14) and 1.8592(14) Å respectively. There is a close intermolecular contact between the terminal alkyne H atom and the triple bond.

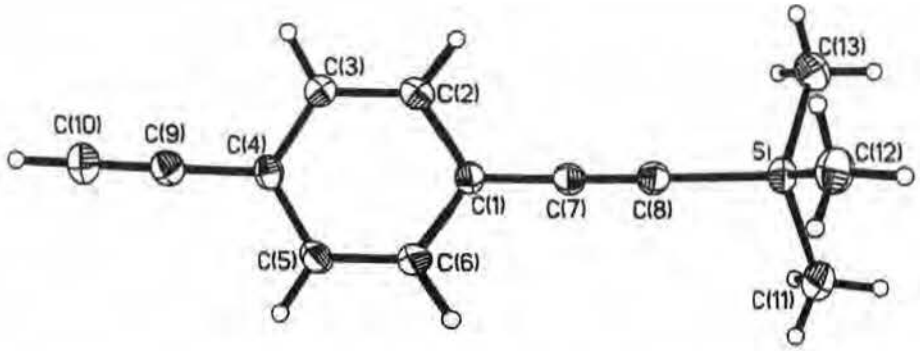


Fig. 2.6: Molecular structure of 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**)

The C(sp)-H bond length was adjusted to the average obtained from neutron diffraction (1.08 Å).[83] The distance between the terminal alkyne H atom and the triple bond of another molecule is 2.63 Å and the angle at the H is 153.8.° (Fig. 2.7).

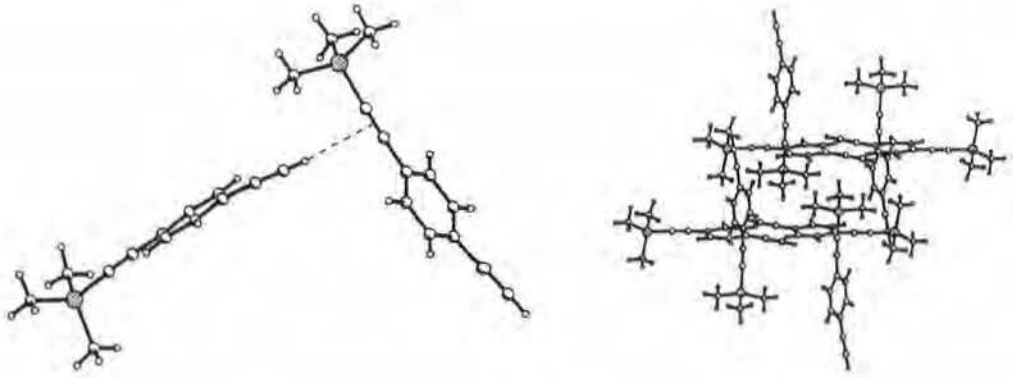
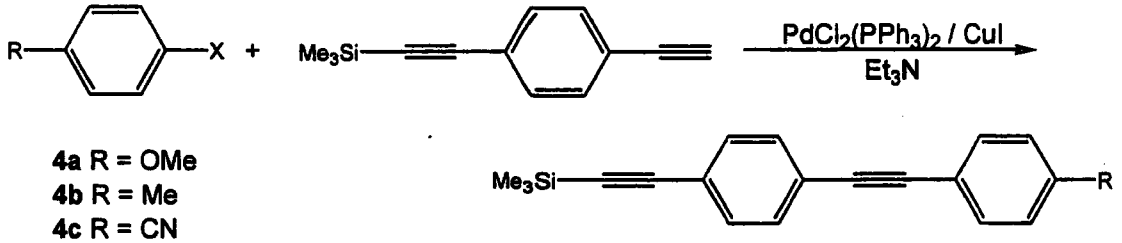


Fig. 2.7: Two views of the molecular packing of 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**)

Recently, Rodríguez *et al.*[84] prepared compound **1** and **2** by the same method and got about the same yield, but they used 1,4-diiodobenzene instead of 4-bromo-1-iodobenene. Under the same conditions, we got compound **3** in 76% yield and they reported a 99%

yield under the same conditions. The difference in the two preparations of compound **3** was that they carried out the deprotection under an argon atmosphere, whereas we carried it out under a flow of nitrogen.

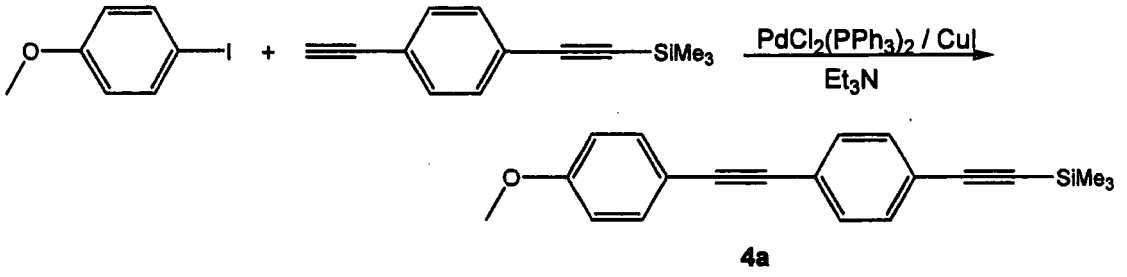
Terminal alkyne **3** served as the starting material for the synthesis of a series of ethynyl tolans and subsequent derivatives. Thus, **3** was reacted with aryl halides containing a variety of functional groups to obtain TMS protected *para*-substituted ethynyl tolans with different electronic properties. Each reaction was carried out under stringently oxygen-free conditions to prevent any oxidation of the Pd(0) catalyst to Pd(II) to avoid homo-coupling of the alkyne to diyne. Use of the Pd/Cu catalyst system 1 mol% and a slight excess of alkyne in the reaction led to completion such that no starting aryl halide was observed by *in situ* GC/MS. The aryl bromides were sufficientally reactive when electron withdrawing substitutents were present at the *para*-position while the iodides were employed with electron donating substitutents.



4a R = OMe
4b R = Me
4c R = CN
4d R = COOMe
4e R = NO_2

Scheme 2.9: General reaction for the synthesis of TMS-protected ethynyl tolans

A selected example of the synthesis of a protected terminal alkyne is discussed below.



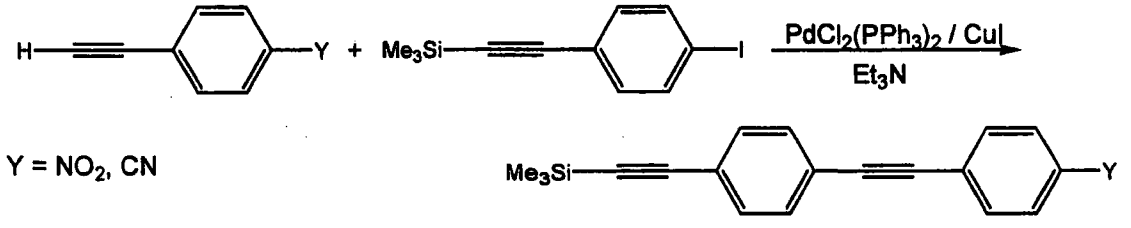
4a

Scheme 2.10: Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-methoxybenzene **(4a)**

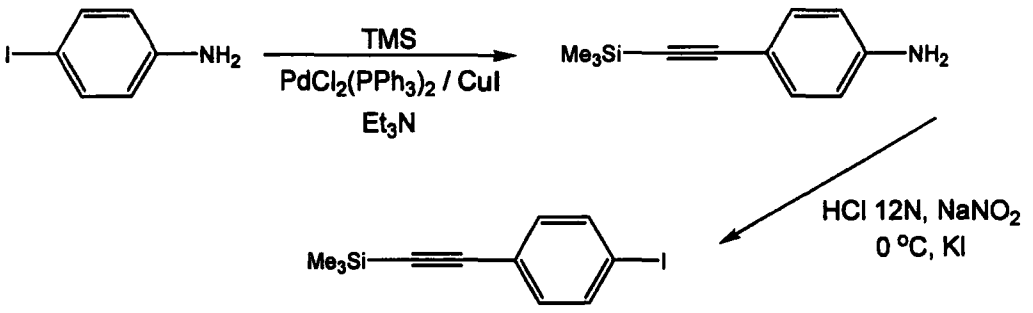
Compound 4-(4-trimethylsilanylethynyl-phenylethynyl)-methoxybenzene **(4a)** was prepared by the use of the Sonogashira palladium and copper catalysed cross-coupling reaction. $PdCl_2(PPh_3)_2$ and CuI were employed in a ratio of 1 mol% each with respect to the starting materials. The reaction was carried out in dry Et_3N and was heated to reflux under nitrogen for 2 hours at 80 °C until it was complete. GC/MS was used to follow the reaction, which not only detected the progress of the reaction, but also the formation of any side products (e.g. homo-coupling). The crude mixture was purified by flash column chromatography eluting with hexane and DCM (9:1), affording the desired pure material in good yield (62%) as a yellow solid. The ^1H NMR spectrum shows resonances for each of the functional groups. One singlet at 0.26 ppm indicated the nine protons of three CH_3 moieties in the ($Si(CH_3)_3$) group, and one singlet at 3.83 ppm was assigned to the three protons of the -OCH_3 group. Two doublets at 6.88 and 7.46 ppm with a coupling constant $^3J_{H\text{-}H} = 9$ Hz represents two protons of one Ar group, and a singlet at 7.43 ppm was due to four protons of the second Ar group (i.e. two coincidentally overlapped signals). A

doublet at 7.46 ppm with coupling constant $^3J_{H\text{-}H} = 9$ Hz represents two protons of one Ar group. We note that the 1, 4-x-C_6H_4-y compounds actually have complex A_2B_2 spin-systems, so the description of a "doublet" and its associated coupling constant given herein are only approximations. The ^{13}C NMR spectrum shows peaks at -0.13 ppm for TMS, at 55.31 ppm for the OMe carbon, at 85.66, 91.40, 96.01 and 104.76 ppm for the four carbons of the two C≡C groups, and at 114.04, 115.09, 122.49, 123.70, 131.20, 131.80, 133.08 and 159.81 ppm for eight unique carbons of the two Ar groups. The molecular ion occurred at *m/z* 304 and a fragment ion at 289 exhibiting the loss of Me was observed in the E.I. mass spectrum.

Compounds **4c** and **4e** were also prepared by Dixneuf and co-workers[85] (Scheme 2.11). The yield was similar for both compounds. The difference was in the preparation of the precursor compound (Scheme 2.12).



Scheme 2.11: Method of Dixneuf and co-workers [85] for preparation of compounds **4c** and **4e**



Scheme 2.12: The different precursors to compounds **4c** and **4e**

The following terminal protected alkynes **4b**, **4c**, **4d** and **4e** were prepared under the same conditions as for **4a**, and the yields are presented in Table 2.1.

Table 2.1: Yields for Sonogashira reactions to prepare TMS-protected alkynes

(R-C_6H_4-C≡C-C_6H_4-C≡C-TMS)

R	Yield %
-OMe **(4a)**	62
-Me **(4b)**	64
-CN **(4c)**	75
-COOMe **(4d)**	48
-NO_2 **(4e)**	78

All the compounds (**4a-e**) were fully characterised by ^{1}H NMR (Fig. 2.8 for **4a** and Fig. 2.9 for **4b**), IR, GC/MS, UV-Vis and fluorescence spectroscopies and by elemental analysis.

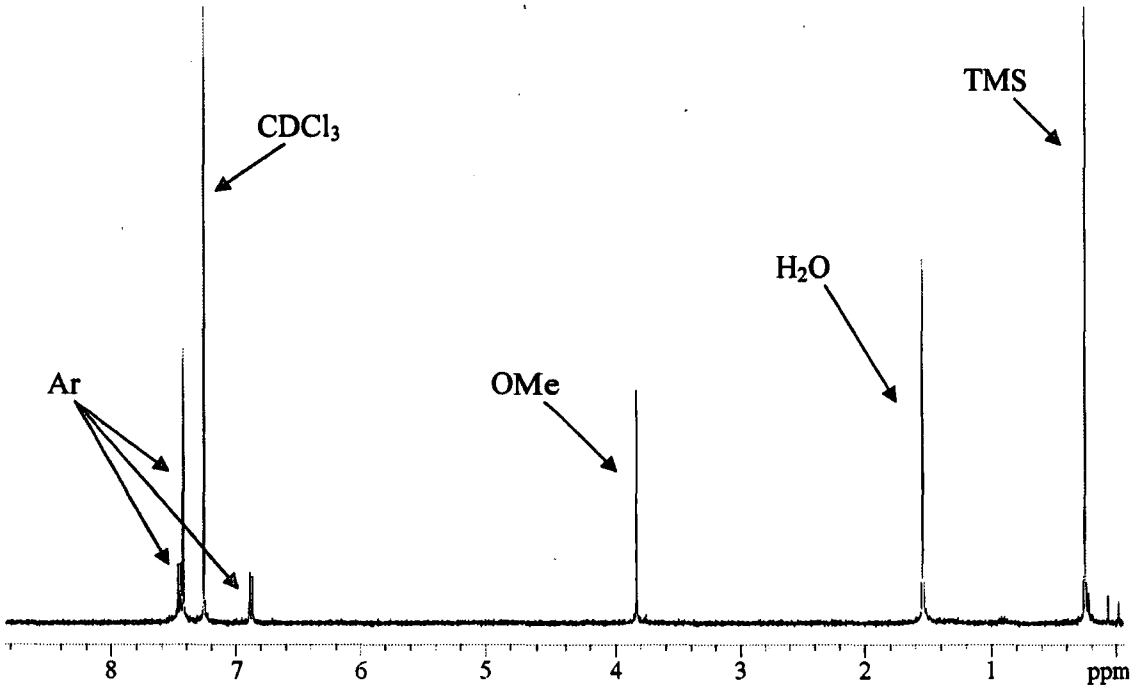


Fig. 2.8: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for *p*-MeO-C_6H_4-C≡C-C_6H_4-C≡C-TMS

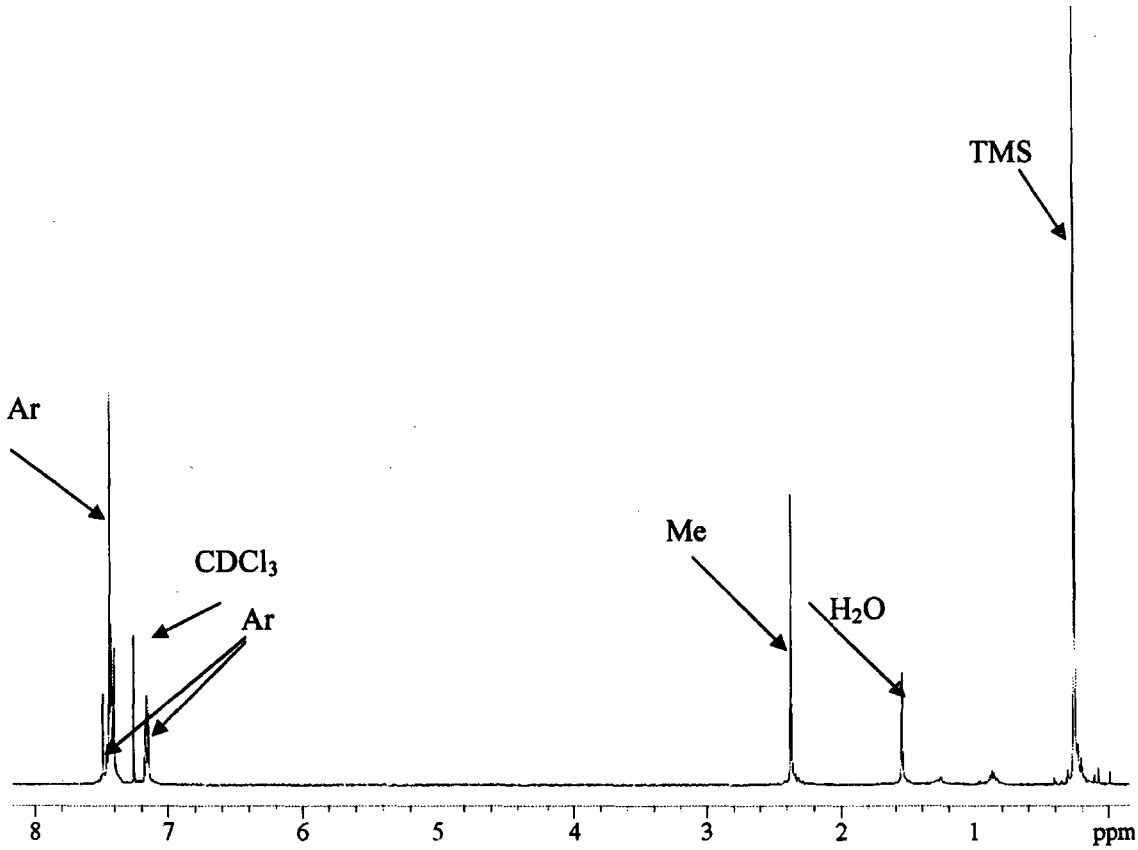


Fig. 2.9: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for *p*-Me-C_6H_4-C≡C-C_6H_4-C≡C-TMS

The absorption and fluorescence spectra of compounds **4a-e**, **5a-e**, **6a-e**, **8**, **9**, **10**, **11**, **12**, and **13** were investigated. Absorbance measurements were made from dilute solutions of the compound in spectroscopically pure chloroform at room temperature.

The absorbance maxima was kept between 1.2 and 0.8 absorbance units in order to get a good signal to noise ratio whilst minimizing saturation (concentrations were around 10^{-5} mol l^{-1}). The absorbance maxima of all of these compounds lie in the near UV region, although compound **4e** has a large part of an absorbance band in the near UV-Vis region.

The absorption and emission spectroscopic data are summarised in Table 2.2. Compounds **4a-e** absorb in the near UV (313-346 nm) as shown in Fig. 2.10 and emit in the near UV-Vis (334-384 nm) regions (Fig. 2.11).

Table 2.2: Absorption and emission data for TMS-protected alkynes **4a-e**

Compound	λ_{max} (Abs) nm	ε mol^{-1} cm^{-1} dm^3	λ_{max} (Em) nm	Stokes Shift cm^{-1}
4a	313 333	46,000 42,000	361	4200
4b	307 328	57,000 52,000	334, 348	2600
4c	316 338	51,000 50,000	360, 367	3800
4d	316 338	43,000 40,000	352, 367	3200
4e	346	35,000	384	2800

Molar absorption coefficients (ε) were calculated from the data and are displayed in Table 2.2. The largest values are for **4b** indicating slightly more intense absorbance for this compound at λ_{max}.

It is observed that there is a small difference between the maximum wavelength of the absorption and emission; this is known as the Stokes shift. A Stokes shift occurs due to the fact that the photo excited molecule loses vibrational energy, before re-releasing the remaining energy as light.

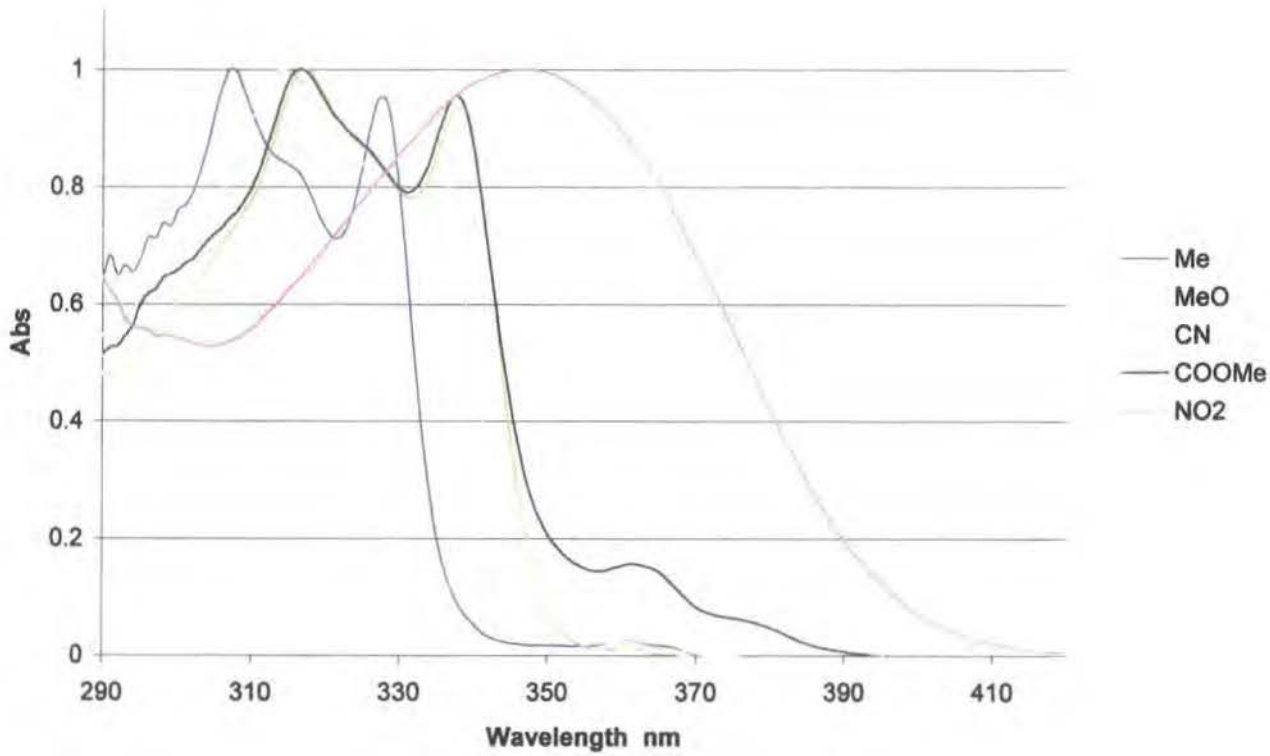


Fig. 2.10: Normalised UV absorption spectra of substituted TMS-C≡C-C_6H_4-C≡C-C_6H_4-R compounds in $CHCl_3$

Fluorescence measurements were made using samples diluted such that the absorption maximum was approximately 0.1 abs units. Concentrations were kept this low in order to nullify the effects of reabsorbing of photons emitted from fluorescence. The samples were irradiated at the wavelength of λ_{max} (Abs) so exciting the molecule to an electronically excited S_1 state. Vibrational relaxation takes the energy down to the lowest vibrational state where either fluorescence or internal conversion can occur the latter meaning that the energy is lost as vibrational energy loss alone, returning the molecules to S_0 (Fig. 2.11).

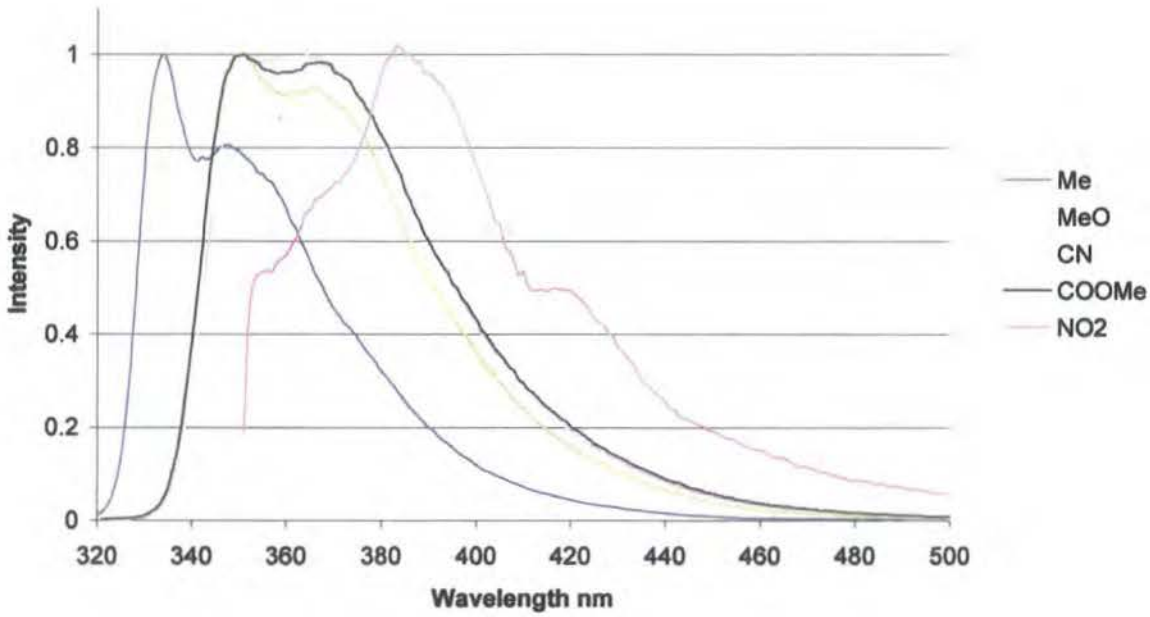
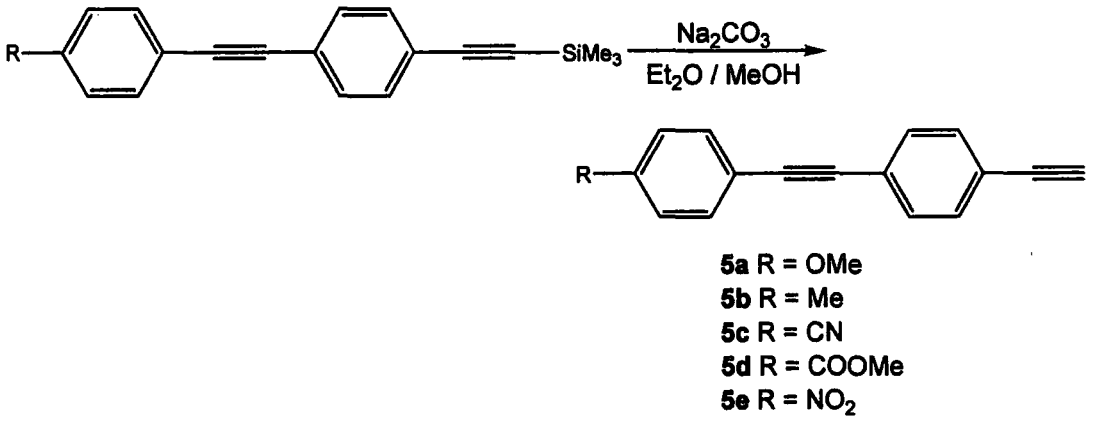


Fig. 2.11: Normalised UV-Vis emission spectra of substituted TMS-C≡C-C_6H_4-C≡C-C_6H_4-R compounds in $CHCl_3$



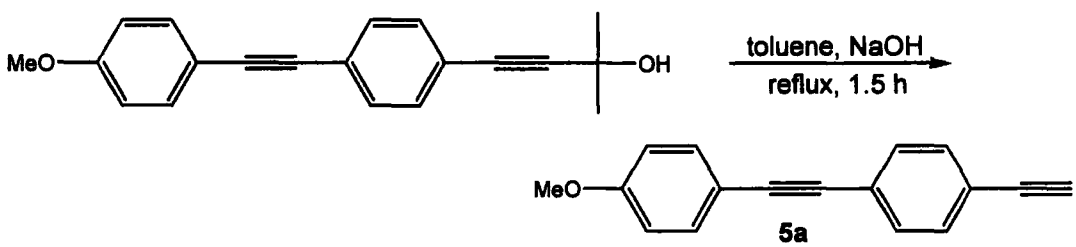
Scheme 2.13: Deprotection reaction to form terminal alkynes

Deprotection was achieved by removal of the TMS group using sodium carbonate in a methanol, diethyl ether and water mixed solvent system.[86] Stirring was required, usually overnight, and the product was filtered to remove sodium carbonate. The filtrate was extracted with diethyl ether which was separated from the aqueous phase, dried over $MgSO_4$, and then the product was isolated by evaporation of the solvent on a rotary evaporator.

The ^1H NMR spectrum for compound **5a** displays a singlet at 3.16 ppm for one proton of the C≡CH group, and one singlet at 3.83 ppm was assigned to three protons of the OMe group. Two doublets at 6.81 and 7.40 ppm with coupling constant $^3J_{H\text{-}H} = 9$ Hz represent four protons of one Ar group, and a singlet at 7.38 ppm was due to four protons of the second Ar group (i.e. two coincidentally overlapped signals). The ^{13}C NMR spectrum shows peaks at 55.67 ppm for the OMe carbon, at 78.88, 82.24, 87.84 and 91.77 ppm for the four carbons of the two C≡C groups, and at 114.42, 115.32, 121.84, 124.60, 131.57, 132.34, 133.50 and 160.04 ppm for eight unique carbons of the two Ar groups. The

molecular ion occurred at *m/z* 232 along with a fragment ion at *m/z* 217, corresponding to the loss of Me, in the EI mass spectrum.

Compound **5a** was prepared previously by Gossauer and co-workers[87] who used 2-methyl-3-butyn-2-ol as the protecting group (Scheme 2.14); they obtained compound **5a** in 91% yield.



Scheme 2.14: The method used by Gossauer and co-workers[87] to prepare **5a**

The following terminal protected alkynes **5b**, **5c**, **5d** and **5e** were prepared under the same conditions as for **5a**, and the yields are presented in Table 2.3.

Table 2.3 Yields for deprotection of TMS protected terminal alkynes

(R-C_6H_4-C≡C-C_6H_4-C≡C-H)

R		Yield%
-OMe	**(5a)**	67
-Me	**(5b)**	73
-CN	**(5c)**	76
-COOMe	**(5d)**	56
-NO_2	**(5e)**	68

Compounds **5a-e** were fully characterised by ^{1}H NMR (Fig. 2.12 for **5d** and 2.13 for **5e**), IR, GC/MS, UV-Vis and fluorescence spectroscopies and by elemental analysis.

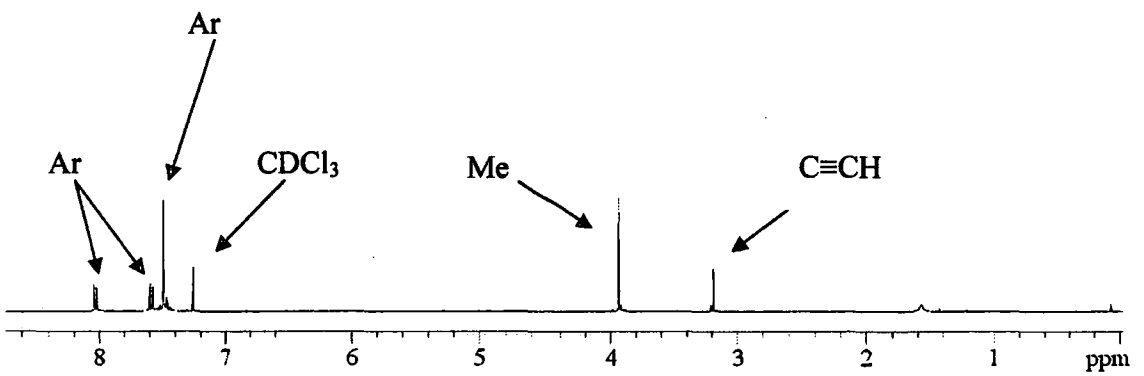


Fig. 2.12: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *p*-$MeCO_2$-C_6H_4-C≡C-C_6H_4-C≡C-H

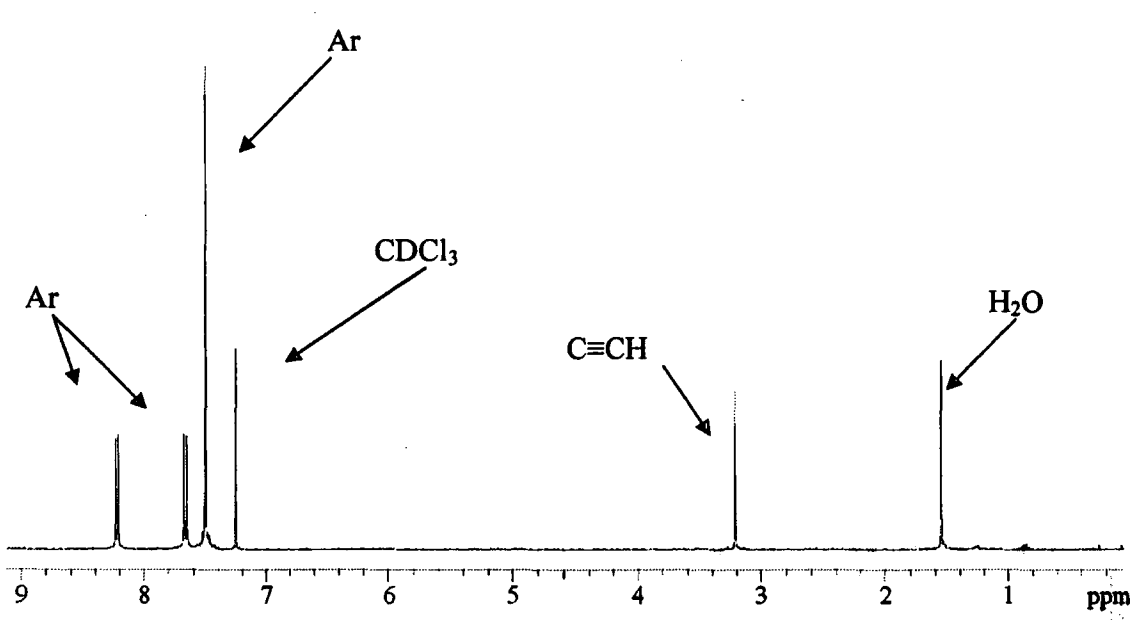


Fig. 2.13: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *p*-NO_2-C_6H_4-C≡C-C_6H_4-C≡C-H

Compounds **5a-e** were investigated by UV-Vis spectroscopy, the absorption and emission spectroscopic data are summrised in Table 2.4. Compounds **5a-e** have absorptions in the near UV (302-338 nm) and emission in the near UV-Vis (333-384 nm) regions.

Table 2.4 Absorption and emission data for deprotected alkynes **5a-e**

Compound	λ_{max} (Abs) nm	ε mol^{-1} cm^{-1} dm^3	λ_{max} (Em) nm	Stokes Shift cm^{-1}
5a	309 328	40,000 37,000	358	4400
5b	302 321	27,000 26,000	336 344	3400
5c	311 331	43,000 41,000	342	2900
5d	311 331	36,000 32,000	343 357	3000
5e	338	31,000	384	3500

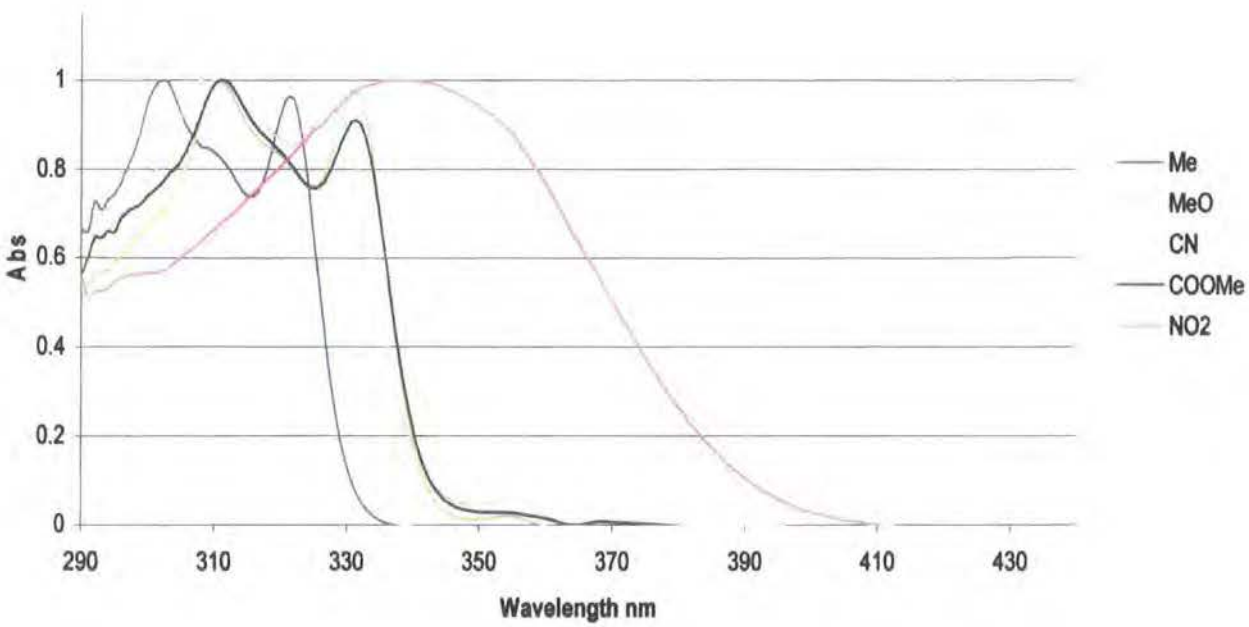


Fig. 2.14: Normalised UV absorption spectra of substituted R-C_6H_4-C≡C-C_6H_4-C≡C-H compounds in $CHCl_3$

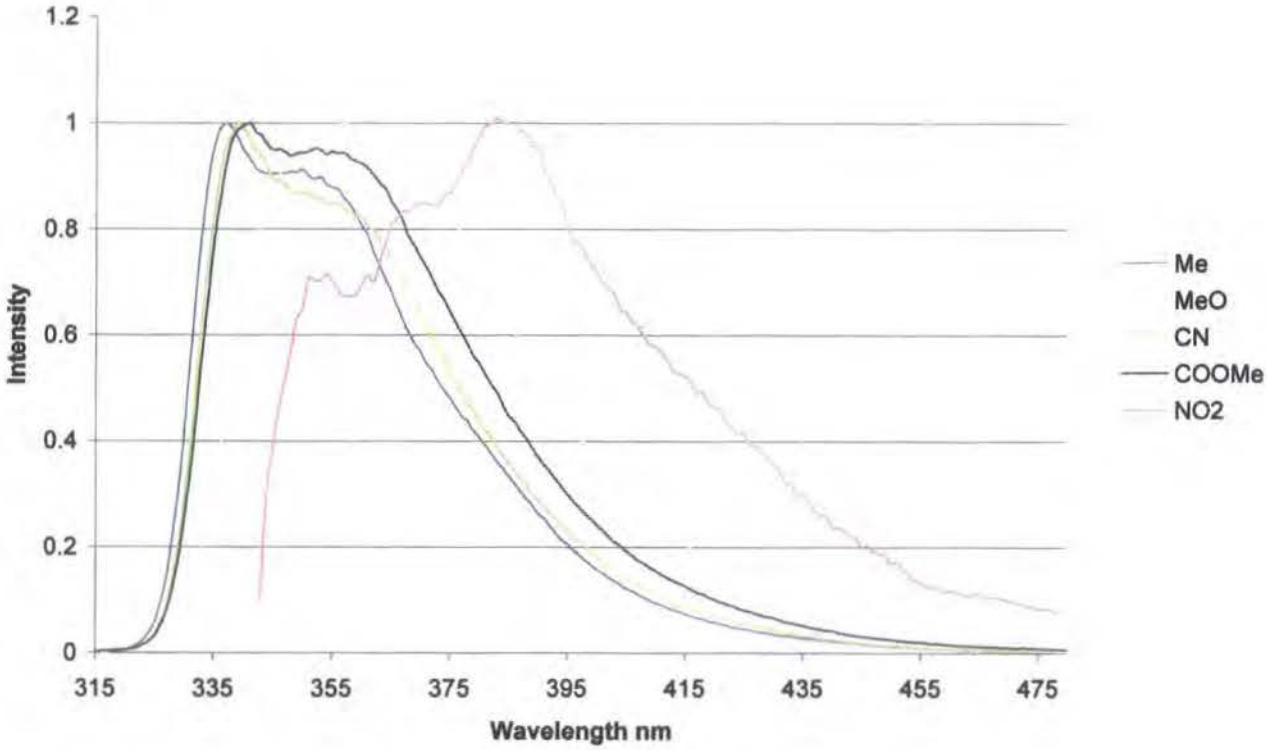


Fig. 2.15: Normalised UV-Vis emission spectra of substituted R-C_6H_4-C≡C-C_6H_4-C≡C-H compounds in $CHCl_3$

2.4 Synthesis of New Diynes

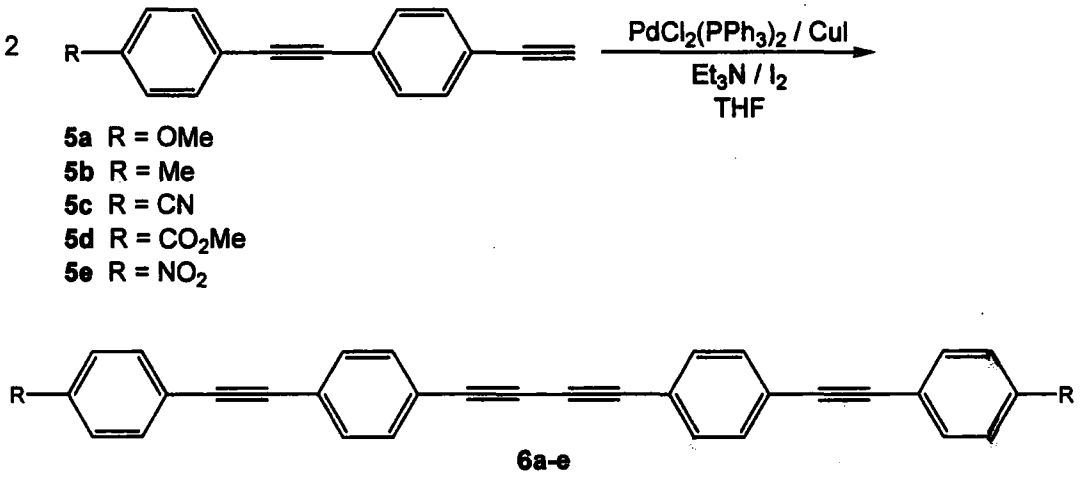
The main aim of this section was the synthesis of new symmetrical, conjugated diynes from the terminal alkynes (**5a-e**). The first issue was to establish the best synthetic method to obtain the diynes in good yields. The method of Li *et al.*[87] was chosen. Thus, 2 mol% $Pd(OAc)_2$, 2 mol% CuI, 3 equiv. of DABCO (1,4-diazabicyclo[2.2.2]-octane) and air have been used for homocoupling the 4-(4-ethynyl-phenylethynyl)-benzonitrile (**5c**) to synthesise the diyne, but only a low yield of the product (11%) was obtained. This diyne

was insoluble which is a problem for obtaining an NMR spectrum. The MALDI mass spectrum for this diyne shows the correct mass of 452.

$PdCl_2(PPh_3)_2$, CuI and I_2 were used to homocouple 4-(4-ethynyl-phenylethynyl) benzoic acid methyl ester (**5d**), in triethylamine, which gave 27% of the corresponding diyne 4,4'-bis-4"-carbomethoxyphenylethynyl)diphenyl-buta-1,3-diyne, **6d**. The compound was soluble enough for NMR spectroscopy and gave the anticipated spectrum, with the MALDI mass spectrum showing the correct mass of *m/z* 518 for the parent ion.

For the homocoupling of 4-(4-ethynyl-phenylethynyl)-nitro benzene (**5e**), DABCO was used, but a low yield was obtained and there was still some unreacted terminal alkyne present. Also, $PdCl_2(PPh_3)_2$, CuI and I_2 were used for homocoupling of **5e**, and the yield was (14%), but again some starting material remained.

To counter the insolubility for the terminal alkynes (**5a, 5b, 5c, 5d** and **5e**) in triethylamine, 10-15 ml of dry THF was added to the reaction to improve the solubility and to allow the reactions to go to completion (Scheme 2.15).



Scheme 2.15: Homocoupling reaction of terminal alkynes

Synthesis of the new diynes (**6a-e**) was achieved by using $PdCl_2(PPh_3)_2$, CuI, 2 equiv. of I_2 and triethylamine in the presence of 10-15 ml of dry THF. The addition of THF proved to be very helpful to obtain these new diynes in improved yields. The purification of these diynes **6a-e** required hot toluene to elute all of the diynes from the silica gel. Diynes **6a-e** were fully characterised by ^1H NMR, Raman, UV-Vis and fluorescence spectroscopies and by elemental analysis. Importantly, all NMR spectroscopic data for these diynes were recorded at high temperature to improve solubility.

For example, compound (**6a**) was prepared using $PdCl_2(PPh_3)_2$ and CuI as catalysts in a ratio of 2 mol% and 5 mol% respectively with respect to the starting material **5a**. The reaction was carried out in Et_3N (15 ml) and dry THF (10 ml) with 2 equivalents of I_2 were added, the mixture was stirred for 24 hours. When GC/MS and TLC showed that complete consumption of **5a** had occurred, the crude mixture was purified by flash column chromatography eluting with hot toluene, affording the desired pure material in 26% yield as a yellow solid. The ^1H NMR spectrum shows a singlet at 3.31 ppm for the six protons of the two Me groups. Two doublets at 6.49 and 6.99 ppm with coupling constants of $^3J_{H\text{-}H} = 9$ Hz are assigned to the eight Ar protons of one type of arene ring, whereas doublets at 7.04 and 7.10 ppm with coupling constants of $^3J_{H\text{-}H} = 8$ Hz represent the eight protons of the other arene group. The ^{13}C NMR spectrum shows peaks at 54.90 ppm for OMe and at 114.09, 130.91, 132.01 and 132.50 ppm for the aromatic carbons. As the compound (like the NO_2 analogue **6e**, vide infra) had very low solubility in any solvent we examined, it was not possible to observe signals for the carbon atoms to which no H's were attached. The mass spectrum showed a peak at 462. The Raman spectrum

displayed a peak at 2205 cm^{-1} for the C≡C-C≡C stretch and three peaks at 1594, 1545, 1530 cm^{-1} for the arene ring vibrational modes.

The diynes **6b, 6c, 6d** and **6e** were prepared under the same conditions as for **6a**, and the yields are presented in Table 2.5.

Table 2.5: Yields for diyne compounds

(R-C_6H_4-C≡C-C_6H_4-C≡C-C≡C-C_6H_4-C≡C-C_6H_4-R)

	R	*Yield%*
-OMe	*(6a)*	*26*
-Me	*(6b)*	*36*
-CN	*(6c)*	*39*
-COOMe	*(6d)*	*36*
-NO_2	*(6e)*	*59*

The electron donating and accepting *para*-substituted diynes **6a-d** formed in low yields, but compound **6e** was isolated in 59% yield.

The Raman spectra for all the of diynes showed C≡C vibrations ranging from 2199 and 2214 cm^{-1} and arene modes between 1588 and 1594 cm^{-1} (Table 2.6).

Table 2.6: Summary of the Raman spectra for diyne compounds

Compound	C≡C cm^{-1}	arene ring cm^{-1}
6a	2205	1594
6b	2199	1588
6c	2202	1593
6d	2214	1594
6e	2201	1588

The ^{1}H NMR spectra for all diynes showed resonances expected for all protons and integrated correctly. Representative examples are shown in Fig 2.16-2.18.

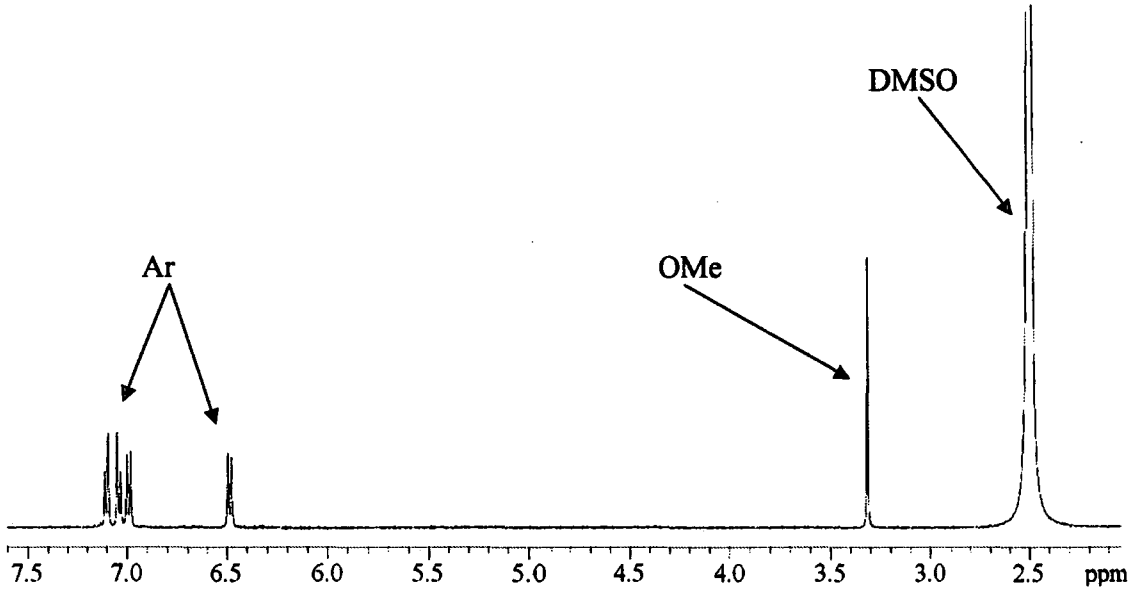


Fig. 2.16: ^{1}H NMR (500 MHz, DMSO) spectrum for *p*-MeO-C_6H_4-C≡C-C_6H_4-C≡C-C≡C-C_6H_4-C≡C-C_6H_4-OMe

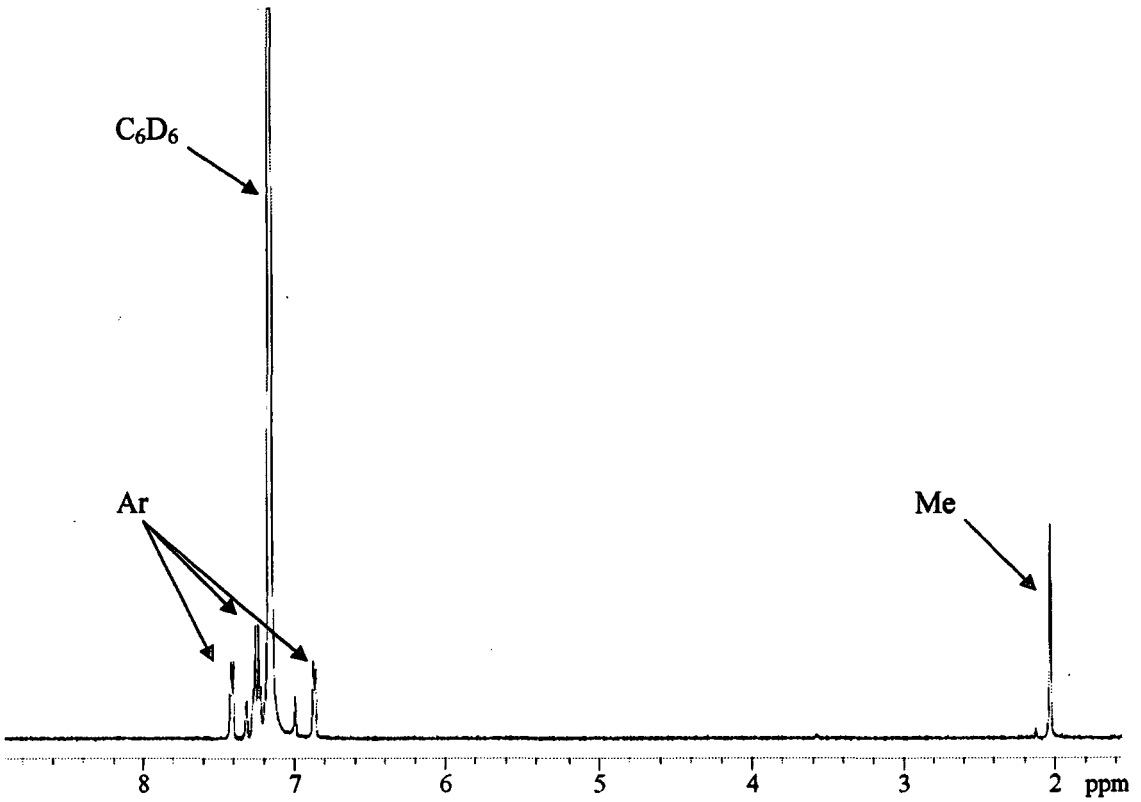


Fig. 2.17: ^{1}H NMR (500 MHz, C_6D_6) spectrum for *p*-Me-C_6H_4-C≡C-C_6H_4-C≡C-C≡C-C_6H_4-C≡C-C_6H_4-Me

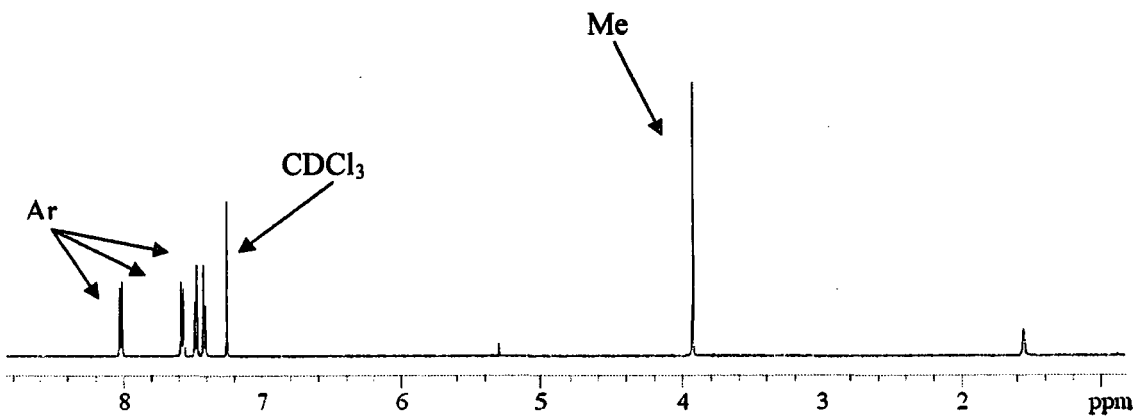


Fig. 2.18: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for *p*-MeO_2C-C_6H_4-C≡C-C_6H_4-C≡C-C≡C-C_6H_4-C≡C-C_6H_4-CO_2Me

All of the symmetric diynes **6a-e** were investigated by UV-Vis spectroscopy, and the absorption and emission spectroscopic data are summarised in Table 2.7. Compounds **6a-e** have absorptions in the near UV (348-370 nm) as shown in Fig. 2.19 and emission maximum in the near UV-Vis (389-397 nm) regions; each compound has a shoulder between 417-426 nm as shown in Fig. 2.20.

Table 2.7: Absorption and emission data for diynes **6a-e**

Compound	λ_{max} (Abs) nm	ε mol^{-1} cm^{-1} dm^3	λ_{max} (Em) nm	Stokes Shift cm^{-1}
6a	356	89,000	397, 424	2900
6b	348	68,000	389, 417	3000
6c	354	85,000	395, 422	2900
6d	353	127,000	393,420	2900
6e	370	70,000	393, 426	1600

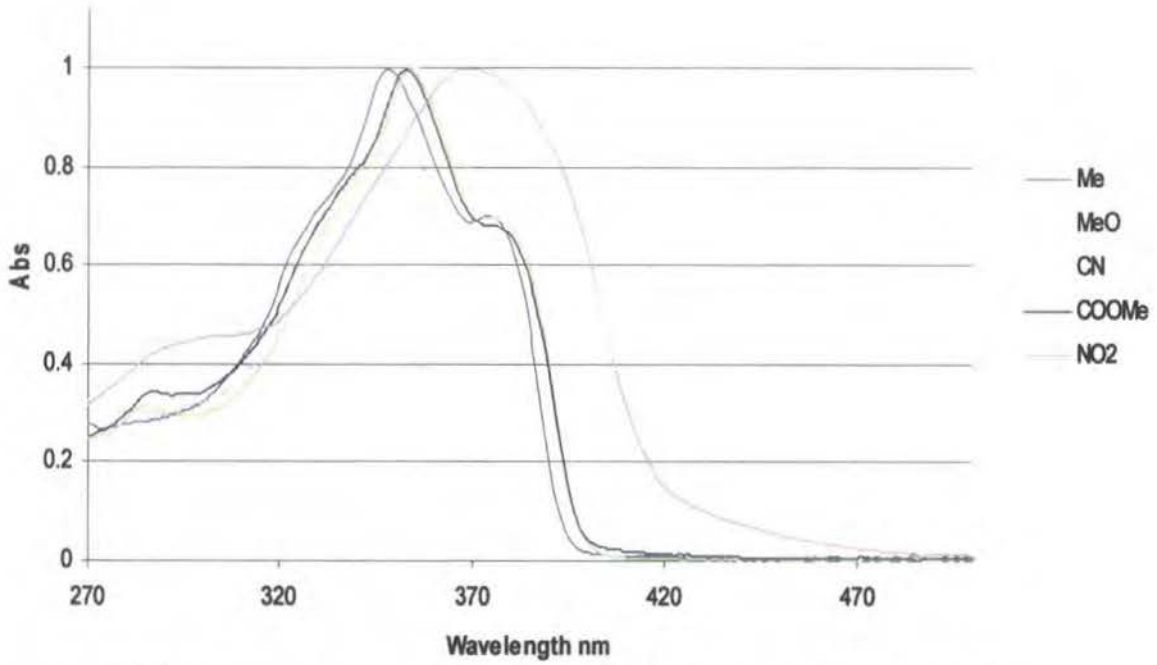


Fig. 2.19: Normalised UV absorption spectra of substituted diynes in $CHCl_3$

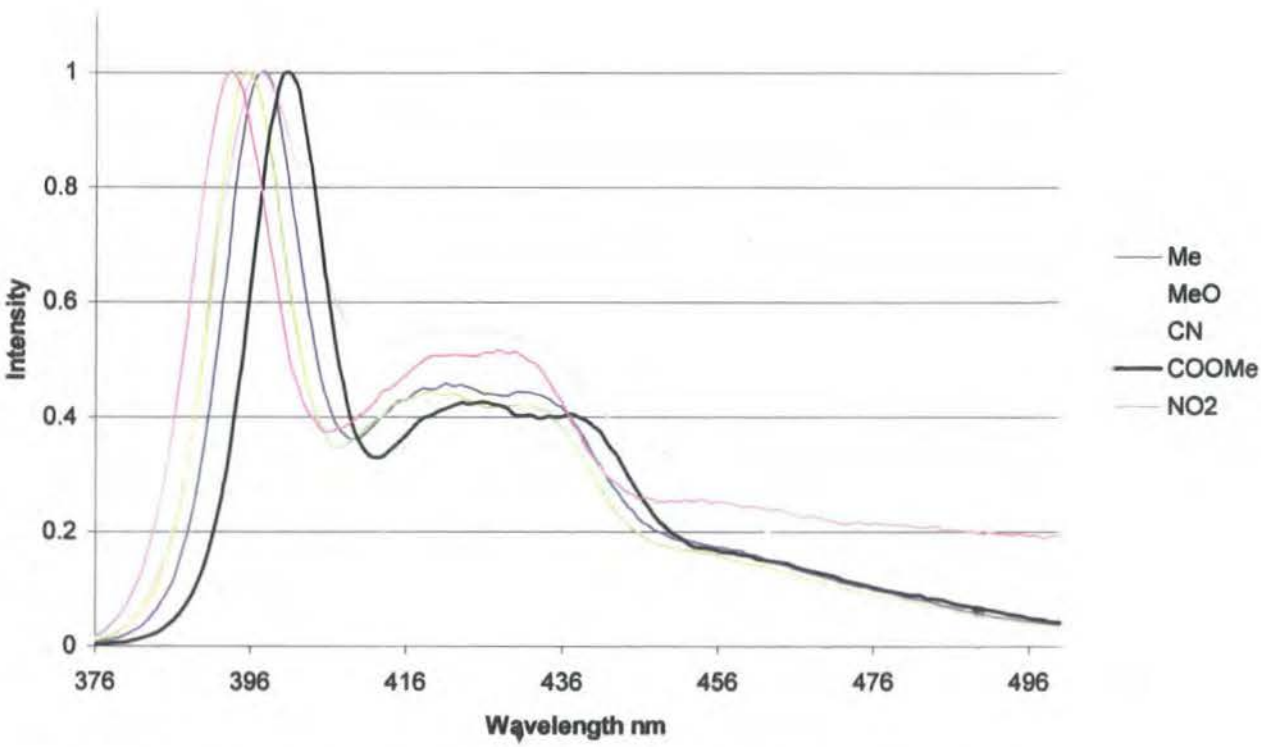


Fig. 2.20: Normalised UV-Vis emission spectra of substituted diynes in $CHCl_3$

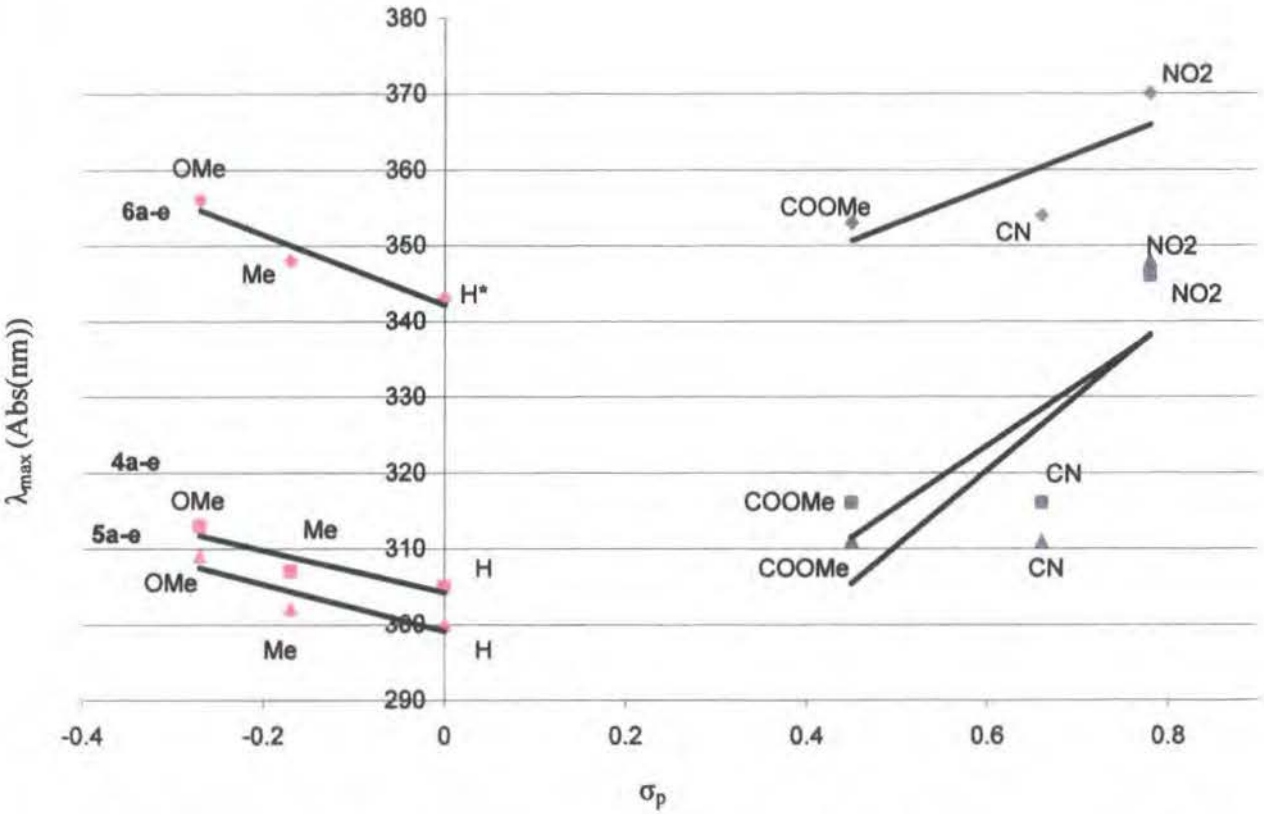


Fig. 2.21: Graph of absorbance maxima of *p*-substituted diynes (diamond), *p*-substituted TMS-protected ethynyl tolans (square) and *p*-ethynyl tolans (triangle) versus Hammett constants σ_p of *p*-substituent.[89,90] Electron-withdrawing substitutents shown in blue and electron-donating substituents shown in red. * The value for λ_{max} of 3 (R=H) was taken from [S. Misumi, Bull. Chem. Soc. Jpn. 1961, 34, 1827] and the spectrum was obtained in EtOH.

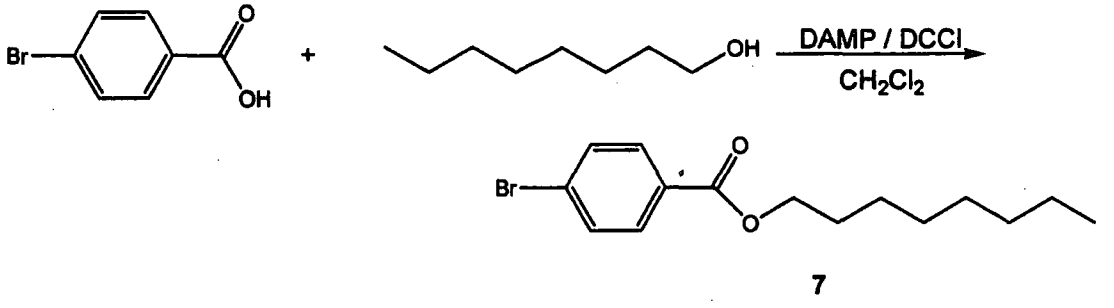
A plot of the absorbance maxima against the Hammett constant[90] for the *para* substitutents (σ_p) (Fig. 2.21) displays the same trend that has been found for the analogous *p*-substituted TMS-protected ethynyl tolans and *p*-ethynyl tolans. The Hammett constants have been shown to provide a measure of the electron accepting or electron donating ability of substitutents on a phenyl ring. A direct correlation has been made between the Hammett constants and the calculated π-conjugation strengths for a number of compounds.[89] It is assumed that these σ_p values represent the extent of electron withdrawl or electron donation through π-conjugation. The graph can be interpreted as showing a red shift of absorbance maxima as the degree of either electron donating or electron withdrawing strength of the substitutents at the *para* position of the phenyl ring increases. A red shift in absorbance provides an insight into the electronic energy levels of the compounds as it signifies that the energy gap between S_0 and the S_1 excited state is reduced by the presence of either stronger electron donating or electron withdrawing *para* substitutents.

We want to make luminescent rhodacyclopentadienes containing acceptor groups, which are processable or at least soluble. As many of my extended, 4-ring diynes were rather insoluble, and the rhodacycles, containing two of these, would be expected to be even less soluble, the next section is concerned with synthesising diynes from esters containing a long aliphatic group to improve solubility.

2.5 Synthesis of Diynes from a Long Chain Esters

This section involved synthesising diynes from esters containing a long chain aliphatic group to improve solubility. Thus, 4-bromobenzoic acid was reacted with octan-1-ol to obtain 4-bromobenzoic acid octyl ester, 7, which has a C_8 chain and a Br group in the

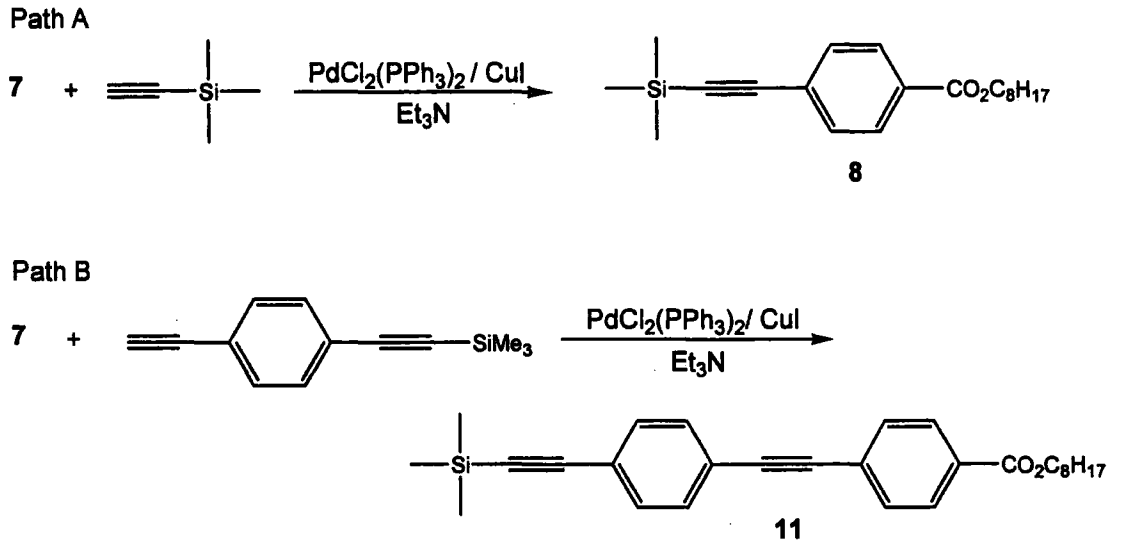
para position for subsequent coupling reactions. The method and conditions were the same as used by Moigne *et al*,[91] but they did not report this derivative (7). The condensation reaction employed dicyclohexylcarbodiimide (DCCI) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) 10 mol% in CH_2Cl_2 (Scheme 2.16).



7

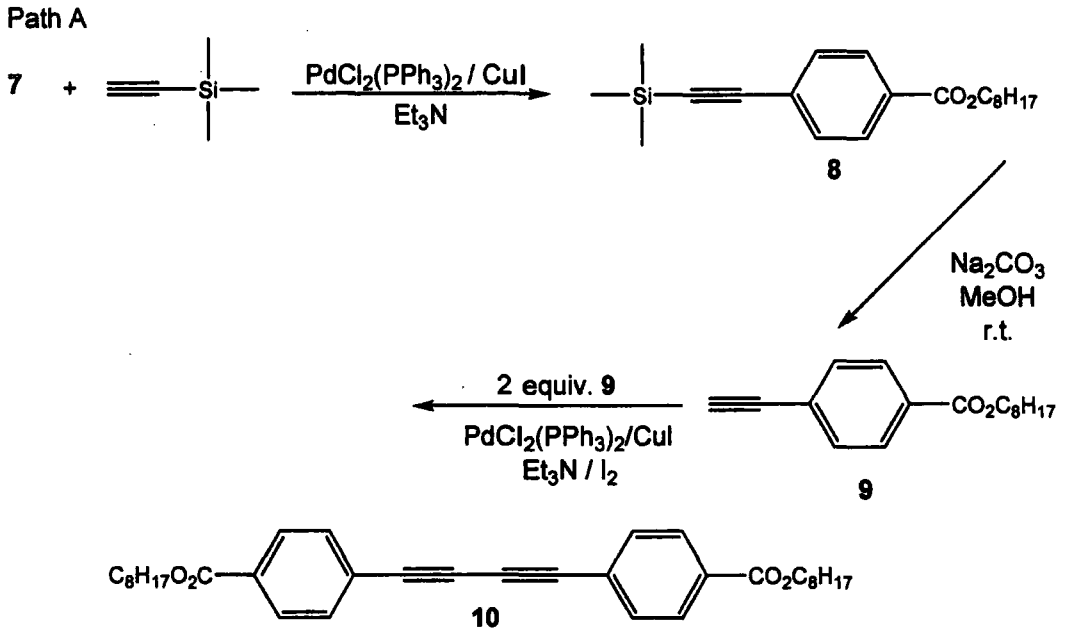
Scheme 2.16: Preparation of 4-bromobenzoic acid octyl ester

The mixture was stirred at room temperature for 24 hours. The dicyclohexyl urea which formed was removed by filtration and the solvent evaporated on rotary evaporator. The crude product was passed through a silica gel column, eluting with hexane. Kugelrohr distillation (120-150 °C, 1.3 x 10^{-4} torr) was used to give the desired product as an analytically pure liquid in 86% yield. Then compound 7 was used in two reaction pathways (Scheme 2.17).



Scheme 2.17: Synthesis of deprotected diynes from esters containing a long aliphatic group

In path A, compound **7** was coupled with TMSA to obtain the protected alkyne, **8** in 63% yield as shown in Scheme 2.18. Then the protecting group TMS was removed under mild conditions (Na_2CO_3 / MeOH / room temperature) to give the terminal alkyne, **9**, in 89% yield, which can then be oxidatively homocoupled to give diyne, **10** (Scheme 2.18). Compound **10** was prepared by using 2 equivalents of **9**. Thus, $PdCl_2(PPh_3)_2$ and CuI were employed as catalysts in a ratio of 2 mol% and 5 mol% with respect to the starting materials. The reaction was carried out in Et_3N (15 ml) with 2 equivalents of I_2 added, the mixture was stirred under N_2 for 24 hours. The yield was 60% and the structure of **I** was confirmed by single-crystal X-ray diffraction (Fig. 2.22).



Scheme 2.18: Preparation of protected alkyne with a TMS group and synthesis of diyne **10**

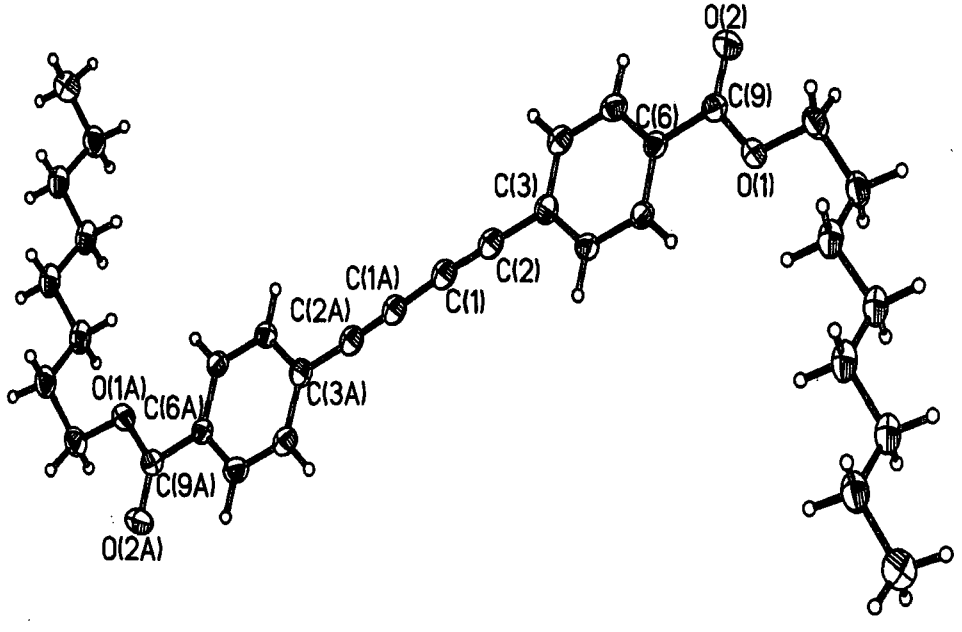


Fig. 2.22: Molecular structure of 4,4'-bis-(carbooctyloxyphenyl)-buta-1,3-diyne (**10**)

Monoclinic single crystals of 4,4'-bis-(carbooctyloxyphenyl)-buta-1,3-diyne (**10**) (space group $P2_1/c$) were obtained by slow evaporation of acetone from a concentrated solution, and these were suitable for X-ray diffraction. The molecule lies on an inversion centre. The triple bond, $C^1 \equiv C^2$ is 1.2062(15) Å in length. The bond length between C^1-C^{1a} is 1.373(2) Å. The two alkyne units are slightly non-linear in the molecule with angles C^2-C^1-C^{1a} and C^1-C^2-C^3 are 179.71(16) and 176.51(11)°, respectively. Carbon-oxygen bond angles for O^1-C^9-O^2, O^2-C^9-C^6, O^1-C^9-C^6 and O^1-C^{10}-C^{11} are 123.52(10), 124.74(10), 111.73(8) and 106.58(8)°, respectively. Torsion angles between C^6-C^9-O^1-C^{10}, C^5-C^6-C^9-O^1 and C^7-C^6-C^9-O^2 are -177.38(8), 6.29(13) and 6.38(16),° respectively.

Compounds **8, 9** and **10** were investigated by UV-Vis spectroscopy and the absorption and emission spectroscopic data are summarised in Table 2.8. Compounds **8, 9** and **10** have absorptions in the near UV (259-351 nm). Compounds **8** and **9** each have a shoulder in their absorption spectra, but compound **10** has several peaks as shown in Fig. 2.23. The emissions were in the near UV-Vis (352-356 nm) regions. No emission was observed for compound **9** (Fig. 2.24).

Table 2.8: Absorption and emission data for compounds **8, 9** and **10**

Compound	λ_{max} (Abs) nm	ε mol^{-1} cm^{-1} dm^3	λ_{max} (Em) nm	Stokes Shift cm^{-1}
8	271	12,000	352	8500
	282	10,000		
9	259	25,000		
	268	20,000		
10	306	37,000	356, 385	2500
	327	49,000		
	351	42,000		

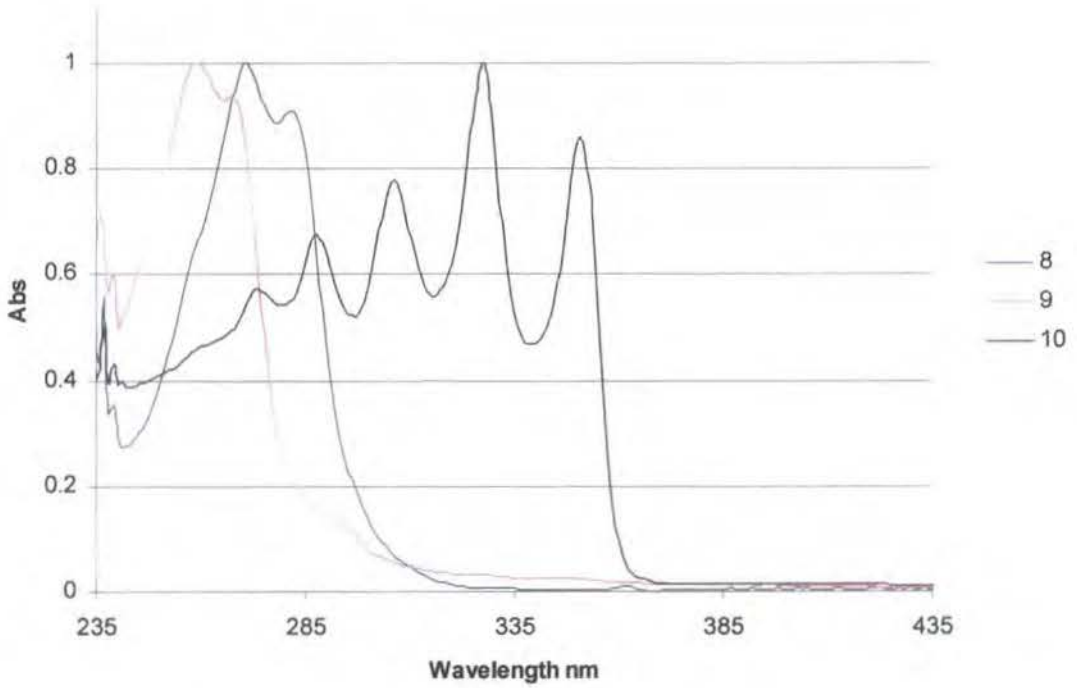


Fig. 2.23: Normalised UV absorption spectra of compounds **8, 9** and **10** in $CHCl_3$

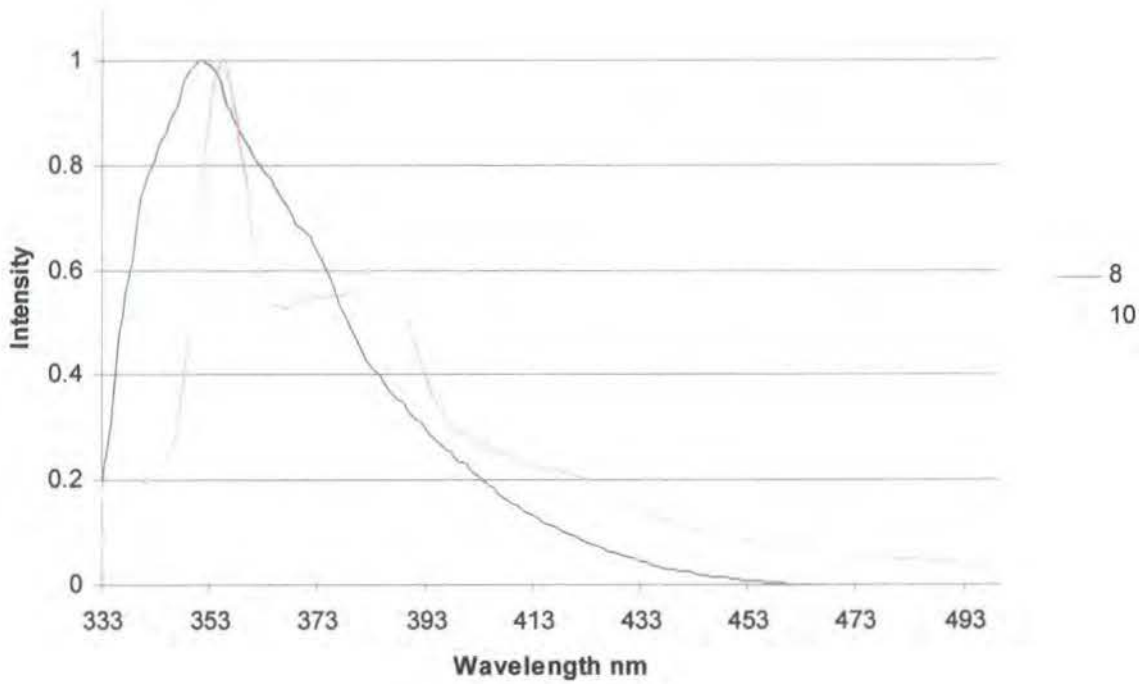
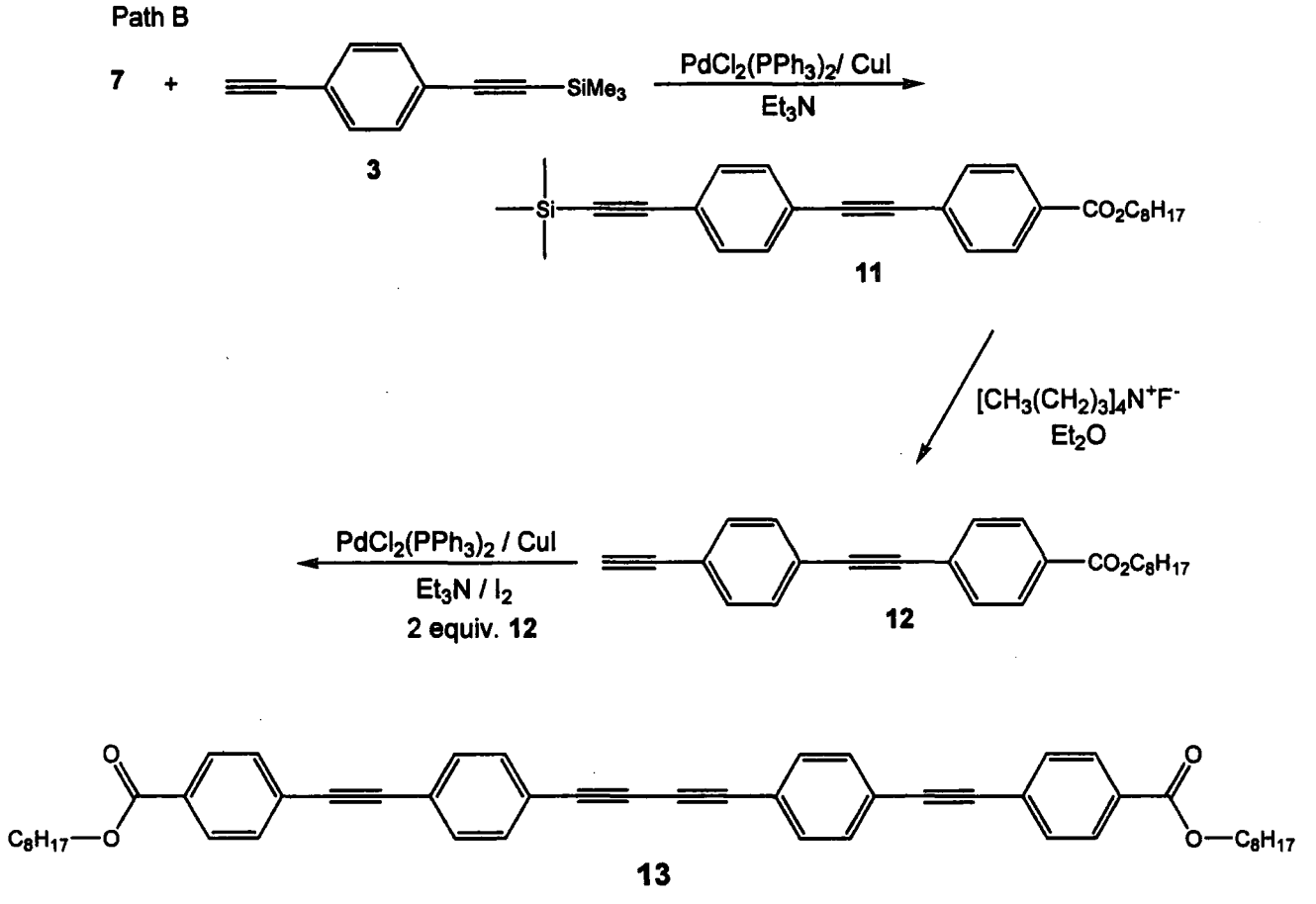


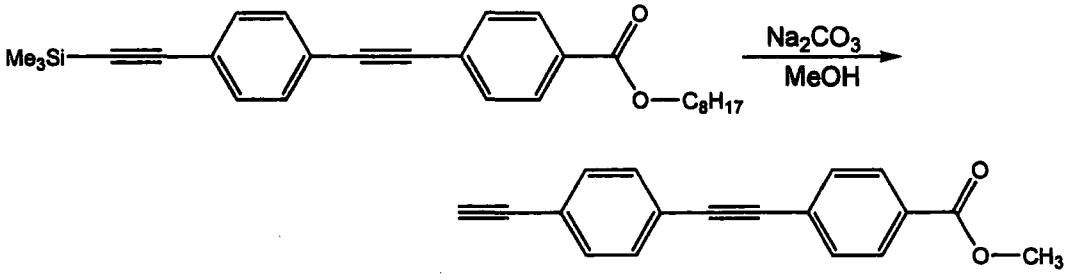
Fig. 2.24: Normalised UV-Vis emission spectra of compounds **8** and **10** in $CHCl_3$

In path B, this time compound **7** was coupled with compound **3** to give 4-(4-trimethylsilanylethynyl-phenylethynyl)-benzoic acid octyl ester, **11**, in the presence of $PdCl_2(PPh_3)$ and CuI in triethylamine Scheme 2.19. The product was formed after 20 hours at 80 °C. The solvent was removed, and then the crude product was passed through a short column of silica eluting with hexane. Recrystallisation from hexane yielded compound **11** in 36% yield as a white solid. The next step was deprotection of compound **11** to form the terminal alkyne 4-(4-ethynyl-phenylethynyl)-benzoic acid octyl ester, **12**, which was achieved in 77% yield as a white solid (Scheme 2.19). Lastly, 2 equivalents of compound **12** can be oxidatively homocoupled to give 4,4'-bis-(4''-carbooctyloxyphenylethynyl)diphenylbuta-1,3-diyne, **13**, in 37% yield (Scheme 2.19).



Scheme 2.19: Preparation of protected alkyne with a TMS group and synthesis of diyne **13**

Interestingly, the deprotection of **11** using Na_2CO_3 in a mixture of MeOH / Et_2O was unsuccessful as the octyloxy group was replaced by OMe to give **5d** (Scheme 2.20). Therefore, $Bu_4N^+F^-$ in Et_2O was used to obtain the terminal alkyne, **12**, which can be oxidatively homocoupled to give diyne, **13**, as shown in Scheme 2.19.



Scheme 2.20: Deprotection reaction for compound **11** by using sodium carbonate which gave compound **5d**

Compounds **11**, **12** and **13** were characterised by ^{1}H NMR, Raman, IR, UV-Vis and fluorescence spectroscopies and by elemental analysis. The ^{1}H NMR spectra for compounds **12** (Fig. 2.25) and **13** (Fig. 2.26) as shown.

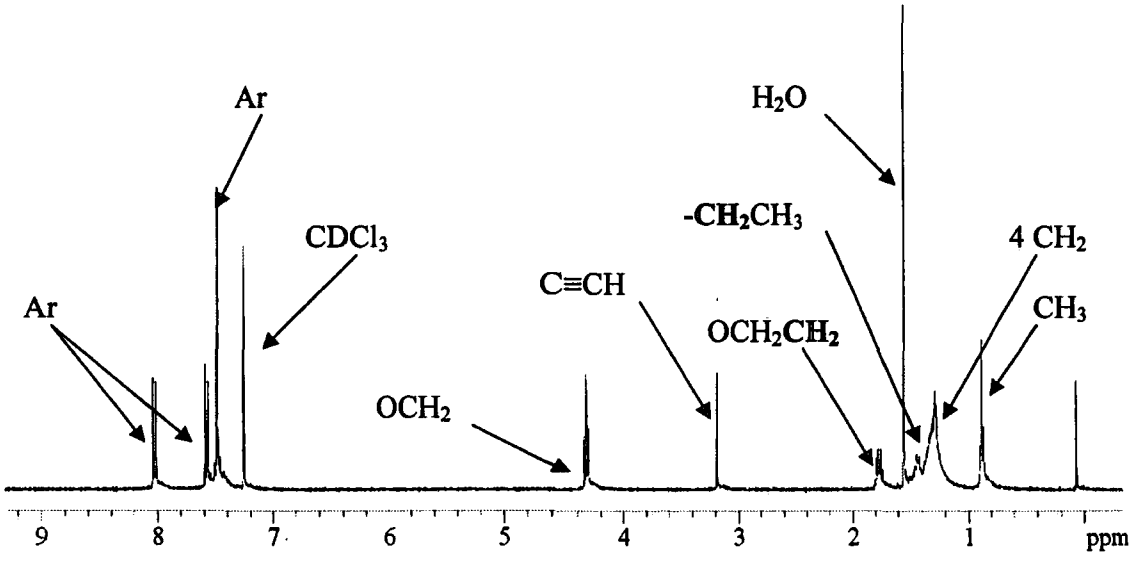


Fig. 2.25: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for $H_{17}C_8OOC\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH$ **(12)**

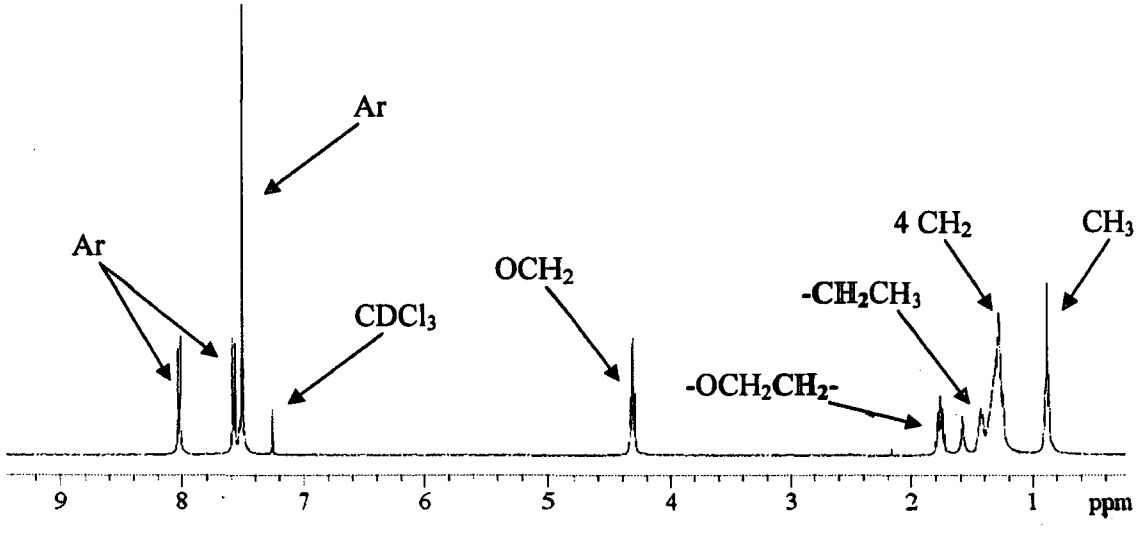


Fig. 2.26: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for $H_{17}C_8OOC\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C_6H_4\text{-}COOC_8H_{17}$ **(13)**

Infrared spectra were recorded for both **11** and **12**. Interestingly, the two spectra are similar, showing C-H, C≡C, C=O and O-C=O bands. The IR spectrum of **12** showed a new band at 3278 cm^{-1}, for the C≡C-H group (Table 2.9).

Table 2.9: Summary of IR spectra for compounds **11** and **12**

Compound	C≡C-H	C-H	C≡C	C=O	O-C=O
11		2954, 2920, 2849	2185	1715	1292
12	3278	2957, 2917, 2848	1921	1711	1281

The Raman spectrum of compound **13**, showing peaks for C≡C at 2207 cm^{-1} and the arene ring at 1596 cm^{-1} is illustrated in Fig. 2.27.

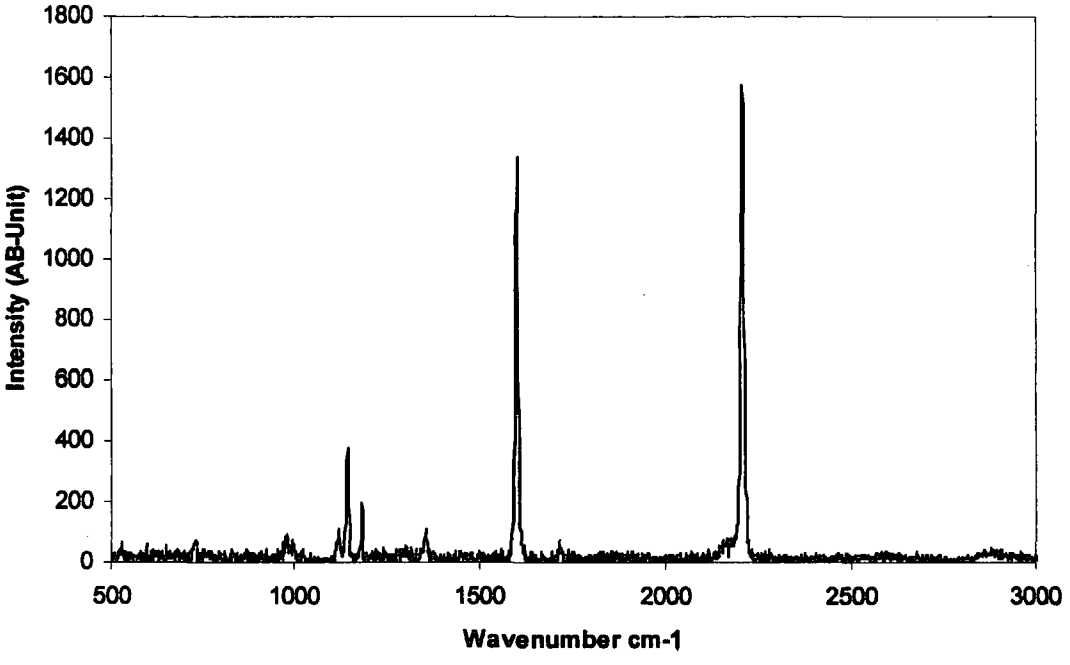


Fig. 2.27: Raman spectrum of compound **13**

Compounds **11, 12** and **13** were investigated by UV-Vis spectroscopy and the absorption and emission spectroscopic data are summarised in Table 2.10. Compounds **11, 12** and **13** have absorptions in the near UV (311-353 nm) and emissions in the near UV-Vis (341-420 nm) regions.

Table 2.10: Absorption and emission data for compounds **11, 12** and **13**

Compound	λ_{max} (Abs) nm	ε mol^{-1} cm^{-1} dm^{3}	λ_{max} (Em) nm	Stokes Shift cm^{-1}
11	317 338	53,000 46,000	349, 365	2900
12	311 331	43,000 38,000	341, 354	2800
13	353	104,000	393, 420	2900

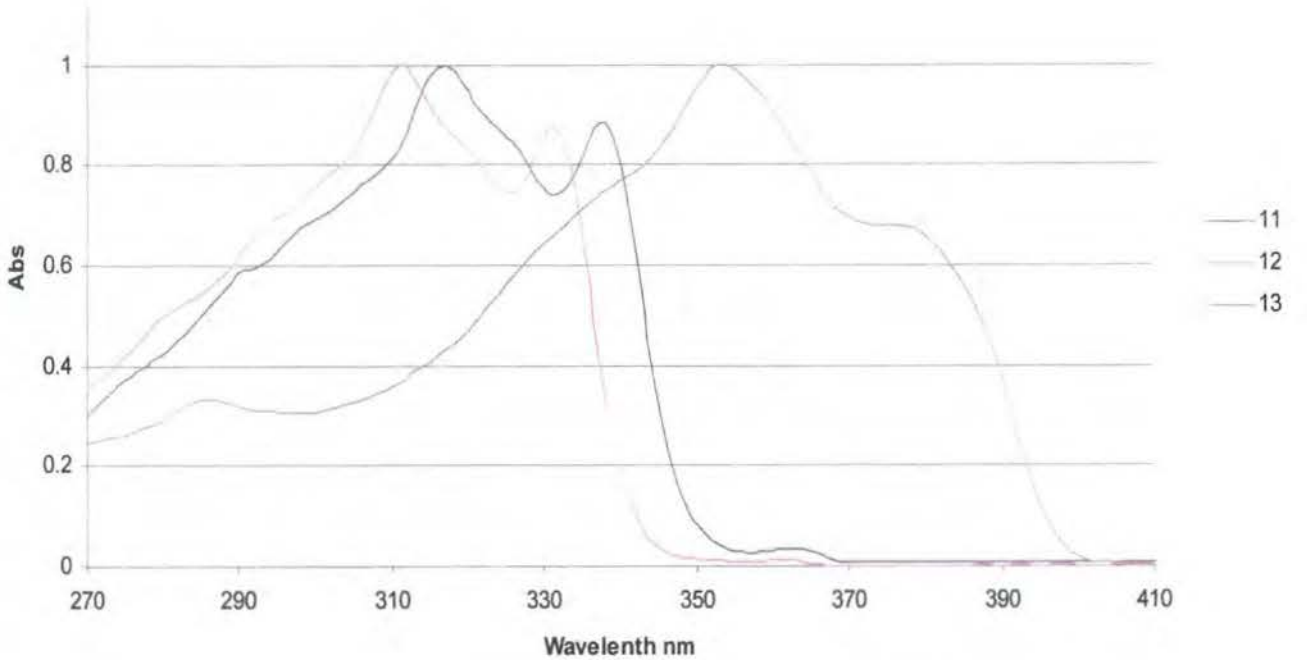


Fig. 2.28: Normalised UV absorption spectra of compounds **11**, **12** and **13** in $CHCl_3$

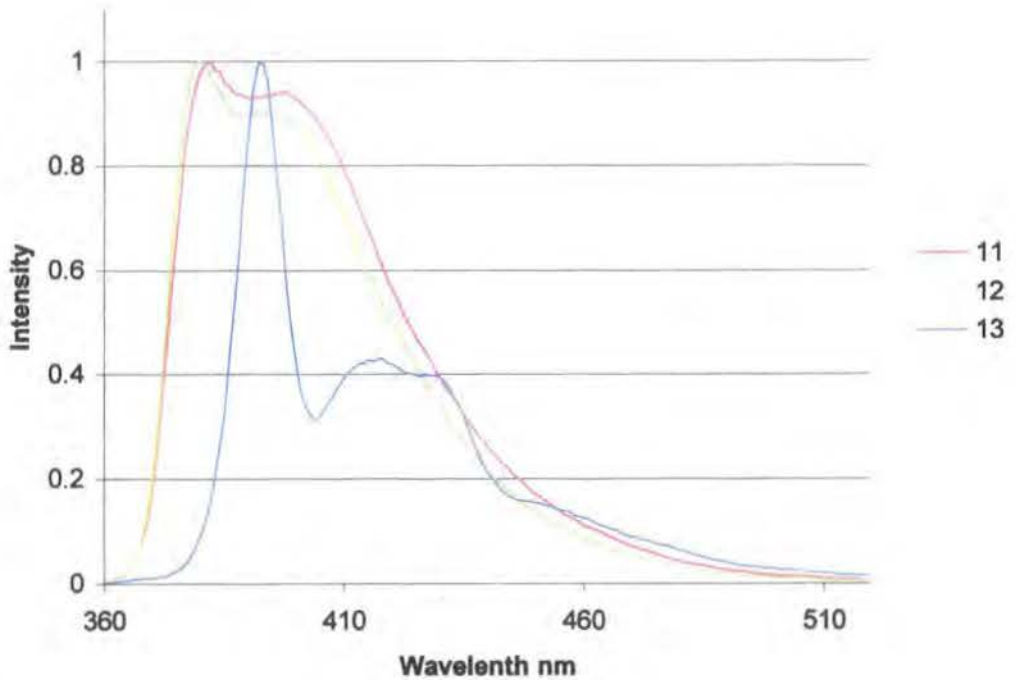


Fig. 2.29: Normalised UV-Vis emission spectra of compounds **11**, **12** and **13** in $CHCl_3$

2.6 Conclusion

Several TMS-protected ethynyl tolans (**4a-e**), *p*-substituted ethynyl-tolans (**5a-e**) and *p*-substituted diynes (**6a-e**) have been synthesised and fully characterised.

The *p*-substituted trimethylsilanylethynyl-phenylethynyl-benzenes (**4a-e**) have been satisfactorily synthesised by means of the Sonogashira cross-coupling reaction between the 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**) and 1-iodo- or 1-bromo-substituted benzenes and their fluorescence properties analysed. The *p*-substituted ethynyl-tolans (**5a-e**) have been efficiently synthesised by deprotection of the TMS group using sodium carbonate. Symmetric conjugated 4,4'-bis-(4''-substitued-phenylethynyl)-diphenyl-buta-

1,3-diynes (**6a-e**) have been synthesised by homo-coupling of *p*-substituted ethynyl-tolans (**5a-e**).

Also, the ester Br-C_6H_4-$COOC_8H_{17}$ has been prepared in good yield. This compound can be used as a starting material to react with TMSA or 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**) to synthesise protected terminal alkynes (**8**) and (**11**). Deprotection has been accomplished affording compounds (**9**) and (**12**) which we used to synthesise the new diynes (**10**) and (**13**).

Finally, the series of 4,4'-bis-(4''-R-phenylethynyl)diphenyl-buta-1,3-diynes (**6a-e**), which were the target of this work, has been prepared successfully. Also, 4,4'-bis-(crbooctyloxyphenyl)-buta-1,3-diyne (**10**) and 4,4'-bis-(crbooctyloxyphenylethynyl)-diphenyl-buta-1,3-diyne (**13**), from the corresponding ester which has a C_8 chain in the *para* position, have been prepared. The diynes (**6a-e**), **10** and **13** were characterised by ^1H NMR, EI/CI MS, Raman, UV-Vis and fluorescence spectroscopies and by elemental analysis. The diynes will be used by other members of the marder group, to prepare a series of new rhodacyclopentadienes which of interest due to linear and nonlinear optical properties.

Chapter 3

Experimental

3. 1 General Expermental

All Sonogashira reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried before use with appropriate drying agents and distilled under nitrogen. The organic reagents used in synthesis were purchased from commercial suppliers and tested for purity by GC/MS before use.

GC-MS analyses were performed on a Hewlett-Packard 5890 Series II chromatograph equipped with a 5971A mass selective detector or on an Agilent 6890 Plus GC equipped with a 5973N MSD and an Anatune Focus robotic liquid handling system / autosampler, and a 10 m fused silica capillary column (5% cross linked phenylmethylsilicone), under the following operating conditions: injector temperature 250 °C, detector temperature 300 °C, the oven temperature was ramped from 50 °C to 280 °C at 20 °C/ min. UHP helium was used as the carrier gas.

NMR spectra were recorded at ambient temperature on Varian Inova 500 (^{1}H, $^{13}C\{^{1}H\}$), Varian C500 (^{1}H, $^{13}C\{^{1}H\}$), and Bruker Avance 400 (^{1}H, $^{13}C\{^{1}H\}$) instruments. Proton and carbon spectra were referenced to external $SiMe_4$ *via* residual protons in the deuterated solvents or solvent resonance, respectively.

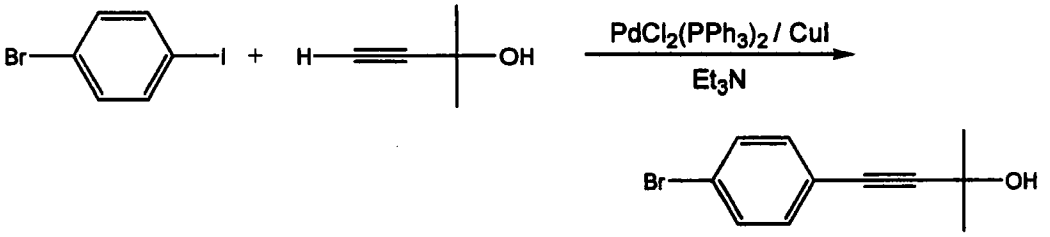
UV/Vis spectra and extinction coefficients were recorded on a Hewlett-Packard 8453 diode array spectrophotometer using standard 1 cm width quartz cells. Fluorescence spectra and quantum yield measurements were recorded on a Horiba Jobin-Yvon Fluoromax-3 spectrophotometer.

Raman spectra were recorded on solid samples using a Horiba Jobin-Yvon LabRamHR Raman microscope with the laser set at 685 nm. IR spectra were recorded as KBr disks using a Perkin Elmer Spectrum 1600 series FT-IR spectrometer.

Elemental analyses were performed using an Exeter Analytical CE-440 analyzer by Mrs. J. Dostal at Durham University. Melting points were obtained using Laboratory Devices Mel-Temp II or Gallekramp melting point apparatus with a thermometer and are uncorrected.

3. 2 Syntheses

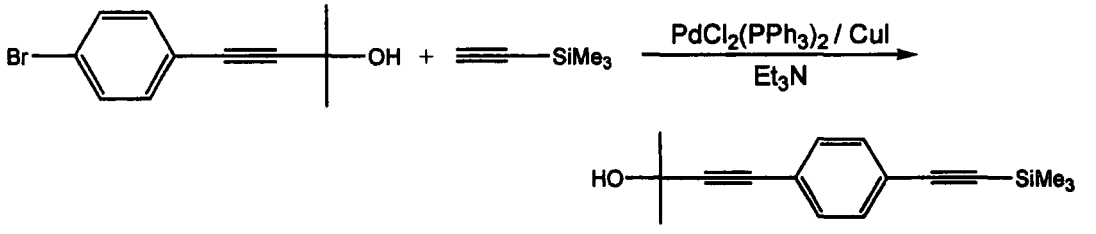
3.2.1 Synthesis of 4-(4-bromophenyl)-2-methyl-but-3-yn-2-ol (**1**)



A 1 L Schlenk flask was charged with 1-bromo-4-iodobenzene (28.2 g, 100 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 1 mmol) and CuI (0.19 g, 1 mmol) and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 500 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was stirred under nitrogen for 16 h. The solvent was removed *in vacuo* and the residue was extracted into hexane and passed through a silica pad, eluting with hexane and CH_2Cl_2, to remove the catalyst residues. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane (yield 19 g, 80%), m. p. 54-56 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 6H; **Me_2**), 1.97 (s br, 1H; **OH**), 7.27 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 7.43 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 31.44 (**Me**), 65.68 (HO-**C**(Me)$_2$), 81.22, 84.92 (**C≡C**), 121.84, 122.61, 131.48, 133.02 (**Ar**). MS (EI) m/z: 240 [M^+], 225 [M-Me^+]. Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64; found: C, 55.10; H, 4.62. IR (KBr) υ_{OH} = 3280, υ_{CH} = 2981, 2928; $\upsilon_{C\equiv C}$ = 1906 cm^{-1}.

3.2.2 Synthesis of 2-methyl-4-(4-trimethylsilanylethynylphenyl)-but-3-yn-2-ol (**2**)

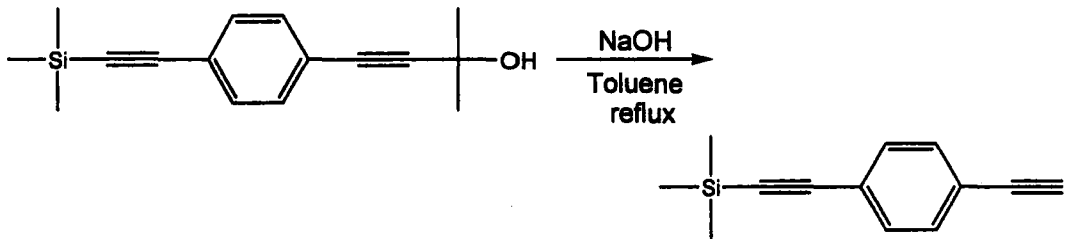


A 500 ml Schlenk flask was charged with 4-(4-bromophenyl)-2-methyl-but-3-yn-2-ol (24.9 g, 100 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 1 mmol) and CuI (0.19 g, 1 mmol) and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 500 ml) was transferred to the reaction flask *via* cannula under nitrogen. TMSA (9.99 g, 102 mmol) was added via pipette under nitrogen. The reaction mixture was heated to reflux for 24 h. The solvent was removed *in vacuo*, and the residue was extracted into 1 L of hexane and passed through a silica pad to remove salts and catalyst residues, eluting with hexane and CH_2Cl_2. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 23.8 g, 93%), m. p. 108-110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 9H; **Me_3**), 1.61 (s, 6H; **Me_2**), 1.94 (s br, 1H; **OH**), 7.33 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.39 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$): δ -0.12 (**Me_3**), 31.42 (**Me_2**), 65.61 (**C-OH**), 81.80, 95.62, 96.07, 104.52 (**C≡C**), 122.78, 122.94, 131.42, 131.79 (**Ar**). MS (EI) m/z: 256 [M^+], 241 [M-Me^+]. Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86; found: C, 74.83; H, 7.95. IR (KBr) υ_{CH} = 3292; $\upsilon_{C\equiv C}$ = 2156 (s), 1919 (w) cm^{-1}.

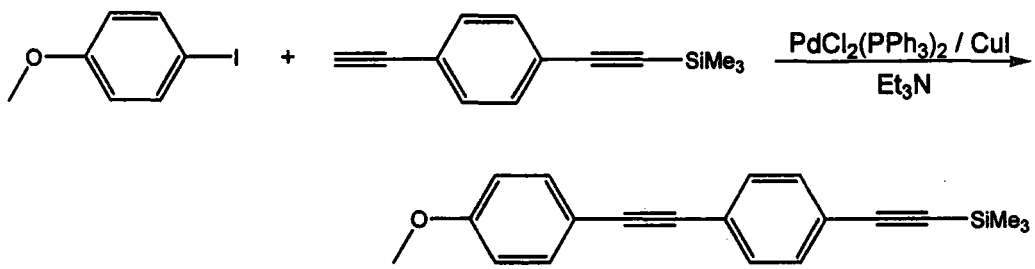
3.2.3 Synthesis of 1-(trimethylsilylethynyl)-4-ethynyl benzene (**3**)



A 500 ml Schlenk flask was charged with ca. 400 ml of toluene, 2-methyl-4-(4-trimethylsilanylethynylphenyl)-but-3-yn-2-ol (20.48 g, 80 mmol) and powdered NaOH (0.32 g, 0.8 mmol) was added. The reaction mixture was heated to reflux for 4 h and then filtered to remove NaOH. The filtrate was evaporated to dryness on a rotary evaporator. The oily residue was eluted through a silica pad with hexane to give a yellow oil, which solidified over time to a white solid (yield 12 g, 76%), m. p. 40-42 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 9H; **Me_3**), 3.16 (s, 1H; **H-C≡C**), 7.41 (s, 4H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -0.16 (**Me_3**), 78.92, 83.26, 96.38, 104.35 (**C≡C**), 122.11, 123.62, 131.80, 131.90 (**Ar**). MS (EI) m/z: 198 [M^+], 183 [M-Me^+]. Anal. Calcd for $C_{13}H_{14}Si$: C, 78.72; H, 7.11; found: C, 78.54; H, 7.10. IR (KBr) $\upsilon_{\equiv C\text{-}H}$ = 3261; $\upsilon_{C\equiv C}$ = 2156; υ_{Ar} = 1496, 1296, 1249; υ_{TMS} = 832 cm^{-1}.

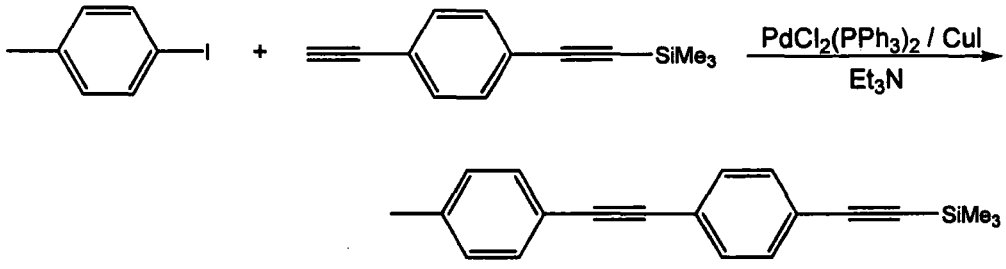
3.2.4 Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-methoxybenzene (**4a**)



A 500 ml Schlenk flask was charged with 1-iodo-4-methoxybenzene (2.34 g, 10 mmol), **3** (2.178 g, 11 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 0.1 mmol) and CuI (I) (0.19 g, 0.1 mmol), and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 250 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 2 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane and CH_2Cl_2. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 1.90 g, 63%), m. p. 120-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me$_3$**), 3.83 (s, 3H; **Me**-O), 6.88 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 7.43 (s, 4H; **Ar**), 7.46 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -0.13 (**Me$_3$**), 55.31 (**Me**-O), 85.66, 91.40, 96.01, 104.76 (**C≡C**), 114.04, 115.09, 122.49, 123.70, 131.20, 131.80, 133.08, 159.81 (**Ar**). MS (EI) m/z: 304 [M^+], 289 [M-Me^+]. Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62; found: C, 78.56; H, 6.67. IR (KBr) υ_{CH} = 2995, 2955, 2898; $\upsilon_{C\equiv C}$ = 2215, 2156; υ_{TMS} = 868, 839 cm^{-1}.

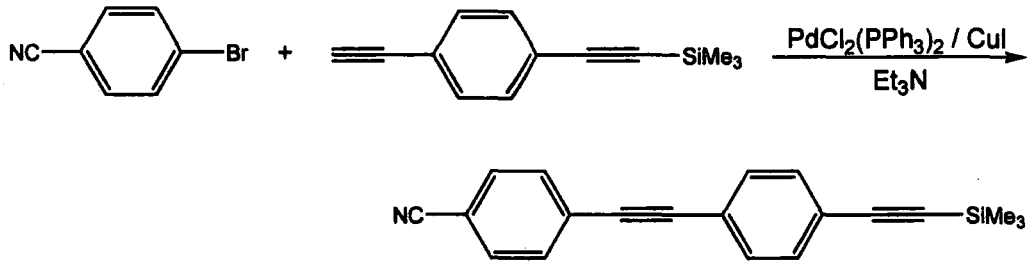
3.2.5 Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-methylbenzene (**4b**)



A 500 ml Schlenk flask was charged with 1-iodo-4-methylbenzene (2.17 g, 10 mmol), **3** (2.178 g, 11 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 0.1 mmol) and CuI (0.19 g, 0.1 mmol) and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 250 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 2 h. The solvent was removed *in vacuo* and the residue was passed through a silica pad eluting with hexane and CH_2Cl_2. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 1.85 g, 64%), m. p. 118-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me$_3$**), 2.37 (s, 3H; **Me**), 7.16 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.41 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.43 (m, 4H; Ar). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -0.12 (**Me$_3$**), 21.50 (**Me**), 86.41, 91.55, 96.10, 104.70 (**C≡C**), 119.93, 122.05, 122.72, 129.11, 131.34, 131.52, 131.83, 138.65 (**Ar**). MS (EI) m/z: 288 [M^+], 273 [M-Me^+]. Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99; found: C, 83.50; H, 6.70. IR (KBr) υ_{Me} = 2956; $\upsilon_{C\equiv C}$ = 2152; υ_{Ar}= 1513, 1406, 1249; υ_{TMS} = 832 cm^{-1}.

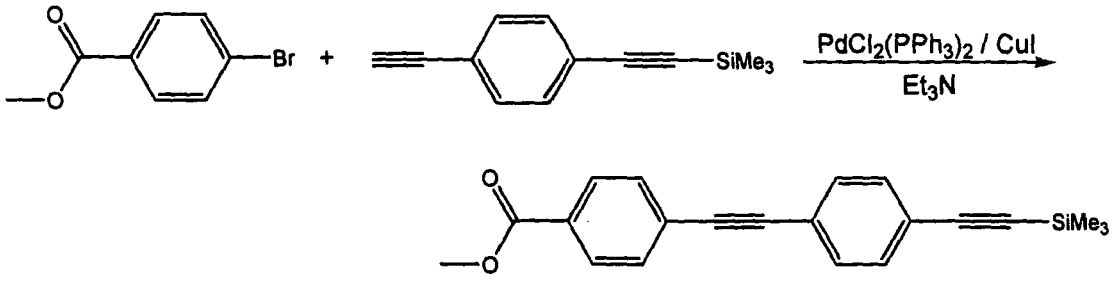
3.2.6 Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-benzonitrile (**4c**)



A 500 ml Schlenk flask was charged with 4-bromobenzonitrile (1.81 g, 10 mmol), **3** (2.178 g, 11 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 0.1 mmol) and CuI (0.19 g, 0.1 mmol), and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 250 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 3 h. The solvent was removed *in vacuo* and the residue was passed through a silica pad eluting with hexane and CH_2Cl_2. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 2.25 g, 75%), m. p. 124-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me$_3$**), 7.47 (s, 4H; Ar), 7.59 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.64 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -0.15 (**Me$_3$**), 89.42, 93.29, 96.99, 97.34 (**C≡C**), 104.31, 111.70 (**Ar**), 118.42 (CN), 123.90, 127.93, 131.55, 131.98, 132.05, 132.24 (**Ar**). MS (EI) m/z: 299 [M^+], 284 [M-Me^+]. Anal. Calcd for $C_{20}H_{17}NSi$: C, 80.22; H, 5.72; N, 4.68; found: C, 79.90; H, 5.63; N, 4.23. IR (KBr) $\upsilon_{C\equiv N}$ = 2228; $\upsilon_{C\equiv C}$ = 2151; υ_{Ar} = 1601, 1507, 1407; υ_{TMS} = 832 cm^{-1}.

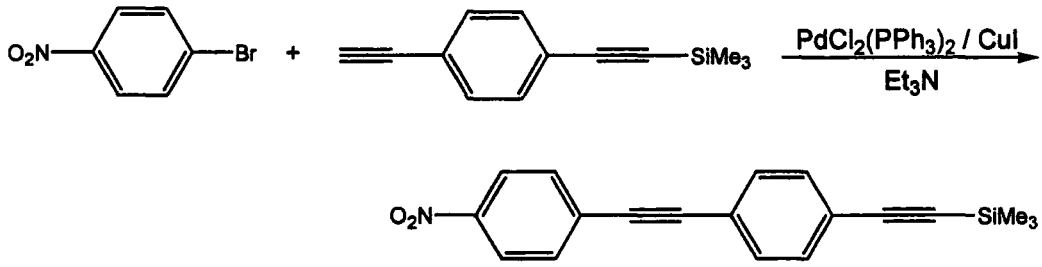
3.2.7 Synthesis of 4-(4-trimethylsilanylethynyl-phyenylethynyl)-benzoic acid methyl ester (**4d**)



A 500 ml Schlenk flask was charged with 4-bromobenzoic acid methyl ester (2.139 g, 10 mmol), **3** (2.178 g, 11 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 0.1 mmol) and CuI (0.19 g, 0.1 mmol) and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 250 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 20 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting cold toluene and next with hot toluene. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane / CH_2Cl_2 (yield 1.6 g, 49%), m. p. 135-137 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me_3**), 3.93 (s, 3H; **Me**), 7.46 (s, 4H; Ar), 7.58 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 8.02 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ -0.13 (**Me_3**), 52.25 (**Me-O**), 90.45, 91.84, 96.67, 104.52 (**C≡C**), 122.69, 123.79, 127.70, 129.52, 129.71, 131.48 (2C), 131.95 (**Ar**), 166.47 (O=C-O). MS (EI) m/z: 332 [M^+], 317 [M-Me^+]. Anal. Calcd for $C_{21}H_{20}O_2Si$: C, 75.86; H, 6.05; found: C, 75.85; H 5.95. IR (KBr) υ_{CH} = 2955; $\upsilon_{C\equiv C}$ = 2153; $\upsilon_{C=O}$ = 1711; υ_{TMS} = 833 cm^{-1}.

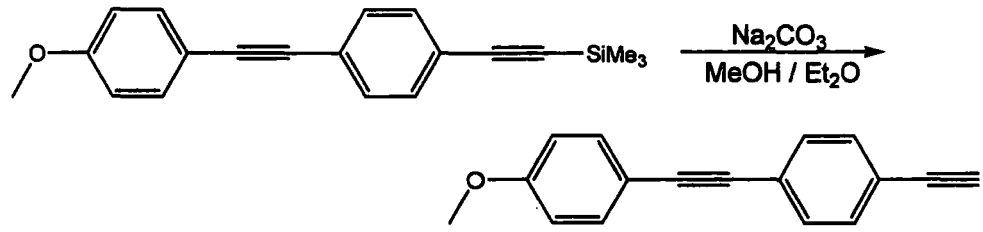
3.2.8 Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-nitrobenzene (**4e**)



A 500 ml Schlenk flask was charged with 1-bromo-4-nitrobenzene (2 g, 10 mmol), **3** (2.178 g, 11 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 0.1 mmol) and CuI (0.19 g, 0.1 mmol), and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 250 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 5 h. The solvent was removed *in vacuo* and the residue was passed through a silica pad eluting with hexane and CH_2Cl_2. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane / CH_2Cl_2 (yield 2.5 g, 79%), m. p. 148-150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me$_3$**), 7.48 (s, 4H; **Ar**), 7.66 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 8.23 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -0.16 (**Me$_3$**), 89.21, 94.17, 97.09, 104.26 (**C≡C**), 129.72, 129.92, 131.61, 131.92, 132.02, 132.25, 132.32, 147.12 (**Ar**). MS (EI) m/z: 319 [M^+], 304 [$M\text{-}Me^+$]. Anal. Calcd for $C_{19}H_{17}NO_2Si$: C, 71.44; H 5.36; N, 4.38; found: C, 70.98; H 5.39; N, 4.33. IR (KBr) $\upsilon_{C\equiv C}$ = 2208, 2151; υ_{Ar} = 1535, 1500; υ_{NO} = 1349; υ_{TMS} = 844 cm^{-1}.

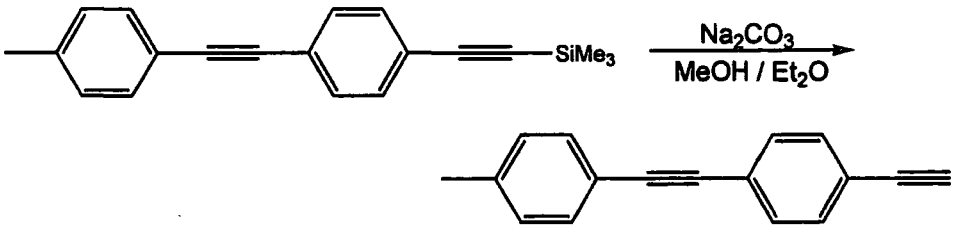
3.2.9 Synthesis of 4-(4-ethynyl-phenylethynyl)-methoxybenzene (**5a**)



A 250 ml Schlenk flask was charged with **4a** (0.76 g, 2.5 mmol), Na_2CO_3 (1.05 g, 1 mmol), MeOH (ca. 50 ml), Et_2O (ca. 50 ml) and H_2O (ca. 5 ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate, The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hot hexane (yield 0.37 g, 65%), m. p. 158-160 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 3.16 (s, 1H), 3.83 (s, 3H; **OMe**), 6.81 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 7.38 (s, 4H; **Ar**), 7.40 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.67 (**OMe**), 78.88, 82.24, 87.84, 91.77 (**C≡C**), 114.42, 115.32, 121.84, 124.60, 131.57, 132.34, 133.50, 160.04 (**Ar**). MS (EI): m/z (rel. int.): 232 [M^+], 217[M-Me^+]. Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21; found: C, 87.74; H, 5.05. IR (KBr) υ_{C-H} = 3277, 3251; $\upsilon_{C\equiv C}$ = 2214 cm^{-1}.

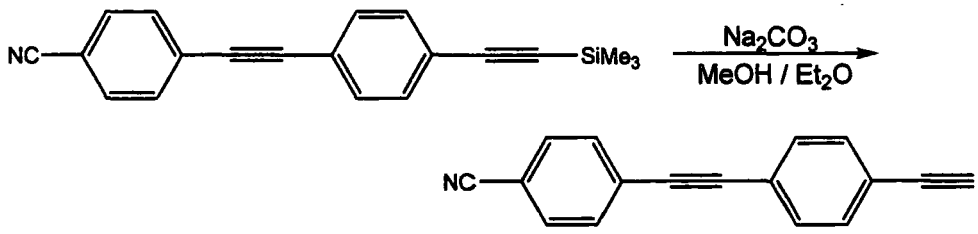
3.2.10 Synthesis of 4-(4-ethynyl-phenylethynyl)-methylbenzene (**5b**)



A 250 ml Schlenk flask was charged **4b** (1.44 g, 5 mmol), Na_2CO_3 (2.12 g, 20 mmol), MeOH (ca. 50 ml), Et_2O (ca. 50 ml) and H_2O (ca. 5 ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate. The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.79 g, 73%), m. p. 130-132 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H; **Me**), 3.16 (s, 1H, **≡CH**), 7.15 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.17 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.46 (s, 4H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.51 (**Me**), 78.73, 83.34, 88.22, 91.62 (**C≡C**), 119.88, 121.66, 124.03, 129.16, 131.41, 131.51, 132.05, 132.35 (**Ar**). MS (EI) m/z: 216 [M^+], 201 [M-Me^+]. Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59; found: C, 93.98; H, 5.57. IR (KBr) υ_{C-H} = 3278; $\upsilon_{C\equiv C}$ = 2212, 2200 cm^{-1}.

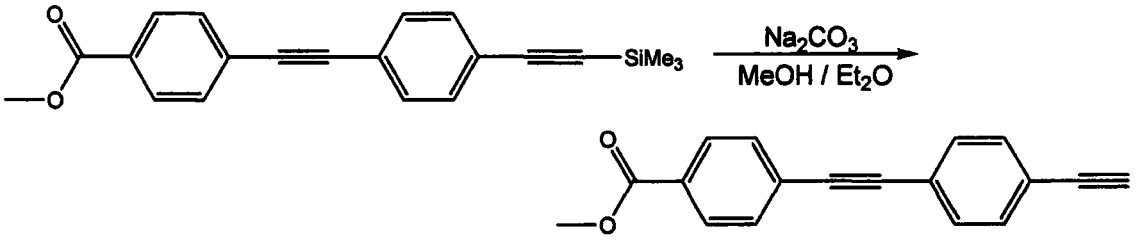
3.2.11 Synthesis of 4-(4-ethynyl-phenylethynyl)-benzonitrile (**5c**)



A 250 ml Schlenk flask was charged with **4c** (1.49 g, 5 mmol), Na_2CO_3 (2.12 g, 20 mmol), MeOH (ca. 50 ml), Et_2O (ca. 50 ml) and H_2O (ca. 5 ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate. The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.87 g, 77%), m. p. 200-202 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13 (s, 1H; ≡C**H**), 7.49 (s, 4H; **Ar**), 7.60 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.65 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 79.44, 83.02, 89.51, 93.07 (**C≡C**), 111.78 (**Ar**), 118.40 (**C**N), 122.64, 122.88, 127.88, 131.65, 132.08, 132.10, 132.16 (**Ar**). MS (EI): m/z (rel. int.): 227 [M^+], 200 [M-CN^+]. Anal. Calcd for $C_{17}H_9N$: C, 89.85; H, 3.99; N, 6.16; found: C, 89.80; H, 3.99; N, 5.98. IR (KBr) υ_{C-H} = 3233; $\upsilon_{C\equiv N}$ = 2227; $\upsilon_{C\equiv C}$ = 2210, 2100 cm^{-1}.

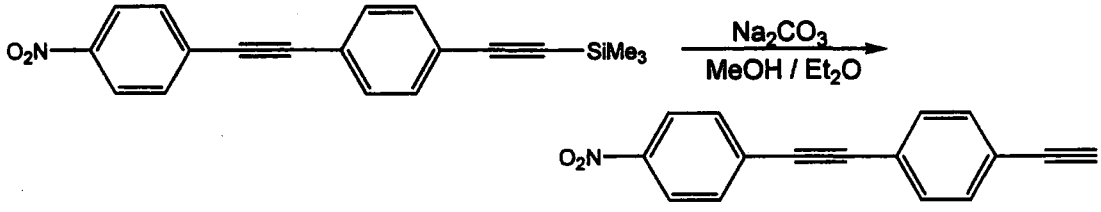
3.2.12 Synthesis of 4-(4-ethynyl-phenylethynyl)-benzoic acid methyl ester (**5d**)



A 250 ml Schlenk flask was charged with **4d** (0.83 g, 2.5 mmol), Na_2CO_3 (1.05 g, 10 mmol), MeOH (ca. 50 ml), Et_2O (ca. 50 ml) and H_2O (ca. 5 ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate. The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hot toluene (yield 0.35 g, 56%), m. p. 176-178 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 3.11 (s, 1H; ≡**CH**), 3.86 (s, 3H; **Me**), 7.03 (s, 4H; **Ar**), 7.37(d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.41 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 52.30 (**Me**), 79.14, 83.21, 90.41, 91.65 (**C≡C**), 122.64, 123.16, 127.63, 129.56, 129.74, 131.52, 131.58, 132.14 (**Ar**), 166.47 (O-**C**=O). MS (EI) m/z: 260 [M^+], 229 [M-Me-O^+]. Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65; found: C, 82.62; H, 4.58. IR (KBr) υ_{C-H} = 3261, 2952; $\upsilon_{C\equiv C}$ = 2211, 2094; $\upsilon_{C=O}$ = 1711 cm^{-1}.

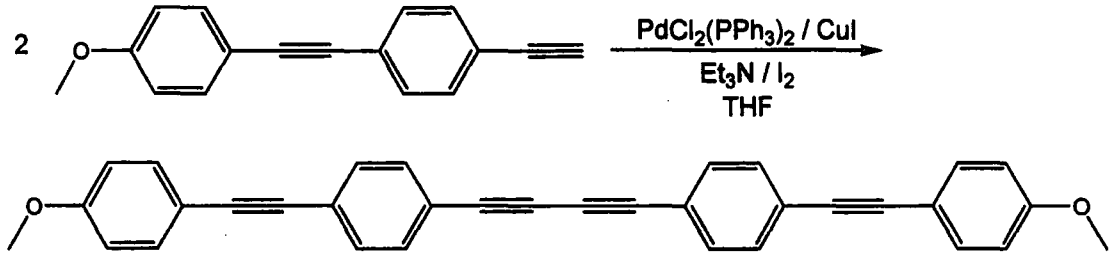
3.2.13 Synthesis of 4-(4-ethynyl-phenylethynyl)-nitrobenzene (5e)



A 250 ml Schlenk flask was charged with **4e** (0.797 g, 2.5 mmol), Na_2CO_3 (1.05 g, 10 mmol), MeOH (ca. 50 ml), Et_2O (ca. 50 ml) and H_2O (ca. 5 ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate. The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane and CH_2Cl_2 (yield 0.4 g, 65%), m. p. 208-210 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, 1H; **≡CH**), 7.51 (s, 4H; **Ar**), 7.66 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 8.23 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 79.52 , 82.96, 89.28, 93.88 (**C≡C**), 122.48, 122.98, 123.64, 129.85, 131.69, 132.20, 132.32, 147.18 (**Ar**). MS (EI) m/z: 247 [M^+], 200 [$M-NO_2H^+$]. Anal. Calcd for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.67; found: C, 77.62; H, 3.78; N, 5.43. IR (KBr) υ_{C-H} = 3256; $\upsilon_{C\equiv C}$ = 2210; υ_{Ar} = 1590, 1507; υ_{NO} = 1340 cm^{-1}.

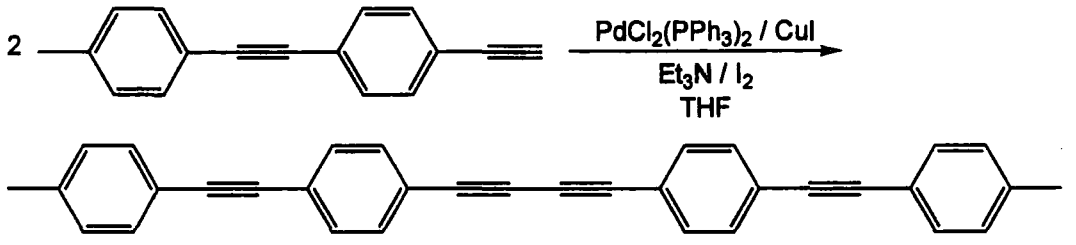
3.2.14 Synthesis of 4,4'-bis-(4''- methoxyphenylethynyl)-diphenyl-buta-1,3-diyne (**6a**)



A 100 ml Schlenk flask was charged with **5a** (0.42 g, 0.90 mmol), $PdCl_2(PPh_3)_2$ (0.025 g, 2 mol%) and CuI (0.02 g, 5 mol%). Dry THF (ca. 20 ml) and triethylamine (ca. 10 ml) was added to the reaction under air. I_2 (0.91 g 1.81 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2 (80:20) to remove all unreacted starting material, and then washed with hot toluene to collect the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hot toluene (yield 0.11 g, 26%), m. p. 243-245 °C (dec).

^{1}H NMR (500 MHz, DMSO, 100 °C): 3.31 (s, 6H; 2**Me**), 6.49 (d, $^3J_{(H,H)}$ = 9 Hz, 4H; **Ar**), 6.99 (d, $^3J_{(H,H)}$ = 9 Hz, 4H; **Ar**), 7.04 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.10 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**). ^{13}C {^{1}H} NMR (125 MHz, DMSO, 100°C): δ 54.90 (**Me**), 114.09, 130.91, 132.01, 132.50 (**Ar**). Carbons not bearing H-substitutents were not observed due to the very low solubility of the sample. EI/CI MS: m/z: 462 [M^+]. Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21; found: C, 87.64; H, 5.05. Raman: $\upsilon_{(C\equiv C)}$ = 2205; $\upsilon_{(arene\ ring)}$ = 1594, 1545, 1530 cm^{-1}.

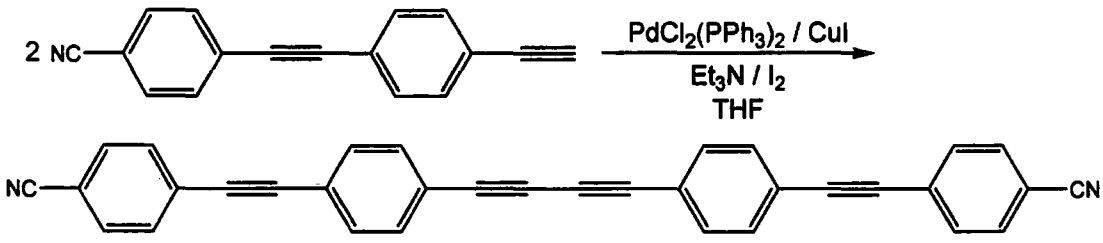
3.2.15 Synthesis of 4,4'-bis-(4''- methylphenylethynyl)-diphenyl-buta-1,3-diyne (**6b**)



A 100 ml Schlenk flask was charged with **5b** (0.42 g, 1.9 mmol), $PdCl_2(PPh_3)_2$ (0.027 g, 2 mol%) and CuI (0.018 g, 5 mol%). Dry THF (ca. 20 ml) and triethylamine (ca. 10 ml) were added to the reaction under air. I_2 (0.24 g 3.8 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2 (80:20) to remove all unreacted starting material, and then washed with hot toluene to collect the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hot toluene (yield 0.15 g, 36%), m. p. 260-262 °C (dec).

^{1}H NMR (500 MHz, C_6D_6, 70 °C): δ 2.02 (s, 6H; **2Me**), 6.86 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.22 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.26 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.40 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**) . ^{13}C {^{1}H} NMR (125 MHz, C_6D_6, 70 °C): δ 21.21 (**Me**), 76.90, 83.12, 88.90, 95.23 (**C≡C**), 120.90, 121.92, 125.15, 129.45, 131.84, 131.95, 132.74, 138.92 (**Ar**). EI/CI MS: m/z: 430 [M^+]. Anal. Calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15; found: C, 94.54; H, 4.95. Raman: $\upsilon_{(C\equiv C)}$ = 2199, 2046; $\upsilon_{(arene\ ring)}$ = 1588 cm^{-1}.

3.2.16 Synthesis of 4,4'-bis-(4''- cyanophenylethynyl)-diphenyl-buta-1,3-diyne (**6c**)

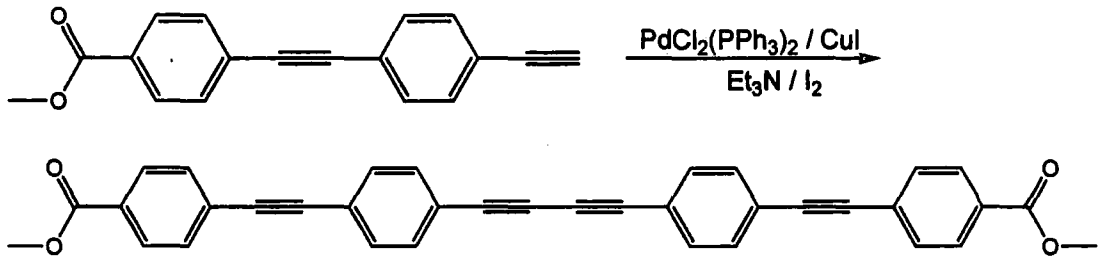


A 100 ml Schlenk flask was charged with **5c** (0.22 g, 0.96 mmol), $PdCl_2(PPh_3)_2$ (0.013 g, 2 mol%) and CuI (0.009 g, 5 mol%). Dry THF (ca. 10 ml) and triethylamine (ca. 10 ml) were added to the reaction under air. I_2 (0.48 g 1.92 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2, (80:20) to remove all unreacted starting material, and then washed with hot toluene to collect the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hot toluene (yield 0.085 g, 39%). m. p. 250-252 °C (dec).

^{1}H NMR (500 MHz, d_8-THF, 85 °C): δ 7.54 (s, 8H, **Ar**), 7.64 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.69 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**). ^{13}C {^{1}H} NMR (125 MHz, d_8-THF, 85 °C): δ 76.52, 82.83, 91.23, 93.30 (**C≡C**), 113.63 (**C≡N**), 123.31, 124.58, 128.44, 128.86, 129.64, 132.66, 132.96, 133.37 (**Ar**). EI/CI MS: m/z: 452 [M^+]. Anal. Calcd for $C_{34}H_{16}N_2$: C, 90.25; H, 3.56; N, 6.19; found: C, 89.97; H, 3.90; N, 5.94. Raman: $\upsilon_{(C\equiv C)}$= 2202; $\upsilon_{(arene\ ring)}$= 1593 cm^{-1}.

3.2.17 Synthesis of 4,4'-bis-(4''-carbomethoxyphenylethynyl)-diphenyl-buta-1,3-diyne

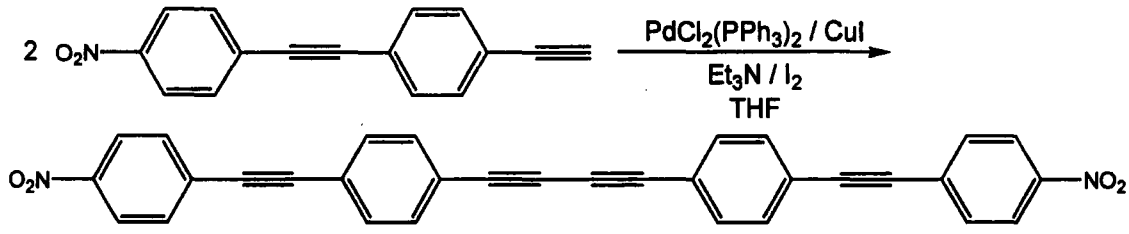
(6d)



A 100 ml Schlenk flask was charged with **5d** (0.22 g, 0.86 mmol), $PdCl_2(PPh_3)_2$ (0.012 g, 2 mol%) and CuI (0.008 g, 5 mol%). Dry THF (ca. 10 ml) and triethylamine (ca. 10 ml) were added to the reaction under air. I_2 (0.436 g 1.72 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2, (80:20) to remove all unreacted starting material, and then washed with hot toluene to collect the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.080 g, 36%). m. p. 263-265 °C (dec).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 6H; **2Me**), 7.42 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.48 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 7.58 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 8.02 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 52.68 (**Me-O**), 91.14, 92.08, 94.09, 1C apparently by solvent resonances (**C≡C**), 123.49, 124.03, 127.99, 129.95, 130.11, 131.92, 131.94, 132.73 (**Ar**), 166.90 (O=C-O). MALDI MS: 518 [M^+]. Anal. Calcd for $C_{36}H_{22}O_4$: C, 83.38; H, 4.28; found: C, 83.12; H, 3.98. Raman: $\upsilon_{(C\equiv C)}$ = 2214, 2165; $\upsilon_{(arene\ ring)}$ = 1594 cm^{-1}.

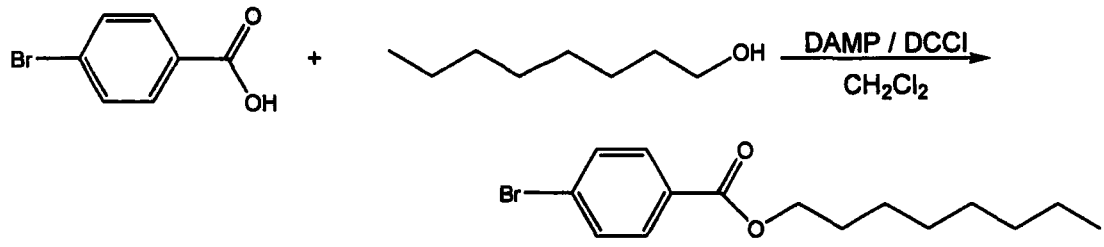
3.2.18 Synthesis of 4,4'-bis-(4''- nitrophenylethynyl)-diphenyl-buta-1,3-diyne (**6e**)



A 100 ml Schlenk flask was charged with **5e** (0.22 g, 0.89 mmol), $PdCl_2(PPh_3)_2$ (0.012 g, 2 mol%) and CuI (0.0085 g, 5 mol%). Dry THF ca. 20 ml and triethylamine ca. 10 ml were added to the reaction under air. I_2 (0.45 g 1.78 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2 (80:20) to removed all unreacted starting material, and then washed with hot toluene to collect the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hot toluene (yield 0.13 g, 59%), m. p. 215-217 °C (dec).

^{1}H NMR (500 MHz, d_8-THF, 85 °C): δ 7.58 (s, 8H; **Ar**), 7.72 (d, $^3J_{(H,H)}$ = 7 Hz, 4H; **Ar**), 8.22 (d, $^3J_{(H,H)}$ = 7 Hz, 4H; **Ar**). ^{13}C {^{1}H} NMR (500 MHz, d_8-THF, 85 °C): δ 124.41, 132.72, 133.23, 133.40 (**Ar**). Carbons not bearing H-substitutents were not observed due to the very low solubility of the sample. EI/CI MS: m/z: 492 [M^+]. Anal. Calcd for $C_{32}H_{16}N_2O_4$: C, 78.04; H, 3.27; N, 5.69; found: C, 77.85; H, 3.32; N, 5.35. Raman: $\upsilon_{(C\equiv C)}$ = 2201; $\upsilon_{(arene\ ring)}$ = 1588; $\upsilon_{(NO)}$= 1341 cm^{-1}.

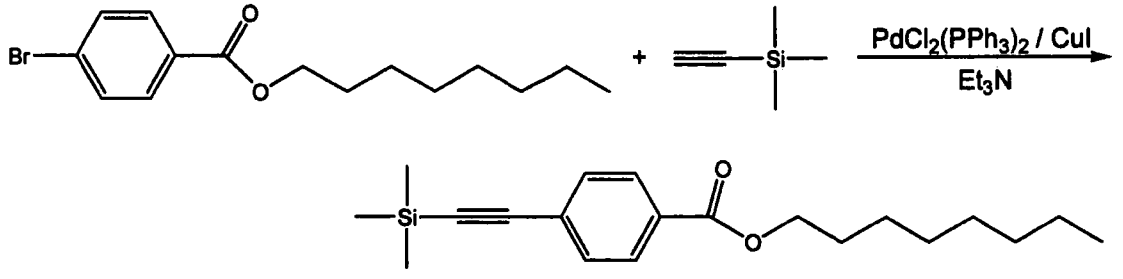
3.2.19 Synthesis of 4-bromobenzoic acid octyl ester (7)



To an ice-cooled and stirred solution of 4-bromobenzoic acid (5 g, 25 mmol), octan-1-ol (3.87 g, 30 mmol) and DAMP (0.302 g, 2.4 mmol) in 150 ml of CH_2Cl_2, was added dropwise a solution of DCCI (9.71 g, 46 mmol) in 10 ml of CH_2Cl_2. The mixture was stirred at room temperature for 24 h. The urea formed was removed by filtration and the solvent evaporated on a rotary evaporator. The crude product was passed through a silica gel column, eluting with hexane. Kugelrohr distillation (120-150 °C, 1.3 x 10^{-4} torr) gave an analytically pure liquid sample. Yield (6.6 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, $^3J(H,H)$ = 7 Hz, 3H; **CH_3**), 1.20-1.38 (m, 8H, 4 **CH_2**), 1.43 (m, 2H; CH_3-**CH_2**), 1.68 (quintet, $^3J_{(H,H)}$ = 7 Hz, 2H; O-CH_2**CH_2**), 4.23 (t, $^3J_{(H,H)}$ = 7 Hz, 2H; O-**CH_2**), 7.50 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 7.82 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.04 (**CH_3**), 22.59, 25.98, 28.64, 29.14, 29.21, 31.73 (**CH_2**), 65.41(O-**CH_2**), 127.86, 129.44, 131.04, 131.63 (**Ar**), 165.90 (O=C-O). MS (EI) m/z: 314 [M^+], 295 [M-Me^+]. Anal. Calcd for $C_{15}H_{21}BrO_2$: C, 57.52; H, 6.76; found: C, 57.36; H, 6.79.

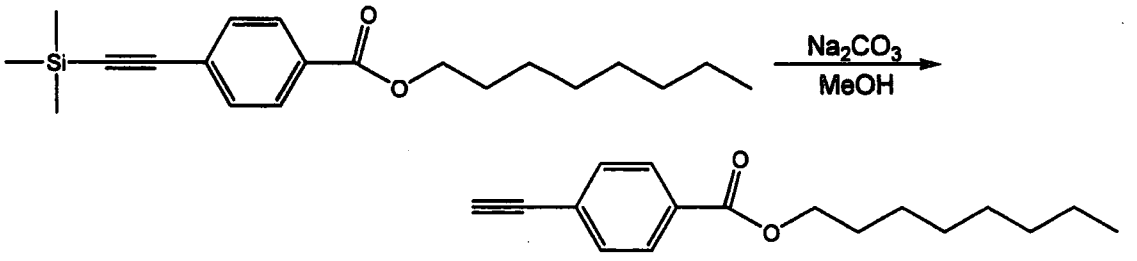
3.2.20 Synthesis of 4-trimethylsilanylethynyl benzoic acid octyl ester (**8**)



A 250 ml Schlenk flask was charged with **7** (3 g, 9 mmol), $PdCl_2(PPh_3)_2$ (0.13 g, 2 mol%) and CuI (0.03 g, 2 mol%), and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 150 ml) was transferred to the reaction flask *via* cannula under nitrogen. TMSA (1.4 g, 14 mmol) was added via pipette under nitrogen. The reaction mixture was heated to reflux for 24 h. The solvent was removed *in vacuo* and the residue was passed through a silica pad eluting with hexane. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane (yield 2 g, 63%), m. p. 36-38 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me_3Si**), 0.88 (t, $^3J_{(H,H)}$ = 6.7 Hz, 3H; **CH_3**), 1.26-1.38 (m, 8H, 4**CH_2**), 1.43 (m, 2H; CH_3-**CH_2**), 1.76 (quintet, $^3J_{(H,H)}$ = 7.3 Hz, 2H; O-CH_2**CH_2**), 4.30 (t, $^3J_{(H,H)}$ = 6.6 Hz, 2H; O-**CH_2**), 7.51 (d, $^3J_{(H,H)}$ = 8.6 Hz, 2H; **Ar**), 7.97 (d, $^3J_{(H,H)}$ = 8.6 Hz, 2H; **Ar**). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.00 (**Me_3Si**), 14.23 (**CH_3**), 22.79, 26.19, 28.86, 29.33, 29.40, 31.94 (**CH_2**), 65.51 (O-**CH_2**), 97.72, 104.31 (**C≡C**), 127.82, 129.49, 131.28, 132.00 (**Ar**), 166.26 (O=**C**-O). MS (EI) m/z: 330 [M^+], 315 [M-Me^+]. Anal. Calcd for $C_{20}H_{30}O_2Si$: C, 72.67; H, 9.15; found: C, 72.53; H, 9.30. IR (KBr) $\upsilon_{C\equiv C}$ = 2164; $\upsilon_{C=O}$ = 1724 cm^{-1}.

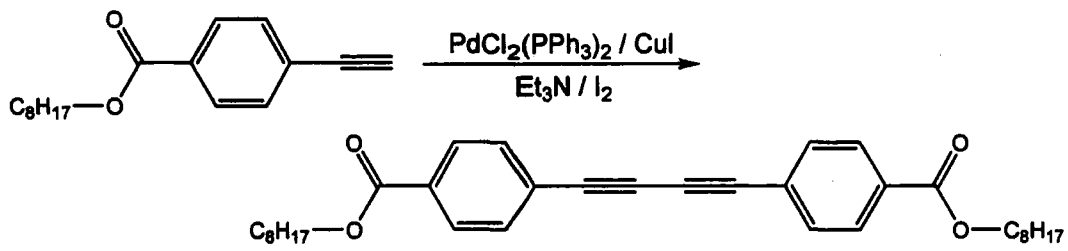
3.2.21 Synthesis of 4-ethynyl benzoic acid octyl ester (**9**)



A 250 ml Schlenk flask was charged with **8** (2 g, 2.5 mmol), Na_2CO_3 (1.05 g, 10 mmol) and MeOH (100ml). The reaction mixture was stirred under nitrogen for 20 h, and then filtered to remove sodium carbonate. The filtrate was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a yellow, oily liquid sample (yield 1.4 g, 90%).

^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, $^3J_{(H,H)}$ = 6.5 Hz, 3H; **CH_3**), 1.22-1.38 (m, 8H, 4 **CH_2**), 1.43 (m, 2H; CH_3-**CH_2**), 1.76 (quintet, $^3J_{(H,H)}$ = 7 Hz, 2H; O-CH_2**CH_2**), 3.22 (s, 1H; ≡**CH**), 4.31 (t, $^3J_{(H,H)}$ = 7 Hz, 2H; O-**CH_2**), 7.55 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**), 7.99 (d, $^3J_{(H,H)}$ = 8 Hz, 2H; **Ar**) . $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.22 (**CH_3**), 22.78, 25.90, 26.18, 28.84, 29.33, 31.99 (**CH_2**), 65.36 (O-**CH_2**), 97.91, 82.83 (**C≡C**), 126.61, 129.40, 130.54, 132.00 (**Ar**), 165.99 (O=C-O). MS (EI) m/z: 258 [M^+], 243 [M-Me+]. Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; found: C, 78.90; H 8.50. IR (KBr) $\upsilon_{\equiv C-H}$ = 3314, 3282, 2948, ; $\upsilon_{C=O}$ = 728 cm^{-1}.

3.2.22 Synthesis of 4,4'-bis-(carbooctyloxylphenyl)-buta-1,3-diyne (**10**)

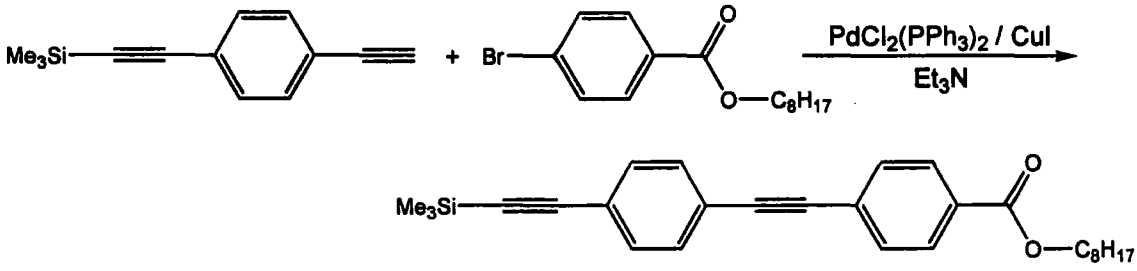


A 100 ml Schlenk flask was charged with **9** (0.2 g, 0.7 mmol), $PdCl_2(PPh_3)_2$ (0.009 g, 2 mol%) and CuI (0.0066 g, 5 mol%), which was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 10 ml) was transferred to the reaction flask *via* cannula under nitrogen. I_2 (0.355 g 1.4 mmol) was added to the reaction mixture under nitrogen. The reaction mixture was stirred under nitrogen for 20 h. The solvent was removed *in vacuo* and the residue was passed through a silica pad eluting with hexane : CH_2Cl_2 (80:20) to remove any starting material, then (60:40) to collecting the product. The solvent was removed on a rotary evaporator to give a yellow solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.12 g, 60%), m. p. 93-95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, $^3J_{(H,H)}$ = 7 Hz, 6H; 2**CH$_3$**), 1.22-1.39 (m, 16 H, 8**CH$_2$**), 1.44 (m, 4H; 2CH$_3$-**CH$_2$**), 1.76 (quintet, $^3J_{(H,H)}$ = 7 Hz, 4H; 2O-CH$_2$**CH$_2$**), 4.32 (t, $^3J_{(H,H)}$ = 7 Hz, 2H; 2O-**CH$_2$**), 7.59 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**), 8.02 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; **Ar**). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.04 (**CH$_3$**), 22.59, 26.01, 28.67, 29.17, 29.23, 31.77 (**CH$_2$**), 65.48 (O-**CH$_2$**), 81.89, 76.19 (**C≡C**), 125.98, 129.53, 130.97, 132.97 (**Ar**), 165.83 (O=**C**-O). MS (EI): m/z (rel. int.): 514 [M^+], 402 [M-C_8H_{16}]. Anal. Calcd for $C_{34}H_{42}O_4$: C, 79.34; H, 8.22; found: C, 78.92; H, 7.84. Raman: $\upsilon_{C\equiv C}$ = 2250; $\upsilon_{C=O}$ = 1715 cm^{-1}.

3.2.23 Synthesis of 4-(4-trimethylsilanylethynyl-phenylethynyl)-benzoic acid octyl ester

(11)

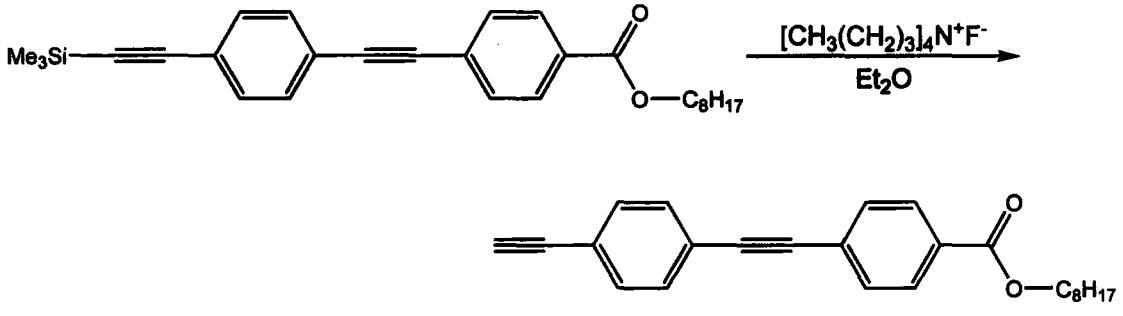


A 250 ml Schlenk flask was charged with **7** (1.5 g, 4.7 mmol), 1-(trimethylsilylethynyl)-4-ethynyl benzene **3** (1.138 g, 5.64 mmol), $PdCl_2(PPh_3)_2$ (0.067 g, 0.1 mmol) and CuI (0.0178 g, 0.1 mmol) and was evacuated and purged with nitrogen 3 times. Triethylamine (ca. 100 ml) was transferred to the reaction flask *via* cannula under nitrogen. The reaction mixture was heated to reflux for 20 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2 (90:10). The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.77 g, 36%), m. p. 70-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H; **Me$_3$Si**), 0.89 (t, $^3J_{(H,H)}$ = 7 Hz, 3H; **CH$_3$**), 1.26-1.40 (m, 8H, 4**CH$_2$**), 1.44 (m, 2H; CH$_3$-**CH$_2$**), 1.77 (quintet, $^3J_{(H,H)}$ = 6 Hz, 2H; O-CH$_2$**CH$_2$**), 4.32 (t, $^3J_{(H,H)}$ = 7 Hz, 2H; O-**CH$_2$**), 7.46 (m, 4H; **Ar**), 7.57 (d, $^3J_{(H,H)}$ =9 Hz, 2H; **Ar**), 8.02 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ -0.10 (**Me$_3$Si**), 14.07 (**CH$_3$**), 22.62, 26.03, 28.69, 29.15, 29.21, 31.76 (**CH$_2$**), 65.35 (O-**CH$_2$**), 90.49, 91.78, 96.63, 104.48 (**C≡C**), 122.74, 123.44, 127.55, 129,49, 130.06, 131.45, 131.48, 131.93 (**Ar**), 166.08 (O=**C**-O). MS (EI) m/z: 430 [M^+], 415 [M-Me]. Anal. Calcd

for $C_{28}H_{34}O_2Si$: C, 78.09; H, 7.96; found: C, 77.97; H, 7.94. IR (KBr) υ_{C-H} = 2954, 2920, 2849; $\upsilon_{C\equiv C}$ = 2185; $\upsilon_{C=O}$ = 1715; $\upsilon_{O-C=O}$ = 1292 cm^{-1}.

3.2.24 Synthesis of 4-(4-ethynyl-phenylethynyl)-benzoic acid octyl ester (**12**)



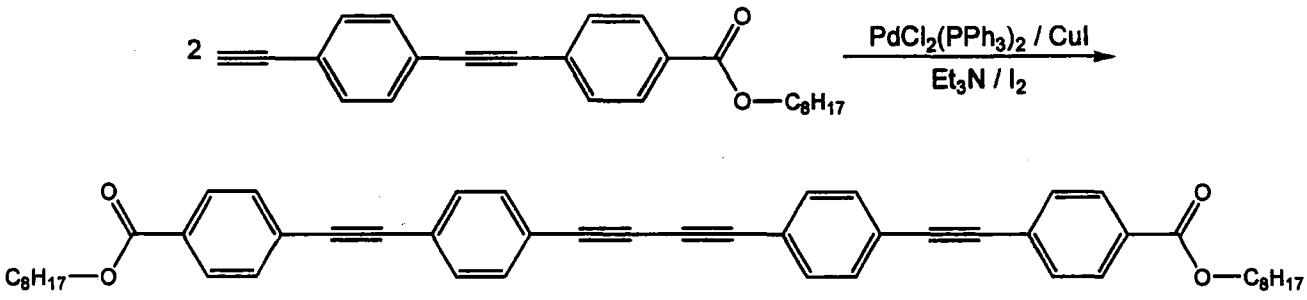
A 250 ml Schlenk flask was charged with **11** (0.86 g, 2 mmol), $[CH_3(CH_2)_3]_4N^+F^-$ (1.0 M in THF, 2 ml) and Et_2O (50 ml). The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo* and the residue passed through a sinter funnel, eluting with hot water. The residue was poured into water (ca. 150 ml) and extracted with Et_2O (ca. 150 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.55 g, 77%), m. p. 65-67 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, $^3J_{(H,H)}$ = 7 Hz, 3H; **CH_3**), 1.26-1.40 (m, 8H, 4 **CH_2**), 1.44 (m, 2H; CH_3-**CH_2**), 1.77 (quintet, $^3J_{(H,H)}$ = 7 Hz, 2H; O-CH_2**CH_2**), 3.19 (s, 1H; C≡**CH**), 4.32 (t, $^3J_{(H,H)}$ = 7 Hz, 2H; O-**CH_2**), 7.49 (s, 4H; **Ar**), 7.58 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**), 8.02 (d, $^3J_{(H,H)}$ = 9 Hz, 2H; **Ar**). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 14.07 (**CH_3**), 22.67, 26.04, 28.70, 29.18, 29.23, 31.77 (**CH_2**), 65.38 (O-**CH_2**), 79.15, 83.14, 90.60, 91.65 (**C≡C**), 122.43, 123.22, 128.17, 129.50, 130.14, 131.50, 131.57, 132.11

(Ar), 166.06 (O=C-O). MS (EI) m/z: 358 [M^+], 343 [M-Me]. Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31 found: C, 83.52; H, 7.25. IR (KBr) $\upsilon_{C\equiv CH}$ = 3278, υ_{C-H} = 2954, 2917, 2848; $\upsilon_{C\equiv C}$ = 1921; $\upsilon_{C=O}$ = 1711; $\upsilon_{O-C=O}$ = 1281 cm^{-1}.

3.2.25 Synthesis of 4,4'-bis-(4"-carbooctyloxyphenylethynyl)-diphenyl-buta-1,3-diyne

(13)



A 250 ml Schlenk flask was charged with **12** (0.22 g, 0.699 mmol), $PdCl_2(PPh_3)_2$ (0.0094 g, 2 mol%) and CuI (0.0064g, 5 mol%). Triethylamine (ca. 50 ml) was transferred to the reaction flask via cannula. I_2 (0.339 g 1.34 mmol) was added and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* and the residue passed through a silica pad eluting with hexane : CH_2Cl_2 (90:10) to removed all unreacted starting material, and then washed with hexane : CH_2Cl_2 (50:50) to collect the product. The solvent was removed on a rotary evaporator to give a white solid which was recrystallised from hexane / CH_2Cl_2 (yield 0.085 g, 37%), m. p. 235-237 °C (dec).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, $^3J(H,H)$ = 7 Hz, 6H; 2CH_3), 1.24-1.39 (m, 16H, 8 CH_2), 1.44 (m, 4H; 2CH_3-CH_2), 1.77 (quintet, $^3J_{(H,H)}$ = 7 Hz, 4H; 2O-CH_2CH_2), 4.32 (t, $^3J_{(H,H)}$ = 5 Hz, 4H; 2O-CH_2), 7.52 (m, 4H; Ar), 7.59 (d, $^3J_{(H,H)}$ = 8 Hz, 4H; Ar), 8.03 (d,

$^{3}J_{(H,H)}$ = 8 Hz, 4H; **Ar**). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.04 (**CH_3**), 22.59, 26.01, 28.69, 29.15, 29.21, 31.76 (**CH_2**), 65.38 (**O-CH_2**), 75.82, 82.09, 91.33, 91.55 (**C≡C**), 121.87, 123.70, 127.35, 129.50, 130.23, 131.51, 131.70, 132.47 (**Ar**), 166.02 (O=**C**-O). MALDI MS: 714 [M^+]. Anal. Calcd for $C_{25}H_{26}O_2$: C, 84.00; H, 7.05 found: C, 83.95; H, 7.10. Raman: $\upsilon_{(C\equiv C)}$ = 2207; $\upsilon_{(arene\ ring)}$ = 1596 cm^{-1}.

3.3 Crystallography

The X-ray diffraction data for compounds **2** was collected on a Bruker Apex CCD diffractometer and for **3** and **10**, on a Bruker SMART 6K CCD detector, using graphite-monochromated sealed-tube Mo-K_α radiation λ = 0.71073 Å. The data collections were carried out at 120(2) K for all crystals using cryostream (Oxford cryosystem) open flow N_2 cryostats. Reflection intensities were integrated using the *SAINT* program.[92] The crystal structures were solve using direct-methods and refined by full matrix least-squares against F^2 of all data using *SHELXTL* software.[93] Crystal data and experimental details are listed in Table 3.1.

Table 3.1: Crystal data and experimental details

Compound	2	3	10
Empirical formula	$C_{16}H_{20}OSi$	$C_{13}H_{14}Si$	$C_{34}H_{42}O_4$
Formula weight	256.41	198.33	514.68
Temperature / K	120(2)	120(2)	120(2)
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	R-3	C2/c	P2(1)/c
a / Å	38.155(4)	18.267(2)	15.944(1)
b / Å	38.155(4)	8.7384(7)	8.4309(4)
c / Å	5.9934(9)	16.426(2)	11.260(1)
α / β / γ / deg.	90 / 90 / 120	90 / 110.77(1) / 90	90 / 102.32(1) / 90
Volume / $Å^3$	7556.2(16)	2451.6(4)	1478.74(14)
Z	18	8	2
D_c / Mg m^{-3}	1.014	1.075	1.156
μ / mm-1	0.128	0.153	0.074
Crystal size / mm^3	0.42 x 0.40 x 0.40	0.51 x 0.28 x 0.07	0.48 x 0.33 x 0.08
Theta range / deg.	1.07 - 30.51	2.38 - 30.00	1.31 - 30.01
Reflections collected	20974	16405	19710
Independent reflections	5114	3571	4310
Goodness-of-fit on F^2	1.083	1.069	1.045
$R_{(int)}$	0.0541	0.0372	0.0417
$wR(F^2)$(all data)	0.0657	0.0976	0.0642
R[I>2σ (I)]	0.1432	0.1058	0.1118
Refined parameters	172	183	174
Largest diff. peak and hole / e $Å^{-3}$	0.425 and -0.301	0.335 and -0.255	0.363 and -0.168

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