
Synthesis of Polycyclic Aromatic Hydrocarbons with Extended π -Conjugation via Multi-Fold C-C Coupling Reactions and their Versatile Applications

A Dissertation

*Submitted in Partial Fulfillment for the Degree of
Doctor of Philosophy*



by

**Khadimul Islam
(Roll No: 176122018)**

Thesis Supervisor: Dr. Akshai Kumar A. S.

**Department of Chemistry
Indian Institute of Technology Guwahati
Guwahati – 781039, Assam, INDIA**

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Dedicated

To

Late Rabiya Bewa (Grandmother)



The logo of the Indian Institute of Technology Guwahati is a circular emblem. It features a central stylized 'S' or 'Om' symbol, which is a common motif in Indian art and religion. The symbol is composed of three interlocking loops. The entire emblem is enclosed within a circular border. The text 'Indian Institute of Technology Guwahati' is written in English around the bottom half of the circle, and 'भारतीय प्रौद्योगिकी संस्थान गुवाहाटी' is written in Hindi around the top half.

***"Learning gives creativity Creativity leads to
thinking Thinking provides knowledge
Knowledge makes you great."***

APJ Abul Kalam



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Indian Institute of Technology Guwahati

Department of Chemistry

Declaration

I do hereby declare that the research work embodied in this thesis entitled “*Synthesis of Polycyclic Aromatic Hydrocarbons with Extended π -Conjugation via Multi-Fold C-C Coupling Reactions and their Versatile Applications*” has been carried out by me in the Department of Chemistry, Indian Institute of Technology Guwahati, Assam-781039, India, under the supervision of **Dr. Akshai Kumar A. S.** for the award of the degree of doctor of philosophy and it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgments have been made wherever the work described is based on the findings of other investigators.

Guwahati

March, 2023

Khadimul Islam

Roll No– 176122018

Department of Chemistry
IIT Guwahati, Guwahati
Assam, INDIA-781039





भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati



Dr. Akshai Kumar Alape Seetharam

Associate Professor, Department of Chemistry, Guwahati – 781039, Assam, INDIA

Tel: +91-3612583479 (O), Mobile: +91-8133036890, Fax: +91-3612582349

Email: akshaikumar@iitg.ac.in, akshaikumara@gmail.com

CERTIFICATE

I hereby certify that the entire work embodied in the thesis entitled “*Synthesis of Polycyclic Aromatic Hydrocarbons with Extended π -Conjugation via Multi-Fold C-C Coupling Reactions and their Versatile Applications*” is the result of investigations carried out by **Mr. Khadimul Islam** (Roll No: 176122018) at the Department of Chemistry, Indian Institute of Technology Guwahati, India under my guidance and the same has not been submitted elsewhere for the award of any degree or diploma.

Guwahati

March 27, 2023

 27/03/2023

Dr. Akshai Kumar A. S.

Supervisor



Abbreviation

T	Temperature	IR	Infrared
°C	Degree Celsius	<i>m/z</i>	Mass to charge ratio
δ	Chemical shifts	<i>e.g.</i>	For example
g	Grams	ca.	around
mg	milligram	<i>et al.</i>	and coworkers
mmol	millimole	<i>i.e.</i>	namely
μ M	micromole	vs.	versus
mL	milliliter	<i>via</i>	through
ppm	parts per million	ⁱ Pr	<i>iso</i> -propyl
r.t.	Room temperature	^t Bu	<i>tert</i> -butyl
h	Hours	Cy	Cyclohexyl
EPR	Electron Paramagnetic Resonance	Ar	Aromatic
MS	Mass spectrometry	THF	Tetrahydrofuran
HRMS	High-resolution mass spectrometry	RDS	rate determining step
Hz	Hertz	TON	Turnover number
MHz	Megahertz	2-MeTHF	2-Methyltetrahydrofuran
NMR	Nuclear Magnetic Resonance	DMAC	dimethylacetamide
<i>J</i>	Spin – spin coupling constant	DMF	<i>N,N</i> -dimethylformamide
s	Singlet	TBAF	tetrabutylammoniumfluoride
d	Doublet	DABCO	1,4-diazabicyclo[2.2.2]octane
dd	Doublet of Doublet	A	acceptor
ddd	Doublet of Doublet of Doublet	D	donor
t	Triplet	QY	Quantum yield
q	Quartet	PAH	Polycyclic aromatic hydrocarbons
m	Multiplate	DME	Dimethoxyethane
bs	Broad singlet	MDA-MB-231	M.D. Anderson - Metastatic Breast 231
ORTEP	Oak Ridge Thermal Ellipsoid Plot	SCXRD	Single crystal X-ray diffraction
CCDC	Cambridge Crystallographic Data Center	UV	Ultra violet
EWG	Electron withdrawing group	CV	Cyclic voltametry
CT	Charge transfer	TRPL	Time-resolved photoluminescence
HDF	Human dermal fibroblast	TICT	Twisted intramolecular charge transfer



Abstract

The contents of the present thesis entitled “*Synthesis of Polycyclic Aromatic Hydrocarbons with Extended π -Conjugation via Multi-Fold C-C Coupling Reaction and Their Versatile Applications*” have been divided into four chapters based on the results achieved from the experimental work carried out during the entire course of the PhD research program.

Chapter I provides a brief literature survey on synthesis of π -conjugated polycyclic aromatic hydrocarbons (PAHs) through C-C cross-coupling reactions. The versatile application on photophysical properties, sensing, optoelectronic device and cytotoxic potential is also discussed. The chapter ends with a discussion on the scope of the current thesis.

Chapter II formulates a single step multi-fold Sonogashira reaction to access nine new symmetrical tetraalkynylatedanthracene employing $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2/\text{cataCXium}^{\text{®}}\text{A}$ with moderate to good yields. Five of these tetraalkynylated anthracenes have been characterized by single crystal X-ray crystallography, with two of them exhibiting numerous interactions that significantly shorten the inter-planar distances in the solid-state structure. Solvatochromism and halochromism are exhibited by these tetraalkynylated anthracenes with one of them showing a low band-gap of 1.79 eV. The rich photophysical properties exhibited by these molecules in solution and in the solid-state offer immense promise for future applications in sensors and optoelectronic devices.

Chapter III investigates the multi-fold Sonogashira coupling reaction of aryl halides with aryl acetylene in the presence of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) as catalysts, CataCXium[®] A (1 mol%) as monodentate phosphine ligand, an equivalent of Cs_2CO_3 under copper-free and amine-free conditions in a readily available green solvent at room temperature. The protocol is applicable for single as well as multi-fold Sonogashira coupling reaction to access various polycyclic aromatic hydrocarbons. Six of these have been tested for their anticancer properties on human triple-negative breast cancer (TNBC) cell line MDA-MB-231 and human dermal fibroblasts (HDF). The compounds being intrinsically fluorescent, their cellular localization was checked by live cell fluorescence imaging. The death of the cancer cells was triggered by polyalkynylatedanthracene molecules through necrosis and apoptosis.

Chapter IV discusses about the development of a new efficient synthetic protocol for single and multi-fold Suzuki coupling reaction in a single step with moderate to excellent yields employing the highly earth abundant, readily available and inexpensive nickel salts with good

functional group tolerance. $\text{ArI} > \text{ArBr} > \text{ArCl}$ is the reactivity order of the halides towards the reaction which follows the corresponding C-X (X=I, Br, and Cl) bond strength. EPR analysis, mercury-drop experiments and reactions with radical scavenger such as TEMPO point to the involvement of well-defined molecular species that operate via a Ni(0)/Ni(II) catalytic cycle where oxidative addition of the aryl halide to Ni(0) is likely to be the rate-determining-step (RDS). For the first time, valuable new polycyclic aromatic hydrocarbons (PAHs) with exciting photophysical properties have been synthesized via Ni(II) catalyzed multi-fold Suzuki coupling.

The current thesis demonstrates a new efficient synthetic protocol for polyarylated/alkynylatedanthracenes via multi-fold C-C cross coupling reactions. They exhibit tunable photophysical properties and are semiconducting in nature. These compounds have been studied for various applications such as sensors and are potential cytotoxic agents.



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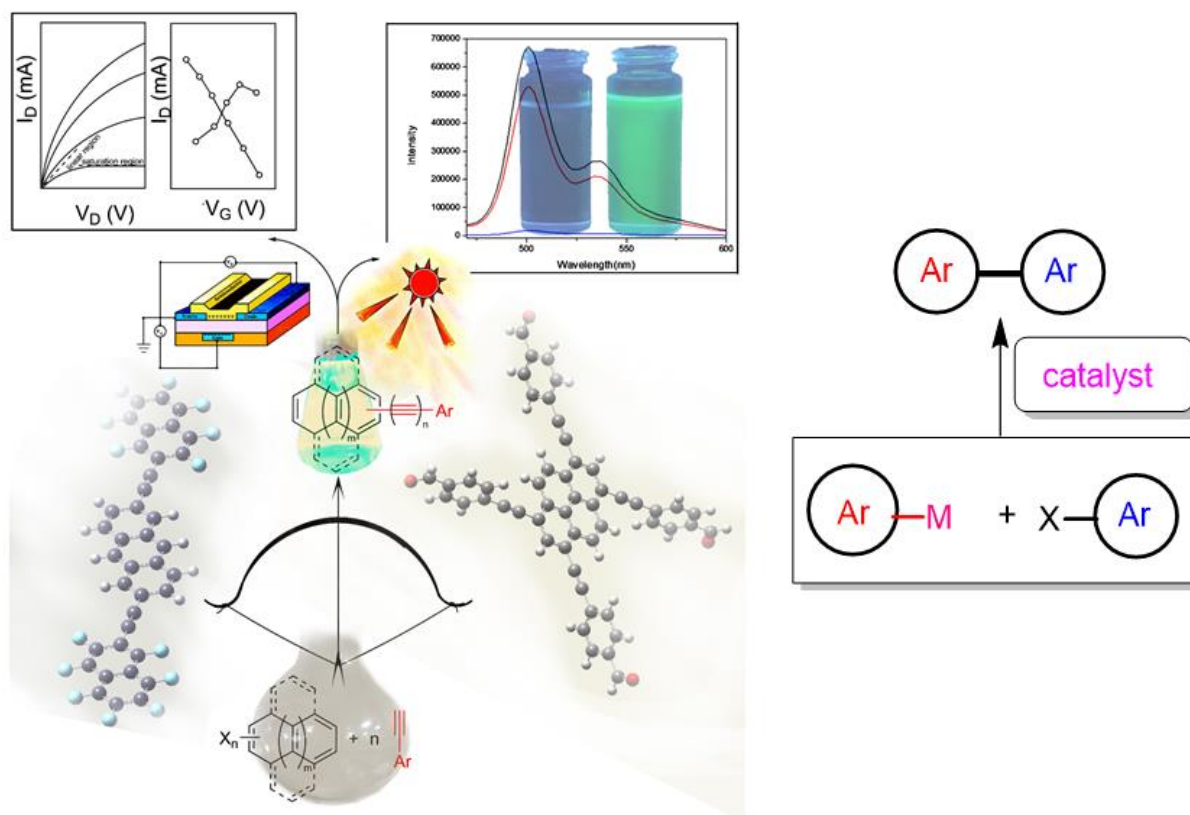
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CHAPTER I

Synthesis of Polycyclic Aromatic Hydrocarbons through C-C Coupling Reaction and their Applications.



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1.1 Introduction

1.1.1 Organic semiconductors

Organic semiconductor research has attracted tremendous interest in recent years.¹ Contrary to the conventional semiconductors based on highly efficient inorganic materials that suffer from high cost,² semiconductors based on organic materials offer unique possibilities such as light weight, mechanical flexibility and low-cost of production.³ These features are very attractive which not surprisingly make organic semiconductors promising candidates for fabricating organic field-effect transistors (OFETs),⁴ organic light-emitting diodes (OLEDs),⁵ solar cells,⁶ liquid-crystal displays⁷ and organic thin film transistors (OTFTs).⁸ OFETs, OLEDs and OTFTs find invaluable applications in integrated circuits, sensors and displays.⁹

Easy solution and vapour processability is one of the striking features of devices fabrication when organic materials are used.¹⁰ Availability of powerful synthetic tools allows one to effectively tailor the functionality on the molecules of interest. This allows one to design new materials with specific utility by significantly manifesting the macroscopic properties in the resulting solid-state structure.^{1, 11} Such a control is an almost impossible task with conventional inorganic materials. In organic semiconductors, electron transition from π - π^* is easier than σ - σ^* , owing to the lesser strength of the π -bond than that of the sigma bond.^{1b} The charge carrier density and mobility are low for organic semiconductors than inorganic semiconductors.¹² In organic semiconductors, the charge carrier density is dependent mainly on the overlap of the π -orbital in the molecules. The charge carrier density can be easily enhanced by doping.¹³

1.1.2. π -Conjugated molecules vs. polymers

The salient requirements that are essential for all charge transport materials for use in electronics include easy synthesis, maximum stability, high mobility, minimal contact resistance, low interfacial barriers and optimal threshold barriers.^{1, 10b-d, 11, 14} The quest of such materials have led to the synthesis of several organic materials either based on conjugated polymers¹⁵ or on π -conjugated molecules containing aromatic moieties such as benzene,¹⁶ naphthalene,^{14a} chrysene,^{14b} anthracene,⁵ and pyrene.¹⁷ Specific to each application, these organic materials may have certain additional design requirements.^{11a} The discovery of polyacetylene in 1977 by Heeger and co-workers paved the way for the development and design of electronics based on conjugated polymers

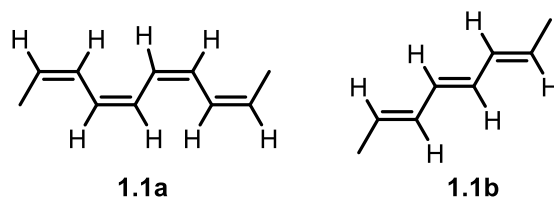


Figure 1.1. Structure of Cis/trans polyacetylene.¹⁸

(Figure 1.1).¹⁸ A large library of conjugated organic molecules are now available for use in organic electronics. In comparison to π -conjugated molecules, semiconductors based on polymers have superior solution processability and mechanical robustness.¹⁹ These solution processed polymers often contain amorphous regimes in addition to crystalline regions which poses a detrimental effect on the charge carrier properties of the fabricated devices.²⁰ Troubleshooting typically involves annealing the polymeric materials at high temperatures under high vacuum conditions.²⁰ However, such methods are not cost effective and hence not suitable for large-scale industrial production.²⁰ Global organic semiconductor research has now shifted the emphasis on the design and development of novel small conjugated molecules as *n*-channel or *p*-channel materials.²¹

A thorough understanding on the various factors that dictate the performance of the devices based on these small conjugated molecules is very essential for fabrication of high efficiency devices.²¹ In devices based on organic semiconductors, the optimal source-drain conductivity depends on the mobility of charge carriers.^{10a,22} Relatively high voltages are required to dislodge the charge carriers if they get stuck in traps.²³ Such potential local minima or traps are occurring mainly due to the presence of chemical impurities or grain boundaries and result in lower mobilities.²⁴ High purity crystalline small conjugated molecules are required for efficient charge transport.^{1b} Extensive π stacking coupled with efficient wave function overlap between the π -systems on adjacent molecules also leads to devices with high mobilities.²⁵ Not surprisingly, pentacene would lead to high mobilities compared to tetracene which in turn would show better mobility than anthracene.^{15a,26}

The match between the work function of the semiconductor and the electrodes plays a pivotal role in the performance of the fabricated devices.^{10a,22} In case of *p*-type organic semiconductors, small injection barriers are achieved by a close match between the Fermi level of the electrode and the highest occupied molecular level.²² On the other hand, for *n*-type semiconductors, the charge injection dynamics are mainly determined by the energetic position of

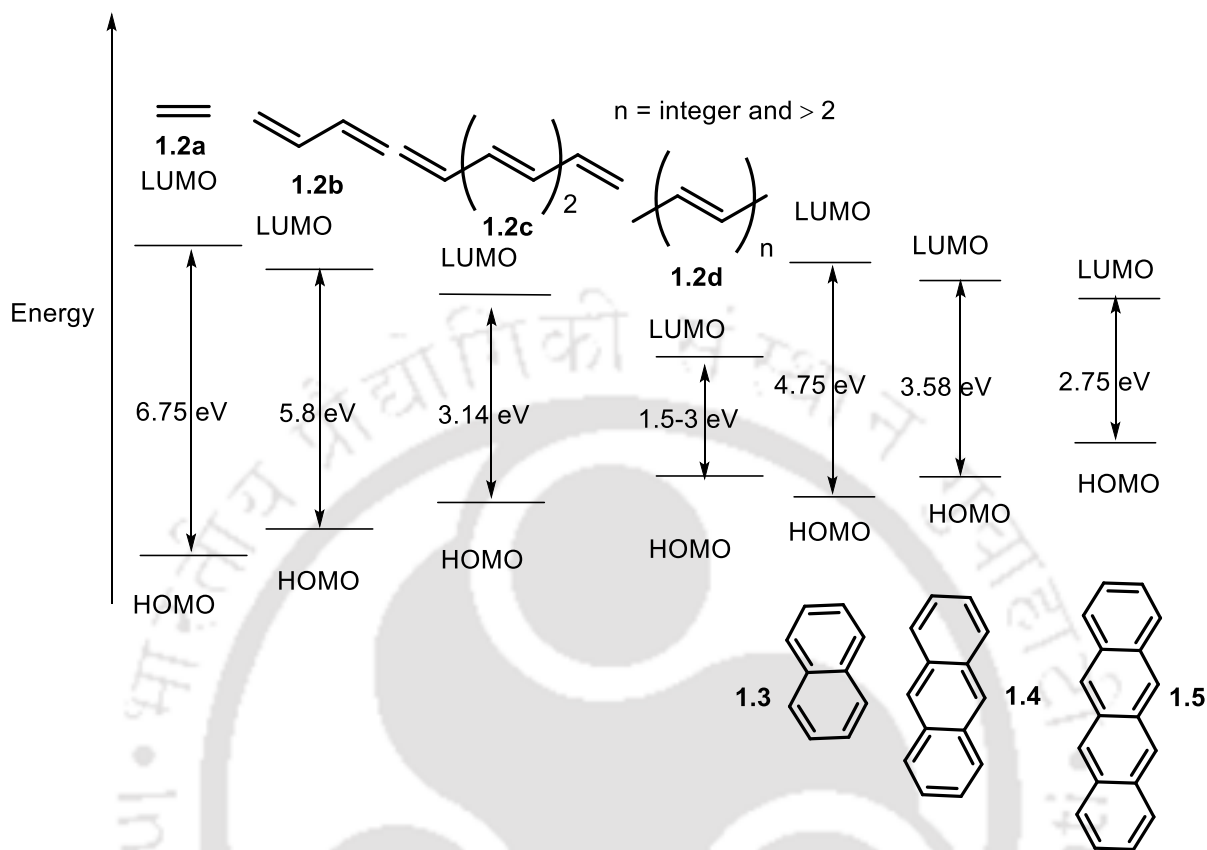


Figure 1.2. The band gap variation with conjugation.²⁷

unoccupied molecular orbitals and their overlap with metallic states.²² Extended π systems generally tend to raise the HOMO (highest occupied molecular orbital) and lower the LUMO (lowest unoccupied molecular orbital) (Figure 1.2).²⁷ This means the molecule can be both easily oxidised and easily reduced. Preferential lowering of LUMO could be achieved either by the introduction of inductively electron withdrawing fluoro groups or by the introduction of π -acceptor groups into the π -systems (Figure 1.3).^{26, 28} Thus on moving from acenes to perfluoroacenes (**1.8**) one can modulate the charge transport mechanism from *p*-type to *n*-type (Figure 1.3).^{3d, 26, 29} In general, *p*-type organic semiconductors can be synthesized by introducing electron-donating groups like thiophene and oligoacenes, while the corresponding *n*-type semiconductors can be obtained by introducing electron withdrawing carbonyl, fluoroalkyl and cyano groups (Figure 1.3).³⁰

1.1.3. Polycyclic aromatic hydrocarbons (PAHs)

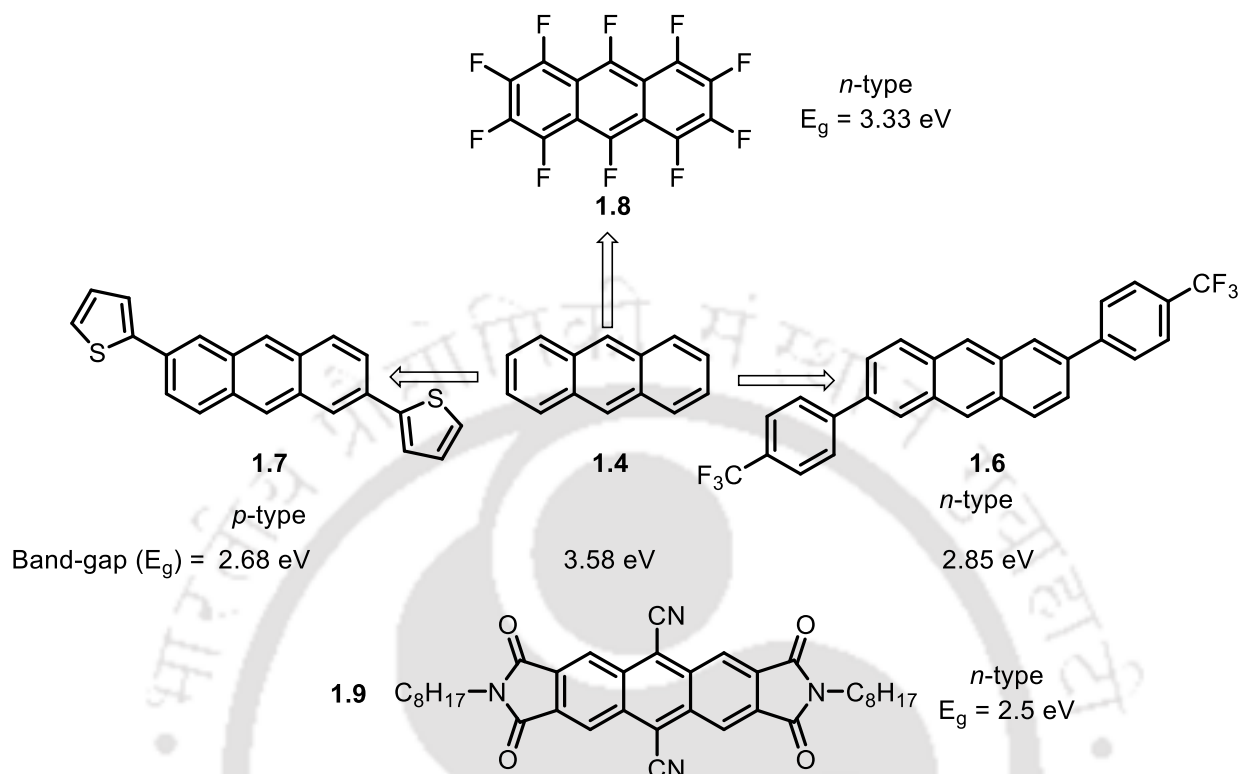


Figure 1.3. Structure of acenes, electron donating (p-type semiconductor) and withdrawing group (n-type semiconductors) connected acenes compounds.^{26,28,3d}

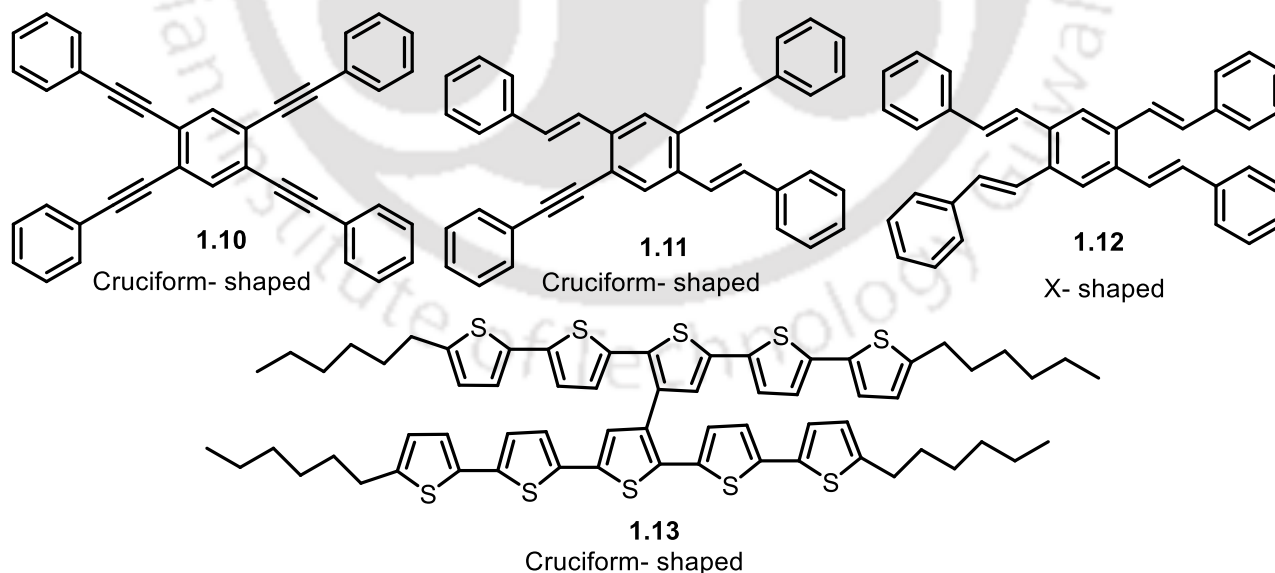


Figure 1.4. Structure of cruciform and X-shaped compounds.³¹

The polyannulated organic π -conjugated molecules like naphthalene,^{14a,32} anthracene,^{29c,33} tetrace-

-ne,³⁴ pentacene,³⁵ and pyrene³⁶ are typically referred to as polycyclic aromatic hydrocarbons (PAHs). The emission in PAHs have been efficiently modulated by introducing various substituents (electron-donating and withdrawing groups) that improve their solubility in organic solvents, enhance their fluorescence efficiency, and control the emission colour.³⁷ The emission colour of organic semiconductors can also be controlled by the introduction of extended π -conjugated groups like phenyl,³⁸ ethynyl,³⁸ and σ - π conjugated group like silyl.³⁹ Furthermore, the shape of the molecules has a great influence on the fluorescence as well as the electronic properties of the molecules. Highly conjugated compounds with cruciformshape¹⁷ show interesting electronic and optical properties. In this context it is noteworthy that Haley,^{31b-e} Nuckolls,^{31f} Bunz^{31g-i} and Scherf^{31j} have reported PAHs based on cruciform-shaped 1,2,4,5-tetrasubstituted (phenylethynyl)benzenes, acenes, 1,4-bis(arylethynyl)-2,5-distyrylbenzenes and α,α' -dihexylpentathiophene-based swivel cruciform respectively. On the other hand, the Marks group has studied the X-shaped 1,2,4,5 tetravinylbenzenes (Figure 1.4).^{31a}

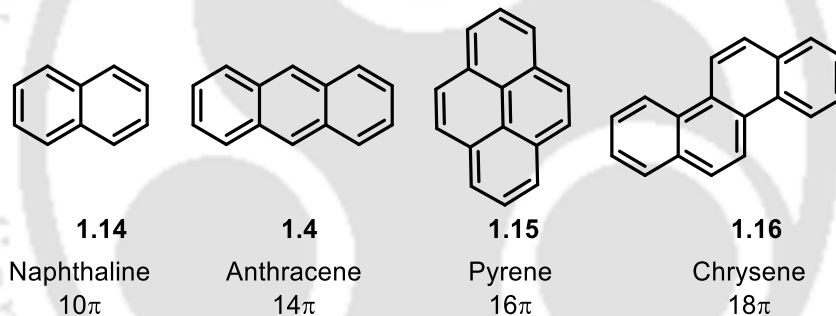


Figure 1.5. Fused cyclic compounds.

The rigidity of the polycyclic backbone imparts high thermal stability to the PAHs,^{14a,b,40,48} which has attracted significant interest in their use in fabrication of optoelectronic devices.⁴¹ Naphthalene, anthracene, pyrene, chrysene molecules having 10π , 14π , 16π and 18π -electrons respectively, contain a rigid fused aromatic structure (Figure 1.5), which decreases the vibronic energy level, resulting in the enhancement of the fluorescence quantum yield.⁴² The efficiency of the devices and emission wavelengths can also be enhanced by the addition of aryl,⁴⁰ amino,⁴⁰ carboxylic acid,⁴³ amino acid ester⁴⁴ and hetero atoms⁴⁰ to the parent PAH framework.

Carbon and graphite are composed of condensed polycyclics with hexagonal network and have electrical conductivity through π -electron in the whole network.⁴⁵ Polycyclic aromatic hydrocarbons (PAHs) with similar molecular structure as that of graphite, also show electrical

conductive behaviour.⁴⁵ In 1954, Inokuchi reported electrically conductive properties of violanthrone and named it as organic semiconductor.⁴⁵⁻⁴⁶ The conductivity properties of the materials depends on the band gap (energy gap between LUMO and HOMO for organic semiconductor). Band gap and conductivity can be modulated by enhancing the π -conjugation through introducing aromatic rings (Suzuki) either directly or *via* double (Heck) and triple bonds (Sonogashira) connected to the parent PAHs.⁴⁷

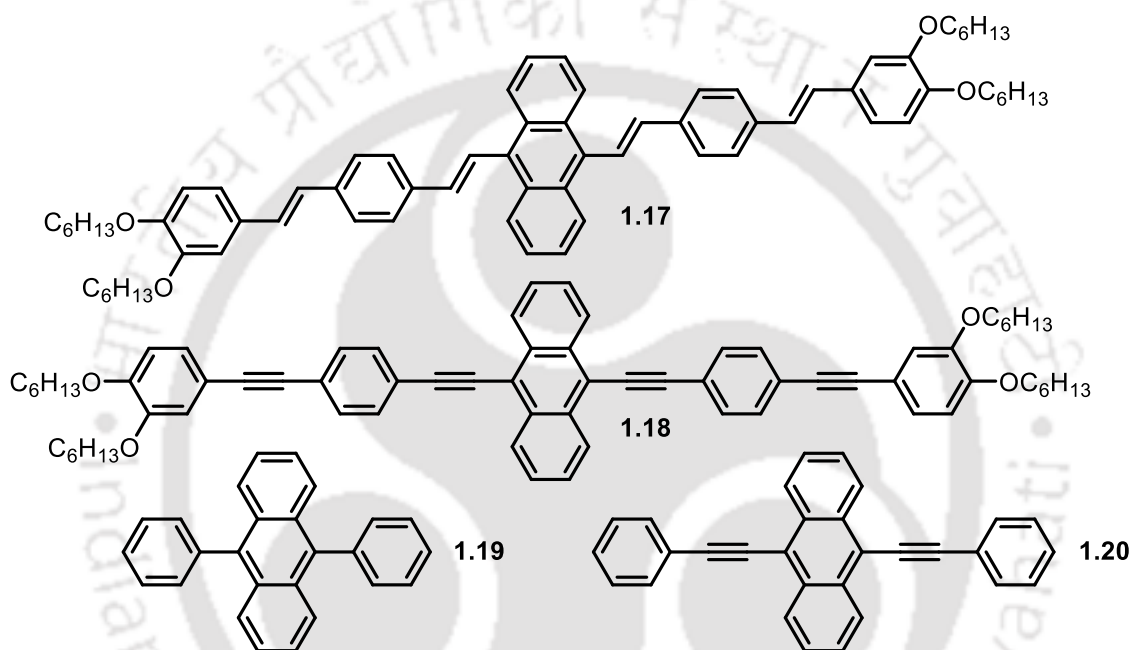


Figure 1.6. Few example PAHs connected aryl groups either directly or *via* double and triple bonds.^{6,15a, 87,88a,47}

Table 1.1. Comparative studies of aryl, alkylene and alkynylated PAHs on photophysical as well as electric properties

compound	Power conversion efficiency (%)	μ (cm ² V ⁻¹ s ⁻¹)	λ_{max} (nm)	Reference
1.17	0.34	10 ⁻⁴	423	6, 87
1.18	1.04	10 ⁻²	464	6,87
1.19	-	0.16	352, 373, 394	15a, 88a
1.20	-	0.73	270, 309, 430, 452	15a, 88a

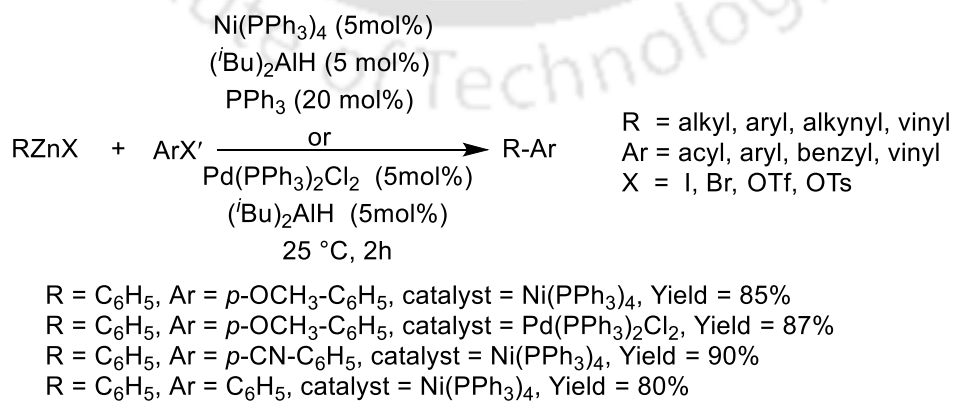
1.2. Synthesis of polycyclic aromatics hydrocarbons through C-C coupling reaction

Following the development of coupling reactions that generate carbon-carbon bonds, a new age of research began. The cross-coupling reactions involving transition metal catalyst such as Negishi⁴⁸, Suzuki,⁴⁹ Stille,⁵⁰ Hiyama,⁵¹ Kumada,⁵² Heck⁵³ and Sonogashira⁵⁴ are powerful tools to form C-C bonds. These reaction protocols have been widely used in the large area of academic as well as industries such as material science,^{47, 55} biological,⁵⁶ supramolecular chemistry,⁵⁷ natural product synthesis,⁵⁸ catalysis chemistry,⁵⁴ fine chemical,⁵⁹ agrochemical⁶⁰ and pharmaceutical industries.⁶¹

In the past five decades, researchers have studied C_{sp2} - C_{sp2} bond formation from an organometal ($Ar'M$, where $M = B, Mg, Si, Sn, Zn$) and organic electrophile ($Ar''X$) employing palladium as catalyst.⁶² The carbon metal ($C^{\delta-}-M^{\delta+}$) bond is polar and the carbon center behaves as nucleophile. Nucleophilic partners such as organoboron ($Ar'B(OH)_2$),⁴⁹ organomagnesium ($Ar'MgX$),⁵² organotin ($Ar'SnX$)⁵⁰ and organozinc ($Ar'ZnX$)⁴⁸ on reaction with aryl halide ($Ar''X$) results in C-C bond formation and this is known as Suzuki-Miyaura, Kumada, Stille and Negishi reaction respectively. The metal catalyzed C-C bond formation coupling reaction is the most vital and powerful tool in a multi-step reaction.

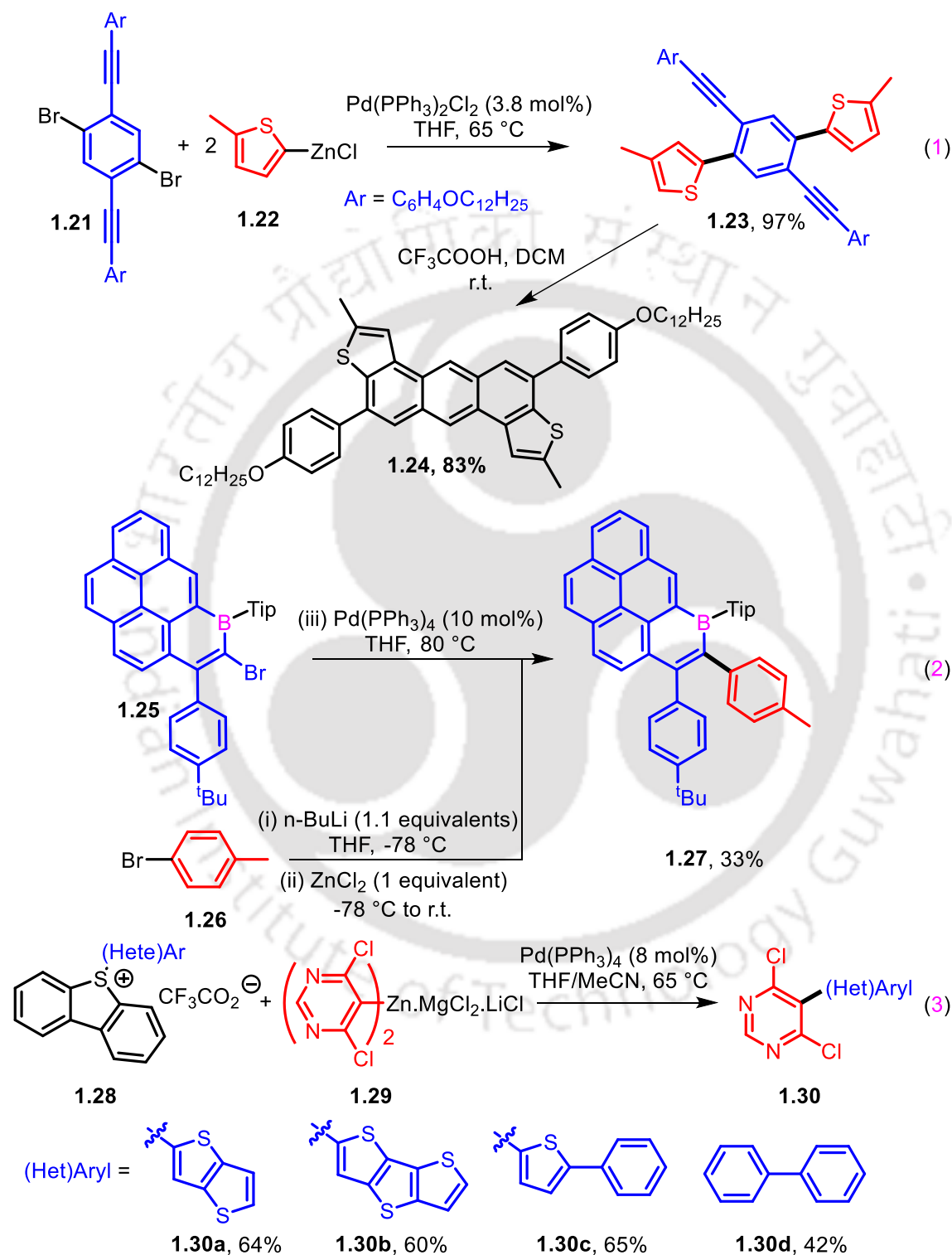
1.2.1. Negishi cross-coupling reaction

Pd or Ni based catalyzed Negishi cross-coupling reaction of organozinc ($RZnX$, where $R = Ar, ArCH_2$ and $X = Br$ or Cl) and aryl halide (ArX , where $X = I$ or Br) to form unsymmetrical biaryls with high chemo and regio selectivity, was reported for the first time in 1977 (Scheme 1.1).⁴⁸



Scheme 1.1. The first report on Negishi coupling reaction.⁴⁸

Number of methodologies have been presented to synthesize fused PAHs but they have some limitations. Swager and co-workers reported promising synthetic pathway to synthesize

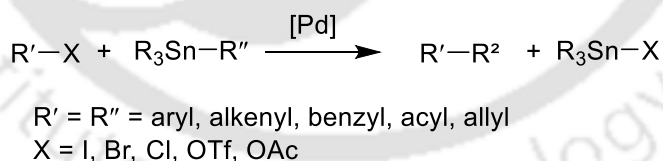


Scheme 1.2. Synthesis of PAHs through Negishi coupling reaction.⁶³

fused PAHs **1.24** where one of the step is Negishi coupling reaction.^{63a} Boron doping PAHs have versatile applications in materials and coupling reactions are the most suitable to functionalize the boron doping compounds. The boron doped PAH compound **1.24** was prepared by Negishi coupling reaction of **1.25** with **1.26** and ZnCl_2 in the presence of $\text{Pd(PPh}_3)_4$.^{63b} Hetero atom containing polycyclic aromatic hydrocarbons (**1.30a-d**) were synthesized through Negishi coupling reaction of zincated dichloropyrimidine with sulfonium salts by Heck group in 2022.^{63c}

1.2.2. Stille cross-coupling reaction

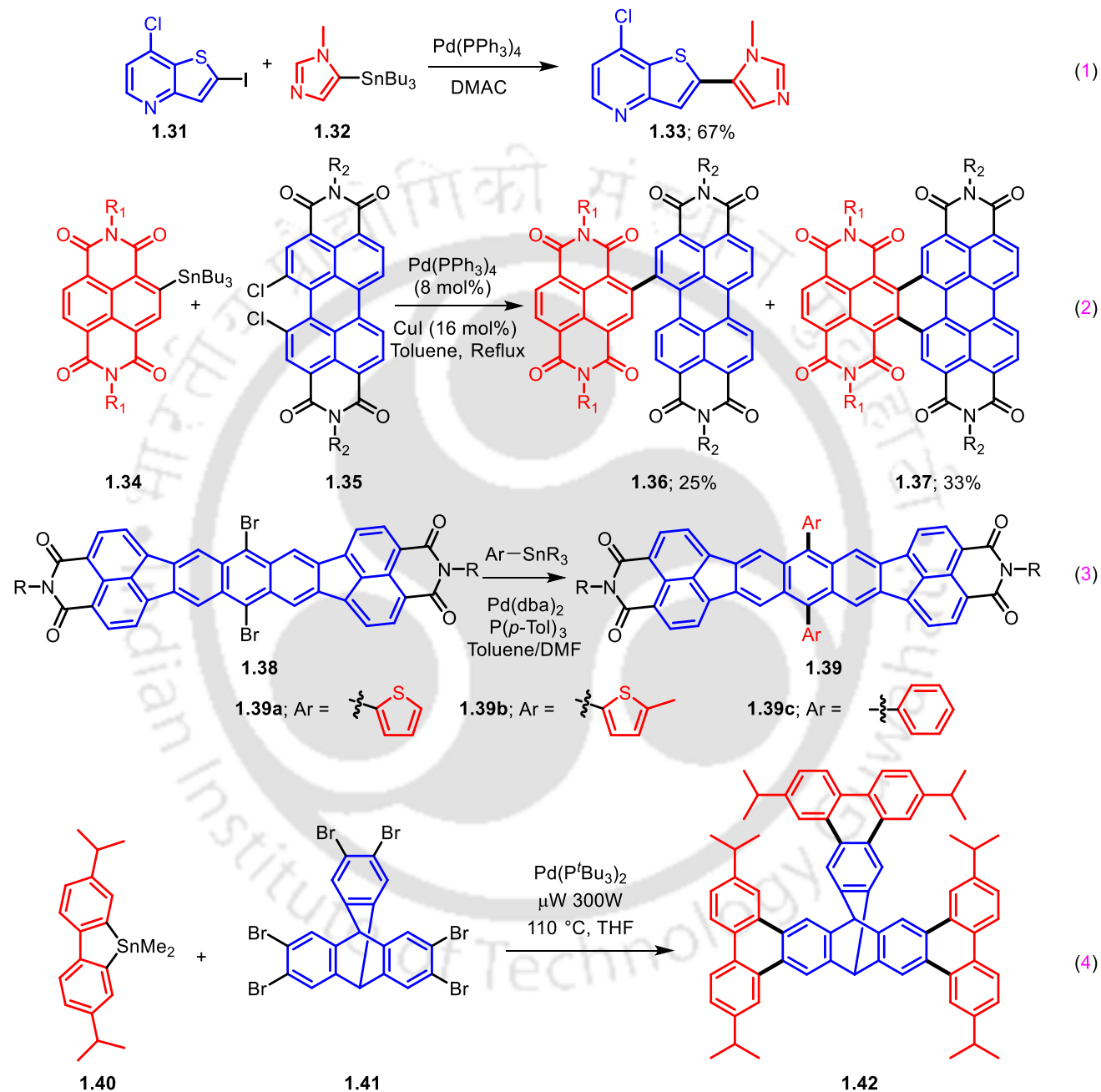
In 1977, Kosugi and co-workers reported the C-C bond formation for the first time of acid chloride/aryl halide and organostannanes in the presence of Pd-catalyst which was further significantly developed as a tool in the organic synthetic chemistry by Stille (Scheme 1.3).⁵⁰ In 2010, Stille was awarded Nobel Prize in chemistry for the Pd-catalyzed coupling reaction. Stille coupling reaction is the most powerful synthetic protocol for the synthesis of five and six member heterocyclic and carbocyclic macromolecules through formation of intermolecular C-C bond.⁶⁴ The main drawback of the process is that, tin compounds are poorly soluble in water owing to their low polarity, toxic and rapid development of other alternative coupling reactions by palladium.⁶⁴ This synthetic methodology is well-suited to synthesize complex molecules such as natural products due to high selectivity and versatile scope.⁶⁴ The reaction conditions are mild and various functional group tolerance is exhibited, apart from the fact that organostannanes are stable in moisture and oxygen, which allows one to perform the reaction at harsh and non-inert conditions.⁶⁴



Scheme 1.3. Schematic representation of Stille coupling reaction.⁵⁰

Many groups have attempted to synthesize imidazole thienopyridine (**1.33**) at large scale by applying various cross-coupling reactions but Ragan and co-workers were successful in obtaining **1.33** in the presence of $\text{Pd(PPh}_3)_4$ as catalyst, starting from **1.31** and **1.32**.⁶⁵ Wang group reported the preparation of NDI based PAHs compound (**1.36** and **1.37**) by the Stille coupling employing the mixture of $\text{Pd(PPh}_3)_4$ and CuI as catalyst from 1,12-dichlorinated perylene diimide (**1.35**) and organostannane **1.34**.⁶⁶ The synthesis of fused polycyclic compounds **1.39a-c** from **1.38**

and aryltin in the presence of $\text{Pd}(\text{dba})_2$ as catalyst were reported by Jenekhe and co-workers.⁶⁷ In 2011, King demonstrated that Stille coupling reaction is the most suitable coupling reaction than others to synthesize compound **1.42**.⁶⁸

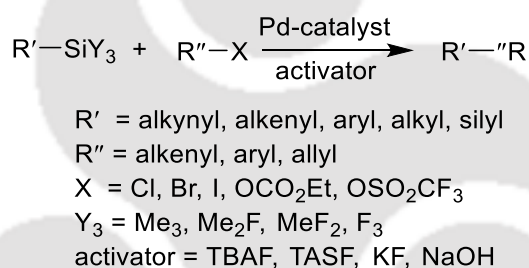


Scheme 1.4. A few PAHs synthesized by Stille coupling reaction.⁶⁵⁻⁶⁸

1.2.3. Hiyama cross-coupling reaction

In 1981, Hiyama started working on the activation of C-Si and Si-Si bond in presence of fluoride.⁵¹

Later, he investigated the coupling reaction of aryl halide and organosilanes employing Pd catalyst in presence of activator fluoride which afforded the C-C coupling product (Scheme 1.5)⁵¹ Fluoride ion coordinates with silicate instead of palladium to form pentacoordinated silicate which accelerates the transmetalation step to complete the coupling cycle.^{51, 69} The activator fluoride can be replaced by other heteroatom substituents such as hydroxyl and alkoxy. Hiyama coupling reaction is preferable for C-C bond formation as organosilicon molecules are stable in nature due to low polarized C-Si bond, are inexpensive, commercially available, and less toxic. The mostly used halides are aryl iodide and bromide than the aryl chloride⁷⁰ and predominantly organosilane used is aryl(alkoxy)silane.⁷¹ Researchers have developed efficient synthetic methodology of Hiyama coupling with varying catalyst or combination of catalyst and ligand (Scheme 1.6)⁷⁰⁻⁷² According to my knowledge, synthesis of PAHs in a single step multi-fold Hiyama coupling reaction has not been reported.

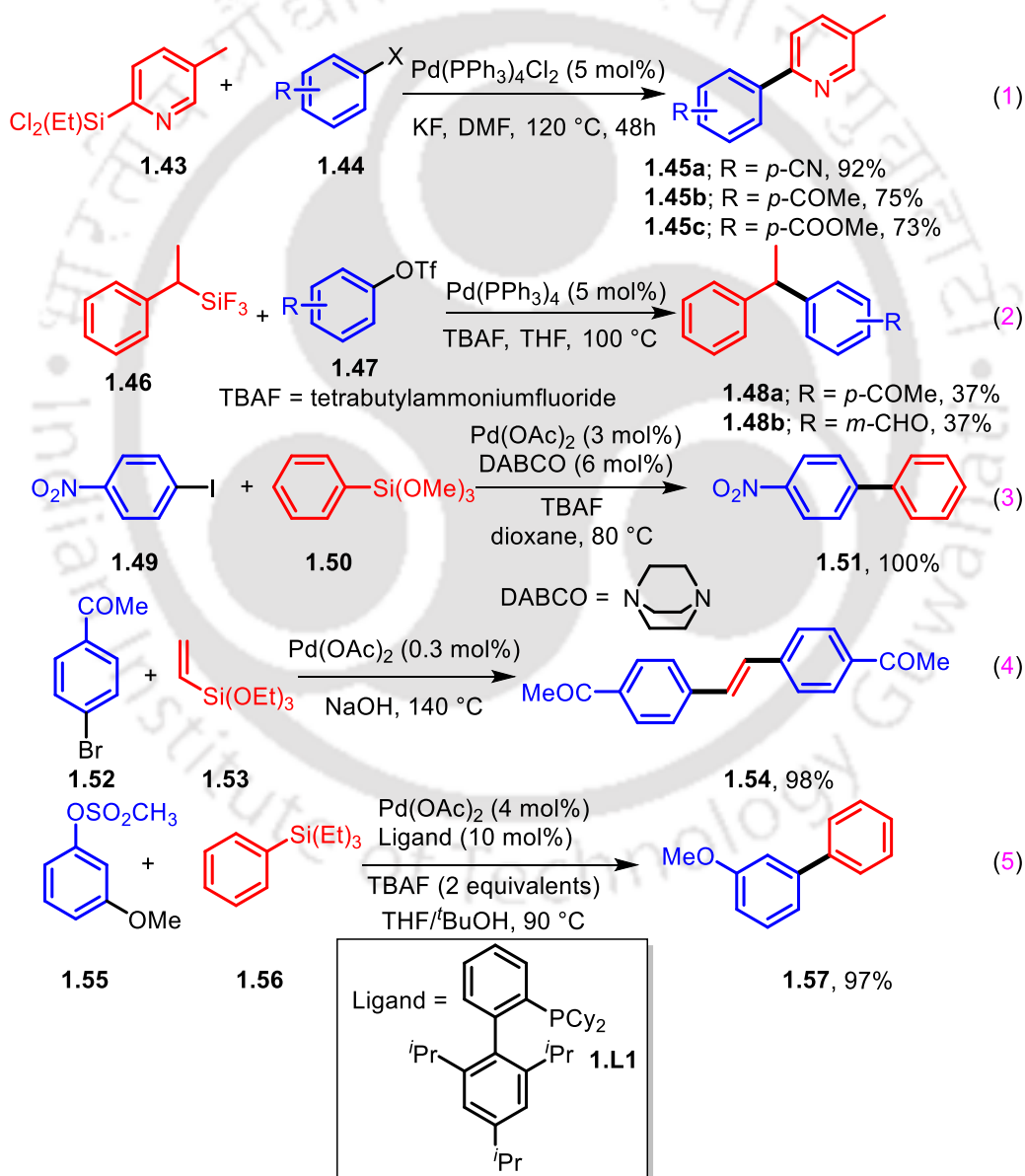


Scheme 1.5. Hiyama coupling reaction.⁵¹

1.2.4. Kumada cross-coupling reaction

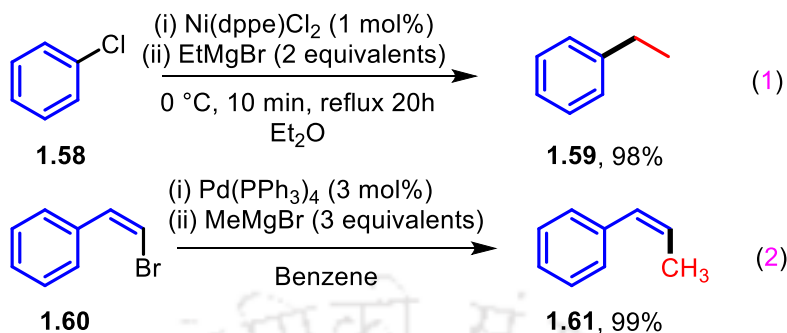
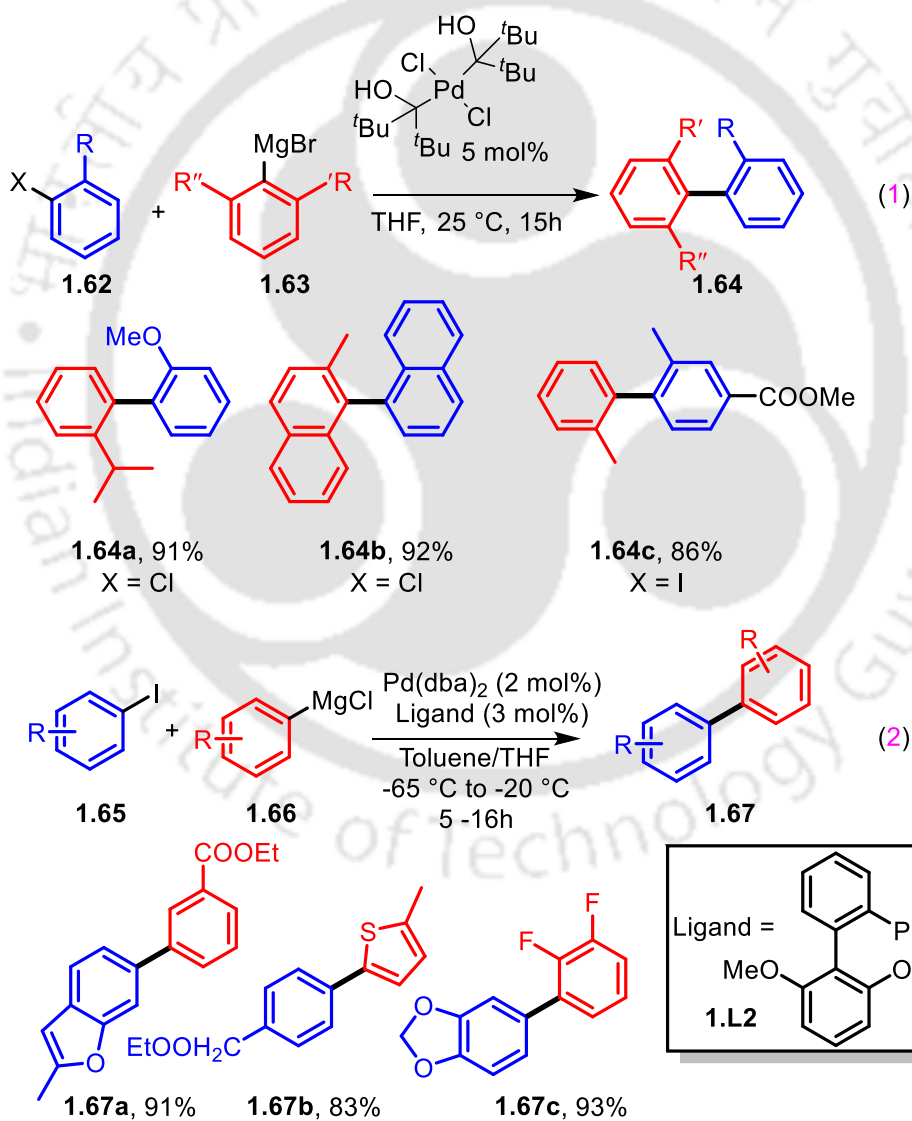
In 1972, Kumada and co-workers discovered the C-C coupling reaction of Grignard reagent with aryl, vinyl and alkyl halide in the presence of Ni catalyst (equation 1, Scheme 1.7).^{52, 73} It was path breaking discovery to form C-C bond which was followed by other coupling reactions such as Suzuki and Sonogashira in the following year. In 1975, Kumada cross coupling reaction was performed in the presence of palladium catalyst by Murahashi and co-workers (equation 2, Scheme 1.7).⁷⁴ Versatile Grignard reagent can be easily synthesized by exchange reaction of metal and halide (I, Br, Cl). The advantage of nucleophilic coupling partner Grignard reagent is its low cost and easy availability. Palladium catalyst are more reactive than nickel catalyst in this reaction but nickel catalysts are preferred when the reactivity is same for both because latter is inexpensive. The homo-coupling product can be formed as a byproduct when reaction is performed in the absence of ligand or presence of labile ligand.⁷⁵ In 2001, Li and co-workers demonstrated that enhanced

the reactivity of deactivated aryl chloride with Grignard reagents in presence of ligand phosphinous acid.⁷⁶ Later, Wolf group reported Kumada coupling reaction in presence of Pd-phosphinous acid catalyst to obtain sterically crowded biaryls with high yields (83-98%) from *ortho*-substituted aryl bromides or chlorides and mono- and di-substituted arylmagnesiumbromide (equation 1, Scheme 1.8).⁷⁷ Martine and Buchwald reported the palladium catalyzed coupling reaction of aryl iodide and Grignard reagents in the presence of biaryl phosphine ligands (equation 2, Scheme 1.8).⁷⁸ To best of my knowledge, synthesis of PAHs in a single step multi-fold Kumada coupling reaction has not been reported.

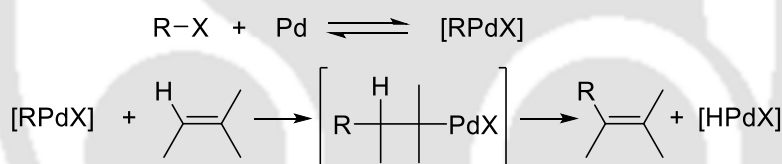


Scheme 1.6. Few example of Hiyama coupling reaction.⁷⁰⁻⁷²

1.2.5. Heck cross-coupling reaction

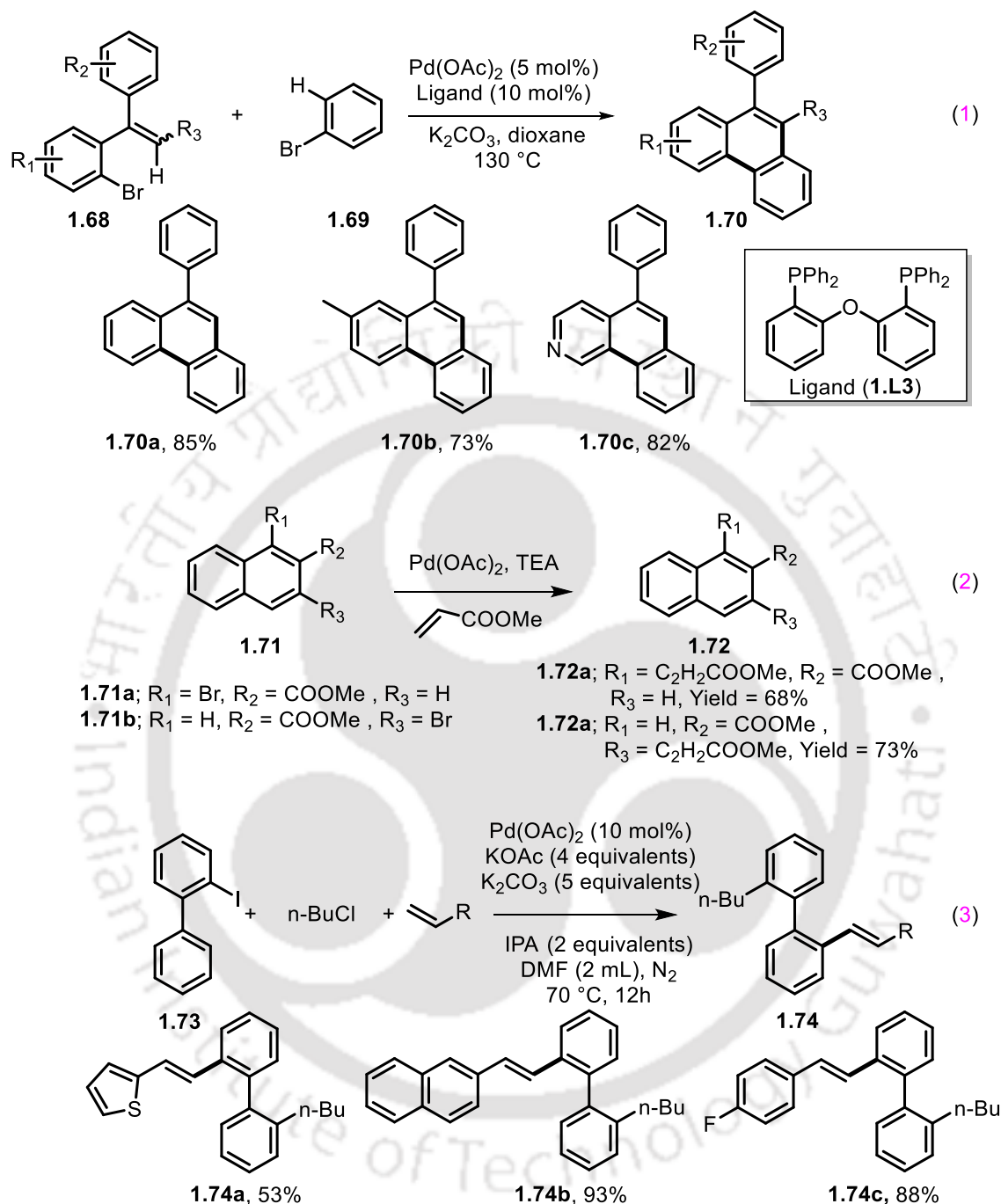
Scheme 1.7. Kumada cross coupling reaction.^{75,74}Scheme 1.8. Few synthetic protocol reported for Kumada coupling reaction.⁷⁷⁻⁷⁸

Over five decades ago, Mizoroki and Heck independently developed arylation of olefinic bonds through C-C coupling reaction in the presence of palladium catalyst (Scheme 1.9).^{53, 79} Due to its high effectiveness, simplicity, excellent chemoselectivity, mild reaction conditions and affordable nature it has received a lot of attention. Olefins from a wide range of sources, such as derivatives of acrylates, styrenes, or intramolecular double bonds, can be employed in the Heck reaction, which is described as an arylation or vinylation of olefins. In addition to the conventional aryl iodides and bromides, several aryl halide variations have been created, including aromatic triflates, aroyl chlorides, aryl sulfonyl chlorides, aromatic diazonium salts, aroyl anhydrides, and aryl chlorides and arylsilanols.⁸⁰ The catalyst is a crucial component of a reaction where a wide range of metals and ligands are examined. Palladium is typically preferred metal owing to its tolerance of a wide range of functional groups and its exceptional capacity to build C-C bonds between adequately functionalized substrates.^{53, 81} The majority of palladium-based reaction proceed with outstanding yields, stereo- and regioselectivity.^{80c} Typically, in the Heck reaction, the less crowded structure is favoured and frequently favours a *trans* product.^{80c}



Scheme 1.9. General protocol of Heck reaction.^{53, 79}

Lin and co-workers developed a direct and modular method to access polycyclic aromatic hydrocarbons compounds (**1.70**) by sequentially cross-coupling and annulating two distinct aromatic bromides (equation 1, Scheme 1.10).⁸¹ Li group reported the synthesis of *o*-carboxyvinyl naphthoates **1.72** by Heck reaction in the presence of Pd(OAc)₂ (equation 2, Scheme 1.10).⁸² Utilizing the different reactivities of a palladacycle and an acyclic arylpalladium species, a novel sequential difunctionalization process of 2-iodobiphenyl has been reported by Zhang.⁸³ In this reaction, selectively alkyl halide reacted with dibenzopalladacyclopentadiene which is formed *in-situ*, and the resulting acyclic arylpalladium species then reacts selectively undergoing Heck reaction with an alkene while resulting in the formation of difunctionalized biphenyl product **1.74** (equation 3, Scheme 1.10).⁸³ According to my knowledge, synthesis of PAHs in a single step multi-fold Heck coupling reaction has not been reported.



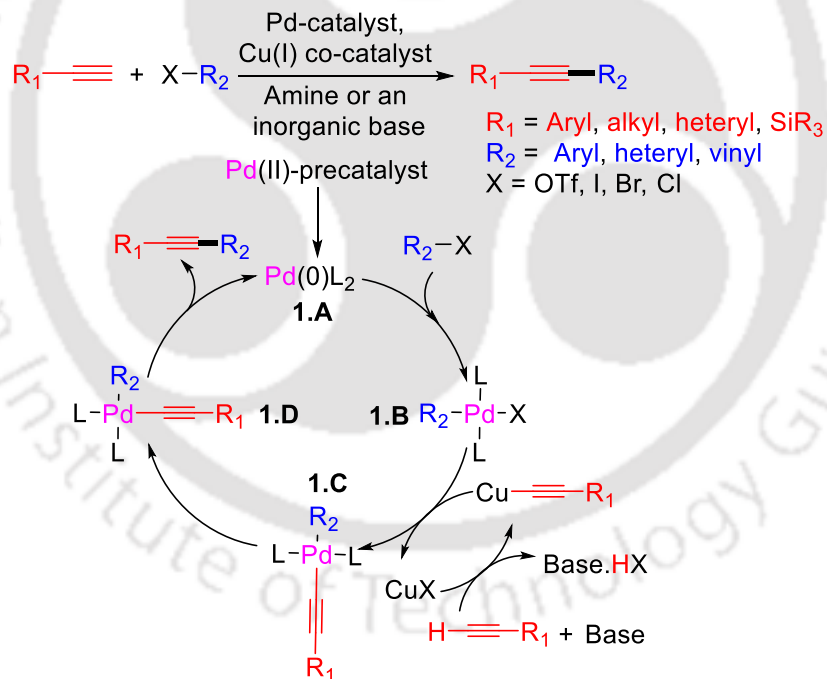
Scheme 1.10. Heck reaction to synthesis of polycyclic aromatic hydrocarbons.⁸¹⁻⁸³

1.2.6. Sonogashira cross-coupling reaction

The Sonogashira reaction is one of the most important reactions in synthetic organic chemistry which is extensively used to carry out C-C bond formation. This reaction is simple to execute, gives high yield and is efficient while being tolerant to the other functional groups.⁸⁴

In 1975, Sonogashira, Tohda, and Hagihara observed that catalytic amounts of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in combination with CuI as a co catalyst brought about the C-C bond formation when haloarenes were reacted with acetylene in the presence of amine as a base (Scheme 1.1).⁵⁴ In these so-called Sonogashira reactions, terminal sp hybridized carbon of alkynes combine to form a bond with the sp^2 (or even sp^3) hybridized carbons present in alkyl halide, aryl halide, and vinyl halides. Cassar,⁸⁵ Dieck and Heck⁸⁶ reported that the reaction can be achieved by using only the palladium catalyst, but it requires a higher temperature.

It is however noteworthy that the Sonogashira reaction is more facile and productive under inert conditions in the presence of the co-catalyst Cu(I) that acts as a mediator for the alkyne transmetalation step in the catalytic reaction pathway. In the presence of oxygen, the copper-mediated reaction leads to the formation of alkyne homo-coupling product, which is known as Hey/Glasser reaction.⁸⁷



Scheme 1.11. General representation of a Sonogashira coupling reaction and the associated mechanism.

The exact mechanism of the Sonogashira reaction is not correctly understood because of the challenges associated with the analysis of the two catalytic cycles involving palladium and copper. It is supposed that in the catalytic cycle of palladium, the cycle starts from the catalytically

active species $\text{Pd}(0)\text{L}_2$ (**1.A**, Scheme 1.1), which is readily formed from the $\text{Pd}(\text{II})$ precursor such as $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$. The catalytically active species is stabilized by base or solvent. In the first and rate-determining step, aryl halide or vinyl halide undergoes oxidative addition to the active catalyst. Subsequently, $\text{R}_2\text{L}_2\text{Pd}(\text{II})(\text{C}_2\text{R}_1)$ (**1.C**, Scheme 1.1) is formed through the transmetalation with copper-acetylide that is formed in the parallel catalytic cycle involving copper. The product is formed and $\text{Pd}(0)\text{L}_2$ (**1.A**, Scheme 1.1) is regenerated in a reductive elimination that follows a *cis/trans* isomerization step (**1.D**, Scheme 1.11).

1.2.6.1. Ethynyl bridged PAHs via Sonogashira coupling

The geometry of the compounds play a great role in conducting as well as photophysical properties.⁸⁸ The ethynyl unit decreases the torsional barrier which indicates that the aromaticity and electricity do not diminish significantly even when it moves away from planarity. This is in

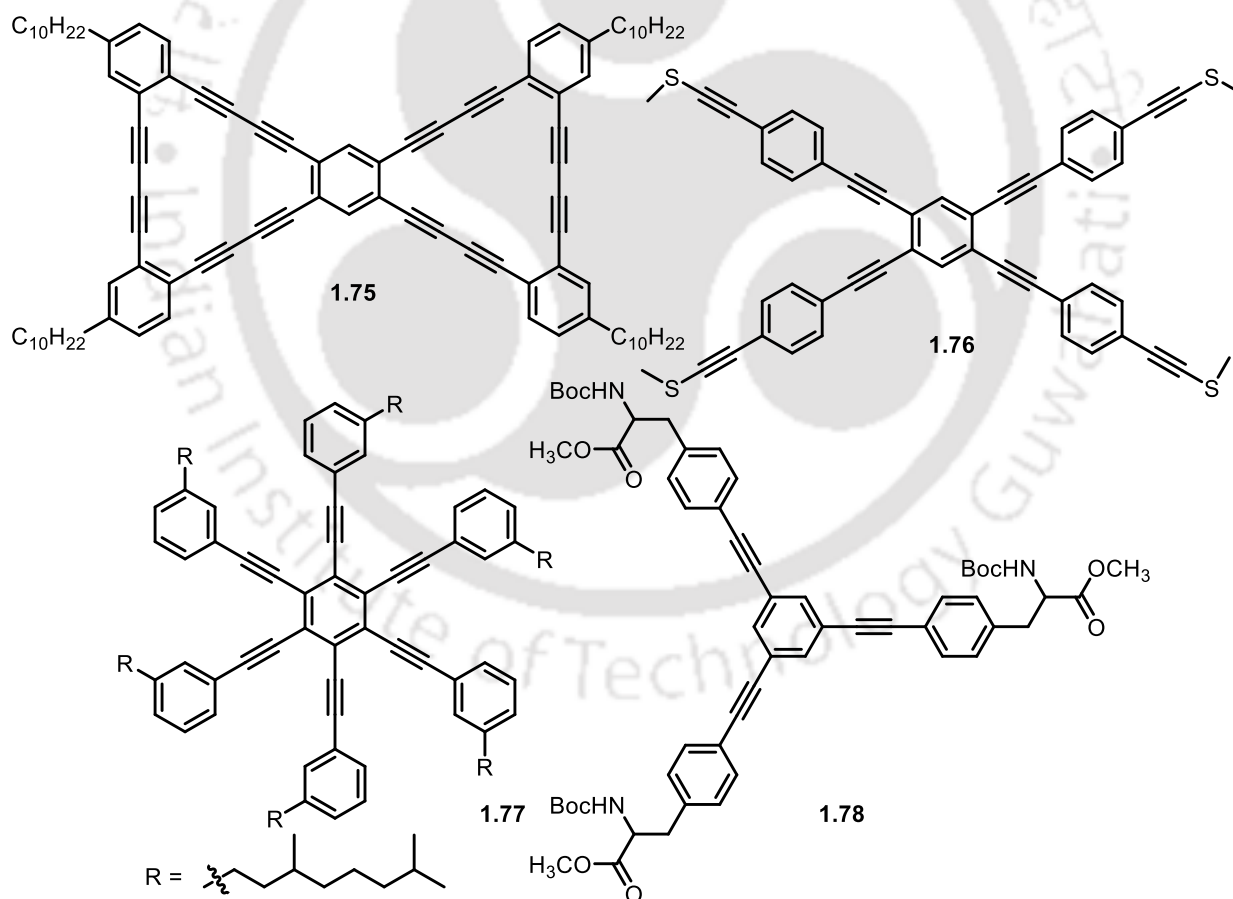
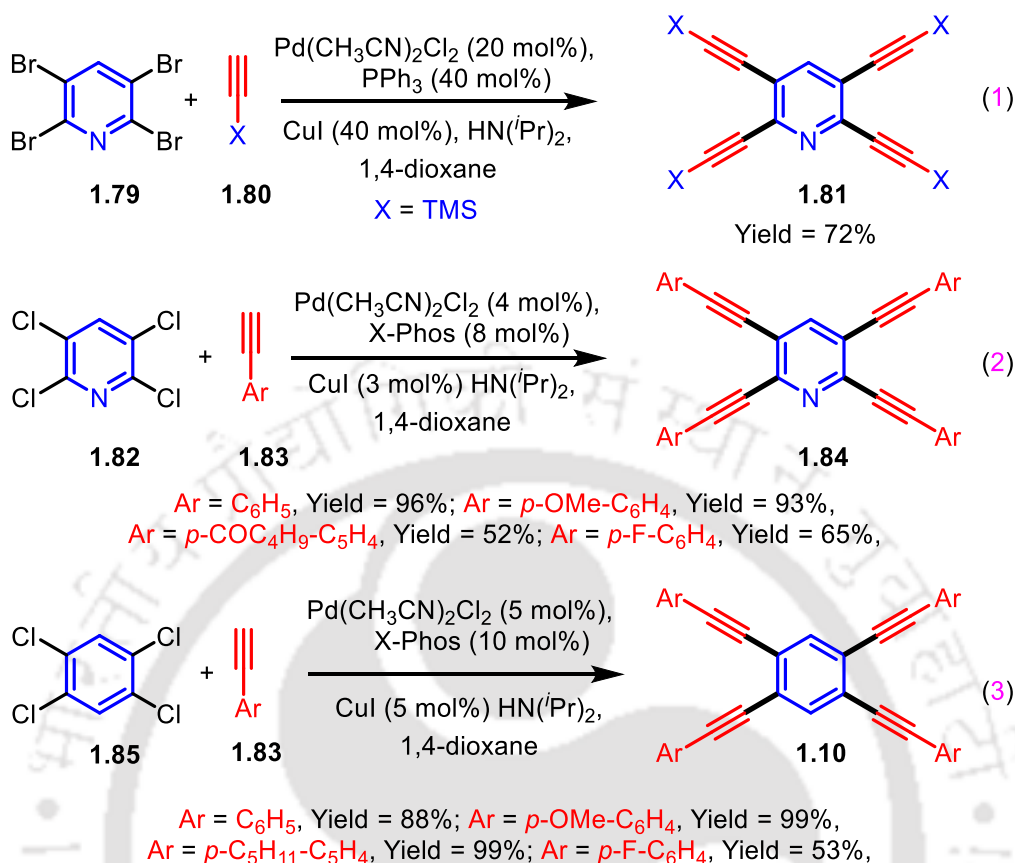


Figure 1.7. Few example of alkynylated PAHs for (a) graphidyne⁹⁷ (**1.75**), (b) nanoparticle⁹⁵ material (**1.76**), (c) liquid crystal compound⁹⁸ (**1.77**) and dendritic material (**1.78**).⁹⁹

stark contrast to other extended π -conjugated groups where the electric conductivity decreases drastically.⁸⁹ The ethynyl unit containing PAHs show bathochromic shift compared to other PAHs in absorption as well as in emission spectra.⁹⁰ The efficiency of acetylenic containing compounds are significantly higher than olefinic containing compounds in bulk hetero-junction (BHJ) solar cells.⁶ By the introduction of the ethyne group, the degree of π -conjugation, thermal stability of the molecules, efficiency of fluorescence and planarity of the molecules are enhanced, which are necessary for effective charge transport and intermolecular interaction.^{14a,91} Due to the increase in the charge transport mobility and efficiency of fluorescence, ethyne bridged compounds are excellent materials for the organic light emitting diodes (OLEDs), liquid crystals, charge transport applications^{4-5,14a,47, 92} and in linear as well as non-linear optical materials.⁹³ These factors have triggered the interest of researchers in the study of extended alkynyl bridged PAHs.⁹⁴ Other applications of polyethynylated PAHs include nanoparticle stabilization,⁹⁵ supramolecular self-assemblies,⁹⁶ and 2D-carbon allotropes building blocks like graphdiyne⁹⁷ which are the core structures for liquid crystals⁹⁸ and dendritic materials (Figure 1.7).⁹⁹ Polyethynylated PAHs also play a pivotal role in safety as they are selective in detection of nitro-aromatic compounds which are not only explosives but also environmental pollutants.^{36b,45,100}

An intriguing method of electronic stabilization is the integration of main group elements (B, N, Si, P, and S) into conjugated PAHs.¹⁰¹ Moreover, the various electrical properties of the main group elements can endow π -conjugated molecules a variety of unique and fascinating properties. The thiophene ring's high aromaticity enhances the benzenoid character, reduces the HOMO energy level, and widens the HOMO-LUMO band gap, which improves the systems' photostability and thermal stability.¹⁰² Furthermore, favoured face-to-face π -stacking patterns are induced by weak intermolecular S-S interactions in the solid state, which can enhance molecular electronic coupling and enable charge and energy transport.¹⁰³

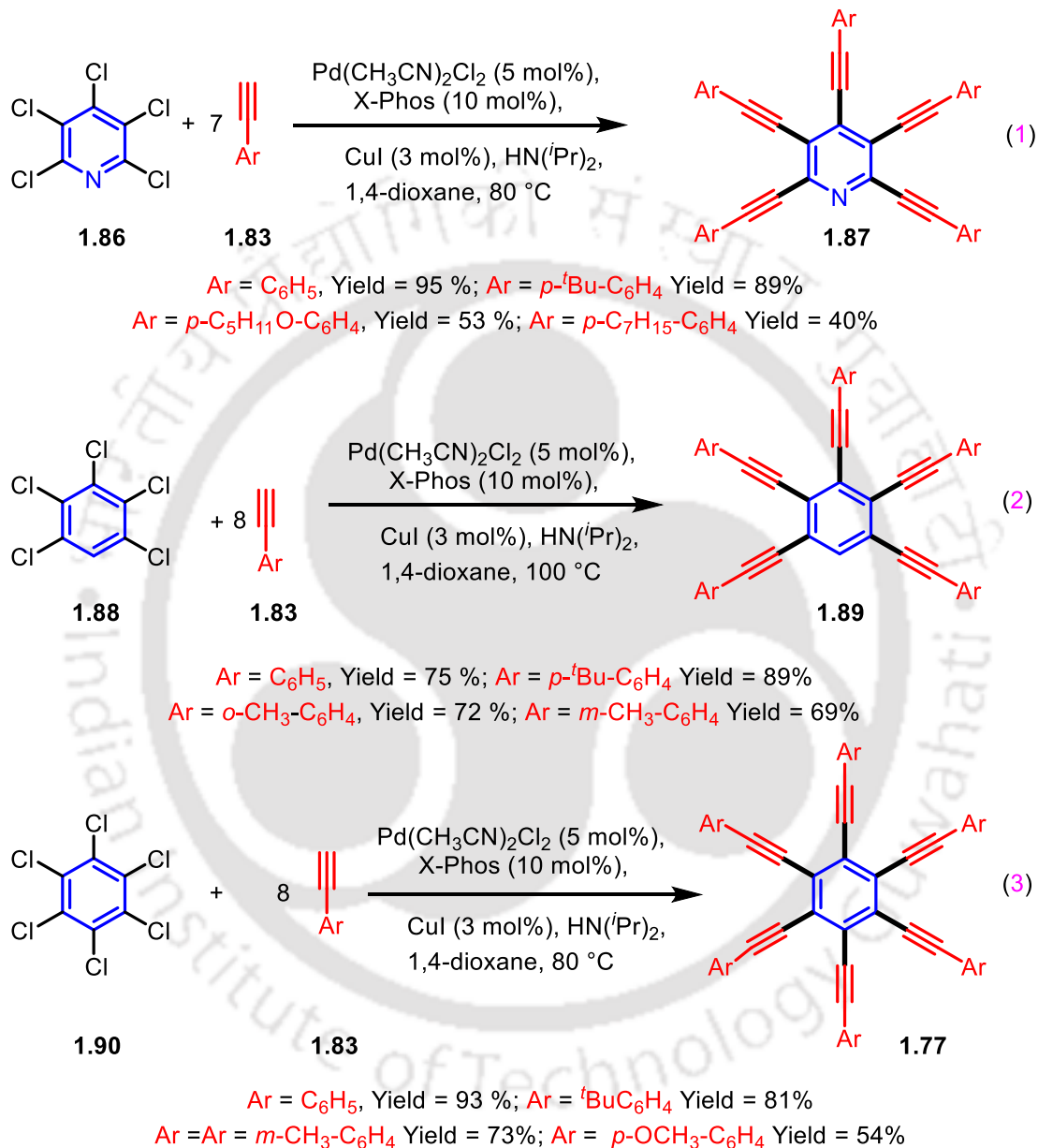
While there are numerous reviews on the chemistry, photophysical properties^{39a,58e,104} and optoelectronic applications^{58d,105} of several π -conjugated molecules and organic polymers, the corresponding studies with polyethynylated PAHs remains sparsely reviewed.¹⁰⁶ In this context, a portion of the current chapter focuses on the synthesis, photophysical properties and applications of polyethynyl containing PAHs. The versatile chemistry of ethynyl bridged PAHs offers immense promise in a plethora of applications.



Scheme 1.12. Synthesis of tetraethynylpyridine and tetraethynylbenzene by multi-fold Sonogashira cross-coupling catalyzed by Pd(CH₃CN)₂Cl₂/CuI.^{52,107}

The synthesis of the 2,3,5,6-tetraalkynylatedpyridine (**1.81**) from 2,3,5,6-tetrabromopyridine (**1.79**) by one step multi-fold Sonogashira cross coupling reaction with seven equivalents of trimethylsilyl (TMS) acetylene (**1.80**) was first reported by the Vollhardt group (Scheme 1.12).¹⁰⁷ The reaction was catalyzed by Pd(CH₃CN)₂Cl₂ (20 mol%) in the presence of PPh₃ (40 mol%) and CuI (20 mol%) as co-catalyst with HN(*i*Pr)₂ as the base. Under otherwise identical conditions, Langer and co-workers developed an alternative synthetic protocol using one-fifth the amount of Pd catalyst and 2-dicyclohexylphosphino-2,4,6- triisopropylbiphenyl (X-Phos) instead of PPh₃ in dioxane to synthesize **1.84** via the Sonogashira cross-coupling of 2,3,5,6- tetrachloropyridine (**1.82**) with five equivalents of **1.83** (Scheme 1.12). The studies were extended to obtain 2,3,5,6-tetraalkynylatedbenzene (**1.10**) from the corresponding Sonogashira cross-coupling of 2,3,5,6-tetrachlorinatedbenzene (**1.84**) with aryl acetylene (**1.83**) (Scheme 1.12).⁵² Excellent yields of **1.10** were obtained when 5 mol% of Pd(CH₃CN)₂Cl₂ was used along with eight equivalents of **1.83**. In

comparison with electron-withdrawing groups, electron donating substituents on **1.82** significantly improved the yields of **1.84** and **1.10**. This is attributed to the fact that the electron withdrawing group decreases the nucleophilicity of acetylenic unit in transmetalation step.



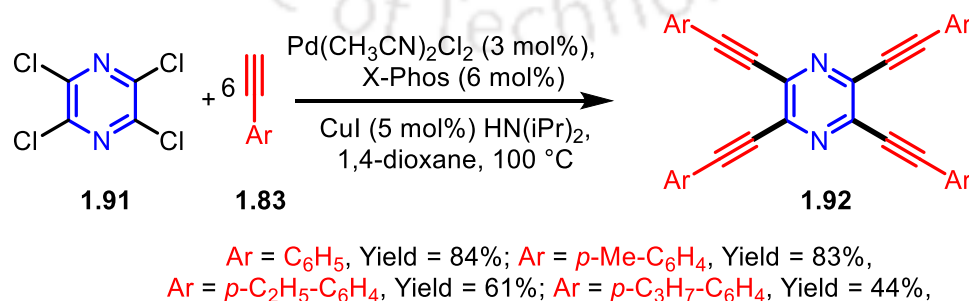
Scheme 1.13. Synthesis of pentaethynylpyridine pentaethynylbenzene and hexaethynylbenzene by multi-fold Sonogashira cross-coupling catalyzed by Pd(CH₃CN)₂Cl₂/CuI.¹⁶

In the same year as Vollhardt,¹⁰⁷ Langer¹⁶ independently has demonstrated a multi-fold

Sonogashira coupling strategy to synthesize hexaalkynebenzene (**1.77**), pentaalkynebenzene (**1.89**), and pentaalkynepyridine (**1.87**) from the respective polychlorinated precursors under identical conditions as discussed for synthesis of **1.77** (Scheme 1.13).¹⁶ Notably, in these synthetic protocols, multiple C-C bonds are formed and less than 1 mol% Pd-catalyst are required for a single C-C bond formation.

Buchwald and Beller have reported that CuI inhibits the single-step Sonogashira reactions while using monochloroarenes as starting materials.¹⁰⁸ However the studies carried out using the protocol developed by Langer¹⁶ proved that CuI co-catalyst is necessary for the multi-fold Sonogashira reaction of polychlorobenzene, and polychloropyridine precursors. The reaction time for the alkylalkyne substituents (20 h) are longer than the arylalkyne substituents (8–20 h). While pyridine core is present as in **1.86**, the C-C bond is first formed at 2- and 6-position, followed by the 4-position and then finally at the 3- and 5- positions.¹⁶ This selectivity was demonstrated by the use of 2.4 equivalents alkyne **1.83** in the reaction with **1.86** which led to penta(ethynyl) pyridine **1.87** as the major product along with minor amounts of 3,4,5-trichloro-2,6-bis(ethynyl)pyridine. While **1.77** having a benzene core is formed in 36% yield, the corresponding pyridine core compound **1.87** was obtained in 95% yield under identical conditions at 80 °C. Better electron withdrawing effect of pyridine core in **1.86** ensures a lower barrier for the rate determining oxidative addition step in comparison with **1.90** that has a benzene core moiety. Higher yields (up to 93%) of **1.77** could be obtained by extending the reaction time (20 h) and by operating at an elevated temperature (100 °C).

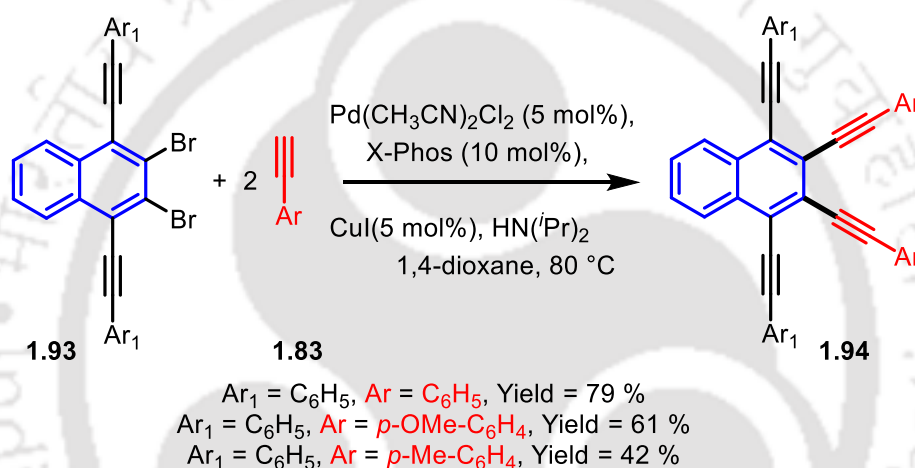
Langer went on to synthesize 2,3,5,6-tetraethynylpyrazine (**1.92**) via the multi-fold Sonogashira reaction of **1.91** with **1.83** catalyzed by Pd(CH₃CN)₂Cl₂ (3 mol%) + X-Phos (6 mol%) and



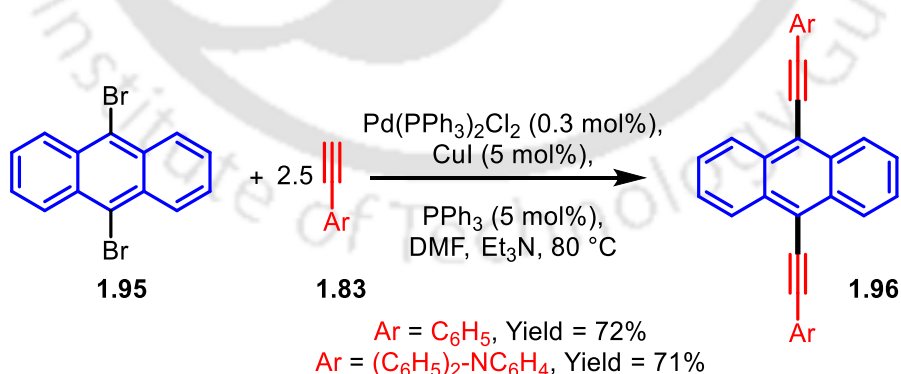
Scheme 1.14. Synthesis of tetraethynylpyrazine by multi-fold Sonogashira cross-coupling catalyzed by Pd(CH₃CN)₂Cl₂/CuI.¹⁰⁹

CuI co-catalyst (5 mol%) in the presence of diisopropylamine using dioxane as solvent at 100 °C (Scheme 1.14).¹⁰⁹ Notably, upon using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (5 mol%) + X-Phos (10 mol%), moderate yields (65%) of **1.92** were obtained in the absence of CuI cocatalyst when phenyl acetylene was used, which increased to 88% in the presence of 5 mol% CuI.

The newly developed multi-fold Sonogashira synthetic protocol was extended by the Langer group to synthesize polyethynylated naphthalene **1.94** from **1.93** (Scheme 1.15).^{14a} While they continued to use $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ as a catalyst and CuI as co-catalyst, they optimized the reaction conditions by varying the phosphine ligands. Among the various phosphines used, the product yields were higher with monodentate phosphine ligands such as X-Phos in comparison



Scheme 1.15. Synthesis of tetraethynylated naphthalene by multi-fold Sonogashira cross-coupling catalysed by $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2/\text{CuI}$.^{14a}

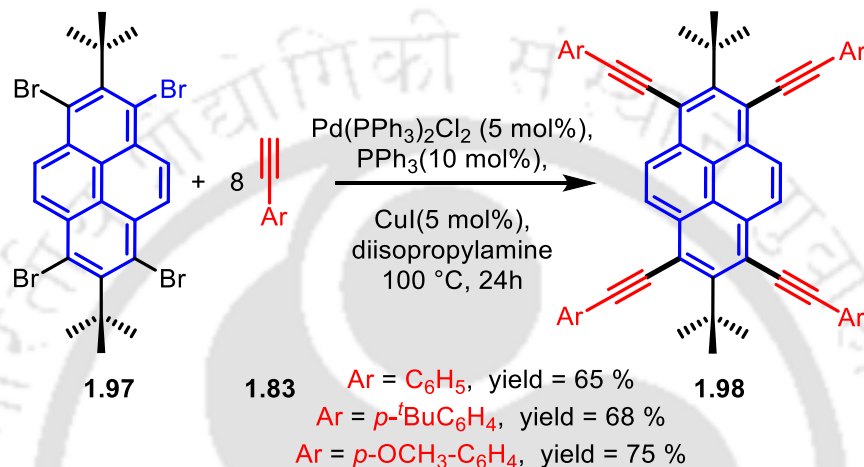


Scheme 1.16. Diethynylanthracene synthesis catalysed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$.¹¹⁰

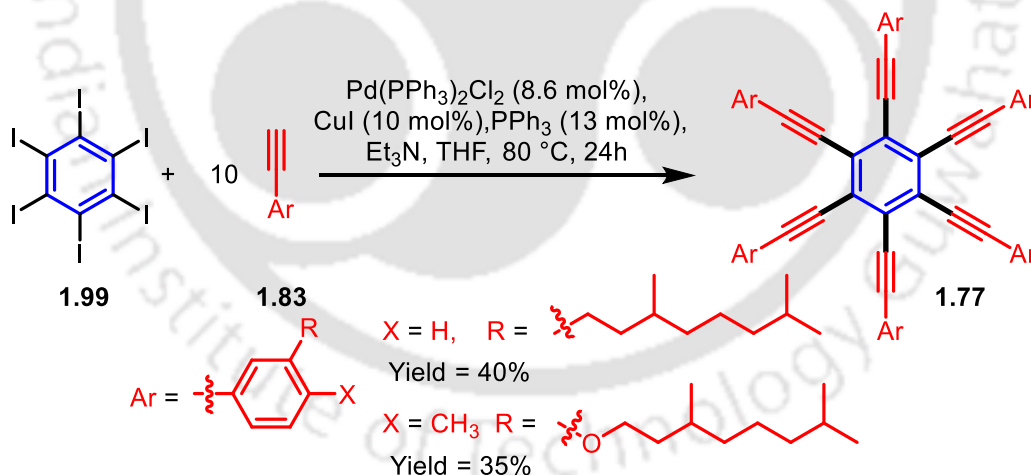
with bidentate phosphine ligands. Further, use of bidentate ligands gave inseparable mixtures of products. Temperature played a key role in the fate of the reaction. Success was obtained only

when the reaction was carried out at 80 °C. While mixture of products are formed at 100 °C, the reaction remained incomplete at 60 °C even after prolonged times.

The alkynylation at 9,10-position of anthracene is widely explored.^{110a, 111} Wang and Grozema have reported the synthesis of 9,10 diarylethynylantracene **1.96** in good to excellent yields starting from 9,10-dibromoanthracene **1.95** and **1.83** by using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2 + \text{PPh}_3$ as catalyst, CuI as a co-catalyst, Et_3N as base and DMF as a solvent at 80 °C (Scheme 1.16).¹¹⁰



Scheme 1.17. Synthesis of polyethynylpyrene catalysed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$.¹⁷

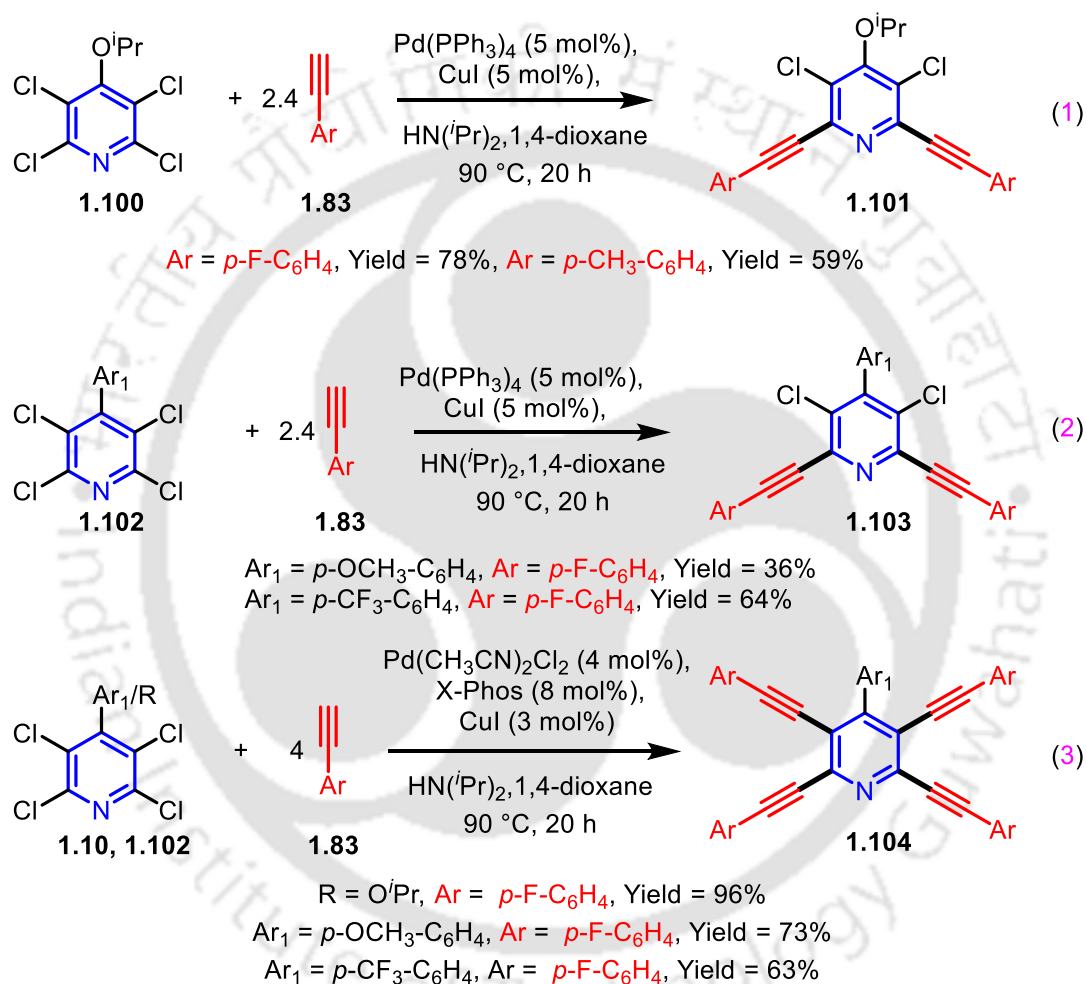


Scheme 1.18. Hexaalkynylatedbenzene synthesis catalyzed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$.¹¹²

There are a few reports on the synthesis of 1,3,6,8- substituted polyalkynylated pyrenes.¹¹³ Yamato and co-workers have reported the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2 + \text{PPh}_3/\text{CuI}$ catalyzed synthesis of tetraalkynylated pyrene **1.98** starting from 1,3,6,8-tetrabromopyrene **1.97** in the presence of diisopropylamine that acts as a base as well as a solvent (Scheme 1.17).¹⁷

In addition to reports by Langer (Scheme 1.13), Takezoe have demonstrated that several other hexa-arylethynylatedbenzene variants of **1.77** could also be obtained *via* the coupling of hexaiodo benzene **1.99** with aryl alkynes such as **1.83** that are catalyzed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2 + \text{PPh}_3$ /CuI in the presence of Et_3N and THF (Scheme 1.18).¹¹²

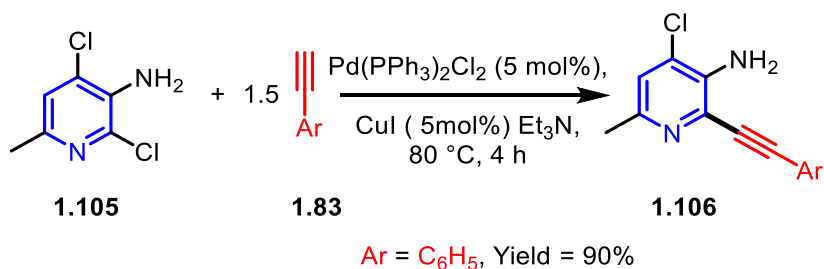
1.2.6.2. Site-selective Sonogashira reaction



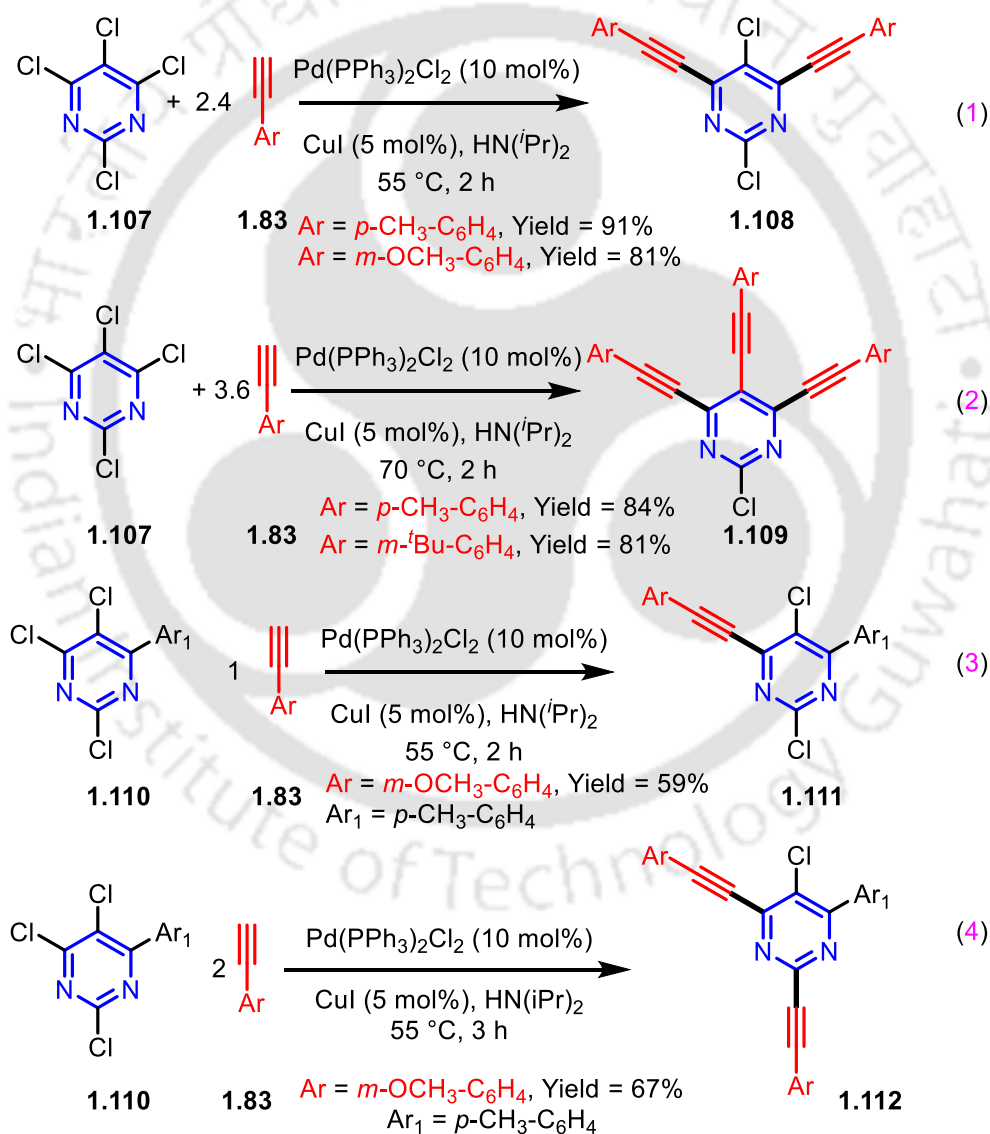
Scheme 1.19. Site-selective Sonogashira reaction catalyzed by $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ and $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2/\text{CuI}$.⁷⁵

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In many instances during the synthesis of the polyalkynylatedpyridine compounds, the Langer group observed site-selectivity in the Sonogashira reactions (equation 1, Scheme 1.19).¹¹⁴ Starting from 4-isopropoxy-2,3,5,6-tetrachloropyridine **1.100**, the 2,6-dialkynylated product **1.101** could be selectively obtained.

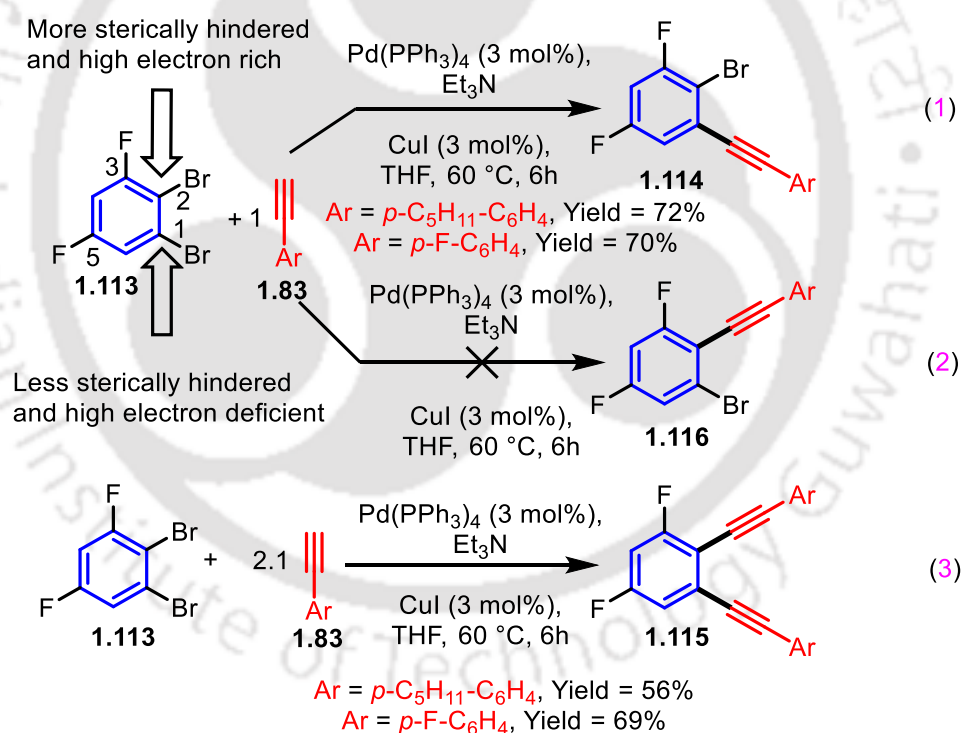


Scheme 1.20. Site-selective Sonogashira coupling at 2-position of 2,4-dihalopyridine that is catalyzed by Pd(PPh₃)₂Cl₂/CuI.¹¹⁵



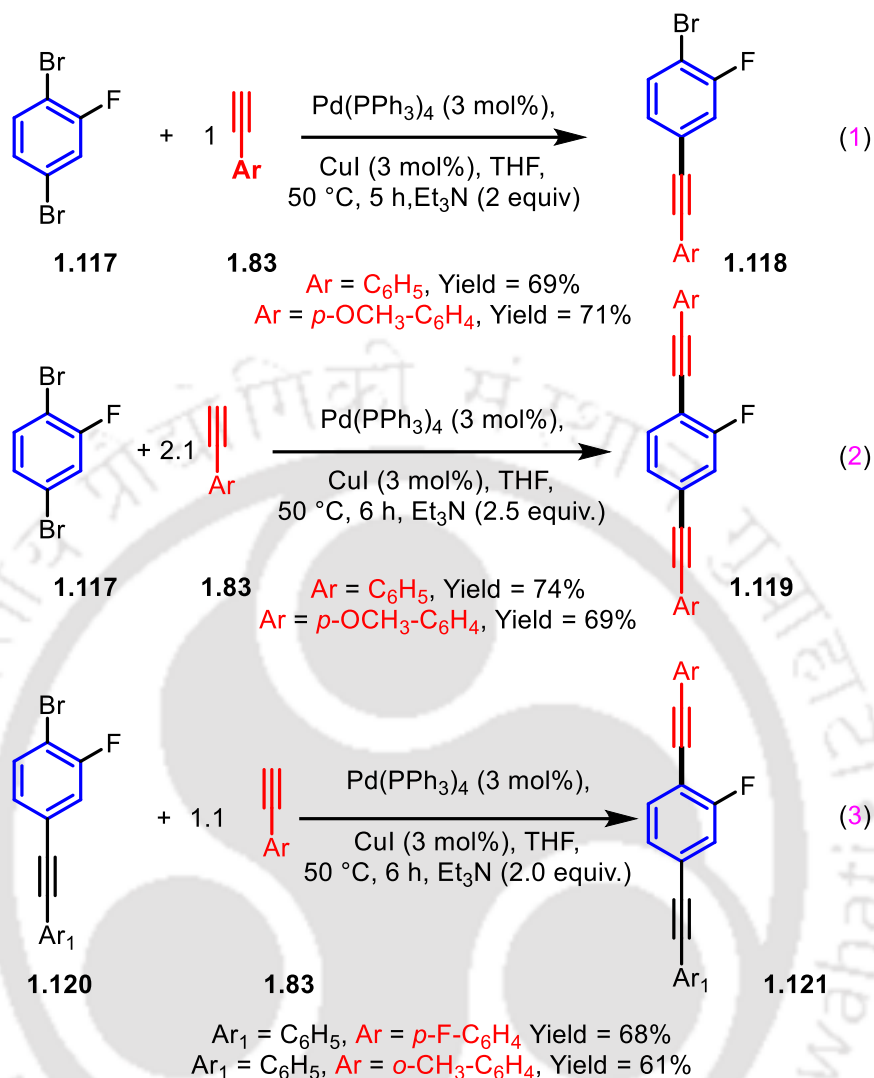
Scheme 1.21. Synthesis of alkynylated pyrimidine compounds via site-selective Sonogashira coupling catalyzed by Pd(PPh₃)₂Cl₂/CuI.¹¹⁶

Presence of isopropoxy group at the 4-position plays a dual role by not only making the 3,5-positions more electron rich and less susceptible to oxidative addition but also by increasing the steric bulk to disfavor the possibility of alkynylation (equation 1, Scheme 1.19). The reactivity of catalysts $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2 + \text{PPh}_3$ were similar. The product yields are higher with alkynes containing electron-withdrawing aryl groups than with alkynes having electron-donating aryl groups (equation 1, Scheme 1.19). Furthermore, electron-donating groups at the 4-position of 2,3,5,6-tetrachloropyridine derivative **1.102** gave lower yield of products in comparison to those with electron deficient group at 4-position (equation 2, Scheme 1.19).¹¹⁴ Notably, tetraalkynyl pyridine **1.104** could be obtained when four equivalents of the alkyne were used in the presence of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (4 mol%) and electron-rich monodentate phosphine ligand X-Phos (8 mol%) (equation 3, Scheme 1.19).⁷⁵ The corresponding reaction hardly took place when $\text{Pd}(\text{PPh}_3)_4$ was used as a catalyst.⁷⁵



Scheme 1.22. Synthesis of fluorinated mono and dialkynylbenzene derivatives through site-selective Sonogashira coupling catalyzed by $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$.¹¹⁷

In 2000, Norman and co-workers reported the catalytic site-selective Sonogashira coupling at 2-position of 2,4-dihalopyridine **1.105** to give **1.106** in excellent yield (90%) in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$ (Scheme 1.20).¹¹⁵

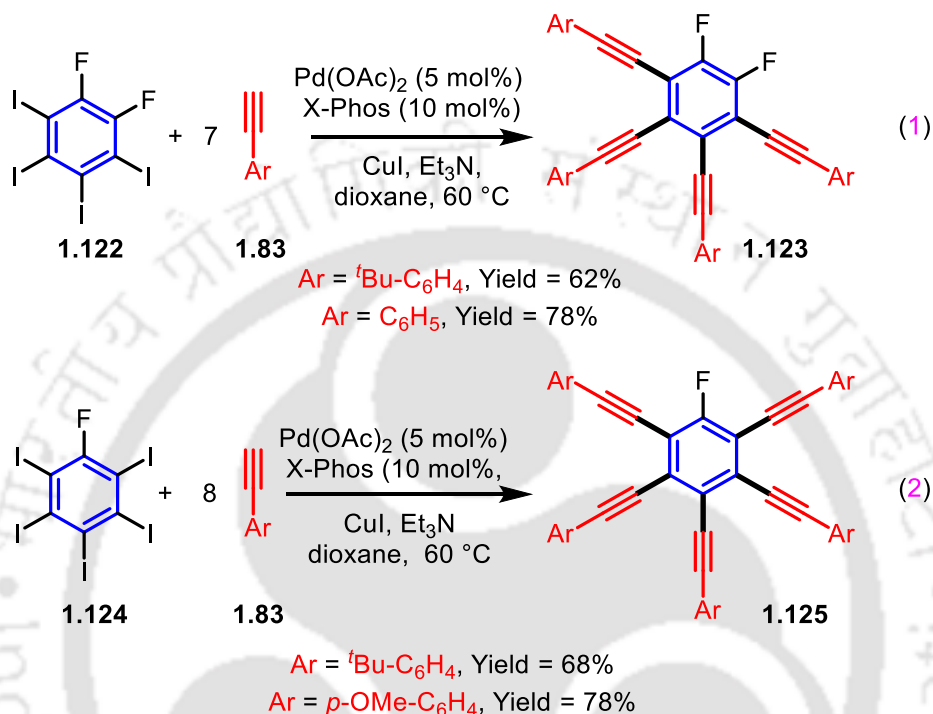


Scheme 1.23. The $\text{Pd(PPh}_3)_4/\text{CuI}$ catalyzed selective substitution of bromine groups with arylalkynes in the presence of fluoro substituents.¹¹⁸

Later, Langer carried out site-selective alkynylation of chloro-pyrimidine compounds employing the $\text{Pd(PPh}_3)_2\text{Cl}_2$ (10 mol%)/ CuI (5 mol%) catalyzed Sonogashira coupling with aryl alkynes (Scheme 1.21)¹¹⁶ using diisopropylamine as base and dioxane as solvent at 55 °C (**1.108**, **1.111**, **1.112**) (equation 1,3,4, Scheme 1.21) and 70 °C (**1.109**) (equation 2, Scheme 1.21).

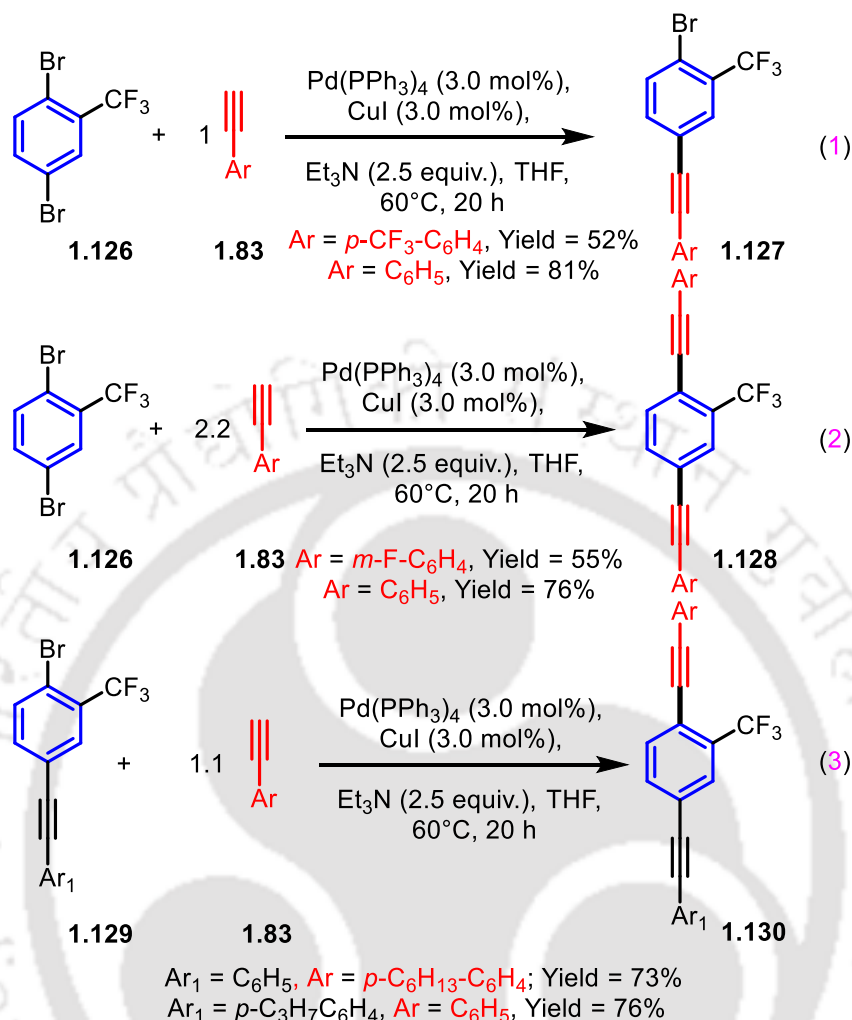
The Langer and co-worker demonstrated the synthesis of fluorinated mono- and dialkynylbenzene from 1,2-dibromo-3,5-difluorobenzene (**1.113**) (Scheme 1.22).¹¹⁷ The 1-alkynyl-substituted 2-bromo- 3,5 difluorobenzene derivatives were obtained in moderate to good yields in the $\text{Pd(PPh}_3)_4$ (3 mol%)/ CuI (3 mol%), catalyzed reactions of an equivalent of alkyne

1.83 performed for 6 h with Et₃N as base and THF as solvent at 60 °C (equation 1, Scheme 1.22). The other isomer (2- substituted product **1.116**) was not formed under these reaction conditions. Disubstituted ethynyl-difluorobenzene (**1.115**) was synthesized under the identical reaction conditions with 2.1 equivalent of arylalkyne **1.83** (equation 3, Scheme 1.22).



Scheme 1.24. Site-selective alkynyl substitution of iodo groups in the presence of fluoro groups via Sonogashira coupling catalyzed by Pd(OAc)₂/CuI.¹¹⁹

In 2012, Langer reported the selective coupling of bromo-substituents with aryl alkynes in the presence of fluoro groups on the aryl ring (Scheme 1.23) to obtain fluorinated alkynylbenzenes with moderate to good yields (Scheme 1.23).¹¹⁸ The bromo group present adjacent to fluorine in **1.117**, is less likely to undergo the first alkynyl substitution due to steric hindrance and high electron density (equation 1, Scheme 1.23). However upon use of excess aryl alkyne **1.83**, the bromo group adjacent to fluorine in **1.117** could be substituted by the alkynyl group (equation 2, Scheme 1.23). The alkynylation of **1.120** (equation 3 in Scheme 1.23) is clearly indicative of the preference for alkynyl substitution of a bromo moiety over a fluoro group during the Pd catalyzed Sonogashira reactions.



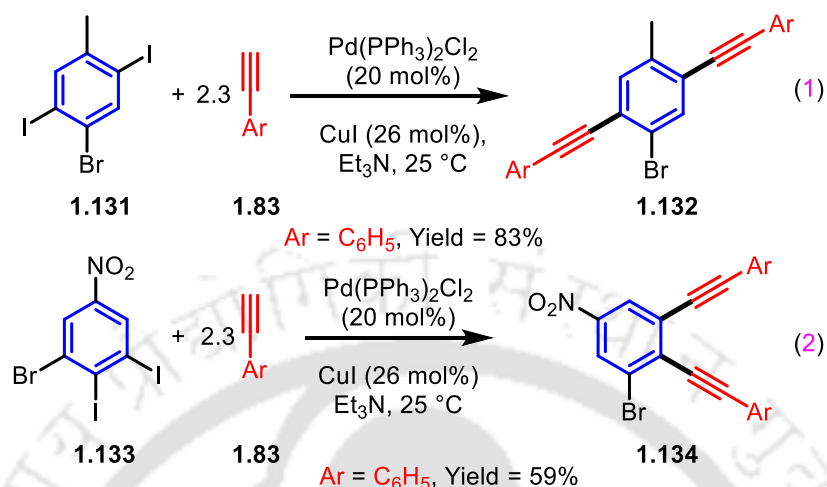
Scheme 1.25. The $\text{Pd(PPh}_3)_4/\text{CuI}$ catalyzed Sonogashira coupling aryl bromides containing trifluoromethyl substituent with arylalkynes.¹²⁰

Langer followed up these studies with the report on $\text{Pd(OAc)}_2 + \text{X-Phos}/\text{CuI}$ catalyzed cross-coupling of fluoroiodobenzenes (**1.122**, **1.124**) (Scheme 1.24),¹¹⁹ in the presence of excess terminal alkyne, Et_3N and dioxane, to afford fluorinated alkynylbenzenes. In this case, site-selective coupling reaction occurred on iodine containing carbon over the fluorine containing carbon atoms.

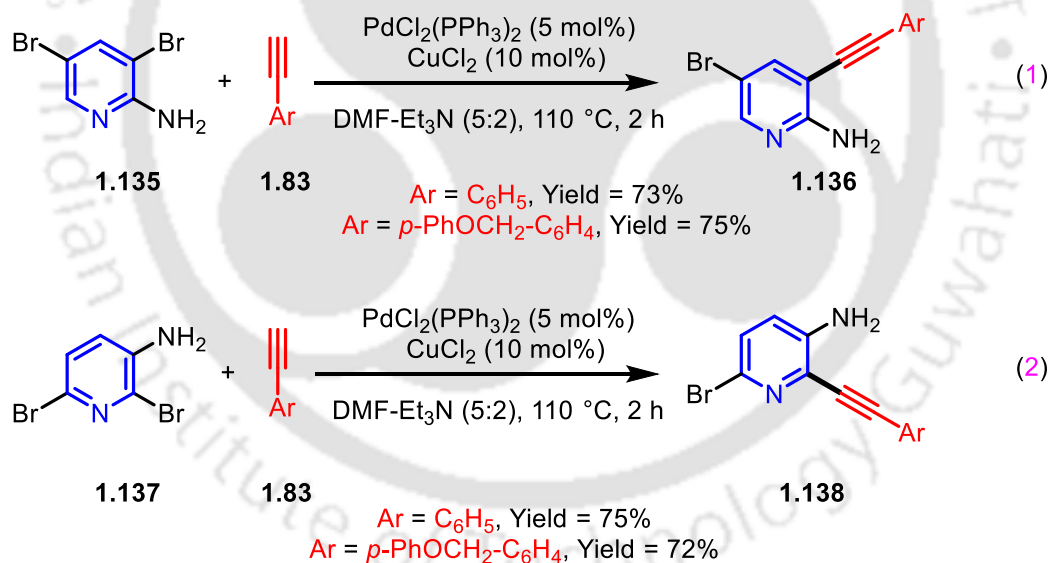
The Langer group went on to describe the synthesis of mono and dialkynylbenzene starting from aryl bromides (Scheme 1.25)¹²⁰ in presence of trifluoromethyl group.

Heck and co-workers reported the selective alkynylation of iodo substituents present in 4-bromo-2,5-diiodotoluene **1.131** and 5-bromo-3,4-diiodonitrobenzene **1.132** by using 2 equivalent of phenylacetylene in the $\text{Pd(PPh}_3)_2\text{Cl}_2/\text{CuI}$ catalyzed Sonogashira reaction (Scheme 1.26).¹²¹ On

the other hand, the selective substitution of bromo groups in aromatic amines was reported by Mojumdar and co-workers in 2007¹²² (Scheme 1.27). The bromo groups present at ortho-position



Scheme 1.26. Selective coupling of iodo substituents in 4-bromo-2,5-diiodotoluene with aryl alkynes via the Sonogashira coupling catalyzed by $\text{Pd(PPh}_3)_2\text{Cl}_2/\text{CuI}$.¹²¹



Scheme 1.27. Selective alkylation of bromo substituents in aromatic amines.¹²²

1.2.6.3. Photophysical properties of PAHs

Every molecule has an unique photophysical property that arises from its interaction with light.¹²³ The photophysical properties of a molecule such as luminescence has various applications in sensing,^{58e} bio-imaging,¹²⁴ medical diagnosis,¹²⁵ military applications,^{58e} and optoelectronic

devices like organic light emitting diodes (OLEDs).^{33, 126} In the context of the current review, this section is devoted to the discussion of the photophysical properties of PAHs.

1.2.6.3.1. Quantum yield of PAHs

The fluorescence quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed by the fluorophore.¹²⁷ Relative fluorescence quantum yield is calculated by the equation shown below (equation 1),^{71b} where ϕ_F and ϕ_R are the relative quantum yields of the analyte and standard respectively; I and I_R are the area of emission of the analyte and the reference; A and A_R are the maximum absorbance of the analyte and reference; η and η_R are the refractive index of analyte and reference solutions respectively.

$$\phi_F = \phi_R \times \left(\frac{I}{I_R}\right) \times \left(\frac{A_R}{A}\right) \times \left(\frac{\eta^2}{\eta_R^2}\right) \quad (1)$$

In 2013, Langer reported the UV/PL studies of the compounds **1.84** and **1.10** (Figure 1.8).⁵² Moderate to good fluorescence quantum yields were obtained for pyridine (**1.84a**; $\phi = 42\%$, **1.84b**; $\phi = 45\%$, and **1.84c**; $\phi = 43\%$) as well as benzene (**1.10a**; $\phi = 45\%$, **1.10b**; $\phi = 50\%$, and **1.10c**; $\phi = 39\%$) based alkynylated compounds. The alkynylated compounds consisting of electron-donating groups undergo bathochromic shift with hardly any significant change in the Stokes shift. This indicates that the intramolecular charge transfer (ICT) that takes place in ground state is similar to the ICT in the excited state.

In 2011, Langer studied the photophysical properties of the compounds **1.87**, **1.89** and **1.77** (Figure 1.8).¹⁶ The compounds containing electron-donating groups attached to phenyl ring (**1.87b**, **1.89b** and **1.77b**) showed red shift for absorption (18 nm, 17 nm and 17 nm respectively) as well as emission (21 nm, 13 nm and 14 nm respectively) maxima when compared to compounds with no substituents on the phenyl ring (**1.87a**, **1.89a** and **1.77a**). On the other hand, blue shift is observed in the case of compounds having electron-withdrawing groups present at the phenyl moiety (**1.87c**, **1.89d** and **1.77d**). The fluorescence quantum yield is higher for pyridine core compounds (**1.87a**; $\phi = 55\%$, **1.87b**; $\phi = 81\%$ and **1.87c**; $\phi = 47\%$) than the corresponding values of benzene core molecules (**1.89a**; $\phi = 26\%$, **1.89b**; $\phi = 53\%$, **1.89c**; $\phi = 41\%$, **1.89d**; $\phi = 43\%$, **1.77a**; $\phi = 43\%$, **1.77b**; $\phi = 55\%$ **1.77c**; $\phi = 44\%$ and **1.77d**; $\phi = 25\%$).

All the pyrazine-based compounds **1.92a–f** (Figure 1.8) reported by Langer showed two peaks in the absorption spectra but a single peak (429 to 461 nm) in the corresponding emission spectra.⁷⁰ The compound **1.92e** ($\lambda_{em} = 461$ nm) displayed higher bathochromic shift when

compared to **1.92b** (λ_{em} = 439 nm) due to presence of π -donating methoxy group in the former. Excellent quantum yields (**1.92a**; ϕ = 81%, **1.92b**; ϕ = 83%, **1.92c**; ϕ = 77%, **1.92d**; ϕ = 85%, and **1.92e**; ϕ = 79%) were exhibited by these pyrazine core compounds.

Langer performed a systematic comparison of the photophysical properties of various pyridine core tetraalkynylated compounds (**1.104 A–C**, **1.141**) (Figure 1.8).⁷⁵ These molecules exhibited moderate to good fluorescence quantum yields (**1.104Aa**; ϕ = 31%, **1.104Ab**; ϕ = 37%, **1.104Ac**; ϕ = 30%, **1.104Ba**; ϕ = 25%, **1.104Bb**; ϕ = 31%, **1.104Bc**; ϕ = 25%, **1.104Ca**; ϕ = 44%, **1.104Cb**; ϕ = 60%, and **1.104Cc**; ϕ = 41%). A higher bathochromic shift was observed with the compounds containing electron-donating groups (**1.104Ab**, **1.104Bb** and **1.104Cb**) in comparison

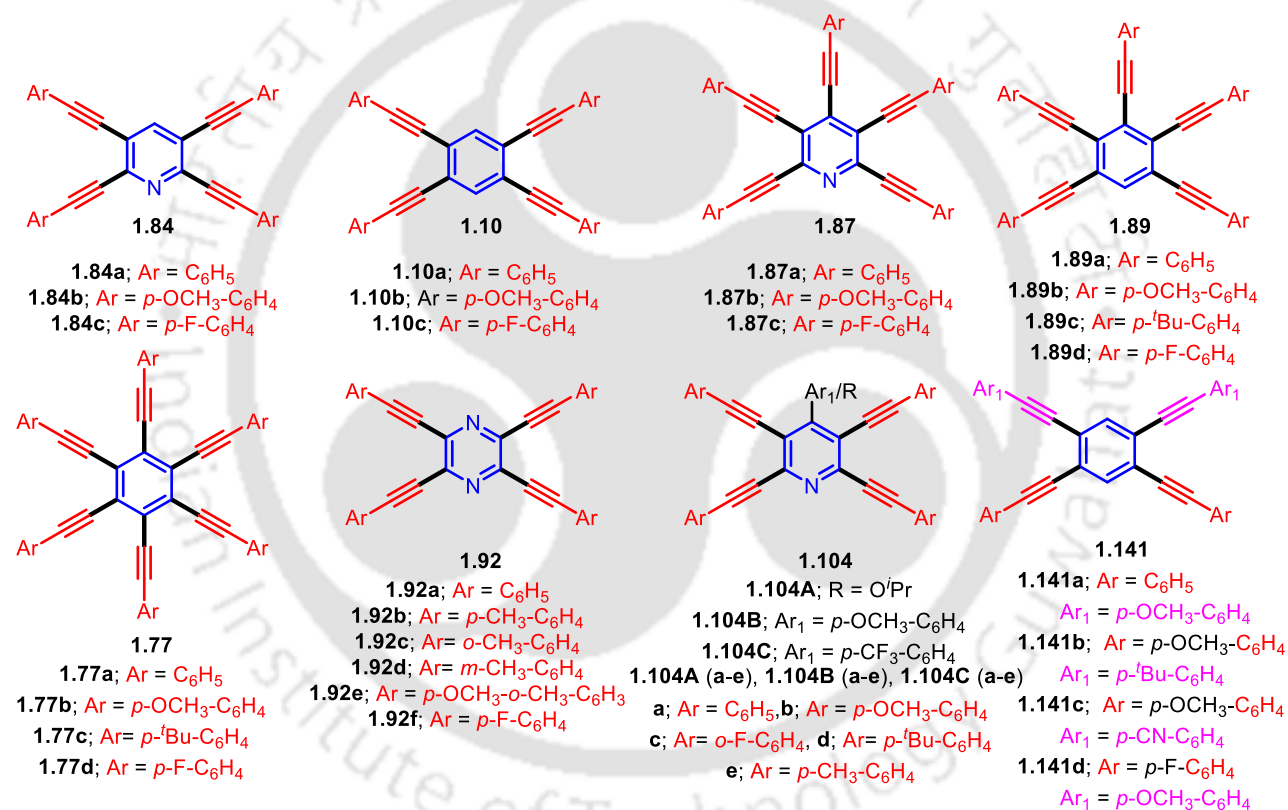


Figure 1.8. A few of PAHs based on benzene, pyridine and pyrazine core for which the photophysical properties have been reported.

to the compounds having no substituents (**1.104Aa**, **1.104Ba** and **1.104Ca**). The compounds **1.141a** and **1.141b** showed higher Stokes shift (ca. 3000–3100 cm⁻¹). In comparison with **1.141b**,

the compound **1.141c** that contains a combination of electron-withdrawing cyanide group and an electron-donating methoxy moiety exhibited bathochromic shift up to 431 nm.

Langer and co-workers' studies on the photophysical properties of pyrimidine core compounds (**1.108**, **1.112**, and **1.142**) (Figure 1.9) revealed their absorbance around 297–371 nm with the corresponding emission in the range of 395–470 nm.⁷⁷ Moreover, high Stokes shift was also observed with these compounds (**1.108a**; 55 nm, **1.108b**; 41 nm, **1.108c**; 103 nm, **1.142a**; 115 nm, **1.142b**; 110 nm, **1.142c**; 136 nm, and **1.112**; 108 nm).

Langer observed that among the fluorinated polyalkynylated compounds (**1.123**, **1.125**, **1.139** and **1.140**), (Figure 1.9) that exhibited emission spectra in the range of 352–454 nm, **1.125g** resulted in the highest bathochromic shift.⁸⁰ Presence of penta-alkynylated moieties consisting of electron donating methoxy group at *para*-position was key to this interesting property of **1.125g**. It was observed that with increase in alkynylation, there was a concomitant increase in the bathochromic shift.

It is observed that the absorbance maxima for **1.119** (λ_{max} = 321–331 nm) is higher than that of **1.118** (λ_{max} = 285–318 nm).⁷⁹ This is attributable to the greater extended π -conjugation in the former (Figure 1.2). The compounds **1.118e–f** and **1.119e–f** containing *tert*-butyl and methoxy groups show redshift in absorption maxima when compared to **1.118a** and **1.119a**. In comparison with **1.119e**, the compound **1.119f** shows a higher Stokes shift (65 nm) owing to the push-pull effect of electron donating nature of $-\text{OCH}_3$ and electron-withdrawing nature of $-\text{F}$.

Among the trifluoromethyl substituted alkynylated compounds **1.127**, **1.128** and **1.130** (Figure 1.9), both **1.127** and **1.128** displayed four transitions in their absorption spectra.⁸¹ Due to the mesomeric and electron inductive effect, the compounds containing electron-donating groups (**1.127b–g**, **1.128b–g**) demonstrated redshift in absorption as well as in emission spectra. Notably, 4,4'-((2(trifluoromethyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(methoxybenzene) (**1.128g**) exhibited the highest Stokes shift (47 nm) which can be attributed to the push-pull effect of electron-donating nature of $-\text{OCH}_3$ and electron-withdrawing nature of $-\text{CF}_3$.

In 2017, Langer reported UV/PL studies of polyalkynylated naphthalene molecules (**1.94**, **1.143**, **1.144** and **1.145**) (Figure 1.10).^{14a} The compounds **1.94** and **1.144** show absorption and emission wavelength in the range 300–400 and 400–450 nm, respectively. The fluorescence quantum

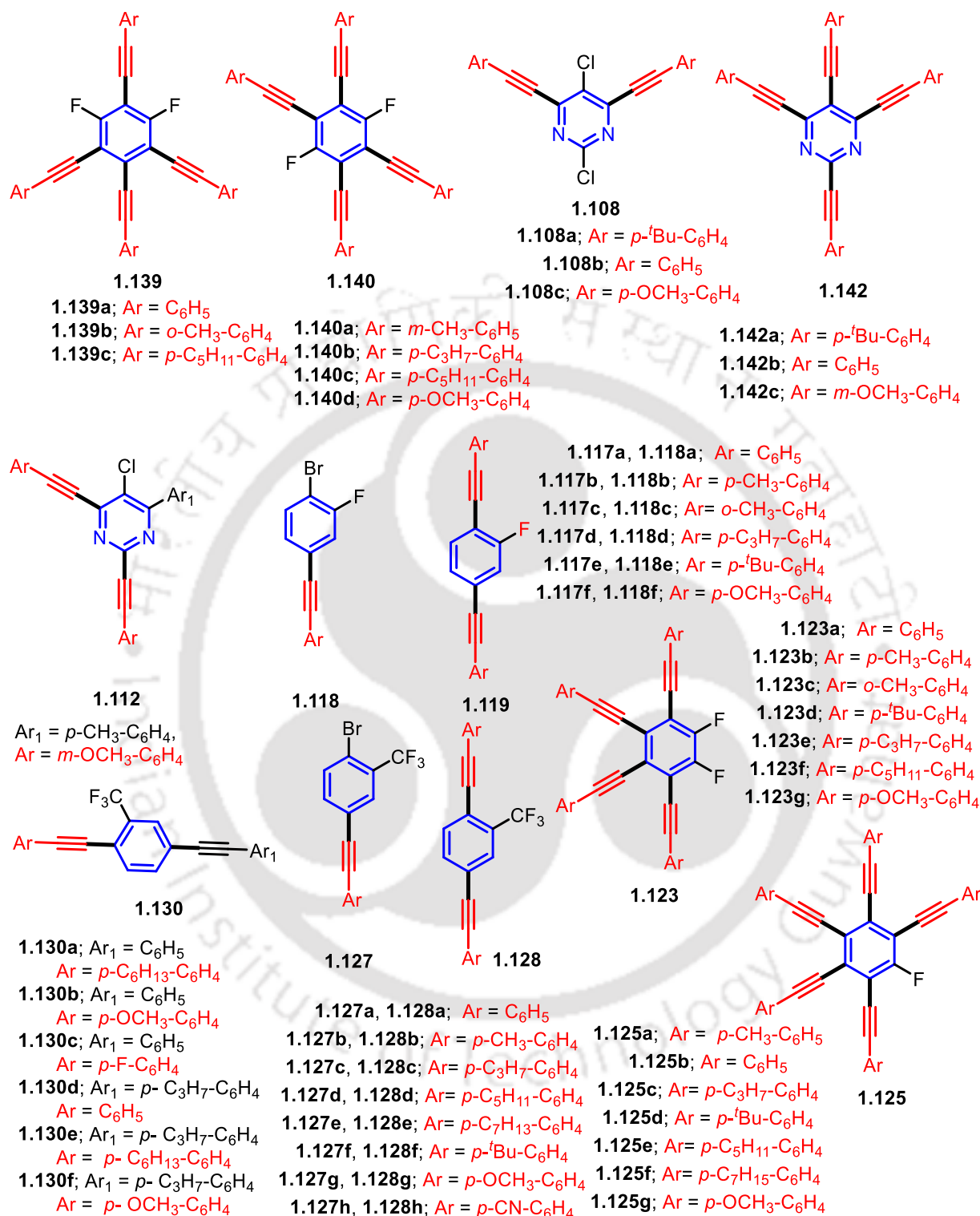


Figure 1.9. A few of PAHs based on benzene and pyrimidine core for which the photophysical properties have been reported.

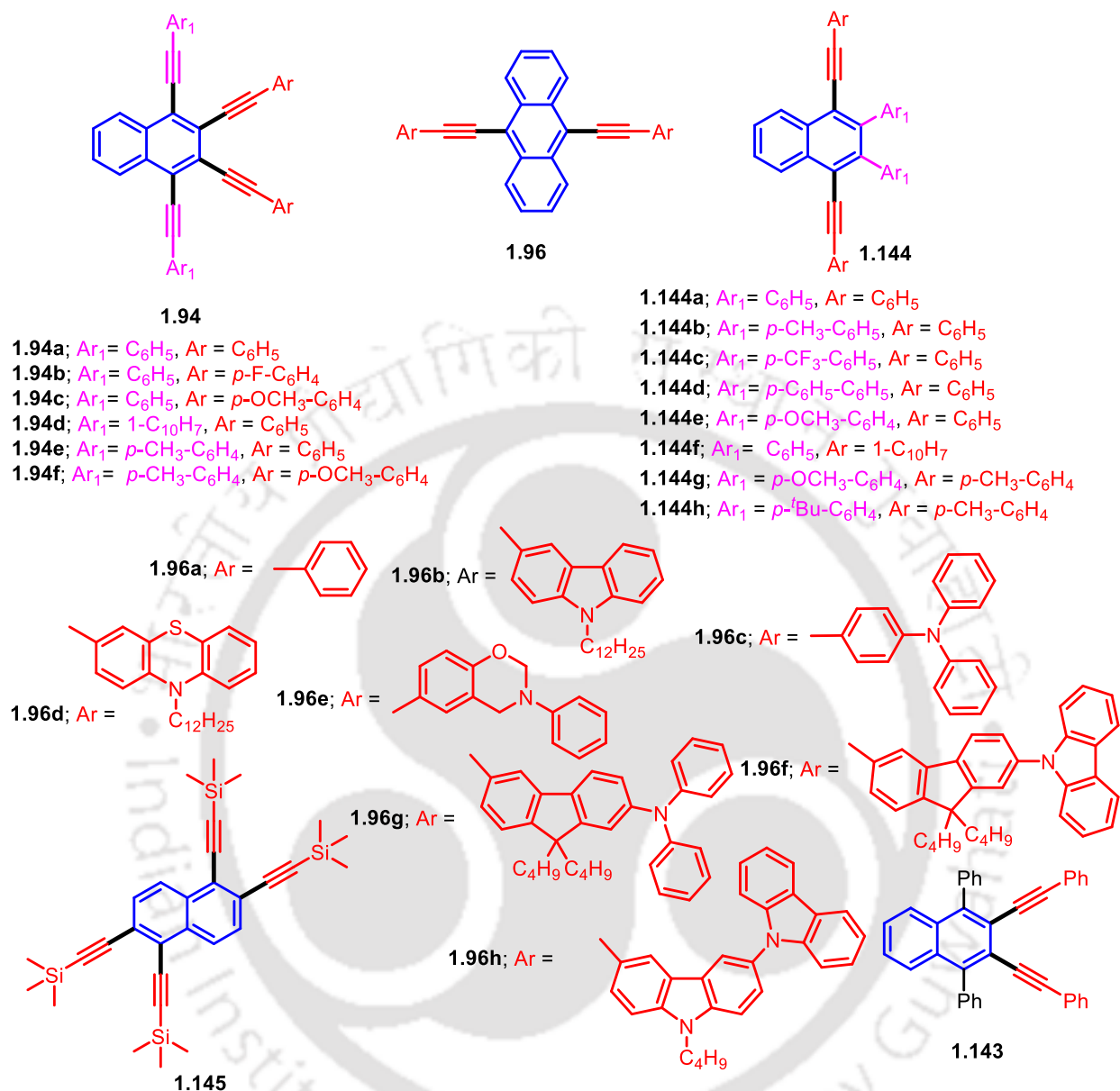


Figure 1.10. A few of PAHs based on naphthalene and anthracene core for which the photophysical properties have been reported.

yield depends on the substituents on phenyl group in case of both these molecules. Higher quantum yield was observed for polyalkynylated naphthalene molecules containing the electron-withdrawing groups ($-\text{CF}_3$ and $-\text{F}$), than for the corresponding naphthalene derivatives with electron-donating groups (**1.94b**; 78%, and **1.144c**; 78% vs. **1.94d**; 39%, **1.144g**; 28%, and **1.144h**; 19%). The high quantum yield (61%) of **1.145** was considered to be the result of the presence of ethynyl unit. The extended π conjugation available to molecules containing ethynyl moiety plays

a vital role in enhancing the absorption (**1.94a**; $\lambda_{\text{max}1} = 382$, $\lambda_{\text{max}2} = 403$ nm, **1.144a**; $\lambda_{\text{max}1} = 369$, $\lambda_{\text{max}2} = 387$ nm) as well as emission maxima (**1.94a**; $\lambda_{\text{em}1} = 424$, $\lambda_{\text{em}2} = 428$ nm, **1.144a**; $\lambda_{\text{em}1} = 401$, $\lambda_{\text{em}2} = 416$ nm). The compound **1.143** (Figure 1.10) which is a regioisomer of **1.144**, shows blue shift in absorption as well as emission maxima. This indicates that the photophysical properties depends on the position of alkynyl substituent on the naphthalene ring.

Small organic molecules containing anthracene core have gained great attention as blue light emitters because of their extended π -conjugated structure, thermal stability, attractive photoluminescence and electroluminescence properties. The introduction of an electron-withdrawing acceptor (A) and an electron-donating donor (D) group to anthracene moiety helps to prevent aggregation, enhances π -conjugation, and improves the luminescence performance.³⁰

In this context, Matussek and co-workers studied the luminescence properties of the alkynylated anthracene molecules (**1.96f–h**) (Figure 1.10).⁵ For this purpose, with anthracene as an acceptor, several D- π -A- π -D motifs were synthesized using donors such as carbazole, diphenylamine, and fluorene. Notably, the electron donating groups are connected to the anthracene core molecule by an ethynyl bridge. While the compounds **1.96f** and **1.96h** that have end-capping carbazole derivatives demonstrated a single absorbance band ($\lambda_{\text{max}} = 342$ and 322 nm respectively), the compound **1.96g** that is endcapped by diphenylamine showed two peaks at 316 and 372 nm. Furthermore, among these alkynylated anthracene molecules, **1.96f** and **1.96g** that have di-butyl substitution on the fluorene unit exhibit high quantum efficiency of 93% and 98% respectively. On the other hand, **1.96h** that has only one butyl group on the fluorene unit exhibited a lower quantum efficiency of 77%. Interestingly, in contrast to one's expectation, **1.96g** demonstrates very high quantum efficiency ($\phi = 98\%$) despite the fact that it has non-rigid diphenylamine group (in comparison to the carbazole moiety of **1.96f** and **1.96h**) that can potentially reduce the fluorescence intensity *via* rotation induced non-radiative emission.

Very recently, Sanda and co-workers described the photoluminescence properties of anthracene core benzoxazine molecules (**1.96a** and **1.96e**) (Figure 1.10).¹²⁸ Owing to the presence of π -conjugation between lone pair electrons of oxygen atom and anthracene moiety in **1.96e**, it exhibited λ_{onset} and λ_{max} that are longer than the corresponding absorptions in **1.96a** by 30 nm and 12 nm respectively. Both **1.96a** and **1.96e** displayed absorption spectra with similar splitting patterns in the range 440–480 nm with **1.96e** exhibiting two distinct peaks at 494 and 524 nm in emission spectra. While **1.96e** and **1.96a** gave a quantum yield of 80% in DCM, the corresponding

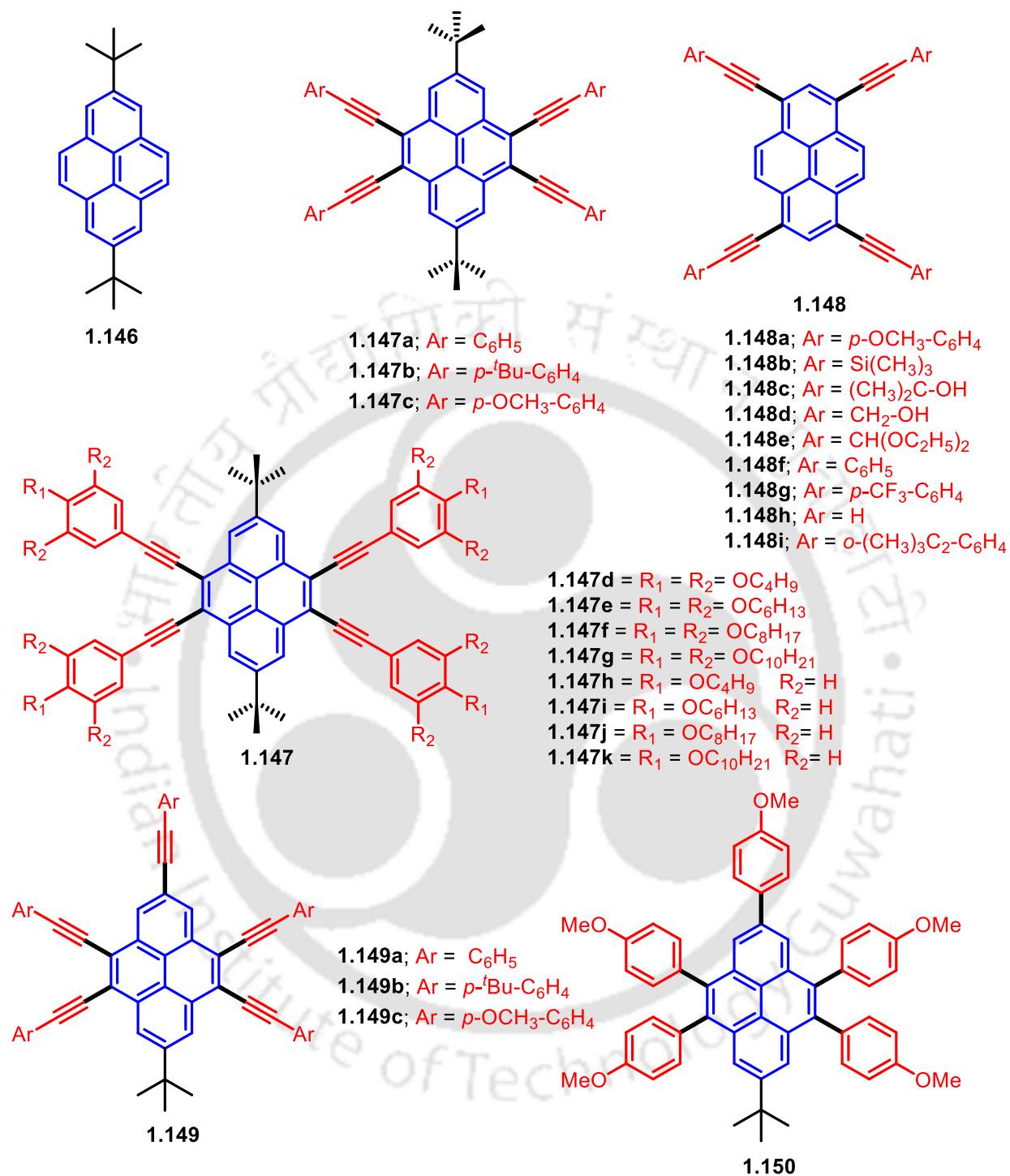


Figure 1.11. A few of PAHs based on pyrene core for which the photophysical properties have been reported.

values were 65% and 93% for **1.96e** and **1.96a** respectively in sulfolane. The relatively lower quan-

-tum yield of **1.96e** in polar solvents such as sulfolane is attributed to aggregation because of the synergistic effect involving the interaction between anthracene-ethynyl units and terminal phenyl groups much like that present in the solid-state.⁸⁹ On lowering the temperature from 25 °C to 0 °C, the quantum yield of **1.96e** increased from 80% to 86% in DCM and 65% to 72% in sulfolane medium.

Pyrene molecules have π -conjugated planar structure, and therefore they easily form excimer/aggregate in solution as well as in solid state which reduces the quantum yield. Pyrene molecules typically show absorption and emission in the UV-region. However, after the introduction of alkynyl unit to the pyrene molecule, the emission band shifts to the visible region due to the increase in the π -conjugation which in turn increases the fluorescence intensity of the molecule.^{48,129,130} Aggregation can be mitigated by the introduction of bulky *tert*-butyl group ('Bu) at 2- and 7-position of pyrene which inhibits the face-to face π -stacking in solution as well as in the solid state.

Yamato studied the photophysical properties of cruciform shaped polyalkynylated pyrene molecules **1.147a–c**, **1.146** and **1.148a** (Figure 1.11).¹⁷ Single-crystal X-ray analysis indicates that contrary to the interplanar distance of 3.5 Å between the unsubstituted strongly π - π stacked pyrene molecules, the intermolecular distance in corresponding *tert*-butyl substituted polyalkynylated pyrene molecules of **1.147c** is about 5.82 Å. This is indicative of the fact that the bulky *tert*-butyl group inhibits the π - π and face-to-face, stacking in the solid-state structure of **1.147c**.

In comparison to the pyrene molecule that shows absorption in the range 300–350 nm, the absorption bands of **1.146** is slightly bathochromic shifted by 3 nm owing to the electron donating 'Bu group at 2- and 7-positions. On the other hand, the compound **1.148a** without 'Bu groups but with polyalkynylation shows a bathochromic shift by about 140 nm in comparison to **1.146**. This is attributed to the enhancement of π -conjugation at 1, 3, 6, 8-positions of the pyrene ring.

Interestingly, **1.147** having both 'Bu groups and tetraalkynylated substituents at 4, 5, 9, 10-position demonstrates a bathochromic shift of about 71–76 nm compared to **1.146** with the corresponding λ_{max} values at 410, 413 and 415 nm for **1.147a**, **1.147b** and **1.147c** respectively. While the compounds **1.147a–c** show blue-light (single band) emission at 441, 448 and 453 nm respectively, the compound **1.148a** exhibited a green emission with lowest energy emission band at 496 nm. The fluorescence Stokes shift in DCM is higher for **1.147c** (2021 cm^{-1}) than **1.147b** (1892 cm^{-1}) and **1.147a** (1714 cm^{-1}). The quantum efficiency for pyrene derivative **1.146** without

tetra electron-donating acetylene substituents was lower in comparison to corresponding pyrene derivatives with acetylene substituents (**1.146**; $\phi = 12\%$ vs. **1.147a**; $\phi = 66\%$, **1.147b**; $\phi = 72\%$, **1.147c**; $\phi = 98\%$ and **1.148a**; $\phi = 96\%$). At high concentration of **1.148a**, there is a decrease in fluorescence emission intensity due to the formation of excimer while a reverse trend is followed in case of **1.147c**. These studies indicate that the bulky *tert*-Bu groups in **1.147** prevents the molecules to come closer and disfavors excimer formation, while this is clearly not the case with **1.147a** that lacks bulky *tert*-Bu groups.

For pyrene core alkynylated compounds (**1.148b–i**) (Figure 1.11),⁹⁰ Sankararaman observed three absorption bands within the range of 350–475 nm. In comparison to pyrene, **1.148b–i** demonstrated bathochromic shifts (85–130 nm) in the emission spectra owing to the extended π -conjugation. These compounds exhibited moderate to good fluorescence quantum yields (**1.148b**; $\phi = 42\%$, **1.148c**; $\phi = 49\%$, **1.148d**; $\phi = 68\%$, **1.148e**; $\phi = 36\%$, **1.148f**; $\phi = 18\%$, **1.148g**; $\phi = 16\%$, and **1.148h**; $\phi = 59\%$).

Hu and Yamato reported the photophysical properties of hand shaped 2-*tert*-butyl-4,5,7,9,10-pentakis(phenylethynyl) pyrene derivatives, **1.149–1.150** (Figure 1.11).⁴⁸ The five ethyne units in **1.149** ensured that they displayed a bathochromic shift of about 100 nm when compared to the parent pyrene molecule ($\lambda_{\text{max}} = 336$ nm). While the compound **1.150** without any ethyne units showed a deep blue emission at 411 nm in addition to a shoulder at 430 nm, the corresponding ethynyl containing pyrene derivatives **1.149a–c** showed maximum emission at 454 nm, 456 nm, and 463 nm respectively along with shoulder emissions at 481 nm, 484 nm, and 488 nm respectively. With the increase in the concentration of **1.149c** from 1×10^{-8} M to 1×10^{-4} M, the emission intensity gradually increased which indicates that the presence of bulky *tert*-Bu group at 2-position on pyrene prevents aggregation and eventual excimer formation. The quantum efficiency was found to be low for compound **1.150** ($\phi = 24\%$) with no alkynyl unit when compared to the alkynyl unit containing pyrene compounds, **1.149a** ($\phi = 46\%$), **1.149b** ($\phi = 72\%$) and **1.149c** ($\phi = 86\%$). This observation can be explained on the basis of extension of π -conjugation length in case of **1.149** and exciton migration associated energy loss for **1.150**. The good quantum efficiency observed in solution for **1.149** could however not be extrapolated to thin films where a decrease in quantum yield is observed (**1.149a**; $\phi = 12\%$, **1.149b**; $\phi = 32\%$, **1.149c**; $\phi = 16\%$). This lowering of quantum efficiency arises due to the formation of intermolecular π - π aggregation between central pyrene cores in solid state.

Giese and Albrecht reported the photophysical properties of alkoxy pyrene derivatives **1.147d–k** (Figure 1.11).¹³¹ The compounds exhibited absorption bands at 300–350 nm and additional absorption maximum at 417 nm. While in the case of trialkoxy substituted pyrene compounds (**1.147d–g**), intensive emission is seen at about 470 nm, the monoalkoxy substituted pyrene compounds (**1.147h–k**) displayed intensive emission at about 450 nm. The lower energy gap between the ground and excited state in trialkoxy substituted pyrene core compounds **1.147d–g** resulted in a bathochromic shift of 20 nm in comparison to the mono-alkoxy substituted pyrene core compounds. The emission spectrum of **1.147d–k** remained unchanged on increasing the concentration from 1×10^{-5} to 1×10^{-2} M in DCM, which indicates the absence of self-aggregation. However, due to self-aggregation, the fluorescence intensity is quenched in the solid-state as well as in polar solvents like acetonitrile and DMF. With increase in the polarity of the solvent, the bathochromic shift gets enhanced due to formation of aggregates. Accordingly, in DMF, **1.147d** had a bathochromic shift of 100 nm when compared to **1.147d** ($\lambda_{\text{max}} = 433$ nm) in cyclohexane. For the monoalkoxyphenyl substituted pyrene **1.147h–k**, smaller solvatochromic shift was observed (ca. 30–50 nm). Due to the increase of hydrophobicity with increase in the number of the attached alkoxy groups, the compounds **1.147d–g** were sparingly soluble in polar solvents leading to formation of π -aggregation at high concentrations. When compared to solution-phase, the thin films of **1.147d–k** displayed bathochromic shift of about 57 nm because of the self-aggregation in solid-state. These results indicate that the self-aggregation is not prevented in the solid-state by the bulky *tert*-Bu groups at 2- and 7-position of the pyrene ring.

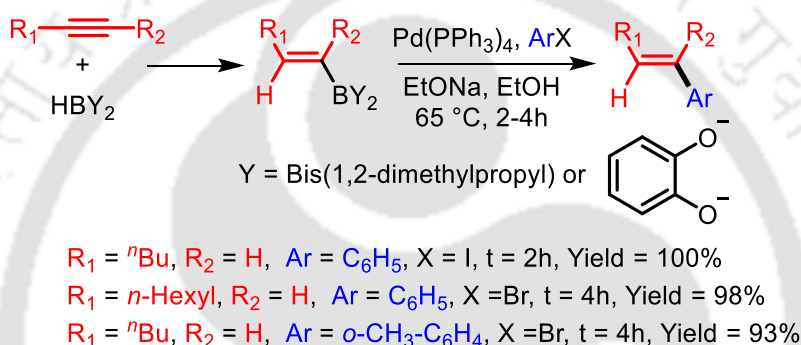
Castellano group had reported that the bulky *tert*-Bu groups at 3, 8-position of pyrene molecules prevent the excimer formation.¹³² The quantum efficiency for the substituted pyrene compounds **1.147d–k** were in the range 43–73% in non-polar and partially-polar solvents like cyclohexane, toluene, THF, and DCM. However, in solid-state and in polar solvents (MeCN, DMF), the quantum efficiency drastically decreased to the range 2–42% due to self-aggregation and excimer formation. The extent of decrease in quantum efficiency for trialkoxy substituted pyrene compounds **1.147d–g** was higher than the corresponding decrease observed in monosubstituted compounds, **1.147h–j**. However, the compound **1.147k** exhibited a similar effect as trialkoxy substituted pyrene compounds **1.147d–g**, due to the enhancement of hydrophobicity by alkane chain ($\text{C}_{10}\text{H}_{21}$) in **1.147k**. A few representative polyalkynylated π -conjugated PAHs that demonstrates fluorescence quantum yield (ϕ) that are greater than 50% are provided in Table 1.2.

Table 1.2. A few polyalkynylated conjugated PAHs which demonstrates fluorescence quantum yields (ϕ) that are greater than 50 %

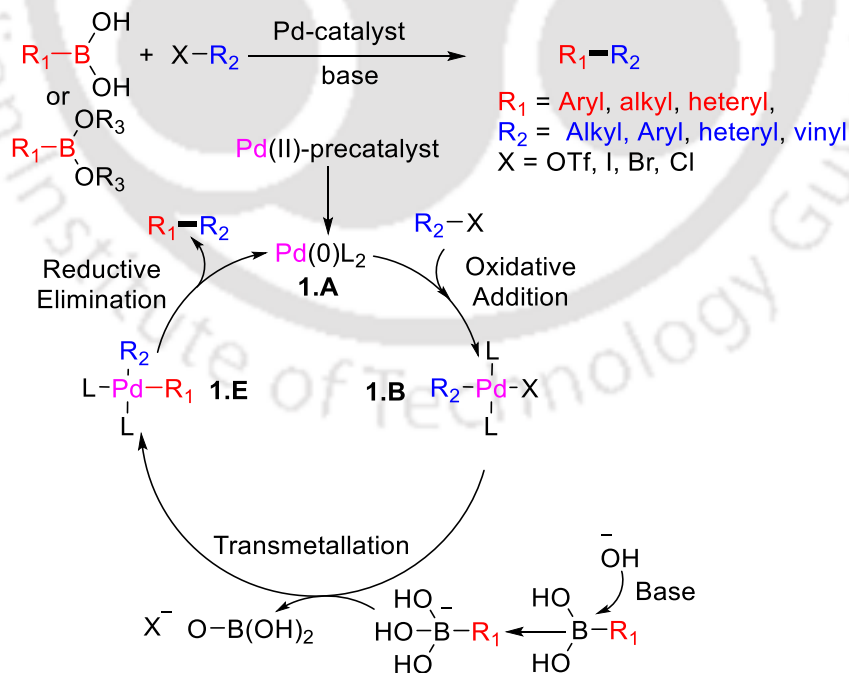
Entry	compound	Quantum Yield ϕ (%)	Reference
1	1.10a	50	94
2	1.87a	55	16
3	1.87b	81	16
4	1.89b	53	16
5	1.89b	55	16
6	1.92a	81	109
7	1.92b	83	109
8	1.92c	77	109
9	1.92d	85	109
10	1.92e	79	109
11	1.94a	60	14a
12	1.94b	78	14a
13	1.94e	59	14a
14	1.96a	93	128
15	1.96e	80	128
16	1.96f	93	5
17	1.96g	98	5
18	1.96h	77	5
19	1.147a	66	17
20	1.147b	72	17
21	1.147c	98	17
22	1.147d	63	110a
23	1.147e	63	110a
24	1.147f	62	110a
25	1.147g	66	110a
26	1.147h	73	110a
27	1.147i	64	110a
28	1.147j	65	110a
29	1.147k	60	110a
30	1.104Cb	60	114
31	1.144a	76	14a
32	1.144d	70	14a
33	1.144c	78	14a
34	1.144d	59	14a
35	1.144e	52	14a
36	1.145	61	14a
37	1.148a	96	17
38	1.148d	68	129
39	1.148h	59	129
40	1.148b	72	90a
41	1.149c	86	90a

1.2.7. Suzuki-Miyaura cross-coupling reaction

In 1979, Suzuki reported carbon-carbon cross-coupling reaction of arylhalide and alkenylboranes by employing $\text{Pd}(\text{PPh}_3)_4$ as catalyst (Scheme 1.28).^{49, 133} This reaction is called Miyaura-Suzuki as well as Suzuki-Miyaura reaction (SMR). Norio Miyaura used to work in the Suzuki lab and also contributed in the development of the reaction. In 2010, Suzuki was awarded the Nobel Prize for the discovery of carbon-carbon cross-coupling reaction in field of catalysis. This reaction involves cross-coupling between different type of organoboron reagents (alkyl, aryl, and alkenylboronic acid and/or ester, organotrifluoroborate, tetraphenylborate) with organic electrophiles (alkyl, aryl halides or triflates) using palladium as a catalyst.

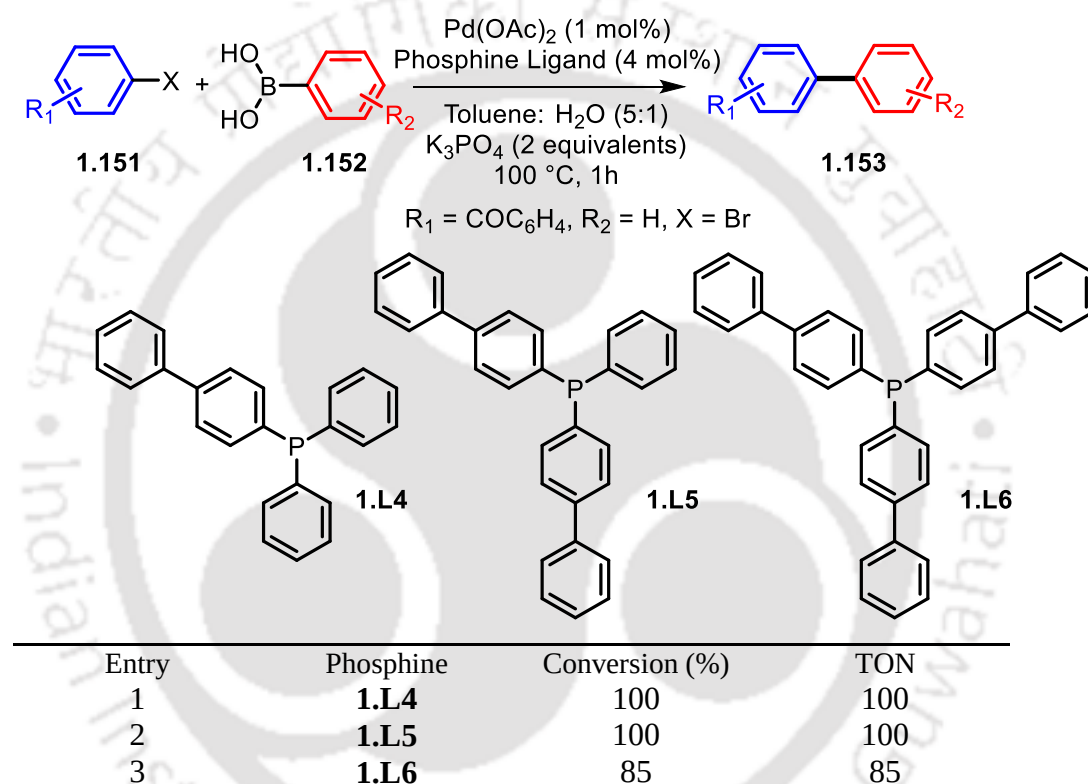


Scheme 1.28. Suzuki-Miyaura cross-coupling reaction.^{49,133}

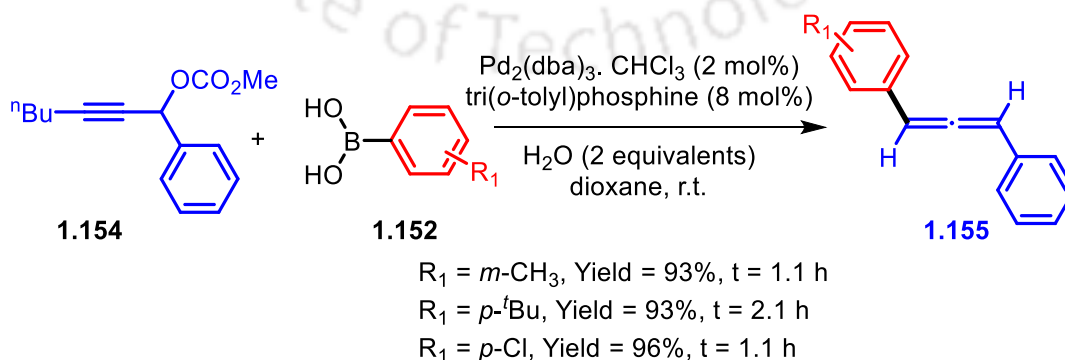


Scheme 1.29. General representation of Suzuki cross-coupling reaction and its possible mechanism.¹³⁴

Alkyl, aryl and alkenyl boronic acid and/or ester are stable towards moisture as well as air and they can be synthesized through numerous simple pathways.¹³⁴ The reaction is found to be highly tolerant towards a range of functional groups. This reaction holds various applications in agrochemical, fine chemical industries, pharmaceutical industries etc for the formation of C-C bond.⁶¹ As per the literature survey on SMR, the most effective catalysts are based on palladium. Since past four decades, researchers have been developing the reaction condition by modification of catalyst and ligand.¹³⁵

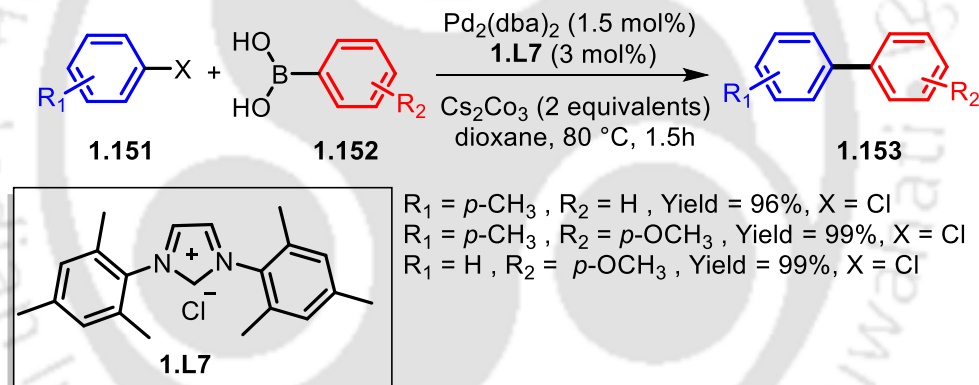


Scheme 1.30. Suzuki cross-coupling reaction employing phosphine ligand.



Scheme 1.31. Suzuki cross-coupling reaction in the presence of *tris(o-tolyl)*phosphine ligand.¹³⁷

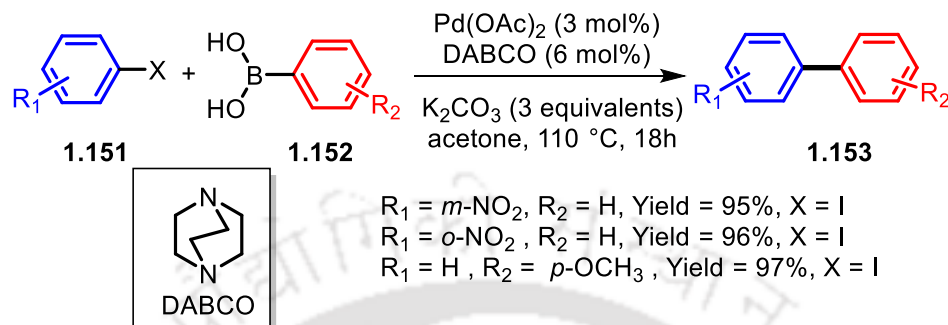
Mechanistically, in the first step of Suzuki reaction, the oxidative addition of organohalides to catalytically active species of palladium ($\text{Pd}(0)\text{L}_2$, **1.A**, Scheme 1.29) takes place to form organopalladium complex ($\text{Pd}(\text{II})\text{R}_2\text{L}_2\text{X}$, **1.B**, Scheme 1.29). This step is the rate determining step. Oxidative addition step is accelerated by addition of sigma-donating ligands, which will enhance the overall reaction rate. The next step is transmetalation, where the base binds to the organoborate and exchanges the halide from the organopalladium complex, making the R group in the organoborate more nucleophilic and shifting it to the palladium complex. Instead of the neutral boronic acid, the borate anion is the species of organoboron that is most reactive towards the transmetalation step. The base's primary function in the reaction mechanism is to increase the boronic acid's reactivity towards the Pd-halide complex (**1.B**, Scheme 1.29) by transforming it into the appropriate organoborate.¹³⁶ The strength of base is important in the transmetalation step. In the final step, product is formed by reductive elimination which will lead to the regeneration of catalytic active palladium species (**1.A**, Scheme 1.29).



Scheme 1.32. Suzuki cross-coupling reaction in the presence of nucleophilic *N*-heterocyclic carbenes ligand.¹³⁸

The role of ligand is very crucial in Suzuki cross-coupling reaction. Initially, triarylphosphine was used as a ligand for this reaction (Scheme 1.30). Researchers have studied the ligand effect on palladium for this reaction. Recently, Shengming reported the activity of bulky *tri-o*-tolylphosphine ligands in this reaction (Scheme 1.31).¹³⁷ The imidazol-2-ylidenes are considered neutral, two electron donor ligands with very poor π -back bonding potential for nucleophilic *N*-heterocyclic carbenes (NHC). As a result, they have received a lot of interest as replacements instead of as phosphine (Scheme 1.32).¹³⁸ Later researchers have developed the ligand as well as catalyst for the reaction. In 2004, Li and co-workers reported highly active

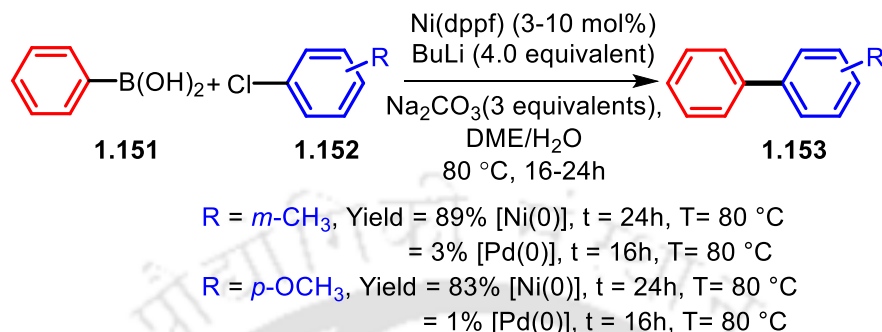
catalytic system $\text{Pd}(\text{OAc})_2/\text{DABCO}$ in the Suzuki coupling reaction (Scheme 1.33).¹³⁹ In the past few decades, the need for new and efficient catalytic system for Suzuki reaction has been the main focus of the researchers worldwide.



Scheme 1.33. Suzuki cross-coupling reaction in the presence of $\text{Pd}(\text{OAc})_2/\text{DABCO}$.¹³⁹

Suzuki-Miyaura coupling reaction of arene bromide and iodide with aryl boronic acid/ester was successfully accomplished with high efficiency and widespread applicability in the presence of Pd-catalyst till 1995.¹³⁴ Though a few examples of electron deficient *N*-heteroaryl chlorides were shown to be viable using palladium catalyst, most of the examples for more accessible and economical arene chlorides were found to be sluggish because of their low reactivity (bond dissociation energy of Ph-X; C-I = 65 kcal/mol, C-Br = 81 kcal/mol, C-Cl = 96 kcal/mol).¹⁴⁰ In order to address this, in 1996 Miyaura and co-workers were first ones to reveal the nickel catalyzed coupling of least reactive aryl chloride with boronic acid (Scheme 1.34).¹⁴¹ In this report, they demonstrate the Suzuki coupling reaction of less reactive aryl chlorides with phenylboronic acid in presence of $\text{Ni}(\text{dppf})$ (3-10 mol%), BuLi or DIBAL-H (4 equivalents) and Na_2CO_3 at 70-80 °C. For comparison, they also performed the reaction with $\text{Pd}(\text{PPh}_3)_4$ which was less reactive towards aryl chlorides. Nickel catalysts have received attention in Suzuki-Miyaura cross-coupling reaction because they are inexpensive and high earth-abundant than palladium metal. Hence, using nickel catalysts would be far more cost-effective unless a coupling process can only be successfully carried out with low loading of palladium catalyst or with high loading nickel catalyst. Owing to its smaller size, the early transition metal nickel is more nucleophilic and typically exhibits Ni(0)/Ni(II) as well as Ni(I)/Ni(III) oxidation states.¹⁴² As a result, nickel cannot simply be viewed as a palladium substitute because it has unique catalytic capabilities that palladium does not. The C-C,¹⁴²⁻¹⁴³ C-N,¹⁸¹ and C-P¹⁴⁴ bond forming reactions of a variety of electrophiles, which are

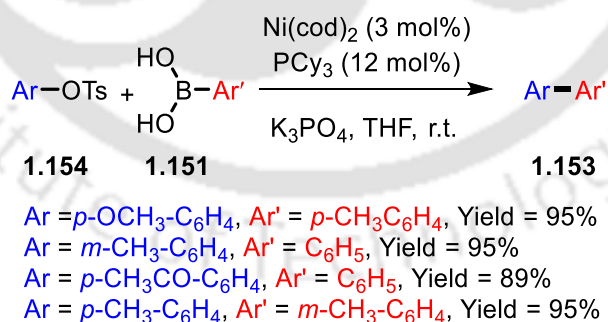
typically difficult in the presence of palladium catalysts, have been traditionally difficult to catalyze. However, extensive studies have clearly shown that the nickel-based catalysts were more versatile and powerful catalysts.



Scheme 1.34. Comparison of Suzuki-Miyaura coupling reaction based on Ni- and Pd-based catalyst.¹⁴¹

In 2004, Hu and Tang display the Suzuki coupling reaction of boronic acid with aryl and alkenyl tosylate or benzenesulfonates in the presence of 3 mol% Ni(cod)₂ as catalyst, PCy₃ as ligand and K₃PO₄ as base at room temperature (Scheme 1.35).¹⁴⁵ In this report they showed vast substrate scope with good to excellent yield for electron donating and withdrawing group of aryl arenesulfonates. They were able to synthesize 4-substituted furanose and 4-substituted coumarins which are applicable in biological applications.

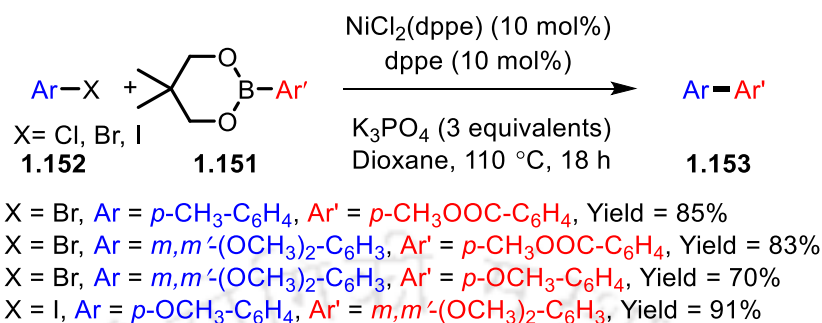
In 2008, Perce and co-workers investigated the Suzuki coupling reaction by screening numerous nickel-phosphine complexes, ligands, leaving group, base and solvents. They observed



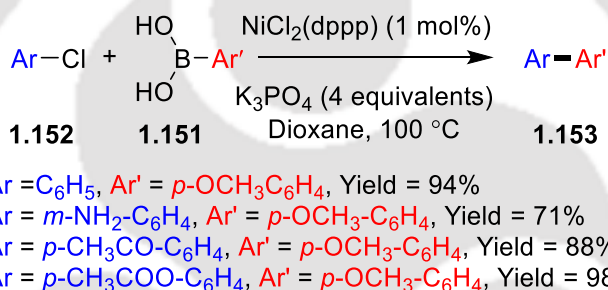
Scheme 1.35. Suzuki coupling reaction of aryl boronic acid and aryltosylate by Ni-catalyst.¹⁴⁵

that the most efficient catalytic system is $\text{NiCl}_2(\text{dppe})$ and dppe or PPh_3 . A good yield was observed for aryl iodide, bromide and chloride in the presence of base K_3PO_4 and dioxane or toluene as solvent. The catalyst system $\text{NiCl}_2(\text{dppe})/\text{dppe}$ is efficient in this reaction for weak

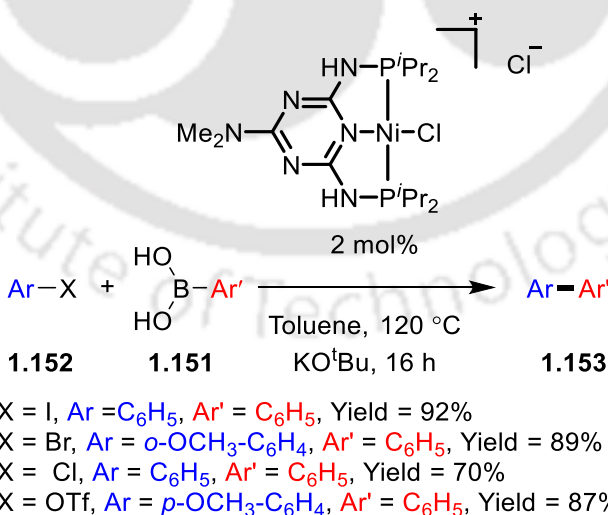
nucleophilic neopentylglycolboronate with catalyst loading 10 mol% at 80 to 110 °C (Scheme 1.36).¹⁴⁶



Scheme 1.36. Suzuki cross-coupling reaction of arylboronic ester and aryl halide employing Ni(dppe)/dppe as catalyst.¹⁴⁶



Scheme 1.37. Suzuki cross coupling reaction between numerous arylboronic acid and aryl chloride employing NiCl₂(dppp) as catalyst.¹⁴⁷



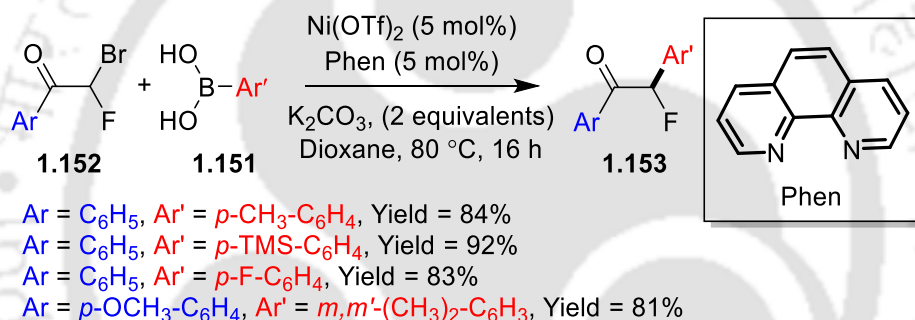
Scheme 1.38. Ni(II)-PNP pincer catalyzed Suzuki coupling reaction.¹⁴⁸

In 2011, Han's group demonstrated stable, readily available NiCl₂(dppp) as an effective catalyst

catalyst for Suzuki coupling reaction of aryl bromide or less reactive aryl chloride even with 1 mol% without any the supporting ligand (Scheme 1.37).¹⁴⁷

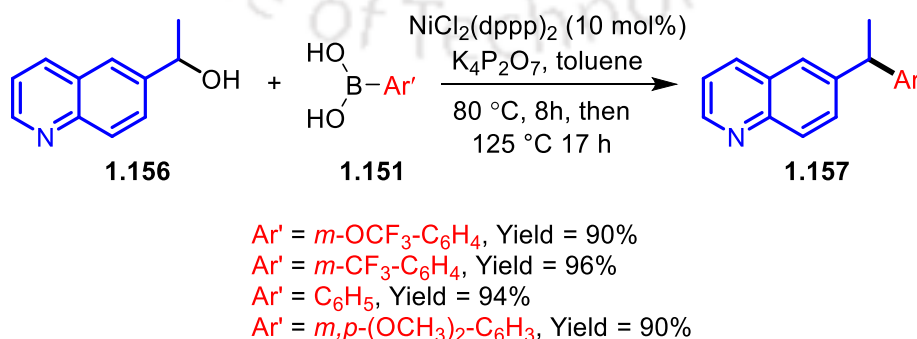
Later, Kirchner's group synthesized air and thermally stable Ni(II)-PNP pincer complex and performed the Suzuki coupling reaction with various aryl halide (primary, secondary and pseudo halides) and aryl boronic acid (Scheme 1.38).¹⁴⁸ Ni(II)-PNP pincer complex displayed reactivity towards coupling reaction with a good to excellent yield of the desired products.

In 2019, Wu and co-workers established catalytic system for Suzuki coupling reaction in the presence of Ni(OTf)₂ as the catalyst, Phen as ligand, K₂CO₃ as base and dioxane as solvent at 80 °C for 16 h (Scheme 1.39).¹⁴⁹ They displayed coupling reaction of boronic acid with α -bromo- α -fluoroketones to form 2-fluoro-1,2-diarylethanone as product with high yield.

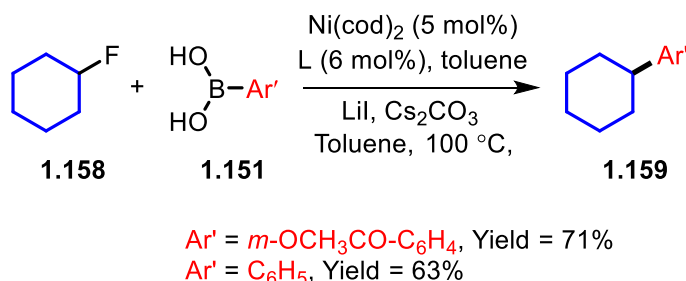


Scheme 1.39. Nickel catalyzed coupling reaction of α -bromo- α -fluoroketones with boronic acid.¹⁴⁹

In 2019, Samec and co-workers studied the efficiency of various nickel catalysts for coupling reaction. They found that 10 mol% NiCl₂(dppp)₂ as catalyst, K₄P₂O₇ as base in toluene at 80 °C for 8 h and 125 °C for 17 h for the coupling reaction of boronic acid with quinolyl alcohol gave high yield of desired product (Scheme 1.40).¹⁵⁰



Scheme 1.40. Nickel catalyzed Suzuki coupling reaction of boronic acid with quinolyl alcohol.¹⁵⁰



Scheme 1.41. Nickel catalyzed Suzuki coupling reaction of alkylfluoride with boronic acid.¹⁵¹

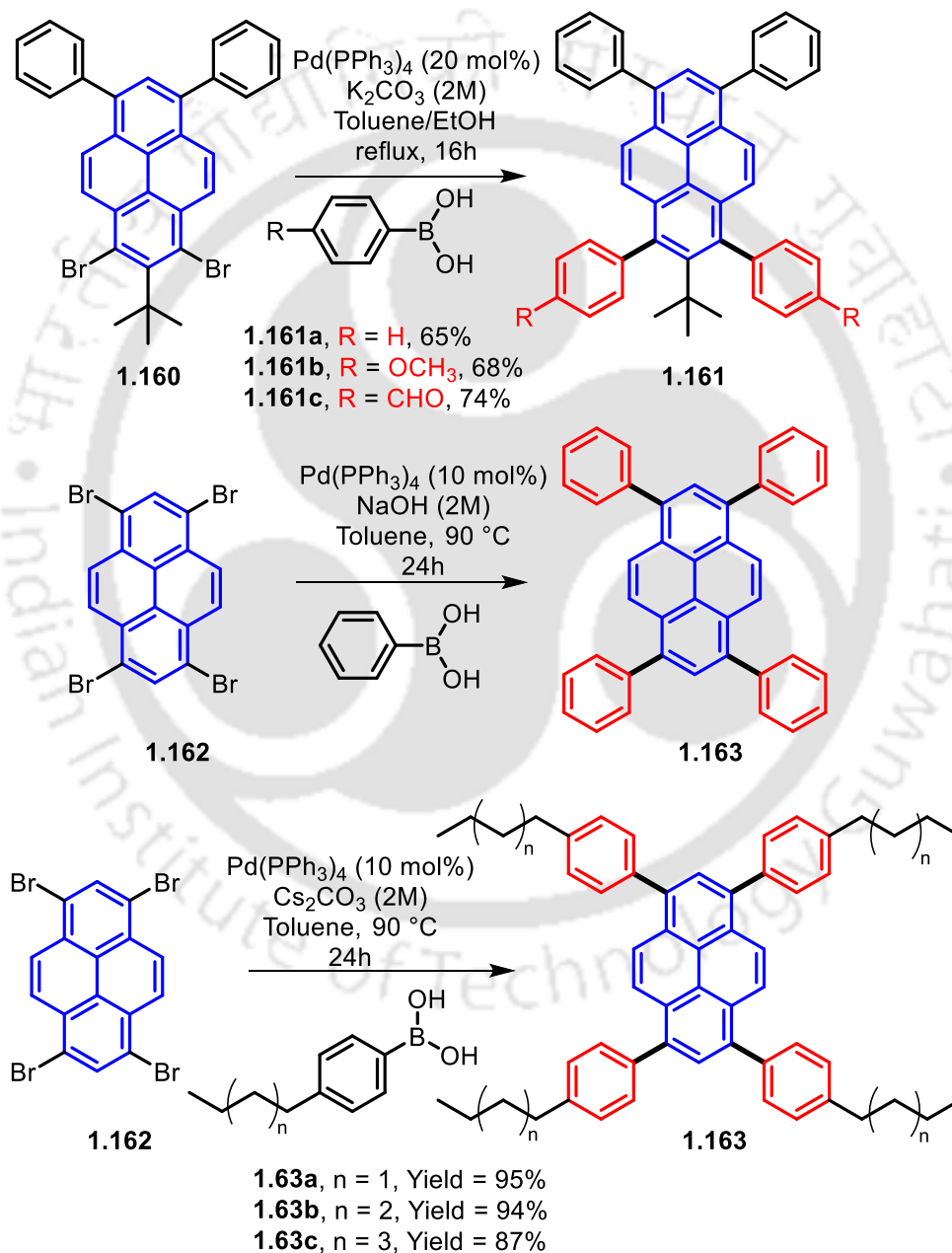
The C-F bond is very less reactive towards Suzuki coupling reaction. To solve this problem, Wolf and co-workers demonstrate the efficient catalyst system for the coupling reaction by employing the combination of nickel-catalyst $[\text{Ni}(\text{cod})_2]$ and nitrogen based ligand (Scheme 1.41).¹⁵¹ They reported an efficient catalytic system for coupling reaction of inactivated alkylfluoride with boronic acid with good yield.

Multi-fold Suzuki cross-coupling reaction has great importance in synthesis of polyarylated polycyclic aromatic hydrocarbons which have immense application in fluorescence¹⁵² as well as electronic devices.¹⁵³ The most effective catalyst is $\text{Pd}(\text{PPh}_3)_4$ towards multi-fold Suzuki coupling reaction.^{152, 154}

Hu and co-workers synthesized polyarylatedpyrene (**1.161**, Scheme 1.42) compounds by Suzuki coupling reaction employing $\text{Pd}(\text{PPh}_3)_4$ as catalyst from 7-tert-Butyl-1,3-diphenyl-5,9-dibromopyrene and arylboronic acids.¹⁵² They demonstrated the optical properties of synthesized compounds (**1.161**) where phenyl group acts as an acceptor for **1.161b** and a donor for **1.161c**. Single-crystal X-ray analysis show that the conformations of **1.161** are extremely twisted, which are advantageous for suppressing the π -aggregations and stand out from the typical 1,3,5,9-tetraarylpyrenes and related 1,3,6,8-tetraarylpyrenes. The modification of emission colour from deep blue to green in solution can be achieved by changing the π -conjugation orientations through a variety of substitution sites, successfully controlling the excited-state ICT pathways. The donor and acceptor containing molecules **1.161b** & **1.161c** are highly emissive in nature with high quantum yield (**1.161b**; $\phi = 74\%$, **1.161c**; $\phi = 61\%$) in the thin-film.

Yamato and co-workers reported multi-fold Suzuki coupling reaction to access polyarylatedpyrene compounds (**1.162**, **1.162a-c**) from 1,3,6,8-tetrabromopyrene in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst.¹⁵⁴ They demonstrated that *tetrakis*-(pentylphenyl)pyrene (**1.163b**) is a photoelectric functional material and it possesses a remarkable crystallization-induced emission

enhancement (CIEE) feature which improves quantum yield up-to 72%. Interestingly, it exhibits high selectivity and sensitivity of detection towards *ortho*-nitroaniline with the limit of detection 9.99×10^{-8} M.^{154b} Bisri fabricated an ambipolar FET devices with the single crystal of **1.163**. A hole mobility and an electron mobility were achieved up-to 9.4×10^{-3} cm²/Vs and 7.7×10^{-2} cm²/Vs of **1.163** in ambipolar FET devices.¹⁵³



Scheme 1.42. Multi-fold Suzuki coupling reaction to access of polyarylatedpyrene.^{152, 154}

1.3. Application of PAHs

1.3.1. Detection of explosive nitroaromatic compounds by PAHs

Recently, researchers have devoted their studies towards the detection of the nitro-aromatic compounds (NACs) (the primary constituents for explosive materials) and polynitro aromatics like picric acid (PA), trinitrotoluene (TNT), dinitrotoluene (DNT) and trinitrobenzene (TNB) among others.^{58f} Polynitro aromatics are one of the most used explosive materials,¹⁵⁵ whose intake may cause severe neurological damage and abnormality in liver functioning.¹⁵⁶ According to the US Environmental Protection Agency (EPA), the permissible concentration of TNT in drinking water is 2 ppb. Picric acid (PA) which widely is used in the pharmaceutical industry, rocket fuel manufacturing, and dye industry is highly soluble in water and is a common groundwater pollutant.^{58c,157} Detection of trace polynitro aromatics is thus of prime importance from the point of view of both efficient defense operations and environmental safety.

In 2011, Mukherjee and co-workers reported the synthesis of organic compounds which consisted of trimethylsilyl group connected through ethyne unit to aromatic core molecules (**1.164–1.166**, **1.96i**, **1.148j**) (Figure 1.12). These molecules were efficient as sensors of picric acid.^{36b} For the detection of TNT and PA, the Stern-Volmer binding constant (K_{sv}) of the compound **1.96i** was $1.97 \times 10^4 \text{ M}^{-1}$ and $2.15 \times 10^5 \text{ M}^{-1}$ respectively. On the other hand, using **1.148j** the corresponding values K_{sv} were found to be $1.4 \times 10^3 \text{ M}^{-1}$ for TNT, $1.1 \times 10^4 \text{ M}^{-1}$ for PA. Both **1.96i** and **1.148j** demonstrated the phenomena of fluorescence quenching by static-quenching mechanisms. These fluorophores show higher fluorescence quenching efficiency for the nitro-aromatic compounds in comparison to other electron-deficient non-nitroaromatic compounds. This is attributed to the formation of charge-transfer complex *via* electrostatic interaction between electron-rich fluorophore and electron-deficient nitro-aromatic compounds. One would expect planar **1.148j** with a higher π -electron density to show higher fluorescence quenching efficiency. This however is mitigated due to the steric effect of four bulky TMS groups. On similar lines and contrary to one's expectation, less electron-rich non-planar **1.165** demonstrated a higher quenching efficiency than highly electron-rich planar **1.148j** owing mainly to the less number of the bulky trimethylsilyl substituents. Notably, **1.96i** is found to be a better sensor than **1.148j** and senses PA up to 0–8 ppb level. The intermolecular distance between picric acid and the fluorophore in the charge transfer complexes with **1.96i** and **1.148j** was calculated to be 3.17 Å and 3.30 Å

respectively. This is indicative of a higher interaction energy for **1.96i** (16.32 kcal mol⁻¹) when compared to **1.148j** (14.09 kcal mol⁻¹).

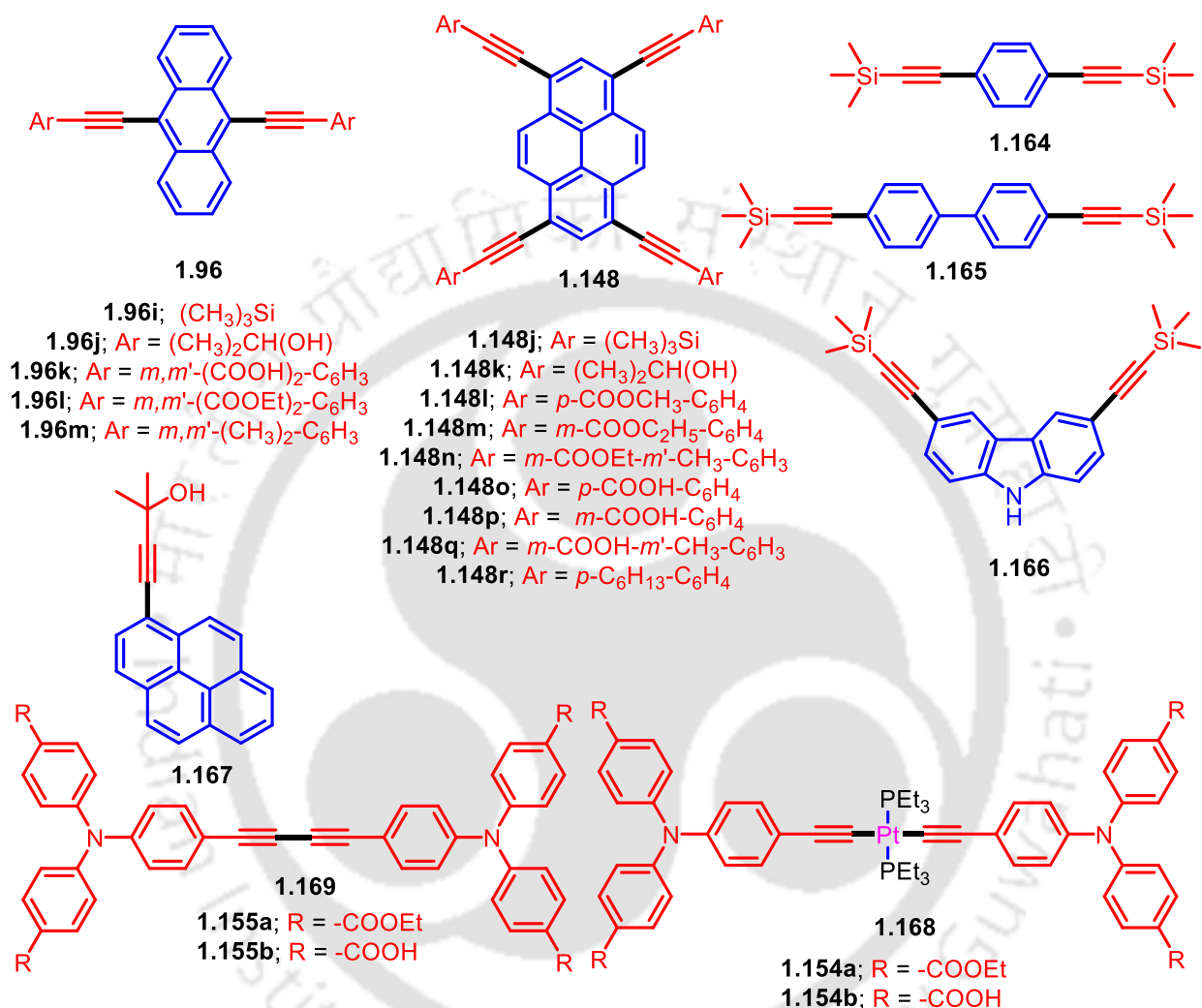


Figure 1.12. A few of polyalkynylated PAHs used as sensors for nitroaromatic compounds.

Mukherjee went on to explore the use of **1.96k–m** (Figure 1.12) in the sensing of PA in solution as well as in the solid-state.^{58a} Among **1.96k–m**, the compound **1.96k** forms non-covalent supramolecular polymer through H-bond due to its electron deficient nature. The K_{sv} value is higher for **1.96k** (2100 M⁻¹) than either **1.96l** (200 M⁻¹) or **1.96m** (130 M⁻¹). In the solid-state for a thin film, while **1.96k** shows emission quenching up to 96%, only 8% quenching was observed with **1.96l**.¹⁵⁸ The unexpectedly high fluorescence quenching efficiency of **1.96k** in comparison with **1.96l** and **1.96m** is traced to the formation of noncovalent supramolecular polymer.

Later in 2013, the Mukherjee group reported supramolecular polymers **1.167**, **1.96j**, **1.148k** (Figure 1.12) containing ethyne units which showed excellent chemosensing behavior to detect nitroaromatic explosive compounds.^{58b} The Stern-Volmer binding constant (K_{SV}) of the fluorophores **1.167**, **1.96j** and **1.148k** towards TNT detection were $1.9 \times 10^2 \text{ M}^{-1}$, $8.7 \times 10^4 \text{ M}^{-1}$ and $6.4 \times 10^3 \text{ M}^{-1}$, respectively. On the other hand, the corresponding values for the detection of DNT were $1.3 \times 10^2 \text{ M}^{-1}$, $8.5 \times 10^4 \text{ M}^{-1}$ and $3.9 \times 10^3 \text{ M}^{-1}$, respectively. In contrast to the general expectation that electron-rich **1.148k** must have a higher fluorescence quenching efficiency (and hence a greater nitroaromatic sensing ability) than **1.96j**, a reverse trend is observed as the bulky 2-hydroxy-propan-2-ide groups in **1.148k** ensures a lower fluorescence quenching efficiency when compared to **1.96j**. On the other hand, **1.167** gave the lowest quenching efficiency due to low π -conjugation. DFT studies indicate the π - π intermolecular interaction distance between the fluorophores **1.96j** and **1.148k** with DNT to be 2.947 Å and 3.279 Å respectively. The corresponding binding energies were 22.55 kcal and 17.10 kcal respectively. The change in HOMO-LUMO gap upon DNT binding was higher for **1.96j** (0.26 eV) in comparison with **1.148k** (0.06 eV). DFT calculations are also indicative of the higher fluorescence quenching efficiency of **1.96j** that is reflected in its better sensing of DNT.

The fluorescence life time of **1.148k** is 2.78 ns and it does not change much with respect to the concentration of DNT. This implies that a static quenching mechanism is followed that involves a charge-transfer complex formation of **1.148k** in the ground state with DNT. It has been observed that **1.96j** senses up to 2 ppb of TNT and 13.7 ppb of DNT. The binding affinity for both **1.96j** and **1.148k** with nitro-aromatic compounds was found to be higher than **1.167**. Not surprisingly, no color change was detected upon addition of TNT to **1.167**. While in solution, **1.96j** shows better DNT sensing ability than **1.148k**, in the solid-state **1.148k** is a better sensor than **1.96j**. Thin films of **1.167**, **1.96j** and **1.148k** exposed to DNT vapour demonstrated a fluorescence quenching of about 30%, 50% and 55% respectively. The presence of OH group in these compounds helps to form the supramolecular polymer *via* H-bonding. In the solid-state, the higher fluorescence quenching efficiency obtained with **1.148k** (55%) in comparison to pyrene (5%) and 1,3,6,8-tetraethynylpyrene (10%) indicates that supramolecular H-bonding interaction plays a pivotal role in enhancing the fluorescence quenching efficiency.^{58b}

Mukherjee also reported π -conjugated polyethynyl bridged pyrene core containing molecules which could sense the nitroaromatic compounds **1.148l-q** (Figure 1.12).⁴⁵ Carboxylic

acid containing compounds (**1.148o–q**) that are capable of forming supramolecular polymers through H-bonding demonstrated a higher quenching efficiency than the ester containing compounds (**1.148l–n**). The hydrogen bonding in supramolecular polymers results in a higher exciton migration. Moreover, the quenching efficiency of all the sensors derived from **1.148l–q** were higher towards the nitro-aromatic compounds than towards the non-nitroaromatic compounds. Upon changing the solvent from polar aprotic DMSO to polar protic methanol, acid containing compounds (**1.148o–q**) exhibited blue shift in absorption (10 nm) as well as in emission (15 nm). While polar aprotic solvents preserve the H-bonded supramolecular polymers of carboxylic acid containing **1.148o–q**, the better solvating polar protic solvents are capable of destroying these H-bonds to form monomers. The higher fluorescence quenching efficiency of **1.148o–q** in polar aprotic solvent is attributed to similar reasons. Notably, the ester group containing compounds gave no noticeable change in fluorescence quenching efficiency either in chloroform or in DMSO. The Stern-Volmer binding constant (K_{SV}) for PA sensing with **1.148l–q** are 9955.17 M⁻¹, 22702.89 M⁻¹, 11953.5 M⁻¹, 32339.63 M⁻¹, 8188.21 M⁻¹ and 37813.85 M⁻¹ respectively. The addition of PA to all the sensors based on **1.148l–q**, caused a downfield shift in ¹H NMR spectra. The shifting of phenyl protons was less prominent than the pyrene protons. It is hypothesized that PA interacted with pyrene moieties of **1.148l–q** via π - π interaction.

Recently, Mukherjee and co-workers demonstrated the triphenylamine based compounds **1.168** and **1.169** (Figure 1.12) which behaved as PA detectors.^{58c} The triphenylamine (TPA) fluorophore have wide applications as aggregation induced emissive (AIE) materials,¹⁵⁹ as biomarkers,¹⁶⁰ and as solid state emitters.¹⁶¹ The π - π interaction in the conjugated polyaromatic compounds allows them to aggregate in solution which reduces the intensity of the fluorescence in a phenomenon known as aggregation-caused quenching (ACQ).¹⁶² The bulky group Pt(PEt₃)₂ in **1.168** prevents the formation of aggregation in solution. The properties of **1.168** were compared with **1.169** that lacks a Pt(PEt₃)₂ group. UV-Vis titration of **1.168b** and **1.169b** with PA revealed strong bands at higher wavelength (420 nm) with change of color from colorless to yellow due to the formation of charge transfer complex. On the other hand, for **1.168a** and **1.169a**, a new weak band is observed at higher wavelength (436 nm). The Stern-Volmer constant (K_{SV}) is 5.72×10^6 M⁻¹ and 2.9×10^5 M⁻¹ for **1.168b** and **1.169b**, respectively that reflects its higher quenching efficiency. The mechanism of this fluorescence quenching is said to involve the formation of charge transfer complex along with a resonance energy transfer.

1.3.2. Application of PAHs in OFET devices

Bardeen, Brattain and Shockley were the first to invent a transistor in 1947,¹⁶³ and were awarded the Nobel Prize in physics for the same in 1956.¹⁶³ At first, the FET devices were fabricated by using inorganic semiconductors. Later in 1998, for the first time FET devices were fabricated with only organic semiconductors at Philips Research Laboratories.^{10a,164} Back then, the charge carrier mobilities (μ_{FET}) obtained were $<10^{-2} \text{ cm}^2/\text{Vs}$ which was much lower than the corresponding values reported for amorphous silicon ($\mu_{\text{FET}} = 10^{-1} \text{ cm}^2/\text{Vs}$).^{10a,103} For fabricating a FET device, the required processing temperature for inorganic semiconductor is above 350 °C, whereas for an organic semiconductor, it is much lesser (ca. 180 °C). Semiconductors can be deposited on the devices from gas phase by physical vapor deposition (PVD), chemical vapor deposition (CVD) and also by inexpensive solution process (screen printing, inject printing and spin coating) techniques. Both polymer and low molecular weight compounds are suitable for the solution process deposition.

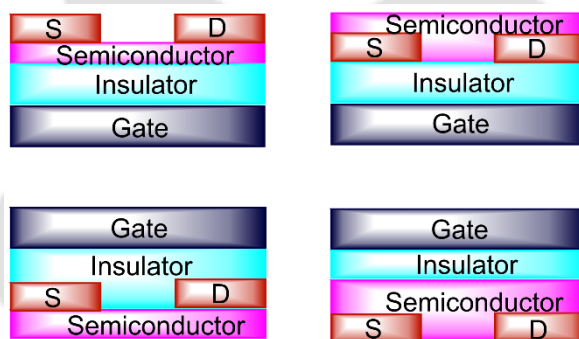


Figure 1.13. Schematic cross-section of common OFET structures: a) bottom-gate and top contact; b) bottom-gate and bottom contact; c) top-gate and top contact, and d) top-gate and bottom contact.

The main components of an OFET device include electrodes (source, drain, and gate electrodes), semiconductors and insulators. These devices are constructed in two configurations of (i) bottom-gate and (ii) top-gate; both of which can be either top contact (a and c, Figure 1.13) or bottom contact (b and d, Figure 1.13). The channel length is the distance between the source and the gate. While silicon wafer is typically used as a substrate and gate electrode, silicon oxide can be used as the dielectric layer.

The operation of a FET device can be understood say for example considering the one with a *p*-type semiconductor. If negative voltage (V_G) is applied to the gate electrode, then an electric

field perpendicular to the dielectric field is created, that results in the generation of positive charge carriers (holes) between the semiconductor and the gate. Simultaneous application of voltage to the drain results in transportation of holes from source to drain. While during the conduction of holes, the device is said to be “on” state, a device operating at $V_D = 0$ is considered “off” state.¹⁶⁵ The most important output characteristics resulting from an OFET device include threshold voltage (V_T), current on/off ratio ($I_{\text{on/off}}$) and charge carrier mobilities (μ_{FET}). The drain current can be calculated by using the following equations (1) and (2).^{10a,166}

$$I_D = \frac{W}{L} \mu_{\text{FET, lin}} C_i [(V_G - V_T)V_D - V_D^2/2] \quad (2)$$

$$I_D = \frac{W}{2L} \mu_{\text{FET, sat}} C_i (V_G - V_T)^2 \quad (3)$$

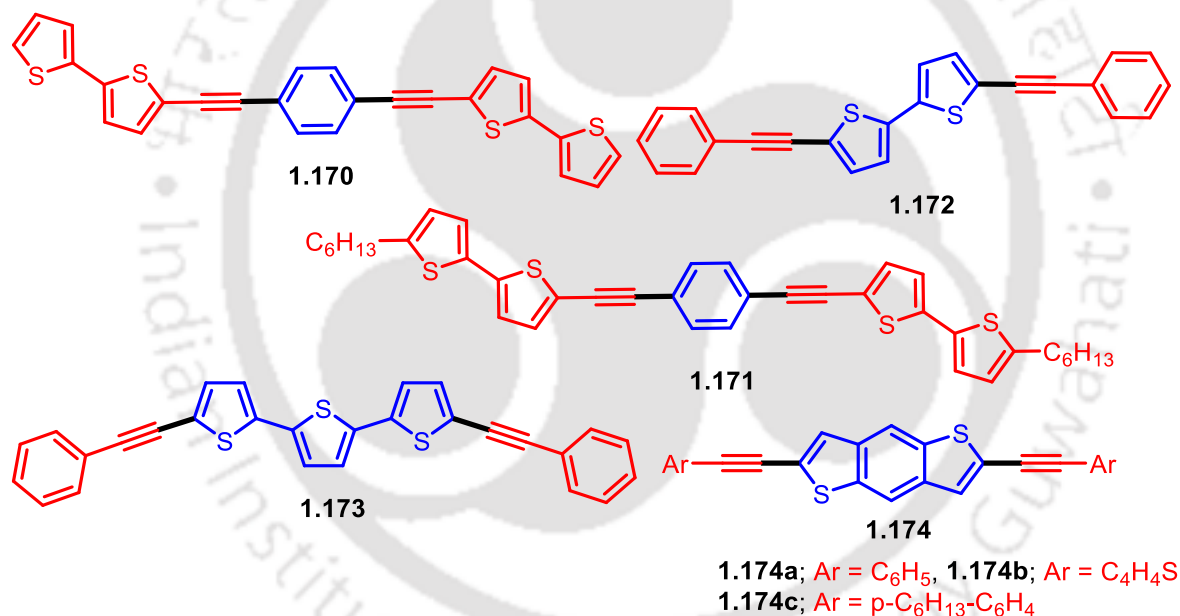


Figure 1.14. PAHs based on benzene and thiophene that have been utilized in OFET devices.

Li and Hu reported organic compounds consisting of ethynyl bridges (**1.170–1.172**) which were employed in construction of OFET devices (Figure 1.14).¹⁶⁷ CV studies revealed the irreversible redox behavior of compounds **1.170** and **1.171** and quasireversibility behavior of **1.172**. These molecules behaved as *p*-type organic semiconductors in top-contact geometry OFET devices, which were fabricated by using octyl-trichlorosilane (OTS) treated with SiO₂/Si as substrates. The obtained values of output characteristics of these OFET devices include, mobility

(**1.170**; $5.6 \times 10^{-2} \text{ cm}^2/\text{Vs}$, **1.171**; $8.4 \times 10^{-2} \text{ cm}^2/\text{Vs}$ and **1.172**; $2.8 \times 10^{-2} \text{ cm}^2/\text{Vs}$), $I_{\text{on/off}}$ ratio (**1.170**; 1.3×10^6 , **1.171**; 1.9×10^5 and **1.172**; 3.9×10^5), and threshold voltage (**1.170**; 6.34 V, **1.171**; 11.8 V and **1.172**; 1.72 V) at $T_{\text{sub}} = 20^\circ\text{C}$. Generally *p*-channel OFET shows negative threshold voltage but **172** had positive threshold voltage due to doping with water or with oxygen.

Porte and co-workers synthesized two *p*-type thiophenophenylene semiconductors **1.170** and **1.173** (Figure 1.14) for fabrication of air-stable organic thin film transistors (OTFT) devices. Porte determined field-effect mobility (ca. $10^{-3} \text{ cm}^2/\text{Vs}$ and $10^{-2} \text{ cm}^2/\text{Vs}$ for **1.172** and **1.173** respectively), current on/off ratio (10^4 and 10^6 for **1.172** and **1.173** respectively), and threshold voltage ($(-5) - 2 \text{ V}$ and $(-4) - 9 \text{ V}$ for **1.172** and **1.173** respectively), at $T_{\text{Sub}} = 25^\circ\text{C}$.¹⁶⁸

Hu reported the ethynylene-containing benzo[1,2-b:4,5-b'] dithiophene (**1.174**) (Figure 1.14) which behaved as *p*-type semiconductors in OFET devices.¹⁶⁹ The compound **1.174a** was found to show one of the most high field effect mobility (up to $1.17 \text{ cm}^2/\text{Vs}$) and current on/off ratio of 10^7 . For the compounds **1.174b** and **1.174c**, the observed mobilities were $0.07 \text{ cm}^2/\text{Vs}$ and $0.28 \text{ cm}^2/\text{Vs}$ respectively with the current on/off ratio of 10^6 and 10^7 respectively.

In 2007, Kashiwagi synthesized polyfluorinated compounds (**1.175**) containing ethyne bridges via Sonogashira coupling reaction. These molecules were used to fabricate top contact OFET devices using Ca and Au as source and drain electrodes at room temperature at 2×10^{-6} Torr (Figure 1.15).²⁷ Fluorine (E.N = 4 on Pauling scale) containing π -conjugated molecules are expected to show high charge carrier mobility.¹⁷⁰ The compounds **1.175b**, **1.175d** and **1.175e** having heptafluoronaphthanyl group responded to FET device under positive gate bias and behaved as *n*-type channel. However, the derivatives of naphthalene having pentafluorophenyl group (**1.175a** and **1.175c**) did not respond to FET device. Interestingly, 2,6-bis-[(naphthalen-2-yl)ethynyl]naphthalene behaves as a *p*-type channel but after the introduction of fluorine groups, the compound **1.175b** behaved as an *n*-type channel.²⁷ These OFET devices gave moderate field effect mobility (**1.175b**; $3.4 \times 10^{-3} \text{ cm}^2/\text{Vs}$, **1.175d**; $2.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and **1.175e**; $1.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$), current on/off ratio (**1.175b**; 5.4×10^3 , **1.175d**; 7.9×10^2 and **1.175e**; 2.4×10^4) and threshold voltages (**1.175b**; 48 V, **1.175d**; 20 V and **1.175e**; 29 V).

Recently, Ai and Jiang reported asymmetric organic semiconductor **1.176a** (Figure 1.15) which showed a mobility of $0.79 \text{ cm}^2/\text{Vs}$ when fabricated as single crystal OFET device. They concluded asymmetry as one of the alternative pathway of achieving high performing semiconductors.¹⁷¹

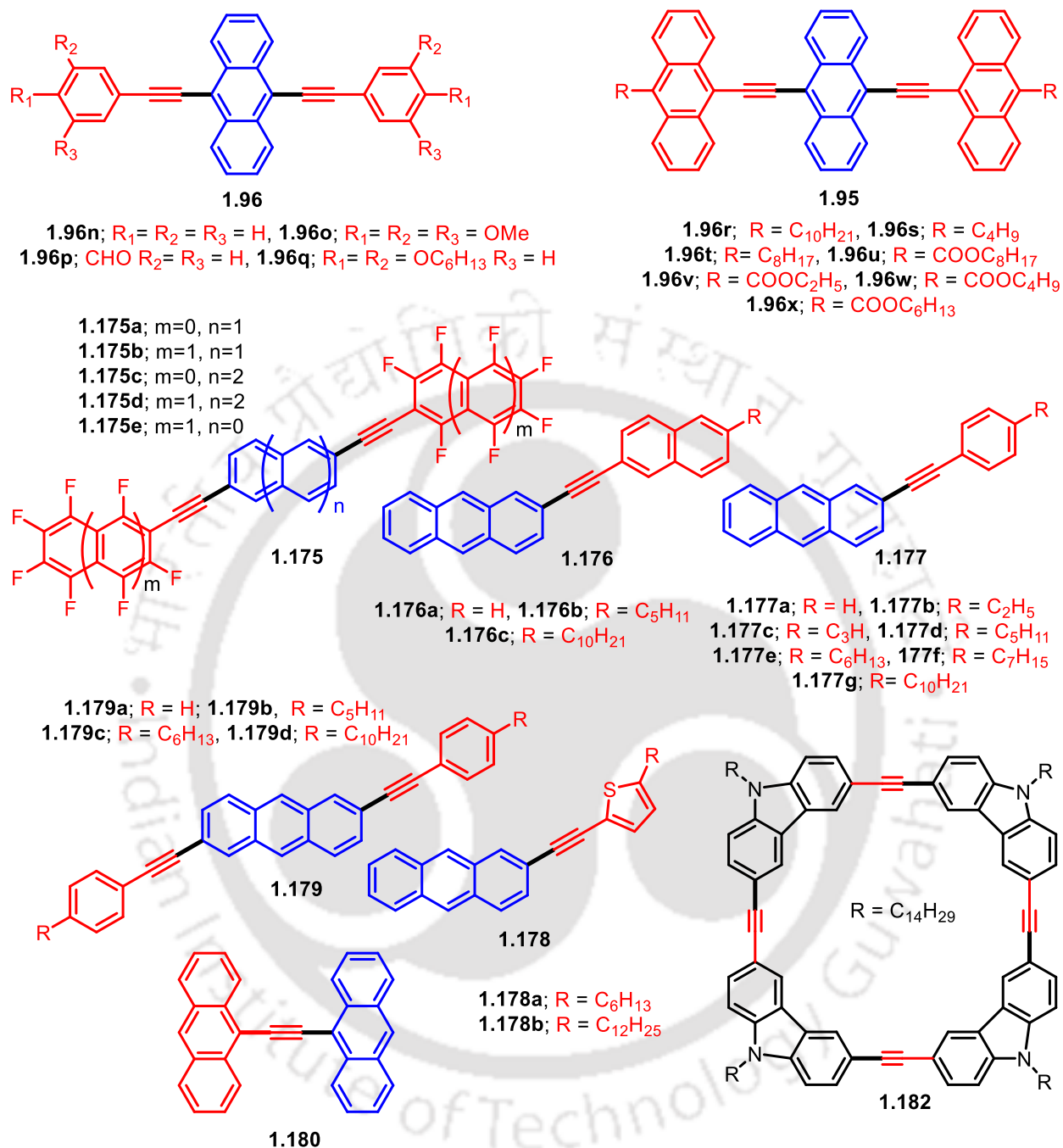


Figure 1.15. A few of polyalkynylated PAHs used for fabricating OFET devices

Kim demonstrated that alkyl side chain length plays a great role not only in increasing the solubility of anthracene based compounds **1.176b–g** (Figure 1.15) but also in enhancing their performance in solution processed OFET devices. Among these six anthracene based compounds

which behaved as *p*-type semiconductors, 2-(*p*-pentylphenylethynyl)anthracene (**1.176d**) showed the highest field-effect mobility of $0.55 \text{ cm}^2/\text{Vs}$ as well as $I_{\text{on/off}}$ ratio (1.9×10^6).¹⁷² The field effect mobility increases on going from ethyl-substituted (**1.176b**; $3.5 \times 10^{-4} \text{ cm}^2/\text{Vs}$) to propylsubstituted (**1.176c**; $0.046 \text{ cm}^2/\text{Vs}$) to pentyl alkylated substrate (**1.176d**; $0.55 \text{ cm}^2/\text{Vs}$) and decreases from heptyl (**1.176f**; $2.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$) to decyl alkylated substrate (**1.176g**; $1.4 \times 10^{-3} \text{ cm}^2/\text{Vs}$).

Kim further demonstrated that linearity and planarity are major factors required in a molecule to attain a close molecular packing that is necessary for fabricating OFET devices.^{50b} Both the compounds **1.177b** and **1.177c** (Figure 1.15) behaved as *p*-type semiconductors, with the former having higher field-effect mobility ($0.036 \pm 0.003 \text{ cm}^2/\text{Vs}$), current on/off ratio (6×10^4) and threshold voltage ($V_T = 29$) than **1.177c** ($\mu = 0.011 \pm 0.002 \text{ cm}^2/\text{Vs}$, $I_{\text{on/off}} = 2 \times 10^4$, $V_T = 12$).

Hu and co-workers demonstrated that position of ethynyl spacer has significant influence on the mobility of anthracene derivatives in OTFTs.¹⁷³ Ethynyl spacer functionalization at 1-position showed zero mobility whereas ethynyl substitution at 2-position of anthracene (**1.177a**) (Figure 1.15) showed mobility up to $1.6 \text{ cm}^2/\text{Vs}$ with a current on/off ratio of 1.0×10^6 and threshold voltage (V_T) of 48 V .¹¹²

Lee demonstrated thermally stable and highly soluble asymmetric alkynyl bridged anthracene-thiophene hybrids **1.178a–b** (Figure 1.15) as good candidates for OTFT devices.¹⁷⁴ The compound **1.178a** displayed mobility of $0.13 \text{ cm}^2/\text{Vs}$, $I_{\text{on/off}}$ ratio of 2.6×10^6 and V_T of 1.43 V . On the other hand, **1.178b** exhibited lower mobility of $0.02 \text{ cm}^2/\text{Vs}$, $I_{\text{on/off}}$ of 1.0×10^6 and V_T of 5 V .¹¹³

Kwon reported end-capped 2,6-bis-phenylethynylanthracene **1.179a** (Figure 1.15) having rod-like anatomy as an organic semiconductor for OTFT devices. The compound **1.179a** showed an average μ of $0.40 \text{ cm}^2/\text{Vs}$ with $I_{\text{on/off}}$ in the range of 10^6 and threshold voltage of 1.48 V .¹⁷⁵

Kobayashi synthesized a crystalline and highly soluble 2,6-bis(4-pentylphenylethynyl)anthracene **1.179b** (Figure 1.15) which displayed comparable hole mobilities. OFET devices could be fabricated either by vacuum-deposited film method ($\mu = 0.94 \text{ cm}^2/\text{Vs}$, $I_{\text{on/off}} = 1.6 \times 10^7$, $V_T = 12.1 \text{ V}$) or by a simple drop-cast method ($\mu = 0.63 \text{ cm}^2/\text{Vs}$, $I_{\text{on/off}} = 6.8 \times 10^6$, $V_T = 20.7 \text{ V}$).^{50a}

Lee and co-workers synthesized novel 4-alkylethynylbenzene end-capped anthracene derivatives **1.179c–d** (Figure 1.15) which could be utilized for solution-processed OTFTs. The compound **1.179c** exhibited higher field-effect mobility ($\mu_{\text{FET}} = 4 \times 10^3 \text{ cm}^2/\text{Vs}$) than **1.179d** (μ_{FET}

= 2×10^3 cm²/Vs), owing not only to the presence of smaller alkyl groups but also due to its more crystalline structure.¹⁷⁶ At 160 °C, **1.179c** and **1.179d** had current on/off ratio of 10^5 and 10^4 respectively and threshold voltage of 11.3 V and 4.2 V, respectively.

Hu demonstrated the use of highly fluorescent compound **1.96n** (Figure 1.15) as a good contender that displays high field-effect as well as very high photoswitch performance, in transistors based on α (nanorods, mobility up to 0.73 cm²/Vs) and β (nanoribbons, mobility less than 0.01 cm²/Vs) phase single crystals.¹⁷⁷ While it adopts a planar conformation in the α (typical herringbone packing) phase, a non-planar conformation is observed in the β (nearly face-to-face packing) phase.¹⁷⁷ A high mobility of up to 3.2 cm²/Vs along with a current on/off ratio of 10^5 was obtained when **1.96n** was anchored onto an Au electrode via a thiophenol group. Organic single crystal transistor (OSCT) device based on **1.96n** have shown high bending durability of about 300 times with a field-effect mobility of around 2.1 cm²/Vs.¹⁷⁸ However, **1.96o** (Figure 1.15) did not show any FET activity.¹⁷⁹ Taticchi in 2010, reported FET active arylacetylene based semiconductor **1.96q** (Figure 1.15) which exhibited *p*-type properties with mobilities of about 10^{-4} cm²/Vs.⁸⁹

In 2008, Aquila developed a series of OTFT devices based on decyl-substituted ternary anthracene **1.96r** (Figure 1.15) which were fabricated in “top” as well as “bottom” contact configurations by utilizing the spin-coating technique. These OTFTs exhibited mobilities up to 5.5×10^{-2} cm²/Vs with current on/off ratio greater than 10^4 .¹⁸⁰ Additionally, these OTFT devices had good NO and NO₂ sensing property.¹⁸¹ When used as an organic semiconductor, **1.96r** showed an average mobility of $2.0 \pm 0.8 \times 10^{-3}$ cm²/Vs and current on/off ratio of 10^4 . Whereas its higher alkyl chain oligomer 9,10-*bis*((10-(2-ethylhexyl)anthracen-9-yl) ethynyl)anthracene **1.96t** (Figure 1.15) showed an average mobility of $1.1 \pm 0.1 \times 10^{-2}$ cm²/Vs that is comparable to **1.175a** with a current on/off ratio of 10^5 .¹⁸²

Giannini, Torsi, Mastrorilli and co-workers reported anthracene core organic semiconductors (**1.96v–x**) (Figure 1.8) for their application in OFET devices of top-contact, bottom-gate geometry fabricated using SiO₂/n-doped Si as substrate by spin-coating.¹⁸³ The compound **1.96v** exhibited lower mobility ($\mu = 10^{-6}$ cm²/Vs) than the corresponding thermally annealed film compounds of **1.96w** and **1.96x** ($\mu = 2.8 \pm 0.3 \times 10^{-2}$ cm²/Vs and $4.4 \pm 0.1 \times 10^{-2}$ cm²/Vs respectively) with a comparable current on/off ratio of 10^4 .

Hu and co-workers used planar “H” type molecule **1.180** (Figure 1.15) (single crystal short ribbon) to fabricate device by developing a new “organic-ribbon mask” method. The short ribbon **1.180** had field-effect mobility of $0.82 \text{ cm}^2/\text{Vs}$ with 1.0×10^5 as an on/off ratio.¹⁸⁴

Xu and Zhu reported for the first time, OFET devices based on the single bundle nanofibers (SBNs) based on cyclic conjugated organic macrocyclic compound **1.182** (Figure 1.15).¹⁸⁵ The *p*-type semiconductor **1.182** was used to fabricate top-gate OFET devices by drop-casting method. Doped *n*-type silicon wafer was used as the gate electrode, while Au was the source as well as drain electrode. OTS-modified SiO_2 served as the dielectric layer. For the single bundle nanofibers (SBN) of **1.182**, the maximum current on/off ratio observed was 10^5 with the average and maximum hole mobilities of $1.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $3.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ respectively. For the thin film OFET devices based on **1.182**, the average hole mobility was $6.7 \times 10^{-5} \text{ cm}^2/\text{Vs}$. The hole mobility for the SBN-OFETs, were higher than that of thin-film OFETs owing to the highly ordered structure of nanofibers.

Choi demonstrated the significant high field-effect mobility of highly conjugated, X-shaped anthracene based highly soluble molecules **1.181a–b** (Figure 1.16) and solution processed these to fabricate thin-film transistors.¹⁸⁶ The highly crystalline as-spun-film of **1.181b** afforded higher mobility ($2.4 \times 10^{-2} \text{ cm}^2/\text{Vs}$) than **1.181a** ($0.4 \times 10^{-2} \text{ cm}^2/\text{Vs}$) owing to the presence of peripheral hexyl groups which helped in its better π -stacking arrangement in 2-dimension and thus making it suitable to be fabricated in OTFT devices.¹²⁵

Choi then studied the application of highly soluble bithiophene and alkyl substituted anthracene based molecules **1.181c–e** (Figure 1.16) as *p*-type semiconductors.¹⁸⁷ Of these two molecules, **1.181e** which showed J-aggregation had higher mobility of $0.07 \text{ cm}^2/\text{Vs}$ compared to **1.181c** ($\mu = 7.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$) in solution processed photovoltaic and TFT devices.¹⁸⁷ Similarly, the 2-D anthracene based π -conjugated crystalline molecules **1.181d** and **1.181f** (Figure 1.16) showed mobility in the range $0.010 - 0.10 \text{ cm}^2/\text{Vs}$ and $I_{\text{on/off}} > 10^3$ when used for fabricating solution processed OTFT and OPV devices. 2-hexylthieno[3,2-b] thiophene substituted anthracene derivative **1.181g–h** (Figure 1.16) displayed high mobility of $0.10 - 0.15 \text{ cm}^2/\text{Vs}$ in TFTs. In FET devices, **1.181g** exhibited higher mobility of $0.70 \text{ cm}^2/\text{Vs}$ compared to **1.181h** ($\mu = 0.23 \text{ cm}^2/\text{Vs}$).¹⁸⁸ The compound **1.181i** that adopts highly ordered j-aggregated molecular arrangement exhibited mobilities of $0.2 - 1.6 \text{ cm}^2/\text{Vs}$ with an on/off ratio $> 10^3 - 10^5$ in OFET devices.^{13b}

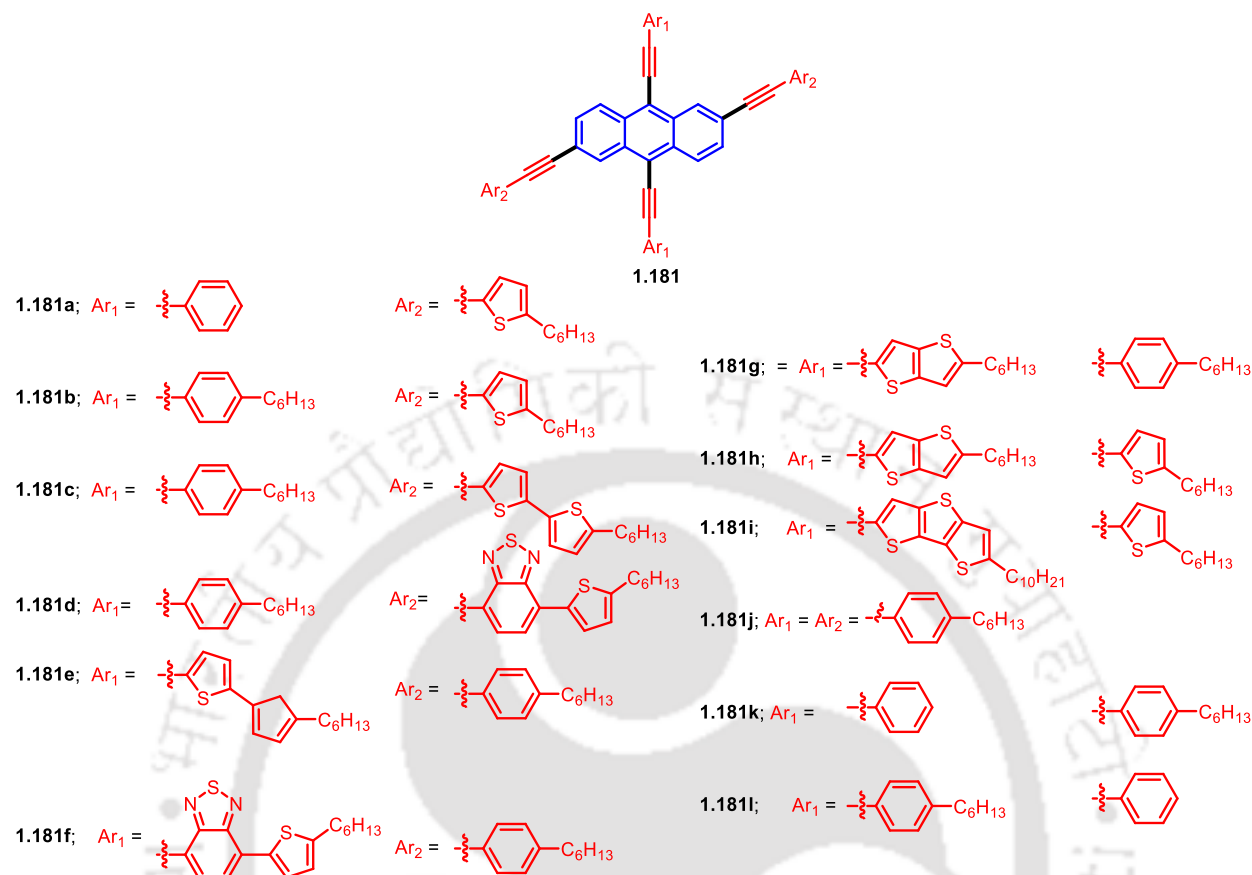


Figure 1.16. A few of polyalkynylated PAHs based on anthracene used for fabricating OFET devices.

In 2012, Choi synthesized solution processable crystalline compound 2,6,9,10-*tetrakis*((4-hexylphenyl)ethynyl)anthracene **1.181j** (Figure 1.16). The crystalline form of **1.181j** showed uniform lamellar π -stacking with very good field effect mobility in both OTFT ($\mu = 0.13 \text{ cm}^2/\text{Vs}$) and SC-FET devices ($\mu = 1 - 1.35 \text{ cm}^2/\text{Vs}$). Notably, mobility of **1.181j** based FET devices ($\mu = 1 - 1.35 \text{ cm}^2/\text{Vs}$) were 7 – 10 folds higher than that obtained for the corresponding OTFT devices.¹⁸⁹

The Choi group synthesized 2,6,9,10-*tetrakis*(arylethynyl) anthracene compounds (**1.181k-l**) (Figure 1.16) and used them for the fabrication of OTFT devices (Figure 1.16).¹⁹⁰ Both the compounds **1.181k-l** behaved as *p*-type semiconductors. The compound 2,6,9,10-*tetrakis*(phenylethynyl)anthracene which was sparingly soluble in common organic solvents, showed an enhanced solubility after the introduction of hexyl chain to the phenyl ring as in 2,6,9,10-*tetrakis*(phenylethynyl)anthracene. Both the compounds were utilized for the fabrication of OTFT devices in bottom-gate, top contact geometry using Au as a drain as well as a source electrode. The mobility of the device fabricated using the compound **1.181k** ($\mu_{\text{FET}} = 0.17 \text{ cm}^2/\text{Vs}$)

was lower than that of the device for **1.181l** ($\mu_{av} = 0.27 \text{ cm}^2/\text{Vs}$; $\mu_{max} = 0.30 \text{ cm}^2/\text{Vs}$). While the current on/off ($I_{on/off}$) ratio for the compound **1.181k** was in the range of $10^6 - 10^7$, the corresponding values for compound **1.181l** were $>10^7$.

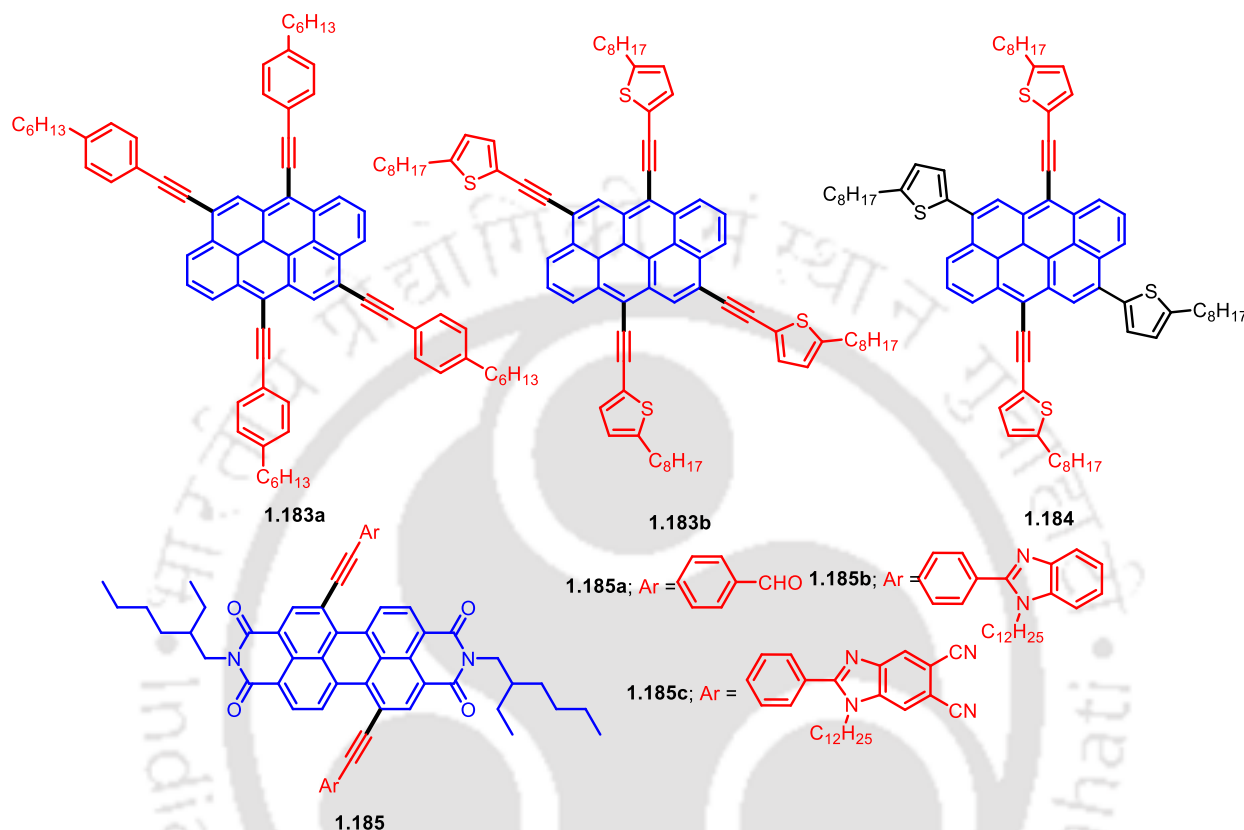


Figure 1.17. FET active PAHs based on polycyclic anthracene and perylene bisimides.

In 2015, Morin reported the synthesis of small polycyclic anthracene compounds (**1.183–1.184**) which behaved as *p*-type organic semiconductor for OFET as well as solar cell (Figure 1.17).¹⁹¹ The compounds were used for fabricating bottom-gate, bottom-contact OFET devices, with Si/SiO₂ as a substrate. For the compounds **1.183–1.184**, the highest hole charge carrier mobility was $10^{-3} \text{ cm}^2/\text{Vs}$ on the as-cast films. While there was no change in the absorption band of **1.183–1.184** in devices that were fabricated *via* as-cast and thermal annealing, the absorption band of **1.183–1.184** occurred at a lower energy in devices fabricated *via* annealing using toluene owing to J-aggregation.¹⁹² The compound **1.183a**, demonstrated a systematic increase in the charge mobility as the device fabrication mode was changed from as-cast ($5.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$) to annealing using toluene ($10^{-2} \text{ cm}^2/\text{Vs}$) and cyclohexane ($0.015 \text{ cm}^2/\text{Vs}$). Among **1.183** and **1.184**, the highest

large mobility ($0.078 \text{ cm}^2/\text{Vs}$) was exhibited by devices fabricated using **1.184** via annealing in toluene. The corresponding $I_{\text{on/off}}$ ratio was 10^6 with a threshold voltage of 6 V.

Table 1.3. A few polyalkynylated π -conjugated PAHs that show mobility greater than $0.1 \text{ cm}^2/\text{Vs}$ in OFETs.

Entry	Compound	Mobility [μ] cm^2/Vs	$I_{\text{on/off}}$	Reference
1	1.174a	1.17	10^7	169
2	1.174c	0.28	10^7	169
3	1.176a	0.79	10^7	171
4	1.176d	0.55	1.9×10^6	172
5	1.176e	0.49	1.5×10^6	172
6	1.177a	1.6	10^6	173
7	1.178a	0.13	2.6×10^6	174
8	1.179a	0.40	10^6	175
9	1.96n	0.94	1.6×10^7	92a
10	1.180	3.2	10^5	177
11	1.181f	0.82	10^5	186
12	1.181g	0.1	10^3	187
13	1.181h	0.7	10^6	188
14	1.181i	0.23	10^6	188
15	1.181j	1.6	10^5	13b
16	1.181k	1.35	-	189
17	1.181l	0.17	$10^6 - 10^7$	190
18	1.181r	0.30	$> 10^7$	190
19	1.148r	0.7	10^6	193

Choi and co-workers reported *p*-channel FETs based on single crystalline microribbon of pyrene core compound **1.148r** (Figure 1.12) which showed mobility of $0.7 \text{ cm}^2/\text{Vs}$ and current on/off ratio of about 10^6 .¹⁹³

Sun and co-workers synthesized anthracene derivatives and perylene bisimides (PBI) which were used to fabricate OFET devices with top-contact/bottom gate geometry. Anthracene derivative **1.96p** (Figure 1.15) was reported to exhibit *p*-channel character whereas the three PBI derivatives **1.185a–c** (Figure 1.17) were found to exhibit *n*-channel character with a positive gate voltage bias. Highest activity was shown by compound **1.185b** which had mobility of $5.2 \times 10^{-5} \text{ cm}^2/\text{Vs}$. However, **1.185a–c** showed very less threshold voltage of about 10 V and very poor $I_{\text{on/off}}$ ratio (10 – 100).¹⁹⁴ Representative examples of polyalkynylated π -conjugated PAHs that show mobility greater than $0.1 \text{ cm}^2/\text{Vs}$ in OFET applications are provided in Table 1.3.

1.3.3. Application of PAHs in cytotoxicity studies

Cytotoxicity is the toxicity brought on by a chemotherapeutic agent's interaction with live cells.¹⁹⁵ The term "cytotoxicity" describes how harmful a substance is to cells.¹⁹⁵ A cytotoxic substance can harm or kill cells through apoptosis or necrosis.¹⁹⁶ Researchers analyse a chemical's cytotoxicity levels to make sure that it won't hurt or even kill patients because some compounds are more cytotoxic than others. Medications used in chemotherapy and specific venoms are two examples of cytotoxic agents. The determination of the suggested biomedical usage of nanoparticles is aided by cytotoxicity assays, which are crucial. Trypan Blue, Alamar Blue and neutral red are only a few of the dyes used in the procedure for determining cytotoxicity and cell viability.¹⁹⁷ The technique uses colour to distinguish between the distinct cells. Based on the ratio of colour uptake by both living and dead cells, the cells are distinguished. The MTT method,¹⁹⁸ the WST test,¹⁹⁹ the tritium-labeled thymidine uptake assay,²⁰⁰ and the dehydrogenase-based assay²⁰¹ are some more techniques for measuring cytotoxicity. In a cytotoxicity bioassay, two classes of compounds may be utilised. Trypan blue or fluorescent DNA binding dyes, for example, belong to the first class of essential dyes since they can pass through damaged cell membranes but not ordinarily into living cells.¹⁹⁷ Cellular markers, which escape from a damaged cell, make up the second class.²⁰² These can either be naturally occurring compounds like enzymes or can be added artificially.

To evaluate the cytotoxic effects of the medicines, the MTT test is carried out. The IC₅₀ value is calculated using MTT, which displays the drug concentration at which 50% of cells died as a result of drug treatment.^{200, 203} Therefore, the medicine is more effective when the IC₅₀ value is lower. It suggests that the medication is exerting cytotoxicity even at very low concentrations.

1.3.3.1. Cytotoxic potential of π -conjugated polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons are regarded as important environmental carcinogens.²⁰⁴ In addition, several planar ring structures have the ability to intercalate with DNA, resulting in a variety of medicines with chemotherapeutic efficacy.^{204b} Most of the widely reported anticancer drugs contain anthracene and pyrene based polycyclic aromatic hydrocarbons (PAHs).²⁰⁵ The synthetic anthracene-9,10-dione mitoxantrone, the antitumoral anthracyclines daunorubicin and doxorubicin are powerful drugs that are currently being used in clinical trials to treat a variety of leukaemias and lymphomas as well as in chemotherapy of solid tumors.²⁰⁶ Banik and co-authors

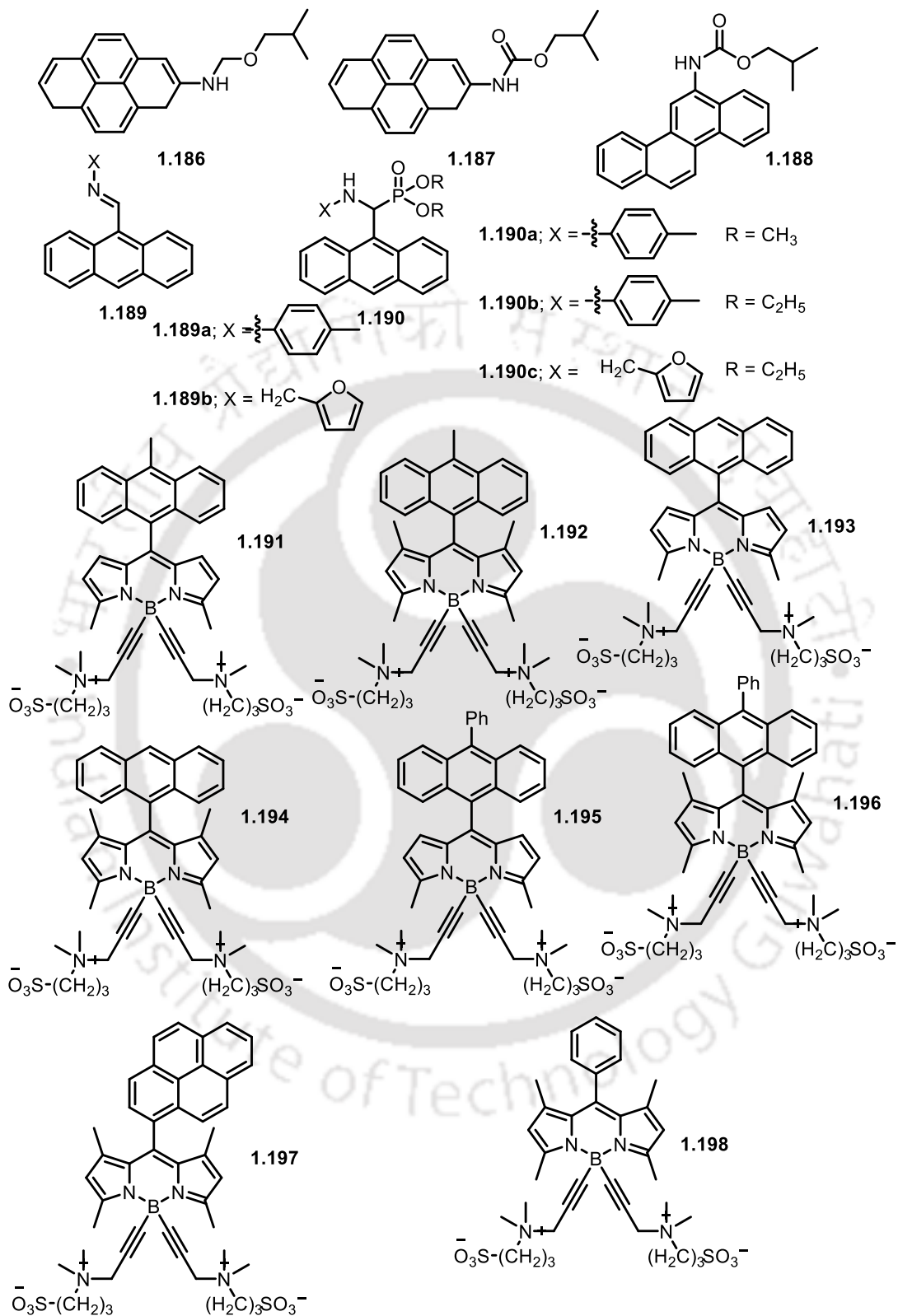


Figure 1.18. Few example of anti-cancer active polycyclic aromatic hydrocarbons.

reported π -conjugated compounds (**1.186**, **1.187**, and **1.188**, figure 1.18) and they were tested for cytotoxicity *in vitro* on a variety of mammalian cell lines.^{204a} When compared to cisplatin, the pyrenyl ether showed greater cytotoxicity against the colon (HT-29) and cervical (HeLa) cancer cell lines.^{204a} Kraicheva and coworkers demonstrated the synthesis process as well as the anticancer activity on a panel of seven human epithelial cancer cell lines for Schiff base 9-anthrylidene-furfurylamine (**1.189**, Figure 1.18) and three new α -aminophosphonates (**1.190**, Figure 1.18).²⁰⁷ Genotoxicity and antiproliferative activities were tested for *in vitro* (3T3 NRU test) and *in vivo* on ICR mice. The most effective cytotoxic drugs against the colon cancer cell line HT-29 were the compounds **1.190b** (Figure 1.18) and **1.190c** (Figure 1.18). Additionally, the others compounds (**1.189a**, **1.190a** and **1.190b**, Figure 1.18) showed antiproliferative effects in HBL-100, MDA-MB-231, and 647-V cells. Senge's group reported the simple synthesis and *in vitro* activity of a library of BODIPY-anthracene, pyrene, and heavy atom-free dyads (**1.191-1.198**, Figure 1.18).²⁰⁸ They showed that at micromolar concentrations, singlet oxygen generated from dyad triplet states, is sufficient to cause cytotoxicity in human breast cancer cells (MDA-MB-468) majorly **1.195**, which exhibits considerable photocytotoxicity at a dose of 5×10^{-7} M with moderate toxicity (89%) in the absence of light. The compounds in this family are intriguing candidates for photodynamic treatment.

Table 1.4. IC₅₀ value of few polycyclic aromatic hydrocarbons

Entry	compound	IC ₅₀ (Molar)	cell
1	1.186	3.1×10^{-5}	small panel of mammalian cell lines
2	1.187	3.0×10^{-5}	small panel of mammalian cell lines
3	1.188	3.9×10^{-5}	small panel of mammalian cell lines
4	1.189a 1.189b	1.5×10^{-4} 9.1×10^{-5}	Tumor cell line (MCF-7)
5	1.190a 1.190b 1.191c	1.1×10^{-3} 4.6×10^{-3} 2.3×10^{-4}	Tumor cell line (MCF-7)
6	1.191	8.7×10^{-6}	human breast cancer cells (MDA-MB-468)
7	1.192	6.1×10^{-6}	human breast cancer cells (MDA-MB-468)
8	1.193	1.3×10^{-6}	human breast cancer cells (MDA-MB-468)
9	1.194	1.7×10^{-5}	human breast cancer cells (MDA-MB-468)
10	1.195	2.8×10^{-7}	human breast cancer cells (MDA-MB-468)
11	1.196	4.2×10^{-6}	human breast cancer cells (MDA-MB-468)
12	1.197	5.2×10^{-6}	human breast cancer cells (MDA-MB-468)
13	1.198	8.2×10^{-4}	human breast cancer cells (MDA-MB-468)

Polyarylated and polyalkynylated PAHs based on anthracene and pyrene have high cytotoxic potential with low IC₅₀ values toward cancer cells (Table 1.4). Polyalkynylated substituents of anthracenes thus have a lot of scope in the study of their cytotoxicity behaviour towards cancer cells.

1.4. Objectives

In the comprehensive literature survey, the synthetic pathway towards polycyclic aromatic hydrocarbons (PAHs), their photophysical properties, and their importance in sensing, cytotoxicity studies as well as organic electronic devices has been demonstrated. Applicability of PAHs in electronic devices depend on their emissive nature, band gap of the molecule and stability. PAHs exhibit high π -conjugation, fused ring structure which helps in their highly emissive and thermally stable nature. The π -conjugation and stability of PAHs can be improved by addition of single, double and triple bond containing aryl substituents. This thesis as a part of doctoral trainings that endeavors to address the following challenges.

- Is it possible to formulate a high yield route to polysubstituted PAHs through multi-fold coupling reaction in one pot and single step process?
- Is it possible to develop a new methodology for the Sonogashira coupling reaction in the absence of copper and amine at room temperature in a green solvent?
- Can one generate an efficient synthetic protocol for the multi-fold Suzuki-Miyaura coupling reaction by employing commercially available nickel salts and would it be possible to accomplish a ligand-free Suzuki reaction?

1.5. References

1. (a) Okamoto, T.; Yu, C. P.; Mitsui, C.; Yamagishi, M.; Ishii, H.; Takeya, J., *J. Am. Chem. Soc.* **2020**, *142*, 9083-9096; (b) Wang, C.; Dong, H.; Jiang, L.; Hu, W., *Chem Soc Rev* **2018**, *47*, 422-500.
2. Park, H.; Gutierrez, M.; Wu, X.; Kim, W.; Zhu, X.-Y., *J. Phys. Chem. A* **2013**, *117*, 10974-10979.
3. (a) Okamoto, T., *Polym. J.* **2019**, *51*, 825-833; (b) Okamoto, T.; Kumagai, S.; Fukuzaki, E.; Ishii, H.; Watanabe, G.; Niitsu, N.; Annaka, T.; Yamagishi, M.; Tani, Y.; Sugiura, H., *Robust, Sci. Adv.* **2020**, *6*, eaaz0632; (c) Katz, H.; Lovinger, A.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin,

- Y.-Y.; Dodabalapur, A., *Nature* **2000**, *404*, 478-481; (d) Usta, H.; Facchetti, A.; Marks, T. J., *Acc. Chem. Res.* **2011**, *44*, 501-510.
4. Yun, H.-J.; Chung, D. S.; Kang, I.; Park, J. W.; Kim, Y.-H.; Kwon, S.-K., *J. Mater. Chem. C* **2012**, *22*, 24924-24929.
5. Slodek, A.; Filapek, M.; Schab-Balcerzak, E.; Grucela, M.; Kotowicz, S.; Janeczczek, H.; Smolarek, K.; Mackowski, S.; Malecki, J. G.; Jedrzejowska, A., *EurJOC* **2016**, *2016*, 4020-4031.
6. Marrocchi, A.; Silvestri, F.; Seri, M.; Facchetti, A.; Taticchi, A.; Marks, T. J., *ChemComm* **2009**, 1380-1382.
7. Chen, Y.; Li, C.; Xu, X.; Liu, M.; He, Y.; Murtaza, I.; Zhang, D.; Yao, C.; Wang, Y.; Meng, H., *ACS Appl. Mater. Interfaces* **2017**, *9*, 7305-7314.
8. (a) Klauk, H., *Chem Soc Rev* **2010**, *39*, 2643-2666; (b) Shao, W.; Dong, H.; Jiang, L.; Hu, W., *Chem* **2011**, *2*, 590-600.
9. (a) Jacob, M. V., MDPI: 2014; Vol. 3, pp 594-597; (b) Elkington, D.; Cooling, N.; Belcher, W.; Dastoor, P. C.; Zhou, X., *Electronics* **2014**, *3*, 234-254.
10. (a) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U., *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 4070-4098; (b) Nikolka, M.; Nasrallah, I.; Rose, B.; Ravva, M. K.; Broch, K.; Sadhanala, A.; Harkin, D.; Charmet, J.; Hurhangee, M.; Brown, A., *Nat. Mater* **2017**, *16*, 356-362; (c) Fukuda, K.; Takeda, Y.; Mizukami, M.; Kumaki, D.; Tokito, S., *Sci. Rep.* **2014**, *4*, 1-8; (d) Yip, H.; Jen, A., *Energy Environ. Sci.* **2012**, *5*, 5994; (e) H. Ma, H.-L. Yip, F. Huang, A.K.Y. Jen, *Adv. Funct. Mater* **2010**, *20*, 1371.
11. (a) Henson, Z. B.; Müllen, K.; Bazan, G. C., *Nat. Chem* **2012**, *4*, 699-704; (b) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D., *Chem. Rev.* **2012**, *112*, 2208-2267.
12. Chueh, C.-C.; Li, C.-Z.; Ding, F.; Li, Z. a.; Cernetic, N.; Li, X.; Jen, A. K.-Y., *ACS Appl. Mater. Interfaces* **2017**, *9*, 1136-1144.
13. (a) Scaccabarozzi, A. D.; Basu, A.; Aníés, F.; Liu, J.; Zapata-Arteaga, O.; Warren, R.; Firdaus, Y.; Nugraha, M. I.; Lin, Y.; Campoy-Quiles, M., *Chem. Rev.* **2021**, *122*, 4420-4492; (b) Chueh, C.-C.; Li, C.-Z.; Ding, F.; Li, Z. a.; Cernetic, N.; Li, X.; Jen, A. K.-Y., *ACS Appl. Mater. Interfaces* **2016**, *9*, 1136-1144; (c) Guo, S.; Kim, S. B.; Mohapatra, S. K.; Qi, Y.; Sajoto, T.; Kahn, A.; Marder, S. R.; Barlow, S., *Adv. Mater.* **2012**, *24*, 699-703; (d) Wei, P.; Menke, T.; Naab, B. D.; Leo, K.; Riede, M.; Bao, Z., *J. Am. Chem. Soc.* **2012**, *134*, 3999-4002.
14. (a) Huy Do, H.; Villinger, A.; Lochbrunner, S.; Ehlers, P.; Langer, P., *Eur. J. Org. Chem.* **2017**, *2017*, 2238-2244; (b) Wu, T.-L.; Chou, H.-H.; Huang, P.-Y.; Cheng, C.-H.; Liu, R.-S., *J. Org. Chem.* **2014**, *79*, 267-274; (c) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A., *Nature* **2009**, *457*, 679-686.
15. (a) Chen, M.; Yan, L.; Zhao, Y.; Murtaza, I.; Meng, H.; Huang, W., *J. Mater. Chem. C* **2018**, *6*, 7416-7444; (b) Gao, L.; Zhang, Z. G.; Bin, H.; Xue, L.; Yang, Y.; Wang, C.; Liu, F.; Russell, T. P.; Li, Y., *Adv. Mater.* **2016**, *28*, 8288-8295.
16. Ehlers, P.; Neubauer, A.; Lochbrunner, S.; Villinger, A.; Langer, P., *Org. Lett.* **2011**, *13*, 1618-1621.
17. Hu, J. Y.; Era, M.; Elsegood, M. R.; Yamato, T., *Eur. J. Org. Chem.* **2010**, *2010*, 72-79.
18. Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J., *J. Chem. Soc., Chem. Commun.* **1977**, 578-580.
19. (a) Choi, J.; Kim, W.; Kim, D.; Kim, S.; Chae, J.; Choi, S. Q.; Kim, F. S.; Kim, T.-S.; Kim, B. J., *Chem. Mater.* **2019**, *31*, 3163-3173; (b) Lee, E. K.; Lee, M. Y.; Park, C. H.; Lee, H. R.; Oh, J. H., *Adv. Mater.* **2017**, *29*, 1703638; (c) Baeg, K. J.; Caironi, M.; Noh, Y. Y., *Adv. Mater.* **2013**, *25*, 4210-4244.

20. Li, Y.; Sonar, P.; Singh, S. P.; Soh, M. S.; Van Meurs, M.; Tan, J., *J. Am. Chem. Soc.* **2011**, *133*, 2198-2204.
21. (a) Mishra, A.; Bäuerle, P., *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 2020-2067; (b) Lin, Y.; Li, Y.; Zhan, X., *Chem Soc Rev* **2012**, *41*, 4245-4272.
22. Waldrip, M.; Jurchescu, O. D.; Gundlach, D. J.; Bittle, E. G., *Adv. Funct. Mater.* **2020**, *30*, 1904576.
23. Debucquoy, M.; Rockele, M.; Genoe, J.; Gelinck, G.; Heremans, P., *Org. Electron.* **2009**, *10*, 1252-1258.
24. Gomar-Nadal, E.; Conrad, B. R.; Cullen, W. G.; Williams, E. D., Effect of impurities on pentacene thin film growth for field-effect transistors. *J. Phys. Chem. C* **2008**, *112*, 5646-5650.
25. Dong, H.; Fu, X.; Liu, J.; Wang, Z.; Hu, W., 25th anniversary article: *Adv. Mater.* **2013**, *25*, 6158-6183.
26. Ando, S.; Nishida, J.-i.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y., *Chem. Mater.* **2005**, *17*, 1261-1264.
27. Costa, J. C.; Taveira, R. J.; Lima, C. F.; Mendes, A.; Santos, L. M., *Opt. Mater.* **2016**, *58*, 51-60.
28. Kashiwagi, K.; Yasuda, T.; Tsutsui, T., *Chem. Lett.* **2007**, *36*, 1194-1195.
29. Bischof, D.; Zeplichal, M.; Anhäuser, S.; Kumar, A.; Kind, M.; Kramer, F.; Bolte, M.; Ivlev, S. I.; Terfort, A.; Witte, G., *J. Phys. Chem. C* **2021**, *125*, 19000-19012.
30. Li, J.; Chang, J.-J.; Tan, H. S.; Jiang, H.; Chen, X.; Chen, Z.; Zhang, J.; Wu, J., Disc-like 7, 14-dicyano-ovalene-3, 4: 10, *Chem. Sci.* **2012**, *3*, 846-850.
31. (a) Kang, H.; Evmenenko, G.; Dutta, P.; Clays, K.; Song, K.; Marks, T. J., *J. Am. Chem. Soc.* **2006**, *128*, 6194-6205; (b) Samori, S.; Tojo, S.; Fujitsuka, M.; Spitler, E. L.; Haley, M. M.; Majima, T., *J. Org. Chem.* **2008**, *73*, 3551-3558; (c) Samori, S.; Tojo, S.; Fujitsuka, M.; Spitler, E. L.; Haley, M. M.; Majima, T., *J. Org. Chem.* **2007**, *72*, 2785-2793; (d) Spitler, E. L.; Shirtcliff, L. D.; Haley, M. M., *J. Org. Chem.* **2007**, *72*, 86-96; (e) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M., *J. Am. Chem. Soc.* **2005**, *127*, 2464-2476; (f) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C., *J. Am. Chem. Soc.* **2006**, *128*, 1340-1345; (g) Wilson, J. N.; Bunz, U. H., *J. Am. Chem. Soc.* **2005**, *127*, 4124-4125; (h) Zuccherro, A. J.; Wilson, J. N.; Bunz, U. H., *J. Am. Chem. Soc.* **2006**, *128*, 11872-11881; (i) Wilson, J. N.; Hardcastle, K. I.; Josowicz, M.; Bunz, U. H., *Tetrahedron* **2004**, *60*, 7157-7167; (j) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T., *J. Am. Chem. Soc.* **2006**, *128*, 3914-3915.
32. (a) Scott, N.; Walker, J.; Hansley, V., *J. Am. Chem. Soc.* **1936**, *58*, 2442-2444; (b) Sun, Y.; Zhao, X.; Zhang, D.; Ding, A.; Chen, C.; Huang, W. E.; Zhang, H., *Chemosphere* **2017**, *186*, 510-518; (c) Bauer, J. E.; Capone, D. G., *Appl. Environ. Microbiol.* **1985**, *50*, 81-90.
33. Aydemir, M.; Haykır, G.; Battal, A.; Jankus, V.; Sugunan, S. K.; Dias, F. B.; Al-Attar, H.; Türksoy, F.; Tavaslı, M.; Monkman, A. P., *Org. Electron.* **2016**, *30*, 149-157.
34. Mackie, C. J.; Candian, A.; Huang, X.; Maltseva, E.; Pettrignani, A.; Oomens, J.; Buma, W. J.; Lee, T. J.; Tielens, A. G., *J. Chem. Phys.* **2015**, *143*, 224314.
35. Lehnher, D.; Murray, A. H.; McDonald, R.; Ferguson, M. J.; Tykwinski, R. R., *Chem. Eur. J.* **2009**, *15*, 12580-12584.
36. Salunke, J. K.; Sonar, P.; Wong, F.; Roy, V.; Lee, C.; Wadgaonkar, P. P., *Phys. Chem. Chem. Phys.* **2014**, *16*, 23320-23328.
37. (a) Abou-Hatab, S.; Spata, V. A.; Matsika, S., *J. Phys. Chem. A* **2017**, *121*, 1213-1222; (b) Becker, H. D., *Chem. Rev.* **1993**, *93*, 145-172.

38. (a) Armitt, D. J.; Crisp, G. T., *J. Org. Chem.* **2006**, 71, 3417-3422; (b) Wang, J.-L.; Zhou, Y.; Li, Y.; Pei, J., *J. Org. Chem.* **2009**, 74, 7449-7456.
39. (a) Asai, K.; Konishi, G.-i.; Nakajima, Y.; Kawauchi, S.; Ozawa, F.; Mizuno, K., *J. Organomet. Chem.* **2011**, 696 (6), 1266-1271; (b) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S., *J. Mater. Chem.* **2011**, 21, 9130-9138.
40. Lin, S.-H.; Wu, F.-I.; Liu, R.-S., *Chem. Commun.* **2009**, 6961-6963.
41. Chien, C. H.; Chen, C. K.; Hsu, F. M.; Shu, C. F.; Chou, P. T.; Lai, C. H., *Adv. Funct. Mater.* **2009**, 19, 560-566.
42. (a) Wei, Z.; Gu, Z.-Y.; Arvapally, R. K.; Chen, Y.-P.; McDougald Jr, R. N.; Ivy, J. F.; Yakovenko, A. A.; Feng, D.; Omary, M. A.; Zhou, H.-C., *J. Am. Chem. Soc.* **2014**, 136, 8269-8276; (b) Becker, R. S.; Pelliccioli, A. P.; Romani, A.; Favaro, G., *J. Am. Chem. Soc.* **1999**, 121, 2104-2109.
43. Gole, B.; Song, W.; Lackinger, M.; Mukherjee, P. S., *Chem. Eur. J.* **2014**, 20, 13662-13680.
44. Wang, H.; Fan, Q.; Chen, L.; Xiao, Y., *Dyes Pigm.* **2019**, 164, 384-389.
45. Inokuchi, H., *Org. Electron.* **2006**, 7, 62-76.
46. Inokuchi, H., *Bull. Chem. Soc. Jpn.* **1954**, 27, 22-27.
47. Chen, M.; Yan, L.; Zhao, Y.; Murtaza, I.; Meng, H.; Huang, W., *J. Mater. Chem. C* **2018**, 6, 7416-7444.
48. Negishi, E.; King, A. O.; Okukado, N., *J. Org. Chem.* **1977**, 42, 1821-1823.
49. Miyauro, N.; Suzuki, A., *J. Chem. Soc., Chem. Commun.* **1979**, 866-867.
50. Milstein, D.; Stille, J., *J. Am. Chem. Soc.* **1979**, 101, 4992-4998.
51. Hiyama, T., *J. Organomet. Chem.* **2002**, 653, 58-61.
52. Corriu, R.; Masse, J., *J. Chem. Soc., Chem. Commun.* **1972**, 144a-144a.
53. Heck, R. F.; Nolley Jr, J., *J. Org. Chem.* **1972**, 37, 2320-2322.
54. Chinchilla, R.; Nájera, C., *Chem Soc Rev* **2011**, 40, 5084-5121.
55. Paun, A.; Hadade, N.; Paraschivescu, C.; Matache, M., *J. Mater. Chem. C* **2016**, 4, 8596-8610.
56. Söğütü, I.; Mahmood, E. A.; Shendy, S. A.; Ebrahimi, S.; Vessally, E., *RSC Adv.* **2021**, 11, 2112-2125.
57. Lima, C. G.; Pauli, F. P.; Madriaga, V. G.; Amaral, A. A.; Graciano, I. A.; Meira, V. L.; da SM Forezi, L.; Ferreira, V. F.; de M. Lima, T.; de Carvalho da Silva, F., *Eur. J. Org. Chem.* **2022**, 2022, e202200904.
58. (a) Chemler, S. R.; Trauner, D.; Danishefsky, S. J., *Angew. Chem., Int. Ed. Engl.* **2001**, 40, 4544-4568; (b) Tabassum, S.; Zahoor, A. F.; Ahmad, S.; Noreen, R.; Khan, S. G.; Ahmad, H., *Mol. Divers.* **2021**, 1-43.
59. Blaser, H.-U.; Indolese, A.; Schnyder, A.; Steiner, H.; Studer, M., *J. Mol. Catal. A Chem.* **2001**, 173, 3-18.
60. Devendar, P.; Qu, R.-Y.; Kang, W.-M.; He, B.; Yang, G.-F., *J. Agric. Food Chem.* **2018**, 66, 8914-8934.
61. Torborg, C.; Beller, M., *Adv. Synth. Catal.* **2009**, 351, 3027-3043.
62. Negishi, E.-i.; Hu, Q.; Huang, Z.; Qian, M.; Wang, G.; Brown, H., *Aldrichimica Acta* **2005**, 38, 71-78.
63. (a) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M., *J. Am. Chem. Soc.* **1997**, 119, 4578-4593; (b) Yuan, K.; Kahan, R.; Si, C.; Williams, A.; Kirschner, S.; Uzelac, M.; Zysman-Colman, E.; Ingleson, M., *Chem.* **2020**, 11, 3258-3267; (c) Yang, C.; Slavětinská, L. P. t.; Fleuti, M.; Klepetářová, B.; Tichý, M.; Gurská, S. a.; Pavliš, P.; Džubák, P.; Hajdúch, M.; Hocek, M., *J. Am. Chem. Soc.* **2022**, 144, 19437-19446.

64. Heravi, M. M.; Hashemi, E.; Azimian, F., *Tetrahedron* **2014**, *70*, 7-21.
65. Ragan, J.; Raggon, J.; Hill, P.; Jones, B.; McDermott, R.; Munchhof, M.; Marx, M.; Casavant, J.; Cooper, B.; Doty, J., *Org. Process Res. Dev.* **2003**, *7*, 676-683.
66. Yue, W.; Lv, A.; Gao, J.; Jiang, W.; Hao, L.; Li, C.; Li, Y.; Polander, L. E.; Barlow, S.; Hu, W., *J. Am. Chem. Soc.* **2012**, *134*, 5770-5773.
67. (a) Li, H.; Earmme, T.; Ren, G.; Saeki, A.; Yoshikawa, S.; Murari, N. M.; Subramaniyan, S.; Crane, M. J.; Seki, S.; Jenekhe, S. A., *J. Am. Chem. Soc.* **2014**, *136*, 14589-14597; (b) Li, H.; Kim, F. S.; Ren, G.; Hollenbeck, E. C.; Subramaniyan, S.; Jenekhe, S. A., *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 5513-5517.
68. Kumar, B.; Strasser, C. E.; King, B. T., *Angew. Chem., Int. Ed. Engl.* **2012**, *77*, 311-316.
69. Hatanaka, Y.; Hiyama, T., *J. Org. Chem.* **1988**, *53*, 918-920.
70. Yuen, O. Y.; So, C. M.; Man, H. W.; Kwong, F. Y., *Chem. Eur. J.* **2016**, *22*, 6471-6476.
71. Foubelo, F.; Nájera, C.; Yus, M., *Chem. Rec.* **2016**, *16*, 2521-2533.
72. (a) Noor, R.; Zahoor, A. F.; Irfan, M.; Hussain, S. M.; Ahmad, S.; Irfan, A.; Kotwica-Mojzych, K.; Mojzych, M., *Molecules* **2022**, *27* (17), 5654; (b) Nakao, Y.; Hiyama, T., *Chem. Soc. Rev.* **2011**, *40*, 4893-4901.
73. Tamao, K.; Sumitani, K.; Kumada, M., *J. Am. Chem. Soc.* **1972**, *94*, 4374-4376.
74. Yamamura, M.; Moritani, I.; Murahashi, S.-I., *J. Organomet. Chem.* **1975**, *91*, C39-C42.
75. Knappke, C. E.; von Wangelin, A. J., *Chem. Soc. Rev.* **2011**, *40*, 4948-4962.
76. Li, G. Y., *J. Organomet. Chem.* **2002**, *653*, 63-68.
77. Wolf, C.; Xu, H., *J. Org. Chem.* **2008**, *73*, 162-167.
78. Martin, R.; Buchwald, S. L., *J. Am. Chem. Soc.* **2007**, *129*, 3844-3845.
79. Cabri, W.; Candiani, I., *Acc. Chem. Res.* **1995**, *28*, 2-7.
80. (a) Le Bras, J.; Muzart, J., *Chem. Rev.* **2011**, *111*, 1170-1214; (b) Crisp, G. T., *Chem Soc Rev* **1998**, *27*, 427-436; (c) Jagtap, S., Heck reaction—State of the art. *Catalyst* **2017**, *7*, 267.
81. Wei, D.; Li, M. Y.; Zhu, B. B.; Yang, X. D.; Zhang, F.; Feng, C. G.; Lin, G. Q., *Angew. Chem.* **2019**, *131*, 16695-16699.
82. Keum, Y. S.; Seo, J. S.; Li, Q. X., *Synth. Commun.* **2005**, *35*, 2685-2693.
83. Chen, D.; Shi, G.; Jiang, H.; Zhang, Y.; Zhang, Y., *Org. Lett.* **2016**, *18*, 2130-2133.
84. (a) Chinchilla, R.; Nájera, C., *Chem. Rev.* **2007**, *107*, 874-922; (b) Doucet, H.; Hierso, J. C., *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 834-871.
85. Cassar, L., *J. Organomet. Chem.* **1975**, *93*, 253-257.
86. Dieck, a. H.; Heck, F., *J. Organomet. Chem.* **1975**, *93*, 259-263.
87. Evano, G.; Blanchard, N.; Toumi, M., *Chem. Rev.* **2008**, *108*, 3054-3131.
88. (a) Granadino-Roldán, J. M.; Garzón, A.; García, G.; Peña-Ruiz, T.; Fernández-Liencre, M. P.; Navarro, A.; Fernández-Gómez, M., *J. Chem. Phys.* **2009**, *130*, 234907; (b) Marsh, N. D.; Mikolajczak, C. J.; Wornat, M. J., *Mol. Biomol. Spectrosc.* **2000**, *56*, 1499-1511.
89. Silvestri, F.; Marrocchi, A.; Seri, M.; Kim, C.; Marks, T. J.; Facchetti, A.; Taticchi, A., *J. Am. Chem. Soc.* **2010**, *132*, 6108-6123.
90. (a) Du, H.; Fuh, R. C. A.; Li, J.; Corkan, L. A.; Lindsey, J. S., PhotochemCAD[‡]: *J. Photochem. Photobiol. A* **1998**, *68*, 141-142; (b) Hu, J.-Y.; Ni, X.-L.; Feng, X.; Era, M.; Elsegood, M. R.; Teat, S. J.; Yamato, T., *Org. Biomol. Chem.* **2012**, *10*, 2255-2262.
91. (a) Gudeika, D.; Grazulevicius, J. V.; Volyniuk, D.; Juska, G.; Jankauskas, V.; Sini, G., *J. Phys. Chem. C* **2015**, *119*, 28335-28346; (b) Teng, C.; Yang, X.; Yang, C.; Li, S.; Cheng, M.; Hagfeldt, A.; Sun, L., *J. Phys. Chem.* **2010**, *114*, 9101-9110; (c) Butler, T.; Alden, S. E.; Taylor,

- M.; Deese, S.; Rider, D. A.; Laskoski, M., *J. Polym. Sci., Part A Polym. Chem.* **2018**, 56, 2630-2640.
92. (a) Takaki, Y.; Wakayama, Y.; Ishiguro, Y.; Hayakawa, R.; Yamagishi, M.; Okamoto, T.; Takeya, J.; Yoza, K.; Kobayashi, K., *Chem. Lett.* **2016**, 45, 1403-1405; (b) Song, H. G.; Kim, Y.; Park, S.-M.; An, T. K.; Kwon, S.-K.; Park, C. E.; Kim, Y.-H., *Dyes Pigment.* **2016**, 131, 349-355.
93. (a) Piao, M. J.; Chajara, K.; Yoon, S. J.; Kim, H. M.; Jeon, S.-J.; Kim, T.-H.; Song, K.; Asselberghs, I.; Persoons, A.; Clays, K., *J. Mater. Chem.* **2006**, 16, 2273-2281; (b) Kondo, K.; Yasuda, S.; Sakaguchi, T.; Miya, M., *J. Chem. Soc., Chem. Commun.* **1995**, 55-56.
94. Ehlers, P.; Hakobyan, A.; Neubauer, A.; Lochbrunner, S.; Langer, P., *Adv. Synth. Catal.* **2013**, 355, 1849-1858.
95. Lim, I.-I. S.; Vaiana, C.; Zhang, Z.-Y.; Zhang, Y.-J.; An, D.-L.; Zhong, C.-J., *J. Am. Chem. Soc.* **2007**, 129, 5368-5369.
96. (a) Kato, S.-i.; Kano, H.; Irisawa, K.-i.; Yoshikawa, N.; Yamamoto, R.; Kitamura, C.; Nara, D.; Yamanobe, T.; Uehara, H.; Nakamura, Y., *Org. Lett.* **2018**, 20, 7530-7534; (b) Fernández, G.; García, F.; Aparicio, F.; Matesanz, E.; Sánchez, L., *Chem. Commun.* **2009**, 7155-7157.
97. Wan, W. B.; Brand, S. C.; Pak, J. J.; Haley, M. M., *Chem. Eur. J.* **2000**, 6, 2044-2052.
98. Kumar, S.; Varshney, S. K., *Angew. Chem., Int. Ed. Engl.* **2000**, 39, 3140-3142.
99. Kayser, B.; Altman, J.; Beck, W., *Chem. Eur. J.* **1999**, 5, 754-758.
100. (a) Gole, B.; Shanmugaraju, S.; Bar, A. K.; Mukherjee, P. S., *Chem. Commun.* **2011**, 47, 10046-10048; (b) Shanmugaraju, S.; Jadhav, H.; Karthik, R.; Mukherjee, P. S., *RSC Adv.* **2013**, 3, 4940-4950; (c) Li, Y.; Sonar, P.; Murphy, L.; Hong, W., *Energy Environ. Sci.* **2013**, 6, 1684-1710; (d) Sun, X.; Wang, Y.; Lei, Y., *Chem. Soc. Rev.* **2015**, 44, 8019-8061; (e) Shanmugaraju, S.; Mukherjee, P. S., *Chem. Commun.* **2015**, 51, 16014-16032.
101. (a) Fukazawa, A.; Yamaguchi, S., *Chem. Asian J.* **2009**, 4, 1386-1400; (b) Bosdet, M. J.; Piers, W. E., *Can. J. Chem.* **2009**, 87, 8-29; (c) Baumgartner, T., *J. Inorg. Organomet. Polym. Mater.* **2005**, 15, 389-409.
102. (a) Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S., *J. Am. Chem. Soc.* **2005**, 127, 13281-13286; (b) Yamada, K.; Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S.; Takeya, J., *Appl. Phys. Lett.* **2007**, 90, 072102.
103. (a) Curtis, M. D.; Cao, J.; Kampf, J. W., *J. Am. Chem. Soc.* **2004**, 126, 4318-4328; (b) Kim, E.-G.; Coropceanu, V.; Gruhn, N. E.; Sánchez-Carrera, R. S.; Snoeberger, R.; Matzger, A. J.; Brédas, J.-L., *J. Am. Chem. Soc.* **2007**, 129, 13072-13081.
104. (a) Chen, C.; Ou, H.; Liu, R.; Ding, D., *Adv. Mater.* **2020**, 32, 1806331; (b) Liu, Y.; Li, C.; Ren, Z.; Yan, S.; Bryce, M. R., *Nat. Rev. Mater.* **2018**, 3, 1-20; (c) Xie, Y.; Li, Z., *Mater. Chem. Front.* **2020**, 4, 317-331; (d) Squeo, B. M.; Gregoriou, V. G.; Avgeropoulos, A.; Baysec, S.; Allard, S.; Scherf, U.; Chochos, C. L., *Prog. Polym. Sci.* **2017**, 71, 26-52; (e) Spano, F. C.; Silva, C., *Annu. Rev. Phys. Chem.* **2014**, 65, 477-500.
105. R. Murad, A.; Iraqi, A.; Aziz, S. B.; N. Abdullah, S.; Brza, M. A., *Polymers* **2020**, 12, 2627.
106. Broggi, A.; Tomasi, I.; Bianchi, L.; Marrocchi, A.; Vaccaro, L., *ChemPlusChem* **2014**, 79, 486-507.
107. Engelhardt, V.; Garcia, J. G.; Hubaud, A. A.; Lyssenko, K. A.; Spyroudis, S.; Timofeeva, T. V.; Tongwa, P.; Vollhardt, K. P. C., *Synlett* **2011**, 2011, 280-284.
108. Gelman, D.; Buchwald, S. L., *Angew. Chem.* **2003**, 115, 6175-6178.
109. Petrosyan, A.; Ehlers, P.; Surkus, A.-E.; Ghochikyan, T. V.; Saghyian, A. S.; Lochbrunner, S.; Langer, P., *Org. Biomol. Chem.* **2016**, 14, 1442-1449.

110. (a) Xue, T.; Zhao, D.; Hao, T.; Li, X.; Wang, T.; Nie, J., *New J. Chem.* **2019**, *43*, 6737-6745; (b) Wang, M.; Ma, X.; Yu, J.; Jia, X.; Han, D.; Zhou, T.; Yang, J.; Nie, J.; Wang, T., *Polym. Chem.* **2015**, *6*, 4424-4435.
111. Fudickar, W.; Linker, T., *J. Am. Chem. Soc.* **2012**, *134*, 15071-15082.
112. Varshney, S. K.; Prasad, V.; Takezoe, H., *Liq. Cryst.* **2011**, *38*, 53-60.
113. (a) Maeda, H.; Tanaka, K.; Aratani, M.; Segi, M., *Photochem. Photobiol.* **2019**, *95*, 762-772; (b) Gama, P. E.; Correa, R. J.; Garden, S. J., *J. Lumin.* **2015**, *161*, 37-46.
114. Ehlers, P.; Petrosyan, A.; Neubauer, A.; Bröse, T.; Lochbrunner, S.; Ghochikyan, T. V.; Saghyan, A. S.; Langer, P., *Org. Biomol. Chem.* **2014**, *12*, 8627-8640.
115. Norman, M. H.; Chen, N.; Chen, Z.; Fotsch, C.; Hale, C.; Han, N.; Hurt, R.; Jenkins, T.; Kincaid, J.; Liu, L., *J. Med. Chem.* **2000**, *43*, 4288-4312.
116. Malik, I.; Ahmed, Z.; Reimann, S.; Ali, I.; Villinger, A.; Langer, P., *Eur. J. Org. Chem.* **2011**, *2011*, 2088-2093.
117. Reimann, S.; Ehlers, P.; Sharif, M.; Wittler, K.; Spannenberg, A.; Ludwig, R.; Langer, P., *Catal. Commun.* **2012**, *25*, 142-147.
118. Reimann, S.; Sharif, M.; Hein, M.; Villinger, A.; Wittler, K.; Ludwig, R.; Langer, P., *Eur. J. Org. Chem.* **2012**, *2012*, 604-615.
119. Sharif, M.; Maalik, A.; Reimann, S.; Iqbal, J.; Patonay, T.; Spannenberg, A.; Villinger, A.; Langer, P., *Tetrahedron* **2013**, *69*, 174-183.
120. Reimann, S.; Wittler, K.; Schmode, S.; Sharif, M.; Fahrenwaldt, T.; Ludwig, R.; Spannenberg, A.; Langer, P., *Eur. J. Org. Chem.* **2013**, *2013*, 8115-8134.
121. Tao, W.; Nesbitt, S.; Heck, R. F., *J. Org. Chem.* **1990**, *55*, 63-69.
122. Majumdar, K.; Mondal, S., *Tetrahedron Lett.* **2007**, *48*, 6951-6953.
123. (a) Banwell, C. N.; McCash, E. M., McGraw-Hill: 1994; (b) Evans, R. C.; Douglas, P.; Burrow, H. D., *Applied photochemistry*. Springer: 2013.
124. Yang, Y.; Zhao, Q.; Feng, W.; Li, F., *Chem. Rev.* **2013**, *113*, 192-270.
125. Guo, T.; Lin, Y.; Zhang, W.-J.; Hong, J.-S.; Lin, R.-H.; Wu, X.-P.; Li, J.; Lu, C.-H.; Yang, H.-H., *Nanoscale* **2018**, *10*, 1607-1612.
126. Huo, J.; Wang, H.; Li, S.; Shi, H.; Tang, Y.; Tang, B. Z., *Chem. Rec.* **2020**, *20*, 556-569.
127. Crosby, G. A.; Demas, J. N., *J. Phys. Chem. A* **1971**, *75*, 991-1024.
128. Goto, M.; Yajima, T.; Minami, M.; Sogawa, H.; Sanda, F., *Macromolecules* **2020**, *53*, 6640-6648.
129. Venkataramana, G.; Sankararaman, S., *Eur. J. Org. Chem.* **2005**, *2005*, 4162-4166.
130. Diring, S.; Camerel, F.; Donnio, B.; Dintzer, T.; Toffanin, S.; Capelli, R.; Muccini, M.; Ziesse, R., *J. Am. Chem. Soc.* **2009**, *131*, 18177-18185.
131. Kapf, A.; Eslahi, H.; Blanke, M.; Saccone, M.; Giese, M.; Albrecht, M., *New J. Chem.* **2019**, *43*, 6361-6371.
132. Zhao, W.; Castellano, F. N., *J. Phys. Chem. A* **2006**, *110*, 11440-11445.
133. (a) Miyaura, N.; Yanagi, T.; Suzuki, A., *Synth. Commun.* **1981**, *11*, 513-519; (b) Miyaura, N.; Yamada, K.; Suzuki, A., *Tetrahedron Lett.* **1979**, *20*, 3437-3440.
134. Miyaura, N.; Suzuki, A., *Chem. Rev.* **1995**, *95*, 2457-2483.
135. (a) Littke, A. F.; Dai, C.; Fu, G. C., *J. Am. Chem. Soc.* **2000**, *122*, 4020-4028; (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L., *J. Am. Chem. Soc.* **1999**, *121*, 9550-9561; (c) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F., *J. Org. Chem.* **2002**, *67*, 5553-5566; (d) Bolliger, J. L.; Frech, C. M., *Chem. Eur. J.* **2010**, *16*, 4075-4081; (e) Eghbali, N.; Eddy, J.; Anastas, P. T., *J. Org. Chem.* **2008**, *73*, 6932-6935.

136. Lima, C. F.; Rodrigues, A. S.; Silva, V. L.; Silva, A. M.; Santos, L. M., *ChemCatChem* **2014**, 6, 1291-1302.
137. Xiao, J.; Luo, H.; Huang, S.; Qian, H.; Ma, S., *Chem. Commun.* **2018**, 54, 10451-10454.
138. Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P., *J. Organomet. Chem.* **2002**, 653, 69-82.
139. Li, J.-H.; Liu, W.-J., *Org. Lett.* **2004**, 6, 2809-2811.
140. (a) Grushin, V. V.; Alper, H., *Chem. Rev.* **1994**, 94, 1047-1062; (b) Kakiuchi, F.; Murai, S., Activation of CH bonds: catalytic reactions. *Activation of Unreactive Bonds and Organic Synthesis* **1999**, 47-79; (c) Han, F.-S., *Chem Soc Rev* **2013**, 42, 5270-5298.
141. Saito, S.; Sakai, M.; Miyauro, N., *Tetrahedron Lett.* **1996**, 37, 2993-2996.
142. Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V., *Chem. Rev.* **2011**, 111, 1346-1416.
143. (a) Li, B. J.; Yu, D. G.; Sun, C. L.; Shi, Z. J., *Chem. Eur. J.* **2011**, 17 (6), 1728-1759; (b) Mesganaw, T.; Garg, N. K., *Org. Process Res. Dev.* **2013**, 17, 29-39.
144. Zhao, Y.-L.; Wu, G.-J.; Han, F.-S., *Chem. Commun.* **2012**, 48, 5868-5870.
145. Tang, Z.-Y.; Hu, Q.-S., *J. Am. Chem. Soc.* **2004**, 126, 3058-3059.
146. Rosen, B. M.; Huang, C.; Percec, V., *Org. Lett.* **2008**, 10, 2597-2600.
147. Zhao, Y. L.; Li, Y.; Li, S. M.; Zhou, Y. G.; Sun, F. Y.; Gao, L. X.; Han, F. S., *Adv. Synth. Catal.* **2011**, 355, 1543-1550.
148. Mastalir, M.; Stöger, B.; Pittenauer, E.; Allmaier, G. n.; Kirchner, K., *Org. Lett.* **2016**, 18, 3186-3189.
149. Liang, J.; Han, J.; Wu, J.; Wu, P.; Hu, J.; Hu, F.; Wu, F., *Org. Lett.* **2019**, 21, 6844-6849.
150. Akkarasamiyo, S.; Margalef, J.; Samec, J. S., *Org. Lett.* **2019**, 21, 4782-4787.
151. Balaraman, K.; Wolf, C., *Org. Lett.* **2021**, 23, 8994-8999.
152. Liu, R.; Ran, H.; Zhao, Z.; Yang, X.; Zhang, J.; Chen, L.; Sun, H.; Hu, J.-Y., *ACS Omega* **2018**, 3, 5866-5875.
153. Bisri, S. Z.; Takahashi, T.; Takenobu, T.; Yahiro, M.; Adachi, C.; Iwasa, Y., *Jpn. J. Appl. Phys.* **2007**, 46, L596.
154. (a) Feng, X.; Tomiyasu, H.; Hu, J.-Y.; Wei, X.; Redshaw, C.; Elsegood, M. R.; Horsburgh, L.; Teat, S. J.; Yamato, T., *J. Org. Chem.* **2015**, 80, 10973-10978; (b) Yu, Z.-D.; Cao, J.-Y.; Li, H.-L.; Yang, G.; Zhao, W.-X.; Wang, C.-Z.; Chen, S.-H.; Elsegood, M. R.; Redshaw, C.; Yamato, T., *J. Lumin.* **2023**, 253, 119439.
155. (a) Bethe, H.; Fuchs, K.; Hirschfelder, H.; Magee, J.; Peierls, R.; von Neumann, J., *Blast Effects* **2018**, 33, 183; (b) Cooper, P. W.; Kurowski, S. R., John Wiley & Sons: 1997.
156. (a) Singh, S., Sensors—an effective approach for the detection of explosives. *J. Hazard. Mater.* **2007**, 144, 15-28; (b) Talmage, S. S.; Opresko, D. M.; Maxwell, C. J.; Welsh, C. J.; Cretella, F. M.; Reno, P. H.; Daniel, F. B., *Rev. Env. Contam. Toxicol.* **1999**, 1-156; (c) Vorbeck, C.; Lenke, H.; Fischer, P.; Knackmuss, H.-J., *J. Bacteriol.* **1994**, 176, 932-934.
157. Beyer, C.; Böhme, U.; Pietzsch, C.; Roewer, G., *J. organometallic Chem.* **2002**, 654, 187-201.
158. McQuade, D. T.; Pullen, A. E.; Swager, T. M., *Chem. Rev.* **2000**, 100, 2537-2574.
159. Wang, J.; Mei, J.; Hu, R.; Sun, J. Z.; Qin, A.; Tang, B. Z., *J. Am. Chem. Soc.* **2012**, 134, 9956-9966.
160. Gao, Y.; Qu, Y.; Jiang, T.; Zhang, H.; He, N.; Li, B.; Wu, J.; Hua, J., *J. Mater. Chem. C* **2014**, 2, 6353-6361.

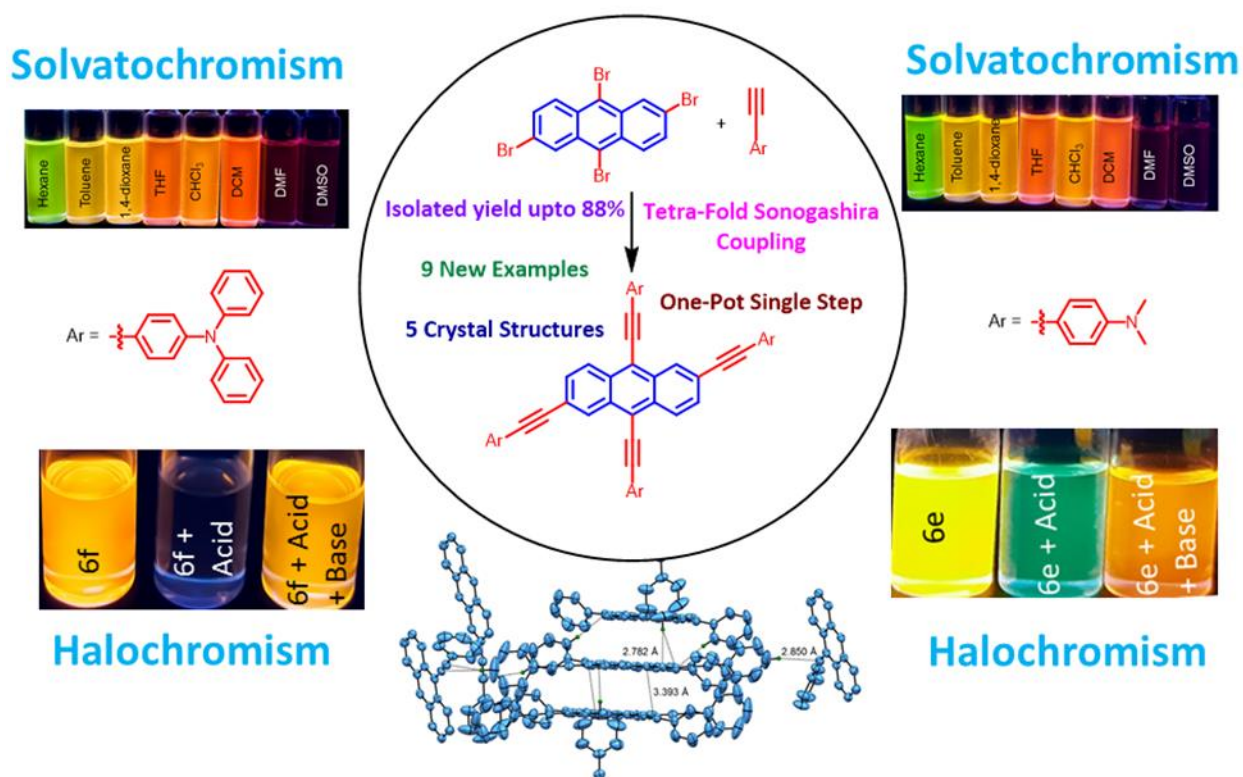
161. Liu, Y.; Chen, X.; Lv, Y.; Chen, S.; WY Lam, J.; Mahtab, F.; Kwok, H. S.; Tao, X.; Tang, B. Z., *Chem. Eur. J.* **2012**, *18*, 9929-9938.
162. (a) Rösch, U.; Yao, S.; Wortmann, R.; Würthner, F., *Angew. Chem.* **2006**, *118*, 7184-7188; (b) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U., *Nat. protoc.* **2013**, *8*, 1535-1550.
163. Bardeen, J.; Brattain, W. H.; Shockley, W., *Phys. Today* **1957**, *10*, 16.
164. Drury, C.; Mutsaers, C.; Hart, C.; Matters, M.; De Leeuw, D., *Appl. Phys. Lett.* **1998**, *73*, 108-110.
165. Koezuka, H.; Tsumura, A.; Ando, T., *Synth. Metal.* **1987**, *18*, 699-704.
166. Horowitz, G.; Hajlaoui, M. E.; Hajlaoui, R., *J. Appl. Phys.* **2000**, *87*, 4456-4463.
167. Meng, Q.; Gao, J.; Li, R.; Jiang, L.; Wang, C.; Zhao, H.; Liu, C.; Li, H.; Hu, W., *J. Mater. Chem.* **2009**, *19*, 1477-1482.
168. Diallo, A. K.; Videlot-Ackermann, C.; Marsal, P.; Brisset, H.; Fages, F.; Kumagai, A.; Yoshimoto, N.; Serein-Spirau, F.; Lère-Porte, J.-P., *Phys. Chem. Chem. Phys.* **2010**, *12*, 3845-3851.
169. Meng, Q.; Jiang, L.; Wei, Z.; Wang, C.; Zhao, H.; Li, H.; Xu, W.; Hu, W., *J. Mater. Chem.* **2010**, *20* (48), 10931-10935.
170. Martinelli, C.; Farinola, G. M.; Pinto, V.; Cardone, A., *Mater.* **2013**, *6*, 1205-1236.
171. Qiu, F.; Dong, Y.; Liu, J.; Sun, Y.; Geng, H.; Zhang, H.; Zhu, D.; Shi, X.; Liu, J.; Zhang, J., *J. Mater. Chem. C* **2020**, *8*, 6006-6012.
172. Back, J. Y.; An, T. K.; Cheon, Y. R.; Cha, H.; Jang, J.; Kim, Y.; Baek, Y.; Chung, D. S.; Kwon, S.-K.; Park, C. E., *ACS Appl. Mater. Interfaces* **2015**, *7*, 351-358.
173. Zhang, X.; Zhao, G.; Zhen, Y.; Tu, Z.; He, P.; Yi, Y.; Dong, H.; Hu, W., *J. Mater. Chem. C* **2015**, *3*, 5368-5371.
174. Shaik, B.; Park, J. H.; An, T. K.; Noh, Y. R.; Yoon, S. B.; Park, C. E.; Yoon, Y. J.; Kim, Y.-H.; Lee, S.-G., *Tetrahedron* **2013**, *69*, 8191-8198.
175. Kim, S.-O.; Lee, M. W.; Jang, S. H.; Park, S. M.; Park, J. W.; Park, M.-H.; Kang, S. H.; Kim, Y.-H.; Song, C. K.; Kwon, S.-K., *Thin Solid Films* **2011**, *519*, 7998-8002.
176. Jang, S.-H.; Kim, H.-J.; Hwang, M.-J.; Jeong, E.-B.; Yun, H.-J.; Lee, D.-H.; Kim, Y.-H.; Park, C.-E.; Yoon, Y.-J.; Kwon, S.-K., *Bull. Korean Chem. Soc.* **2012**, *33*, 541-548.
177. Wang, C.; Liu, Y.; Wei, Z.; Li, H.; Xu, W.; Hu, W., *Appl. Phys. Lett.* **2010**, *96*, 67.
178. Cai, X.; Ji, D.; Jiang, L.; Zhao, G.; Tan, J.; Tian, G.; Li, J.; Hu, W., *Appl. Phys. Lett.* **2014**, *104*, 32_1.
179. Schmidt, R.; Göttling, S.; Leusser, D.; Stalke, D.; Krause, A.-M.; Würthner, F., *J. Mater. Chem.* **2006**, *16*, 3708-3714.
180. Dell'Aquila, A.; Marinelli, F.; Tey, J.; Keg, P.; Lam, Y.-M.; Kapitanchuk, O. L.; Mastroilli, P.; Nobile, C. F.; Cosma, P.; Marchenko, A., *J. Mater. Chem.* **2008**, *18* (7), 786-791.
181. Marinelli, F.; Dell'Aquila, A.; Torsi, L.; Tey, J.; Suranna, G.; Mastroilli, P.; Romanazzi, G.; Nobile, C.; Mhaisalkar, S.; Cioffi, N., *Sens. Actuators B Chem.* **2009**, *140*, 445-450.
182. Keg, P.; Dell'Aquila, A.; Marinelli, F.; Kapitanchuk, O. L.; Fichou, D.; Mastroilli, P.; Romanazzi, G.; Suranna, G. P.; Torsi, L.; Lam, Y. M., *J. Mater. Chem.* **2010**, *20*, 2448-2456.
183. Romanazzi, G.; Dell'Aquila, A.; Suranna, G. P.; Marinelli, F.; Cotrone, S.; Altamura, D.; Giannini, C.; Torsi, L.; Mastroilli, P., *J. Mater. Chem.* **2011**, *21*, 15186-15189.
184. Jiang, L.; Gao, J.; Wang, E.; Li, H.; Wang, Z.; Hu, W.; Jiang, L., *Adv. Mater.* **2008**, *20*, 2735-2740.

185. Guan, Y.-S.; Qin, Y.; Sun, Y.; Wang, C.; Xu, W.; Zhu, D., *Chem. Commun.* **2015**, 51, 12182-12184.
186. Jung, K. H.; Bae, S. Y.; Kim, K. H.; Cho, M. J.; Lee, K.; Kim, Z. H.; Choi, D. H.; Lee, D. H.; Chung, D. S.; Park, C. E., *Chem. Commun.* **2009**, 5290-5292.
187. Shin, J.; Kang, N. S.; Lee, T. W.; Cho, M. J.; Hong, J. M.; Ju, B.-K.; Choi, D. H., *Org. Electron.* **2014**, 15, 1521-1530.
188. Jo, S.-Y.; Hur, J.-A.; Kim, K.-H.; Lee, T.-W.; Shin, J.-C.; Hwang, K.-S.; Chin, B.-D.; Choi, D.-H., *Bull. Korean Chem. Soc.* **2012**, 33, 3061-3070.
189. Hur, J.-A.; Shin, J.-C.; Lee, T.-W.; Kim, K.-H.; Cho, M.-J.; Choi, D.-H., *Bull. Korean Chem. Soc.* **2012**, 33, 1653-1658.
190. (a) Hur, J. A.; Bae, S. Y.; Kim, K. H.; Lee, T. W.; Cho, M. J.; Choi, D. H., *Org. Lett.* **2011**, 13, 1948-1951; (b) Lee, H.; Lee, H.; Hur, J. A.; Cho, M. J.; Choi, D. H.; Kang, T. D., *J. Korean Phys. Soc.* **2013**, 62, 930-936.
191. Giguère, J.-B.; Sariciftci, N. S.; Morin, J.-F., *J. Mater. Chem. C* **2015**, 3, 601-606.
192. Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R., *Angew. Chem. Int. Ed.* **2011**, 50, 3376-3410.
193. Kim, Y. S.; Bae, S. Y.; Kim, K. H.; Lee, T. W.; Hur, J. A.; Hoang, M. H.; Cho, M. J.; Kim, S.-J.; Kim, Y.; Kim, M., *Chem. Commun.* **2011**, 47, 8907-8909.
194. Lee, I. L.; Li, S. R.; Chen, K. F.; Ku, P. J.; Singh, A. S.; Kuo, H. T.; Wen, Y. S.; Chu, C. W.; Sun, S. S., *Eur. J. Org. Chem.* **2012**, 2012, 2906-2915.
195. Mukherjee, P., *Quality Control and Evaluation of Herbal Drugs*; Elsevier: Amsterdam, The Netherlands **2019**, 515-537.
196. Kroemer, G.; Dallaporta, B.; Resche-Rigon, M., The mitochondrial death/life regulator in apoptosis and necrosis. *Annu. Rev. Physiol.* **1998**, 60, 619-642.
197. Dragar, Č.; Kralj, S.; Kocbek, P., *Int. J. Pharm.* **2021**, 597, 120348.
198. (a) Buranaamnuy, K., *Open Vet. J.* **2021**, 11, 251-269; (b) Grela, E.; Kozłowska, J.; Grabowiecka, A., *Acta histochem.* **2018**, 120, 303-311.
199. Lee, K. H.; Kwon, G. H.; Shin, S. J.; Baek, J. Y.; Han, D. K.; Park, Y.; Lee, S. H., *J. Biomed. Mater. Res., Part A* **2009**, 90, 619-628.
200. Adan, A.; Kiraz, Y.; Baran, Y., Cell proliferation and cytotoxicity assays. *Curr. Pharm. Biotechnol.* **2016**, 17, 1213-1221.
201. Radoi, A.; Compagnone, D., *Bioelectrochemistry* **2009**, 76, 126-134.
202. Bussink, J.; Kaanders, J. H.; van der Kogel, A. J., *Radiother. Oncol.* **2003**, 67, 3-15.
203. W Caldwell, G.; Yan, Z.; Lang, W.; A Masucci, J., *Curr. Top. Med. Chem.* **2012**, 12, 1282-1290.
204. (a) Bandyopadhyay, D.; Granados, J. C.; Short, J. D.; Banik, B. K., *Oncol. Lett.* **2012**, 3, 45-49; (b) Lerman, L., *J. Mol. Biol.* **1961**, 3, 18-IN14.
205. (a) Wunz, T. P.; Craven, M. T.; Karol, M. D.; Hill, G. C.; Remers, W. A., *J. Med. Chem.* **1990**, 33, 1549-1553; (b) Iyengar, B. S.; Dorr, R. T.; Alberts, D. S.; Sólyom, A. M.; Krutzsch, M.; Remers, W. A., *J. Med. Chem.* **1997**, 40, 3734-3738; (c) Dorr, R. T.; Liddil, J. D.; Sami, S. M.; Remers, W.; Hersh, E. M.; Alberts, D. S., *Anti-Cancer Drugs* **2001**, 12, 213-220.
206. Lown, J. W., *Pharmacol. Ther.* **1993**, 60, 185-214.
207. Kraicheva, I.; Tsacheva, I.; Vodenicharova, E.; Tashev, E.; Tosheva, T.; Kril, A.; Topashka-Ancheva, M.; Iliev, I.; Gerasimova, T.; Troev, K., *Bioorg. Med. Chem.* **2012**, 20, 117-124.
208. Callaghan, S.; Filatov, M. A.; Savoie, H.; Boyle, R. W.; Senge, M. O., *Photochem. Photobio. Sci.* **2019**, 18, 495-504.



CHAPTER II

Multi-Fold Sonogashira Coupling for Synthesis of Tetraethynylated Anthracenes with Tunable Photophysical Properties



K. Islam; H. Narjinari; A. Bisarya; A. Kumar, *Org. Biomol. Chem.*, **2021**, 19, 9692-9704



2.1 Introduction

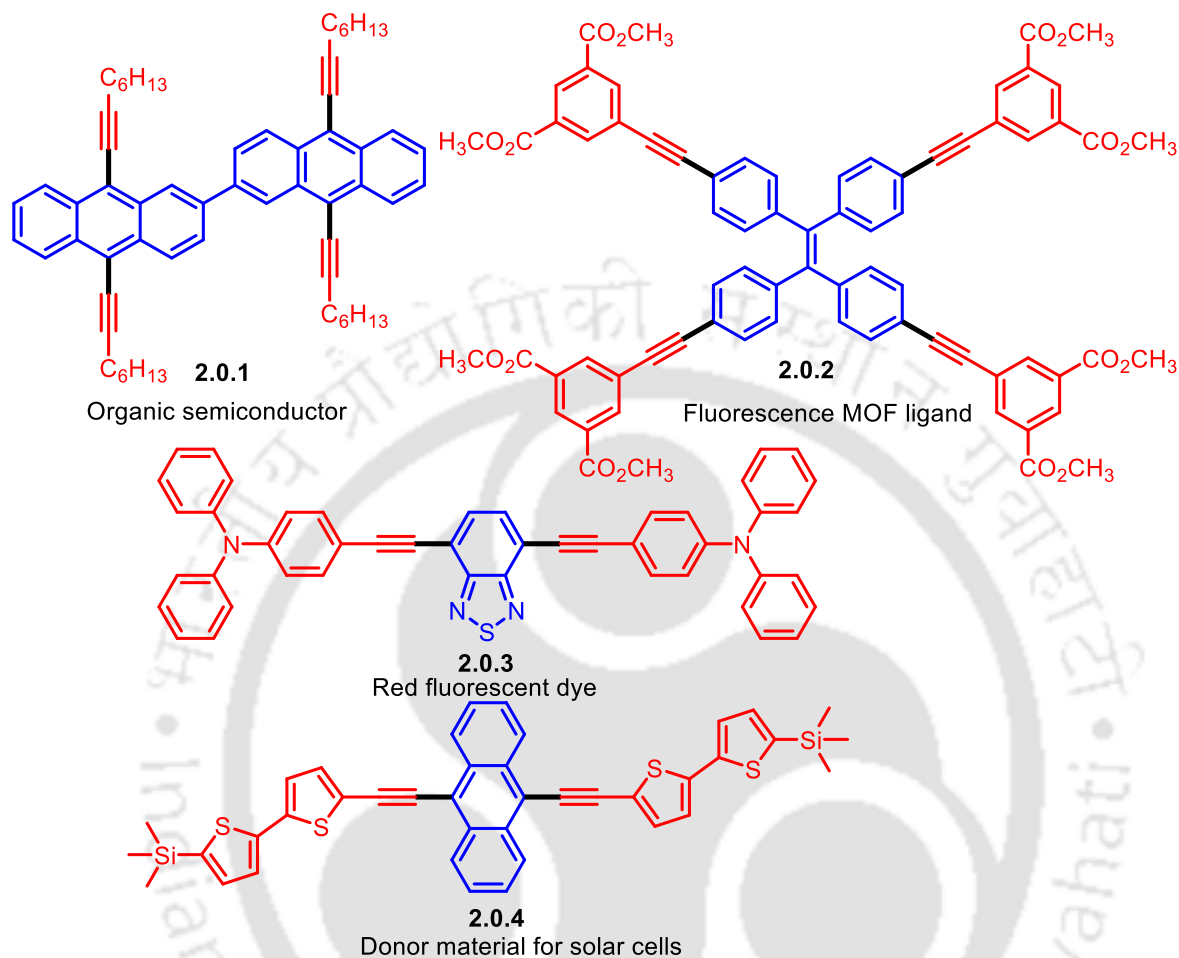


Figure 2.1. Valuable alkynylated compounds.¹

The polyalkynylation² of polyaromatic hydrocarbons (PAHs) containing aromatic cores like benzene,³ naphthalene,⁴ anthracene,⁵ pyrene,⁶ perylenes⁷ and chrysene⁸ has garnered a great deal of global attention in recent years owing to the versatile applications of PAHs in organic fluorescence,^{5,6b} organic light-emitting diodes (OLEDs),⁵ organic field-effect transistors (OFETs),⁹ solar cells,⁹ sensors,¹⁰ and liquid-crystal displays.¹¹ The introduction of an alkynylated unit into PAHs significantly improves their thermal stability while enhancing the π -conjugation that helps in the fabrication of optoelectronic devices with tunable properties.^{4,9} Further control could be achieved by the introduction of either heteroatoms or a variety of functional groups into both the aromatic core of the PAH and the alkynyl carbon.¹² Therefore, the development of

effective synthetic procedures for alkynylated molecules is crucial for the identification of new organic materials.

The most effective and widespread technique for creating C_{sp} - C_{sp^2} bonds is cross-coupling aryl halides with terminal alkynes, also known as the Sonogashira coupling. Generally, Sonogashira cross coupling reaction of various aryl halides and terminal alkyne have been performed in the presence of various ligands (Figure 2.2) with palladium ($Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(dba)_2$, $Pd_2(dba)_3$, $Pd(PhCN)_2Cl_2$, $Pd(CH_3CN)_2Cl_2$, $Pd(OAc)_2$, $Pd(C_3H_5)_2Cl_2$, $Pd(dppe)Cl_2$, $Pd(dppp)Cl_2$, and $[(\pi\text{-allyl})PdCl_2]_2$) and copper(I) co-catalyst.¹³ Sonogashira reaction have been extensively applicable in industry as well as academic fields. Researchers are still developing the efficient synthetic protocol of Sonogashira reaction.

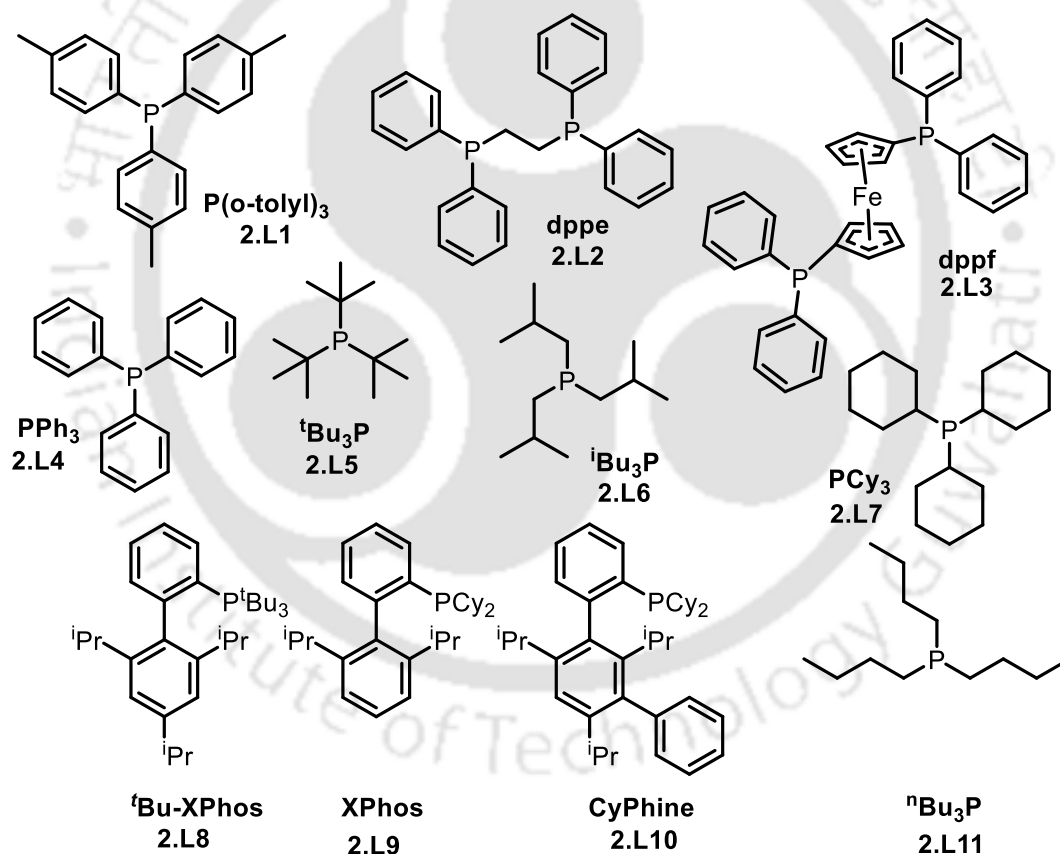
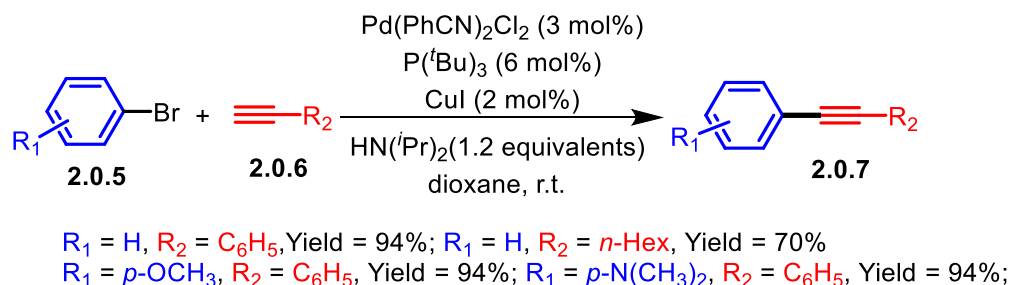


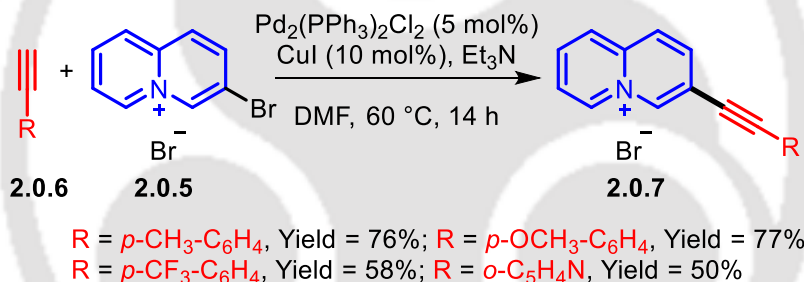
Figure 2.2. Few phosphine based ligands reported for Sonogashira reaction

In 2000, Fu and co-workers reported efficient synthetic protocol of the Sonogashira reaction of aryl bromide and terminal alkyne in the presence electron-rich phosphine ligand ($tBuP$) and $Pd(PhCN)_2Cl_2/CuI$ at room temperature with moderate to excellent yields (Scheme 2.1).^{13a}

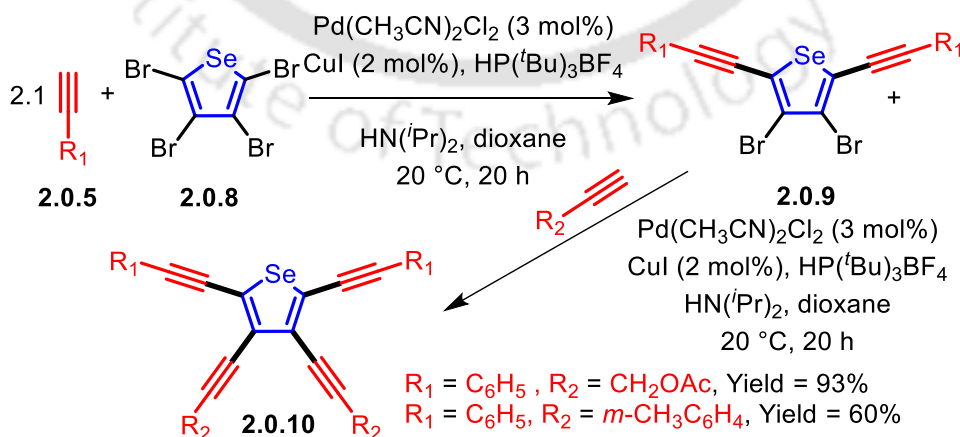


Scheme 2.1. Sonogashira reaction in the presence of $\text{Pd(PhCN)}_2\text{Cl}_2/\text{CuI}/^t\text{BuP}$

For the first time, Cuadro and Vaquero developed a efficient synthetic methodology of Sonogashira reaction of bromoquinolizium bromides (heteroaromatic cation) and aryl/heteroarylacetylenes employing $\text{Pd(PPh}_3)_2\text{Cl}_2$ as catalyst and CuI as co-catalyst (Scheme 2.2).¹⁴ The synthetic procedure enables to perform the reaction of quinolizium system to effectively incorporate aryl- and heteroarylethynyl substituents. The developed methodology also provides an accessible route to prospective π -donor- π -acceptor (D- π -A) systems containing one or more heteroaromatic cationic units.



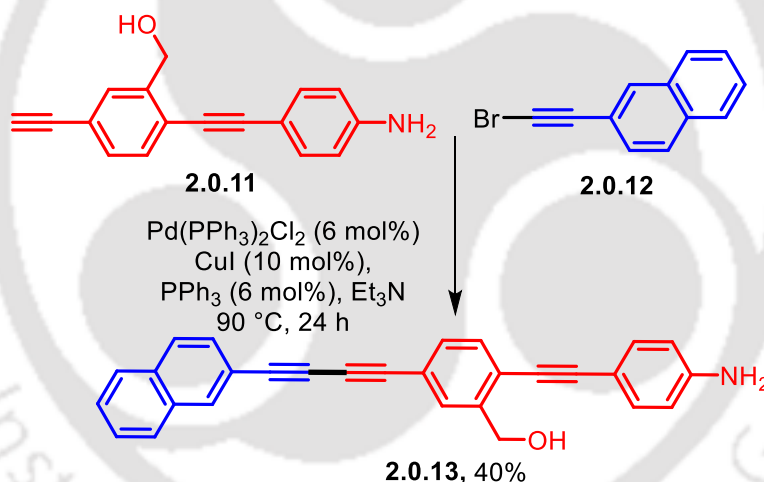
Scheme 2.2. Sonogashira reaction to access π -acceptor/ π -donor systems bearing heteroaromatic cationic units.



Scheme 2.3. Site-selective Sonogashira reaction of polyhalogenatedselenophene

Site-selective multi-fold Sonogashira reaction of polyhalogenated selenophene in the presence of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2/\text{CuI}$ was reported by Langer group in 2013 (Scheme 2.3).¹⁵ First alkyne reaction occurred at 2- and 5-positions of selenophene, then at 3-, 4-positions.

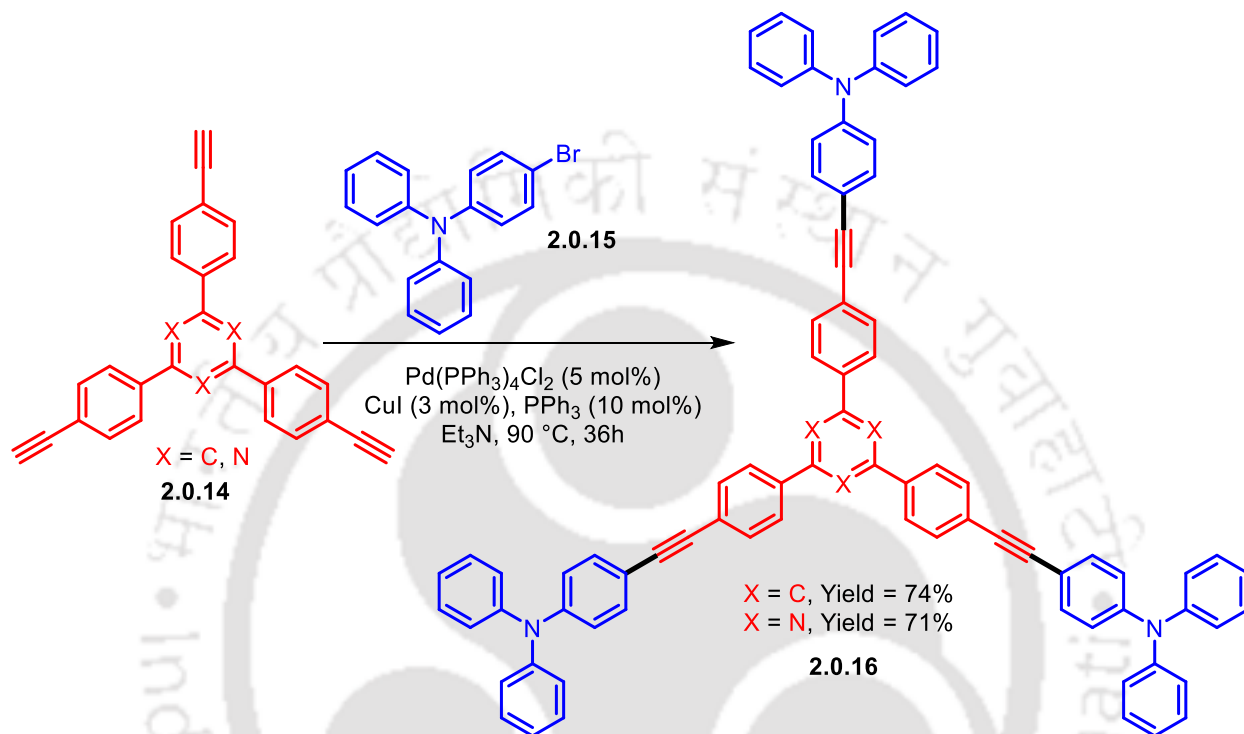
Lei and co-workers synthesized linear polyethynylene π -conjugated compound by Sonogashira reaction and studied its photophysical properties (Scheme 2.4).¹⁶ Amino-substituted phenylene polyethynylene **2.0.13** has shown the bathochromic shift of about 103 nm and broadening of the emission spectra by changing the solvent polarity from less polar toluene to more polar solvent DMF. It changes the color dramatically under UV-irradiation at 365 nm. The positive solvatochromism was observed owing to intramolecular charge transfer from the positive charge on the amino group to the negative charge on the $\text{Ph}-(\text{C}\equiv\text{C})_2^-$ and naphthalene moieties of **2.0.13** in the excited state. The charge-separated excited state can be stabilised more effectively than the ground state in polar solvent, which causes the bathochromic shift of emission maxima.



Scheme 2.4. Synthesis of linear polyethynylene π -conjugated dye by Sonogashira reaction.

Two new donor-acceptor (D-A) type conjugated compounds containing star-shaped phenyl and triazine triphenylamine end-capped arms were synthesized in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$ as catalyst by Mukherjee and co-workers (Scheme 2.5).¹⁷ Both the compounds show bathochromic shift in the emission spectra on changing the solvent polarity from non-polar to polar solvent (hexane to DMSO) owing to the twisted intramolecular charge transfer (TICT) effect in polar solvent. The intensity of fluorescence decreases in polar solvent because of various nonradiative decay process of TICT. In systems with donor and acceptor groups connected by a single bond, TICT is a very typical phenomena. Rotation around this connection causes the orbitals of these two groups to become decoupled, allowing practically full electron

transfer from the donor to the acceptor. In polar solvent, the highly polar TICT state is preferentially stable in comparison to a planar locally excited (LE) state. In nonpolar solvent, the emission arises from the locally excited state but emission is observed from TICT state in polar solvent which gives the bathochromic shift of emission.

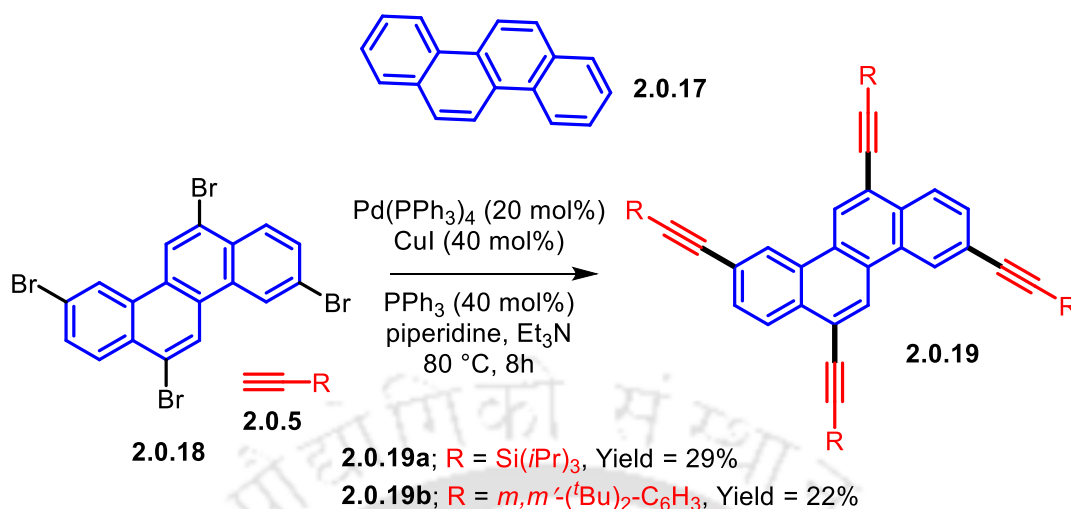


Scheme 2.5. Synthesis of π -conjugated donor-acceptor organic luminogens by Sonogashira reaction.

Liu and co-workers synthesized the 3,6,9,12-tetraalkynylatedchrysenes molecules employing Pd(PPh₃)₄/CuI and studied their photophysical and electronic behaviours (Scheme 2.6).⁸ The absorption as well as emission band showed bathochromic shift for 3,6,9,12-tetraalkynylatedchrysene compounds with respect to chrysene (Table 2.1). Fluorescence quantum efficiency increases and band gap decreases by addition of polyalkynylated substituents to chrysene (Table 2.1).

Table 2.1. Photophysical properties of chrysene and alkynylated substituted chrysene.

Compound	Absorption (λ_{max})	Emission (λ_{em})	Quantum Yield (ϕ)	Band gap (eV)
2.0.17	309, 322	366, 383	12.2	3.77
2.0.19a	308, 372, 394	408, 428	74.1	3.05
2.0.19b	329, 396, 416	439, 466	62.6	2.81



Scheme 2.6. 3,6,9,12-tetraalkynylatedchrysene derivatives synthesis by Sonogashira reaction in the presence of Pd(PPh₃)₄/CuI.

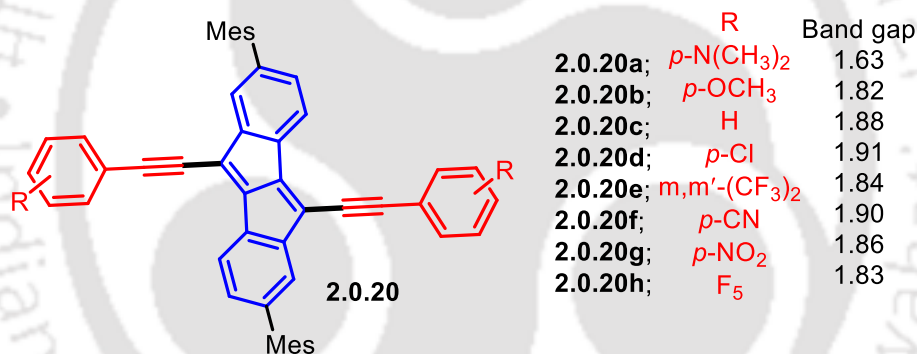
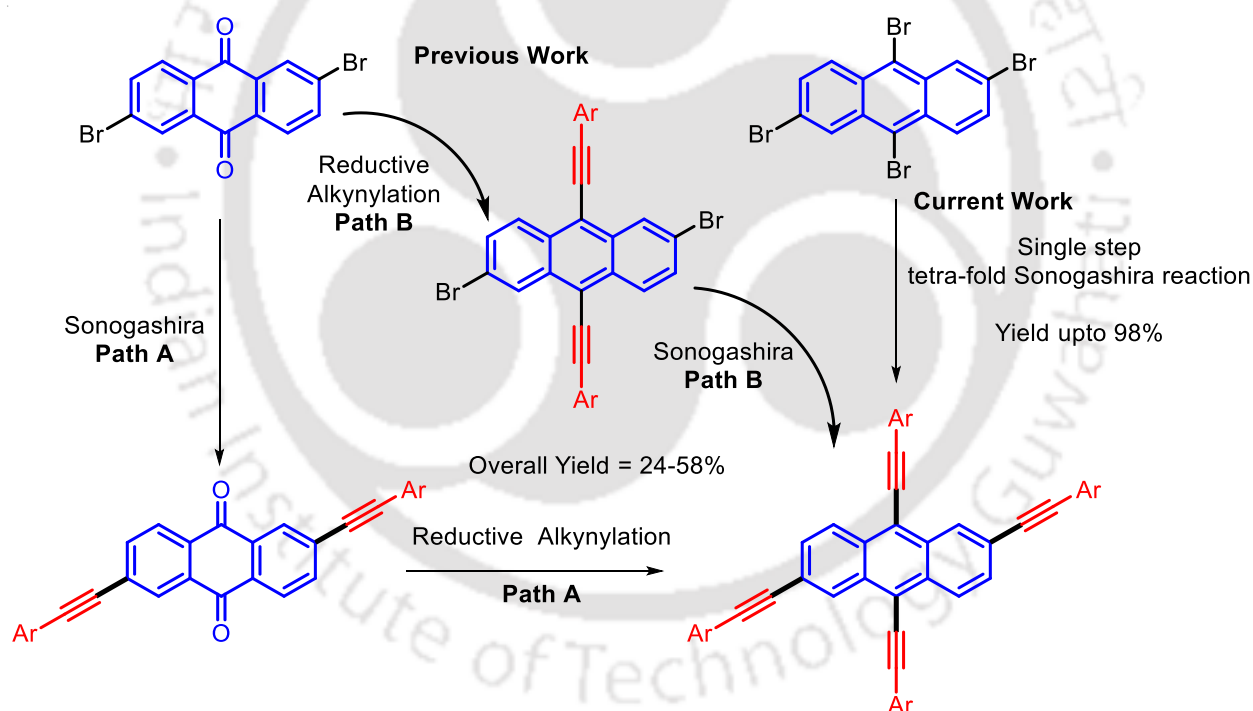


Figure 2.3. The *n*-type materials based on dibenzo[a,e]pentalenes.

Recently, Esser group demonstrated that band gap can be tuned by introducing the various functional groups containing alkynylated unit at 5,10-position of dibenzo[a,e]pentalenes (Figure 2.3).¹⁸

Of particular interest are PAHs with an anthracene core that has three rigid fused aromatic rings containing a 14 π -electron that typically has a bandgap of 3.9 eV and gives a high fluorescence quantum yield owing to optimal vibronic energy levels.¹⁹ The alkynylation^{4,20} of anthracene and its further functionalization^{4,20} have been reported to result in highly π -conjugated organic semiconductors with tailored bandgaps¹² and improved electron mobility and stability and hence better overall properties for device fabrication.²¹

2,6,9,10-tetraalkynylated anthracene molecules have found great application in the fabrication of organic field-effect transistors (OFETs).¹ To date, about twelve²² unsymmetrical 2,6,9,10-tetraalkynylated anthracene molecules have been reported by Choi and co-workers and they are typically synthesized via two-step reactions.^{22f} In the first step, Choi synthesized the symmetrical dialkynylanthracene-9,10-dione starting from 2,6-dibromoanthracene-9,10-dione via Sonogashira coupling. The second pair of alkynyl groups was then introduced into 2,6-dialkynylanthracene-9,10-dione by the treatment of appropriate alkynes in the presence of SnCl_2 and HCl , leading to 2,6,9,10-tetraalkynylated anthracene (Scheme 2.7, Path **A**). Choi has demonstrated the flexibility of the synthetic protocol by accomplishing the reduction of 2,6-dibromoanthracene-9,10-dione to 2,6-dibromo-9,10-dialkynylanthracene followed by the Sonogashira reaction to yield the unsymmetrically substituted 2,6,9,10-tetraalkynylated anthracene (Scheme 2.7, Path **B**) with moderate overall yield 24-58%.^{22f}



Scheme 2.7. Synthetic protocol leading to tetraalkynylatedanthracene.

2.1.1. Objectives

To the best of our knowledge, there are no reports on symmetrical 2,6,9,10-tetraalkynylated anthracene molecules. More importantly, there are no reports on a one step synthetic protocol for obtaining 2,6,9,10-tetraalkynylated anthracene. 2,6,9,10-tetraalkynylated anthracene molecules

are not explored in the field of photophysical properties and solid state interaction. The current chapter attempts to address the following challenges.

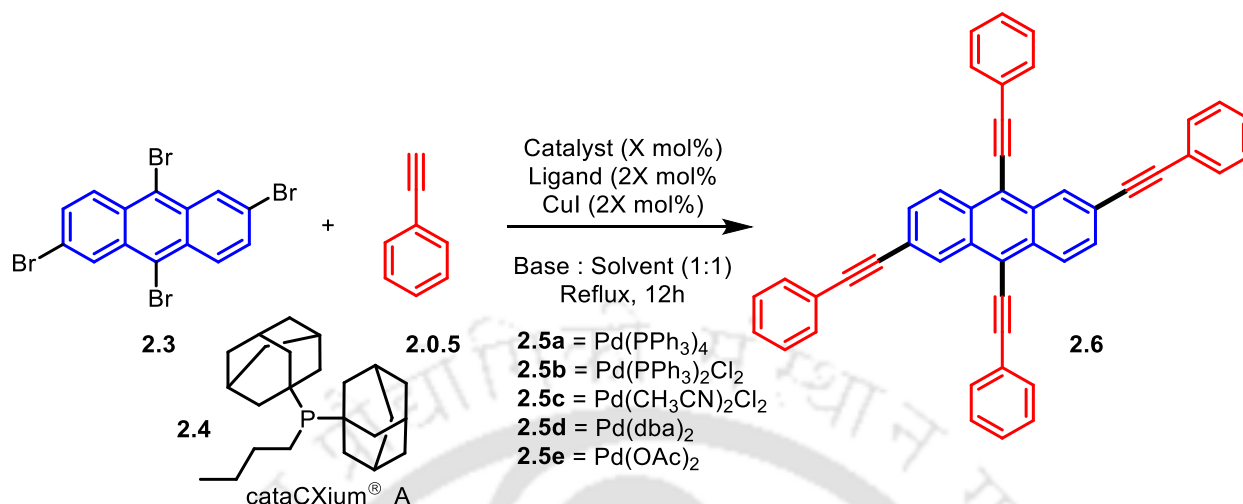
- Is it possible to formulate a new synthetic route to 2,6,9,10-tetraalkynylatedanthracenes by multi-fold Sonogashira coupling reaction in a single step and one pot?
- Is it possible to tune the photophysical properties of their by varying the various substituents?
- Can the synthesized polyalkynylatedanthracenes be used as sensors?

2.2. Results and discussion

2.2.1. Synthesis of tetraalkynylatedanthracenes

The studies were initiated by the synthesis of the precursor 2,6,9,10-tetrabromoanthracene (**2.3**) by a slight modification of the reported procedure.²³ The optimization of the reaction conditions for the tetra-fold Sonogashira coupling of **2.3** was attempted using phenyl acetylene (**2.0.5**) as a model alkyne using a variety of catalytic systems (Table 2.2). The Pd(PPh₃)₄ (**2.5a**) (2.5 mol% per halide) catalyzed tetra-fold Sonogashira coupling of **2.3** with **2.0.5** in the presence of a 1 : 1 solvent mixture of toluene and triethylamine resulted in the desired product **2.6** being obtained in about 47% yield (entry 1, Table 2.2). Upon repeating the reaction with 2.5 mol% per halide of Pd(PPh₃)₂Cl₂ (**2.5b**) under identical conditions, the tetraalkynylated product **2.6** was obtained in 57% yield (entry 2, Table 2.2). Comparable yields (ca. 60%) of **2.6** were obtained at a higher loading (5 mol% per halide) of **2.5b** (entry 4, Table 2.2) which however reduced to 44% upon lowering the loading of **2.5b** to 1.25 mol% per halide (entry 3, Table 2.2). The catalysts Pd(CH₃CN)₂Cl₂ (**2.5c**), Pd(dba)₂ (**2.5d**) and Pd(OAc)₂ (**2.5e**) did not yield the tetra-fold Sonogashira coupled product **2.6** (entries 5–7, Table 2.2). There was a general increase in the yield of the tetra-fold Sonogashira coupled product when cataCXium®A (**2.4**) was used as a ligand (entries 8–12, Table 2.2) with **2.5c** being the most efficient (entry 10, Table 2.1) among the studied catalysts. The catalyst **2.5c** (2.5 mol% per halide) in combination with 5 mol% cataCXium®A per halide led to the formation of **2.6** in 91% yield starting from **2.3** and **2.0.5** when refluxed in a 1 : 1 mixture of toluene and Et₃N.

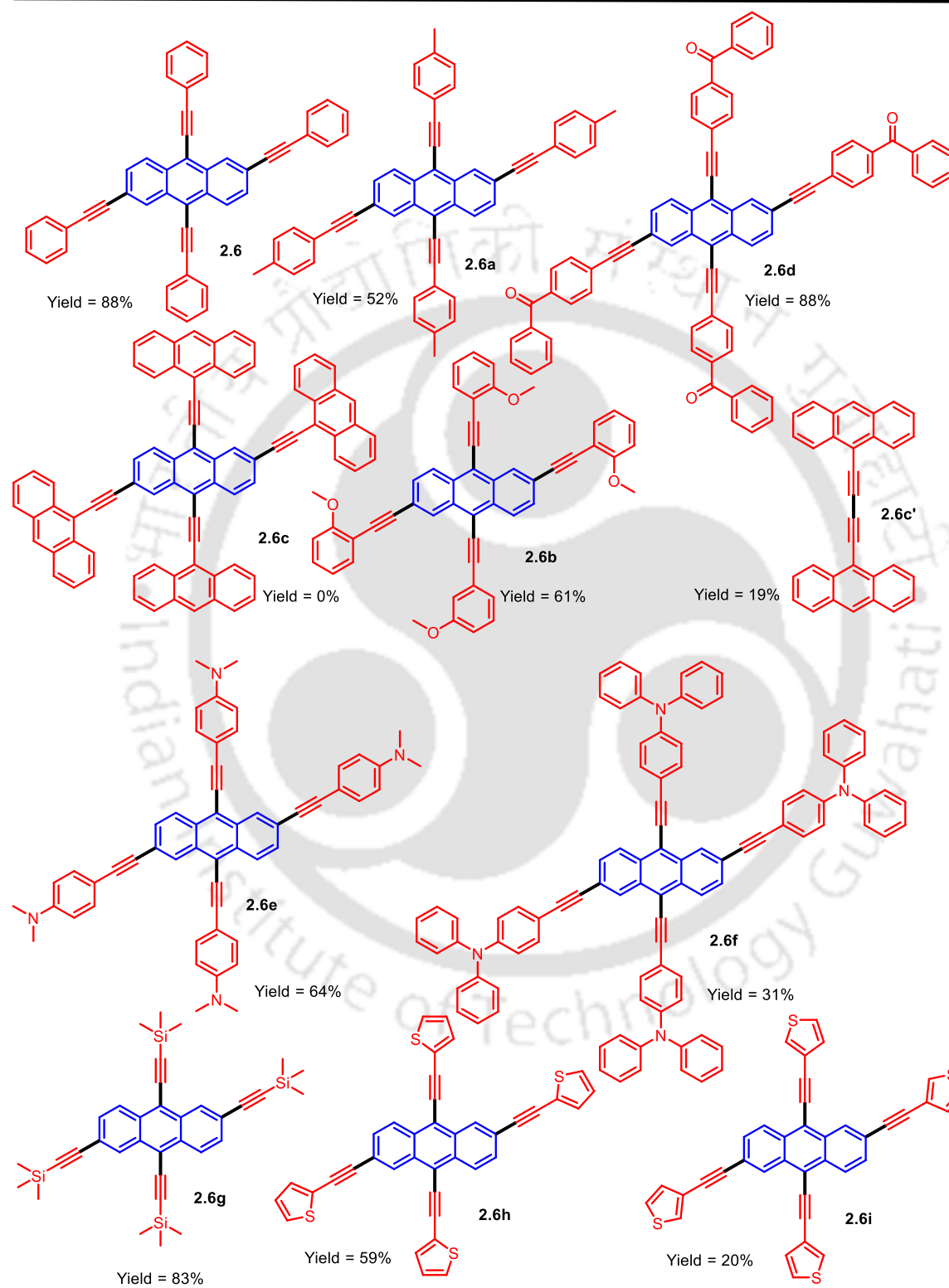
Among the various solvent systems screened (entries 10, 13 and 14, Table 2.1) under the conditions shown in entry 10, the best results (ca. 98% of **2.6**, entry 13, Table 2.2) were obtained with a 1 : 1 solvent mixture of THF and Et₃N. The use of K₃PO₄, NaO^tBu and KO^tBu as bases ga-

Table 2.2. Optimization of tetra-fold Sonogashira coupling of **2.3** with **2.0.5**^a

Entry	Catalyst (x mol%)	Ligand (2x mol%)	Base	Solvent	Yield ^b 2.6 (%)
1	2.5a (2.5)	—	Et ₃ N	Toluene	47
2	2.5b (2.5)	—	Et ₃ N	Toluene	57
3	2.5b (1.25)	—	Et ₃ N	Toluene	44
4	2.5b (5)	—	Et ₃ N	Toluene	60
5	2.5c (2.5)	—	Et ₃ N	Toluene	0
6	2.5d (2.5)	—	Et ₃ N	Toluene	0
7	2.5e (2.5)	—	Et ₃ N	Toluene	0
8	2.5a (2.5)	cataCXium® A	Et ₃ N	Toluene	72
9	2.5b (2.5)	cataCXium® A	Et ₃ N	Toluene	57
10	2.5c (2.5)	cataCXium® A	Et ₃ N	Toluene	91
11	2.5d (2.5)	cataCXium® A	Et ₃ N	Toluene	84
12	2.5e (2.5)	cataCXium® A	Et ₃ N	Toluene	82
13	2.5c (2.5)	cataCXium® A	Et ₃ N	THF	98(88) ^c
14	2.5c (2.5)	cataCXium® A	Et ₃ N	Dioxane	84
15	2.5c (1.25)	cataCXium® A	Et ₃ N	THF	85
16	2.5c (2.5)	cataCXium® A	K ₃ PO ₄	THF	1.5
17	2.5c (2.5)	cataCXium® A	NaO ^t Bu	THF	7
18	2.5c (2.5)	cataCXium® A	KO ^t Bu	THF	6
19	2.5c (2.5)	(^{Ph} 2NNN) ²⁴	Et ₃ N	THF	3
20	2.5c (2.5)	(^{Cy} 2NNN) ²⁴	Et ₃ N	THF	3
21	2.5c (2.5)	(^{Bim} 2NNN) ²⁵	Et ₃ N	THF	0.8
22	2.5c (2.5)	(^{MeBim} 2NNN) ²⁶	Et ₃ N	THF	1.5

^aReaction conditions: 0.101 mmol of **2.3** and 0.606 mmol of **2.0.5** in the presence of 2.5 mol% of **2.5** per halide, 5 mol% of ligand per halide and 5 mol% of CuI per halide in a 1:1 mixture of a base and a solvent under reflux conditions. ^bYield determined from ¹H NMR using 1,4-dioxane as external standard. ^cIsolated yield is provided in parenthesis. ^dTwo equivalents of the base were used with respect to per halide.

Table 2.3. Tetraalkynylated anthracenes synthesized under the optimized conditions (entry 13, Table 2.1)



All are isolated yield

-ve very poor results (entries 16–18, Table 2.2). On the other hand, N-based ligands performed very poorly in comparison with cataCXium[®]A (entries 19–22, Table 2.2). The optimized conditions (entry 13, Table 2.2) were employed to access a variety of tetraalkynylated anthracenes (**2.6a**–**2.6i**) in good to moderate yields (Table 2.3). While all the compounds were fully characterized by NMR, MALDI and HRMS(ESI) analyses, we were fortunate to obtain good quality crystals in a few cases (**2.6**, **2.6a**, **2.6b**, **2.6e** and **2.6g**) which were analyzed by single-crystal X-ray diffraction studies. However, the attempted synthesis of **2.6c** did not proceed in the expected fashion and a homo-coupled product **2.6c'** was isolated and crystallographically characterized.

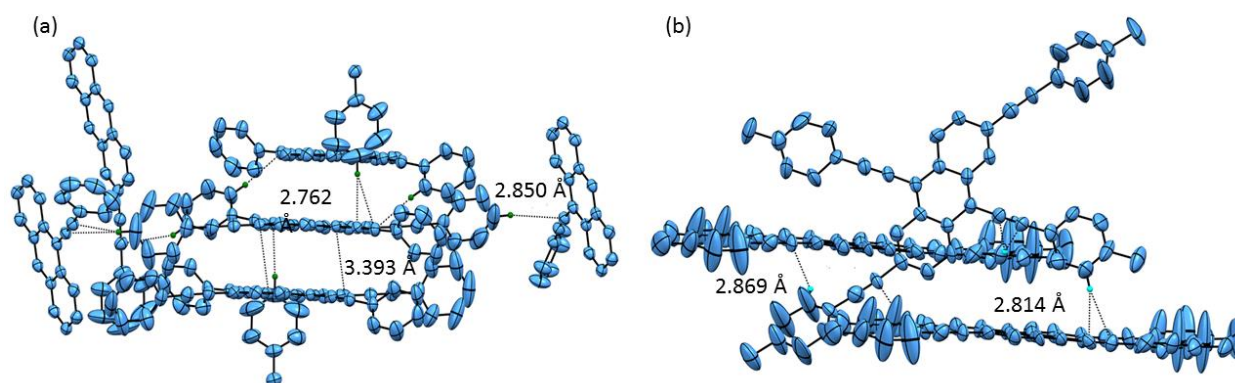


Figure 2.4. Interactions present in the solid-state structure of (a) **6** (b) **6a**

It is noteworthy that in addition to the expected π – π interactions, the acidic aromatic protons are capable of demonstrating weak interactions with the various π bonds present in the conjugated systems which are capable of imparting unique photophysical properties in the resulting molecular solid.²⁷ Among the five new tetraalkynylated anthracenes (**2.6**, **2.6a**, **2.6b**, **2.6e** and **2.6g**) which were characterized by single-crystal X-ray diffraction studies, only **2.6** and **2.6a** exhibited several π – π interactions apart from various $C_{\text{phenyl}}\text{--H}\cdots\pi$ interactions in the solid-state (Figure 2.4). Compound **2.6** showed two effective π – π interactions with an average distance of 3.393 Å (Figure 2.4a). In addition, **2.6** demonstrates a total of seven $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions including two symmetrical bifurcated²⁷ $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions with an average bond distance of 2.762 Å and five other unsymmetrical T-shaped $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions (ca. 2.850 Å). On the other hand, the solid-state molecular structure of **2.6a** showed only four $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions that included two symmetrical bifurcated $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions with an average bond distance of 2.814 Å and two other unsymmetrical T-shaped $C_{\text{phenyl}}\text{--H}\cdots\pi(C\equiv C)$ interactions (ca. 2.869 Å).

H $\cdots\pi$ (C $\equiv$ C) interactions (ca. 2.814 Å) and two unsymmetrical T-shaped C_{phenyl}-H $\cdots\pi$ (C $\equiv$ C) interactions with an average bond distance of 2.869 Å (Figure 2.4b).

2.2.2. Photophysical properties of tetraalkynylated anthracenes

All the nine new tetraalkynylated anthracenes (**2.6**, **2.6a–2.6i**) displayed bright colors both in solution and in the solid-state. The rich photophysical properties of **2.6**, **2.6a–2.6i** are shown in Table 2.4 (Figure 2.5–2.16). The interesting absorption/emission spectra, the good quantum yield, optimal lifetime and easily accessible bandgaps hold great promise in the fabrication of sensors and optoelectronic devices based on these molecules. Molecule **2.6e** that shows the lowest bandgap could be of potential interest for the fabrication of OFET devices.

All the compounds showed absorption in UV as well as in the visible light region (Figure 2.5). The absorption band in the solid powder state differs from the absorption band in solution. The solid powder state absorption band showed a bathochromic shift with respect to the absorption band in the solution phase due to the ground state aggregate formation of tetraalkynylated anthracene derivatives (Figure 2.5b). The absorption maxima (λ_{max}) are not distinctively sharp in the solid powder form for all compounds. The onset (λ_{onset}) of the absorption band in the solid powder state of tetraalkynylated anthracene derivatives extends up to ca. 727 nm, which is comparatively longer than the onset of the absorption band (λ_{onset} = ca. 520 nm) in the solution state. The full width at half maximum (fwhm) of all the compounds are broad, which indicates the strong intermolecular interaction²⁸ of 2,6,9,10-tetraalkynylated anthracene compounds in the aggregated form in the ground state.

Interestingly, all the synthesized compounds are highly emissive in solvents having low–moderate polarity, thin-film and solid powder state. All compounds exhibit emission in the visible region in solution (λ_{em} = 464–575 nm), thin-film (λ_{em} = 543–642 nm), and solid powder state (λ_{em} = 402–653 nm) (Figure 2.12). The emissions in thin-film and solid powder state were found to be different from the emissions in the solution state. Except **2.6e** all the molecules showed a red shift in the thin-film and solid powder state with respect to the solution phase. The presence of the electron donating group –N(CH₃)₂ in **2.6e** led to a blue shift^{28a} in the solid powder state (ca. 173 nm). The hypsochromic shift for compound **2.6e** was probably due to the more twisted conformation in the solid powder state than in the solution state.²⁹ In thin-film, compounds

containing electron-donating groups showed a bathochromic shift (up to 99 nm) with respect to the phenyl group containing 2,6,9,10-tetraalkynylated anthracene (**2.6**). Compounds **2.6**, **2.6a–2.6i** exhibited moderate to good quantum yields (30–69%) in the solution phase (reference: quinine sulfate 0.1 M H₂SO₄). Time resolved photoluminescence of compounds **2.6**, **2.6a–2.6i** was studied and average lifetimes were calculated from the corresponding bi-exponential fitting curves (Table 2.4, Table 2.5, Figure 2.13-2.14).

Table 2.4. Photophysical properties of tetraalkynylated anthracenes synthesized via tetra-fold Sonogashira coupling

Entry	Compound	λ_{max}^a (nm)	Log (ϵ) ^b (LM ⁻¹ cm ⁻¹)	λ_{em}^a (nm)			ϕ_F^e (%)	τ_{av}^f (ns)	E_g^g (eV)			
				Solution ^a	film ^b	powder ^c			Solution	Solid	E_{HOMO}^h	E_{LUMO}^i
1	2.6	345	4.17	500	543	601	69	4.54	2.47	20.4	-5.78	-3.74
2	2.6a	348	3.92	507	595	584	64	4.36	2.44	2.00	-5.58	-3.58
3	2.6b	359	4.03	514	633	653	60	4.83	2.39	1.95	-5.33	-3.33
4	2.6d	368	3.74	517	610	636	46	2.96	2.36	1.92	-4.76 ⁱ	-2.84 ^h
5	2.6e	322	3.54	575	642	402	30	4.18	2.16	1.79	-5.11	-3.32
6	2.6f	344	4.07	572	635	639	35	3.56	2.21	1.99	-5.27	-3.28
7	2.6g	310	4.5	464	556	567	69	6.70	2.62	1.92	-5.39	-3.47
8	2.6i	342	3.95	503	547	567	64	4.79	2.47	2.04	-5.71	-3.67

^aThe absorption (10⁻⁵ M) as well as emission (10⁻⁹ M) spectra recorded in CHCl₃. ^bLog (ϵ) was calculated from the plot of absorbance vs. concentration. ^cEmission spectra were recorded on glass on which a thin film was prepared by drop-cast method. ^dEmission spectra were recorded in powder form of the compounds. ^eQuantum yield as an average calculated at five different concentrations with respect to quinine sulfate in 0.1 M H₂SO₄ as the standard (ϕ_F = 54%).

^fThe average lifetime of the compounds calculated by using the equation

$$\tau_{av} = \frac{B_i \tau_i^2}{B_i \tau_i} \quad (1)$$

Where τ_{av} = average lifetime in the excited state of the luminescence compound,

B = pre-exponential factor, τ_i = decay lifetime of photoluminescence in the excited state for the i^{th} component. ^gThe bandgaps were calculated from the Tauc plot. ^hDetermined from cyclic voltammetry.

ⁱCalculated from the solid state bandgap using the equation $E_g = E_{LUMO} - E_{HOMO}$.

During the CV analysis, while **2.6d** exhibited an irreversible reduction peak, all the other tested compounds underwent irreversible oxidation (Figure 2.16b). Accordingly, the LUMO energy level for **2.6d** and the HOMO energy level for the rest of the compounds were calculated by using equation (7) and (6), respectively (*vide-infra*). As the events involved in the CV analysis were irreversible and to have a good understanding of the counterpart energy level, the E_{HOMO} of

2.6d and E_{LUMO} of the other studied compounds were calculated from the solid-state bandgap (Table 2.3) using equation (8) (*vide-infra*).

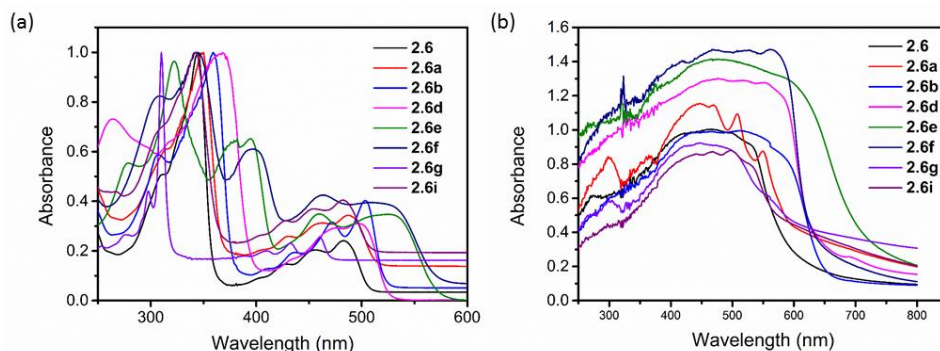


Figure 2.5. (a) Normalized absorption spectra (293 K, 10⁻⁵ M) of **2.6**, **2.6a-2.6i** in CHCl₃ (b) Absorption spectra (293 K) of the compounds (**2.6**, **2.6a-2.6i**) in solid powder state.

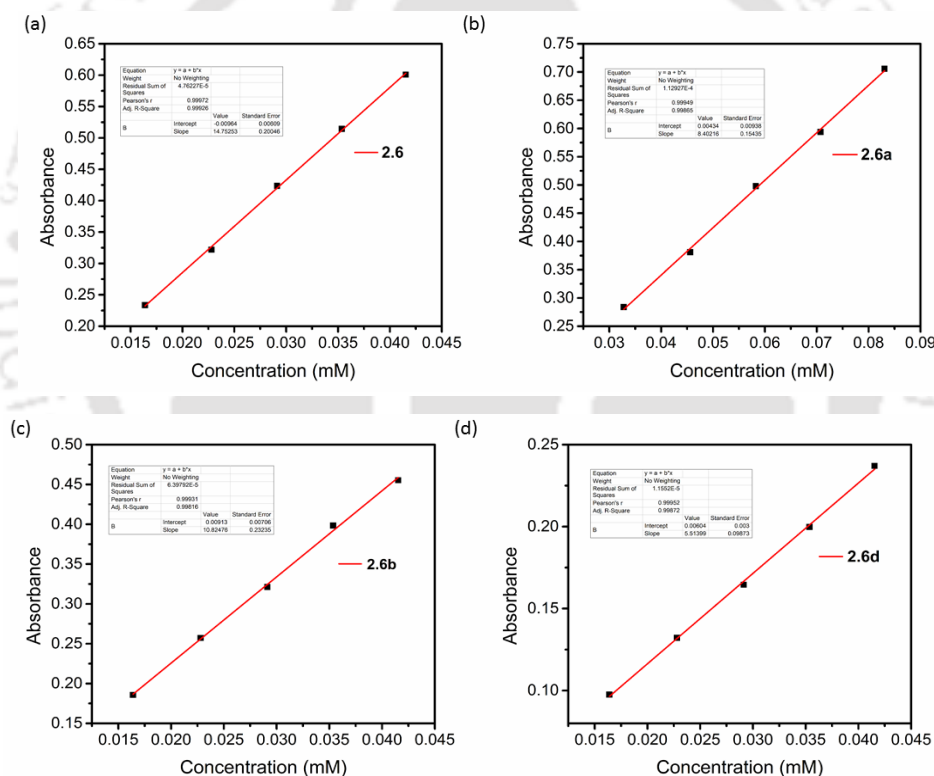


Figure 2.6. (a-d) Absorbance vs. Concentration spectra for the compounds (**2.6**, **2.6a-2.6d**) in CHCl₃.

Molar extinction coefficient can be calculated from the figure 2.6 and 2.7 by using the equation 2. It is a measure of how strongly the light is absorbed by chemical species in a particular wavelength. The absorption of light is proportional to molar extinction coefficient of the chemical species. It is

an inherent property of chemical species that depends on their structure and chemical compositions. In the table 2.3, the molar extinction coefficients of synthesized compounds (**6**, **6a-6i**) are listed and it shows that the compounds strongly absorb the light.

$$\varepsilon = \frac{A}{l.c} \quad (2)$$

Where ε = molar extinction coefficient A = absorption, l = length of the light path, c = concentration

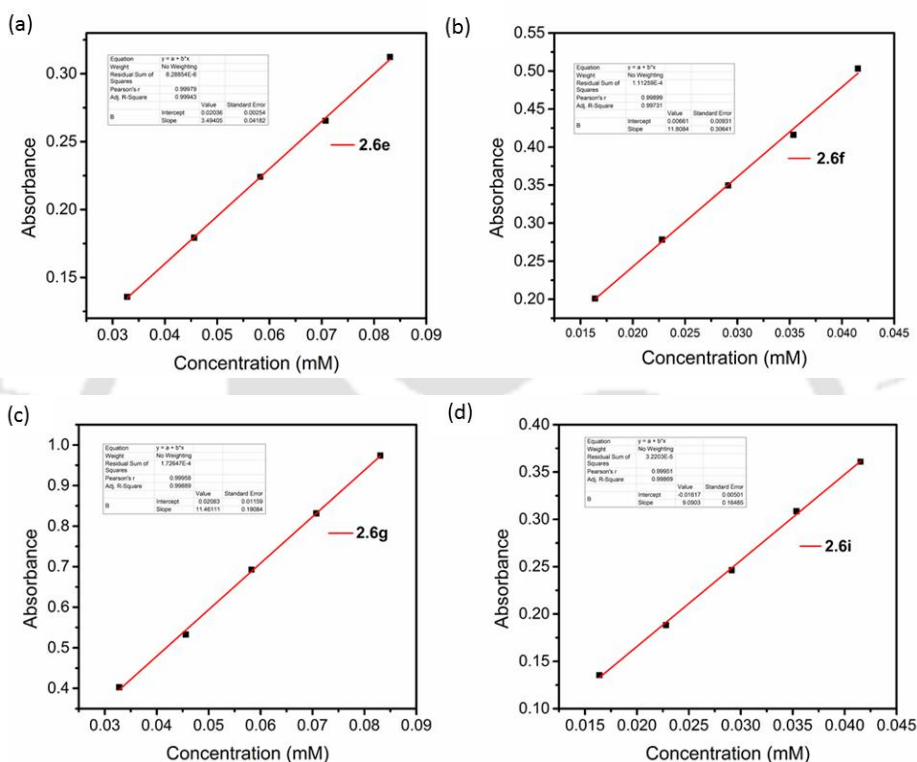


Figure 2.7. (a-d) Absorbance vs. concentration spectra for the compounds (**2.6e-2.6i**) in CHCl_3 .

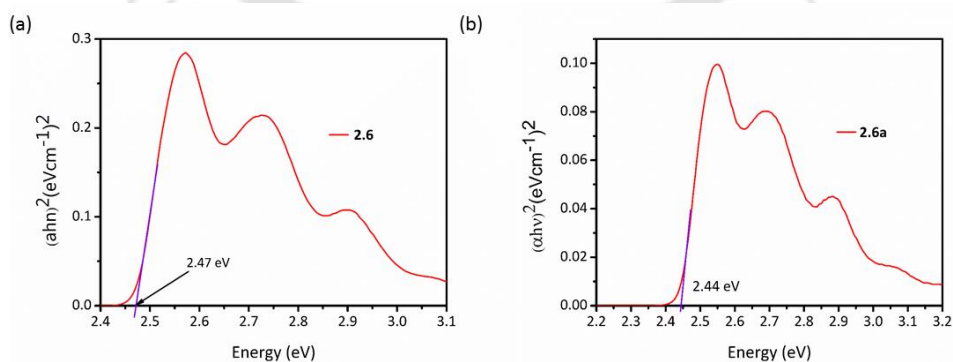


Figure 2.8. (a-b) Tauc's plot from the absorption spectra (293 K, 10^{-5} M) of **2.6**, & **2.6a** in CHCl_3 for energy band gap calculation.

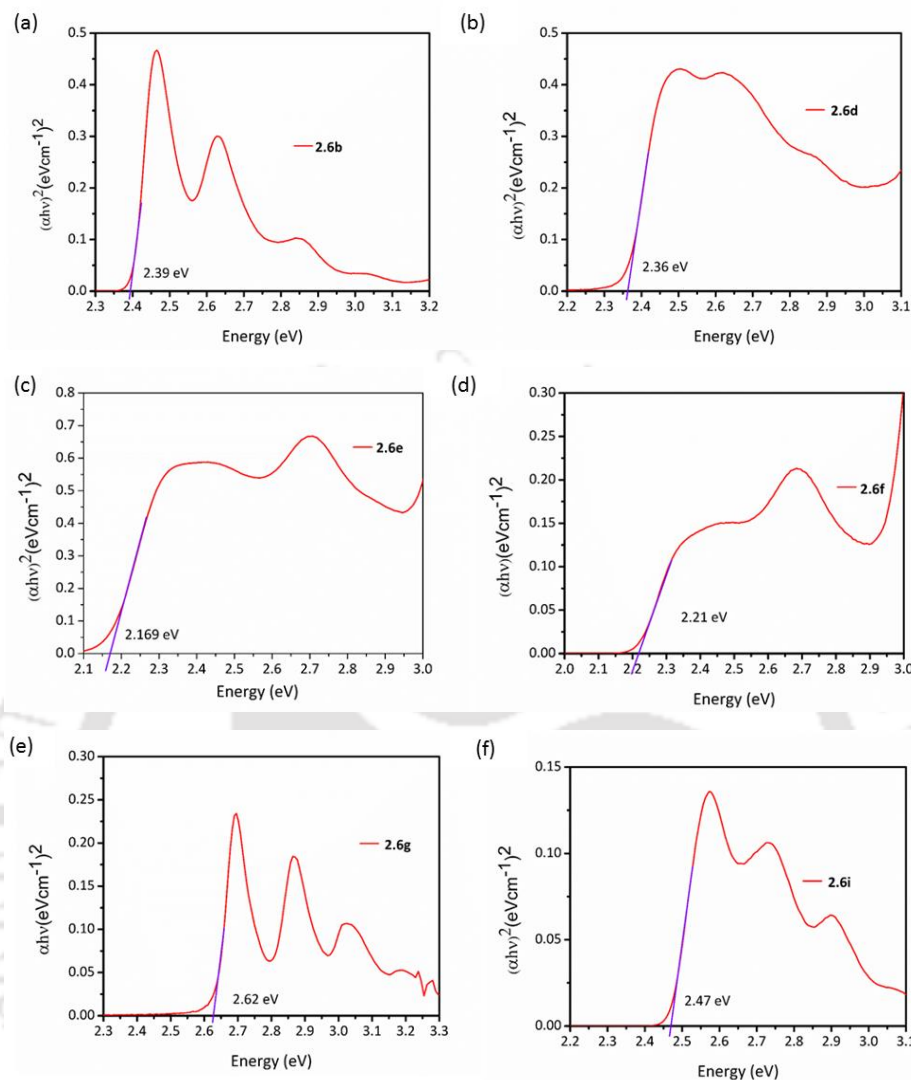


Figure 2.9. (a-f) Tauc's plot from the absorption spectra (293 K, 10^{-5} M) of **2.6b-2.6i** in CHCl_3 for energy band gap calculation.

The energy required to excite an electron from the valence band to the conduction band is known as the band gap energy of a semiconductor. In order to accurately anticipate the photophysical and photochemical properties of semiconductors, the band gap energy must be determined. In 1966, Tauc formulated the equation 3 for calculating the band gap from the absorption spectra.³⁰

$$(\alpha \cdot hv)^{1/\gamma} = B(hv - E_g) \quad (3)$$

Where h = planck's constant, v = photon's frequency, E_g = band gap energy, B = constant. γ is a factor depends on the nature of the electron transition and its values are 1/2 or 2. The band gaps of

synthesized compounds (**2.6**, **2.6a-i**) are calculated from Tauc's plot of figure 2.7-2.11 and listed on table 2.3. The band gap values of **2.6**, **2.6a-i** compounds indicate that they can behave as semiconductor.

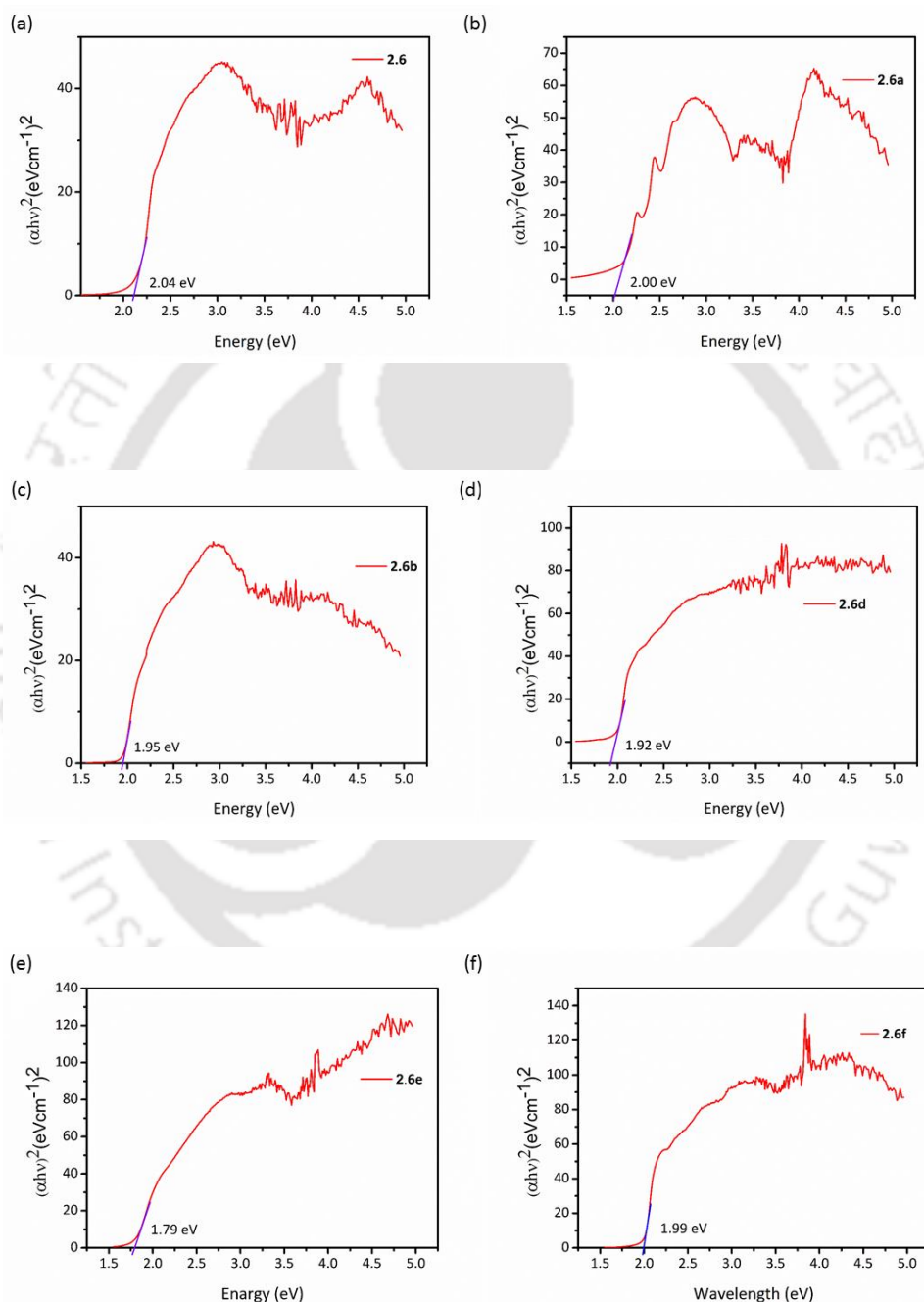


Figure 2.10. (a-f) Tauc's plot from the absorption spectra of **2.6**, **2.6a-2.6f** in solid powder state for energy band gap calculation.

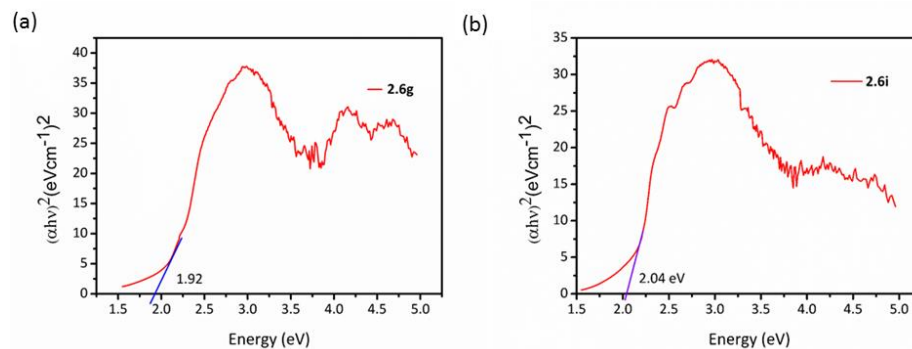


Figure 2.11. (a-b) Tauc's plot from the absorption spectra of **2.6g** & **2.6i** in solid powder state for energy band gap calculation.

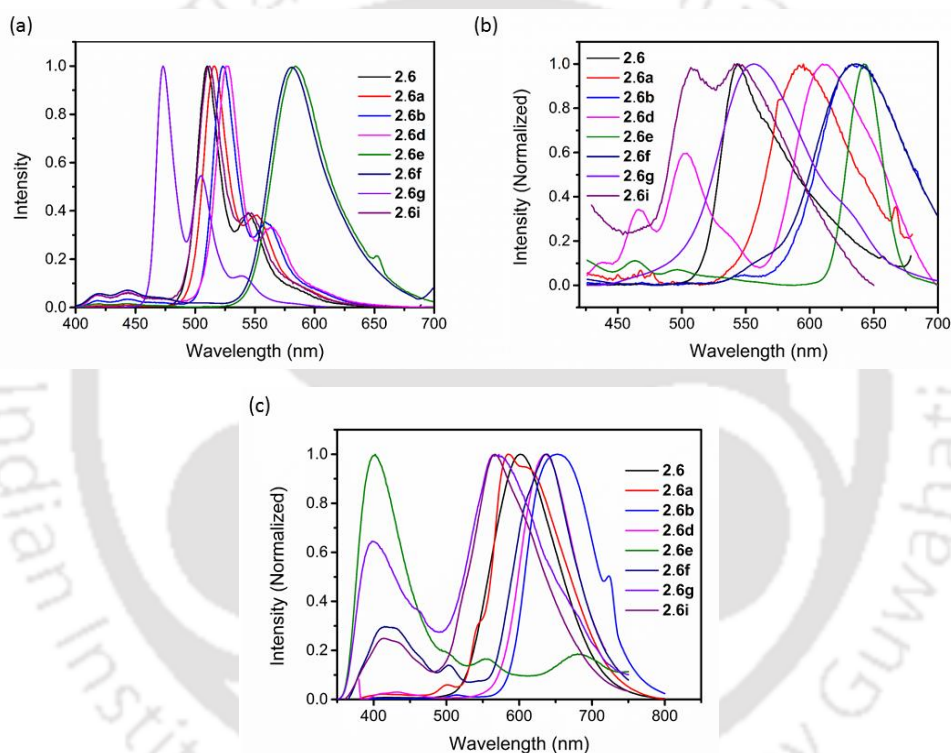


Figure 2.12. Normalized emission spectra in (a) solution (CHCl_3 , 293 K, 10^{-6} M), (b) thin-film (c) solid powder state for the compounds (**2.6**, **2.6a-2.6i**).

A potential method for analysing excited charge carrier recombinations in semiconductors and molecular systems is time-resolved photoluminescence (TRPL) spectroscopy.³¹ It is typically simple to analyse the TRPL decays of many chemical systems (such as organic materials and molecules) and to fit an exponential function that yields the rate constants. The average lifetime (τ_{av} , Table 2.4 & 2.5) of the compound at excited state is calculated from TRPL spectroscopy by applying the equation 1 (Table 2.4).

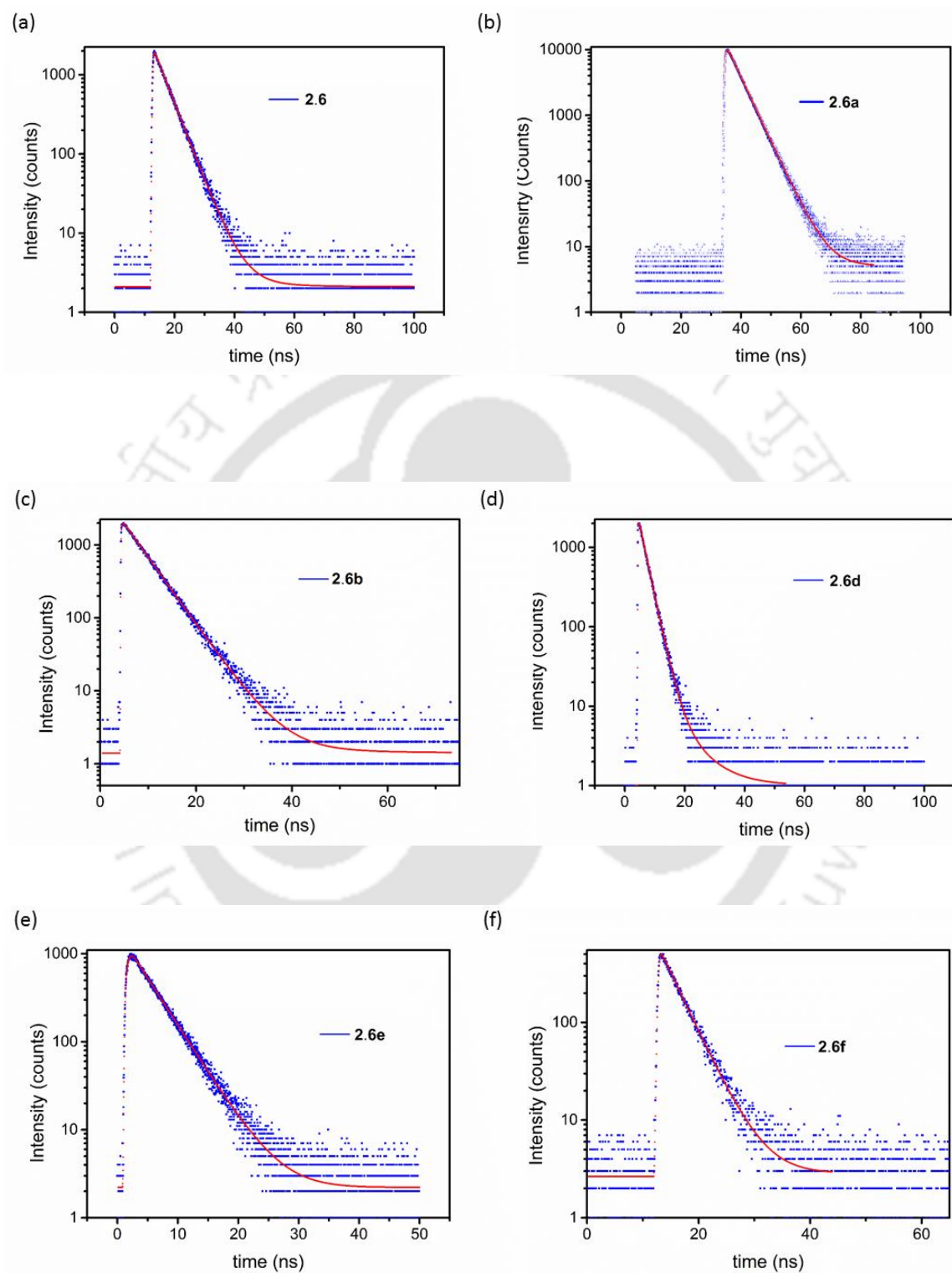


Figure 2.13. (a-f) Time-resolved photoluminescence spectra for the compounds **2.6**, **2.6a-2.6f**.

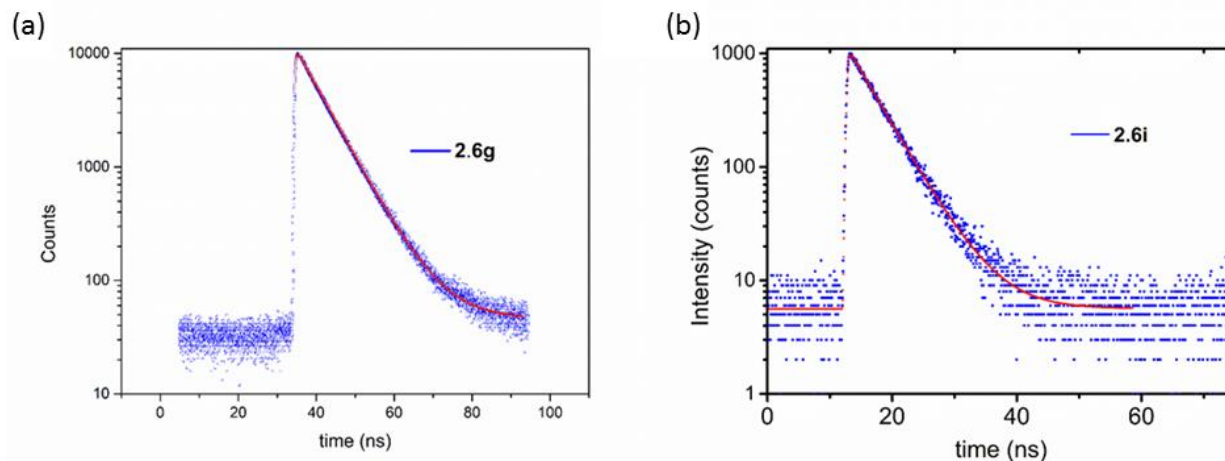


Figure 2.14. (a-b) Time-resolved photoluminescence spectra for the compounds **2.6g** & **2.6i**.

Table 2.5: Time-resolved Photoluminescence data.

Compound	B ₁ (%)	τ_1 (ns)	τ_1^2 (ns)	B ₂ (%)	τ_2 (ns)	τ_2^2 (ns)	τ_{av} (ns)
2.6	99.738	4.434	19.660	0.262	15.825	250.43	4.54
2.6a	25.995	0.192	0.037	74.005	4.423	19.57	4.36
2.6b	99.824	4.714	22.222	0.176	19.922	396.886	4.83
2.6d	96.829	2.392	5.722	3.171	8.069	65.109	2.96
2.6e	96.989	4.085	16.687	3.011	6.246	39.013	4.18
2.6f	0	0	0	100	3.559	12.666	3.56
2.6g	36.844	0.327	0.107	63.156	6.879	47.323	6.70
2.6i	99.877	4.562	20.812	0.123	31.450	989.103	4.79

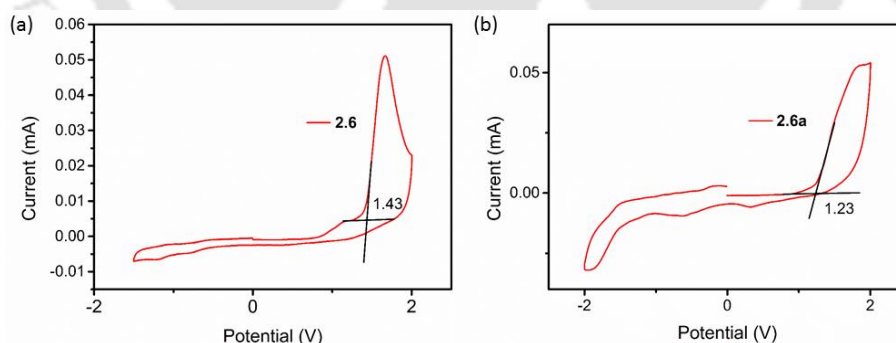


Figure 2.15. Current vs. potential curve for the compounds (a) **2.6**, (b) **2.6a**. During cyclic voltammetry analysis; glassy carbon was used as working electrode, platinum wire was used as counter electrode, Ag/AgCl was used as reference electrode with acetonitrile as solvent. Scan rate is in 50 mV/s. Scan direction, **2.6**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2V, minimum voltage = -1.5 V, **2.6a**, **2.6b**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2 V, minimum voltage = -2 V.

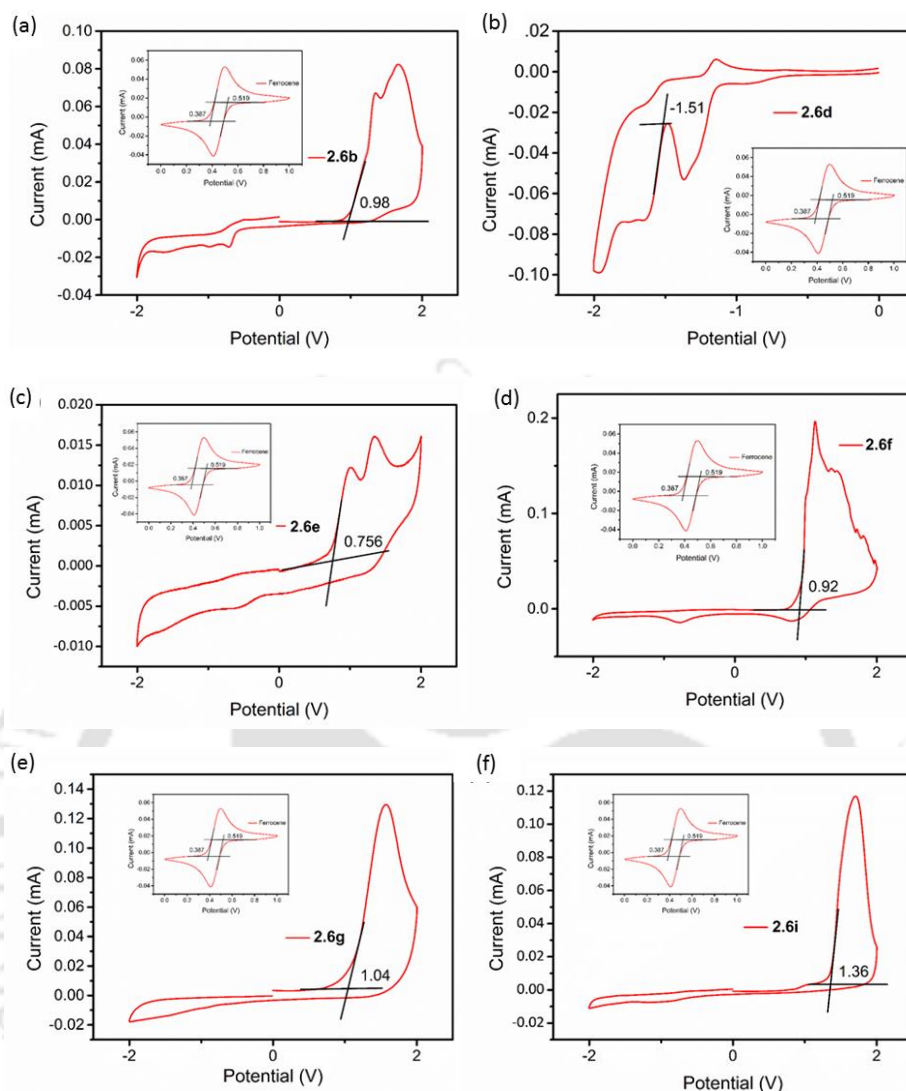


Figure 2.16. Current vs. potential curve for the compounds (a) **2.6b**, (b) **2.6d**, (c) **2.6e**, (d) **2.6f**, (e) **2.6g** and (f) **2.6i**. During cyclic voltammetry analysis; glassy carbon was used as working electrode, platinum wire was used as counter electrode, Ag/AgCl was used as reference electrode with acetonitrile as solvent. Scan rate is in 50 mV/s. Scan direction, **2.6b**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2 V, minimum voltage = -2 V. **2.6d**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = 0.0 V, minimum voltage = -2 V; **2.6e**, **2.6f**, **2.6g** and **2.6i**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2 V, minimum voltage = -2 V.

Solvatochromism is the phenomenon in which the chromophore changes its wavelength at maximum absorption as well as emission upon change in the polarity of the solvents.³² Among the tetraalkynylated anthracenes (**2.6**, **2.6a–2.6i**), compounds **2.6e** and **2.6f** that comprise a donor- π -

acceptor- π -donor motif show positive solvatochromism (Figure 2.17). The structured emission

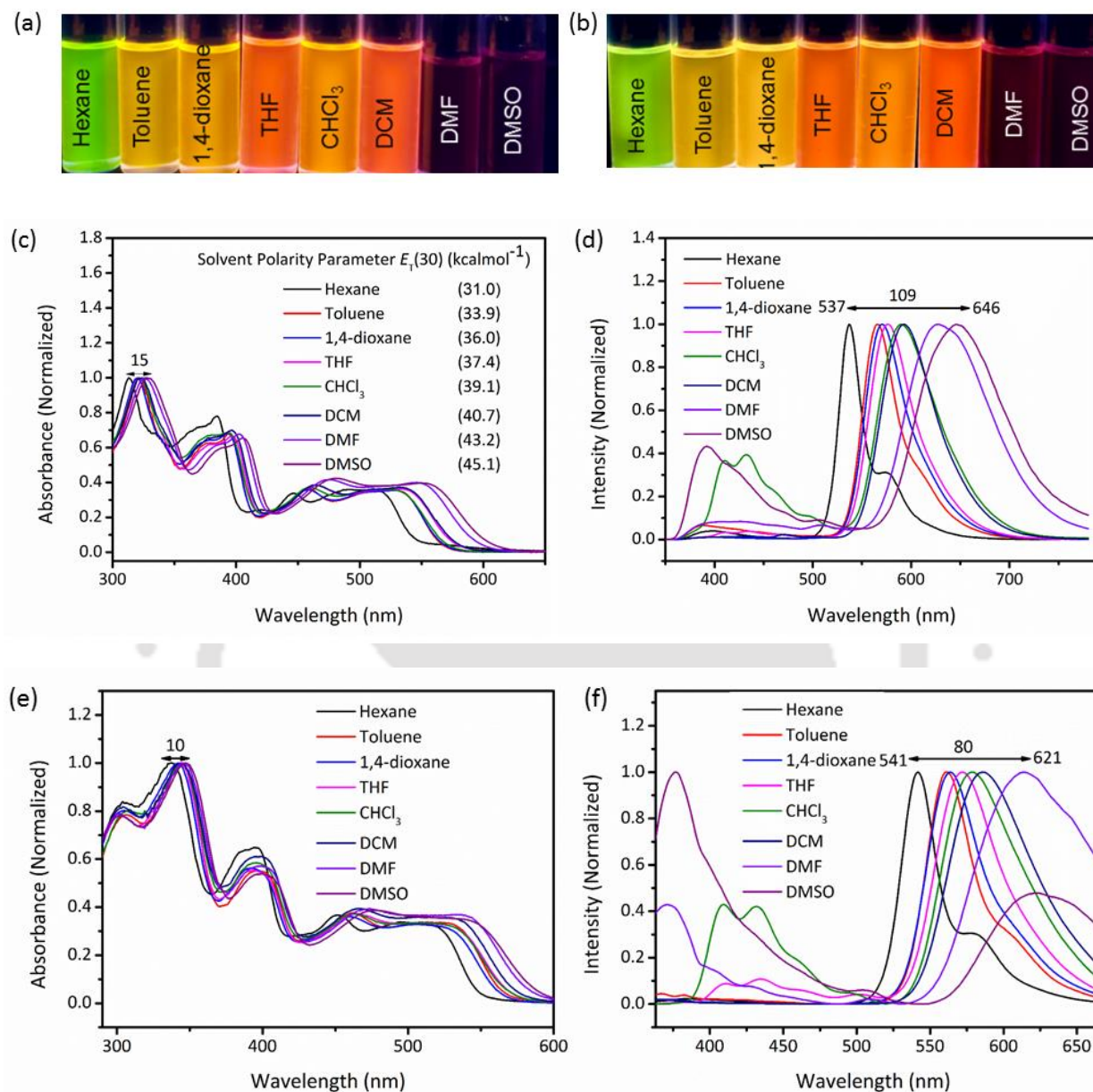


Figure 2.17. Solvatochromism demonstrated by compounds **2.6e** and **2.6f**. The colour in various solvents under 365 nm UV light demonstrated by (a) **2.6e** and (b) **2.6f**. (c) Normalized absorption spectra of **2.6e** according to the Reichardt polarity scale by increasing the solvent polarity from hexane to DMSO. (d) Normalized emission spectra of **2.6e** according to the Reichardt polarity scale by increasing solvent polarity from hexane to DMSO. (e) Normalized absorption spectra of **2.6f** according to the Reichardt polarity scale by increasing the solvent polarity from hexane to DMSO. (f) Normalized emission spectra of **2.6f** according to the Reichardt polarity scale by increasing solvent polarity from hexane to DMSO.

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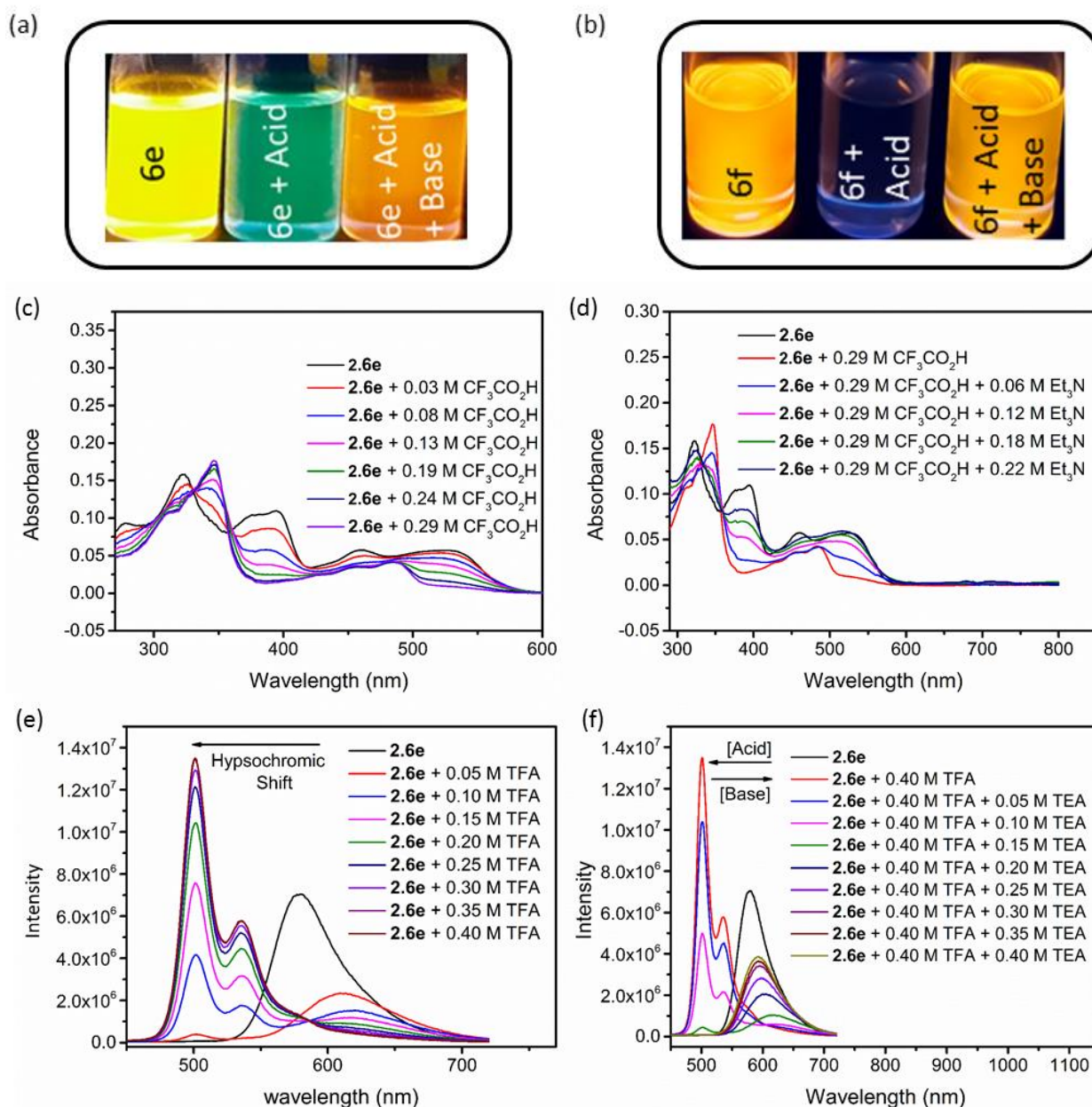


Figure 2.18. Halochromism demonstrated by compounds **2.6e** and **2.6f**. The colour after sequential addition of an acid and a base under 365 nm UV light demonstrated by (a) **2.6e** and (b) **2.6f**. (c) The absorption spectra demonstrating the titration of **2.6e** ($[\mathbf{2.6e}] = 1 \times 10^{-5}$ M) with varying concentration of $\text{CF}_3\text{CO}_2\text{H}$ (d) The absorption spectra demonstrating the titration of **2.6e** with varying concentration of Et_3N (e) Hypsochromic shift in the emission spectra of **2.6e** ($[\mathbf{2.6e}] = 2 \times 10^{-6}$ M) upon gradual addition of $\text{CF}_3\text{CO}_2\text{H}$. (f) Major recovery of the emission spectra of **2.6e** upon neutralization with Et_3N .

band of **2.6e** and **2.6f** in nonpolar hexane gradually broadened with a systematic increase in polari-

-ty from hexane to DMSO (Reichardt polarity scale)³³ with a concomitant bathochromic shift of 109 nm (Figure 2.17d) and 80 nm (Figure 2.17f), respectively. This indicates that the dipole moments in emissive states in **2.6e** and **2.6f** are higher with respect to their ground states³⁴ along with the involvement of the strong intramolecular charge transfer (ICT).³⁵ The molecules **2.6e** and **2.6f** show some extent of emission in the NIR region in the polar solvent. While a bathochromic shift of the high-energy ($\pi \rightarrow \pi^*$) absorbance maxima ($\lambda_{\text{max}} = 322$ nm) (Figure 2.18c) is observed upon addition of $\text{CF}_3\text{CO}_2\text{H}$ (TFA) to the solution of **2.6e** in chloroform, a hypsochromic shift is

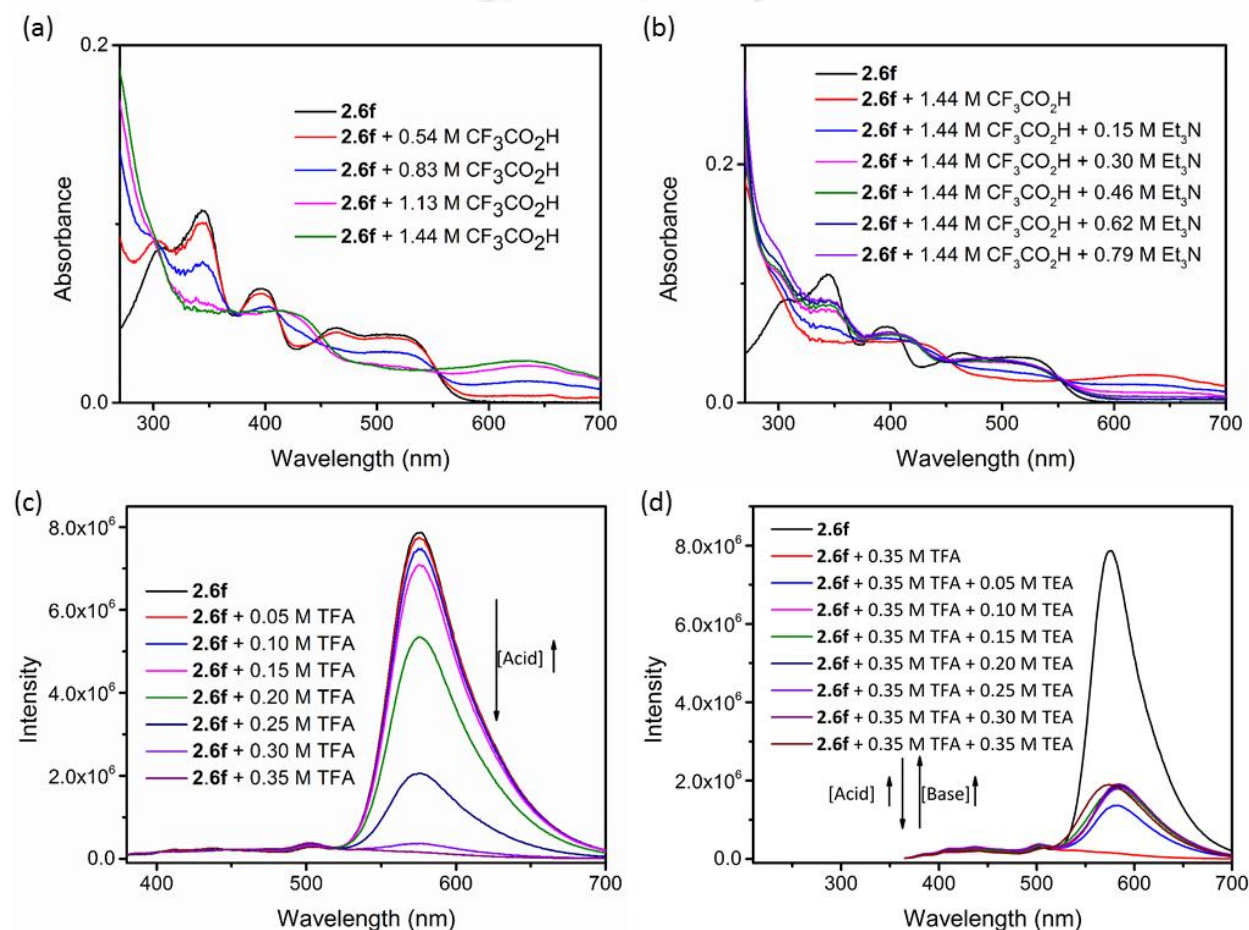


Figure 2.19. (a) The absorption spectra demonstrating the titration of the **2.6f** ($[\mathbf{2.6f}] = 1 \times 10^{-5}$ M) with varying concentration of CF_3COOH (b) The absorption spectra demonstrating the titration of **2.6f** with varying concentration of Et_3N (c) Disappearance of the emission maxima of **2.6f** ($[\mathbf{2.6f}] = 2 \times 10^{-6}$ M) upon gradual addition of $\text{CF}_3\text{CO}_2\text{H}$. (d) Major recovery of the emission spectra of **2.6f** upon neutralization with Et_3N .

observed for the low energy (charge-transfer (CT)) absorbance band (Figure 2.18d). The addition of acid would result in a facile protonation of the $-\text{NMe}_2$ groups.^{36,34}

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The bathochromic shift of the $\pi \rightarrow \pi^*$ band can be attributed to the increased solvent polarity upon addition of $\text{CF}_3\text{CO}_2\text{H}$.^{36b} The hypsochromic shift of the CT band of **2.6e** is expected as post-protonation, the protonated- NMe_2 groups are no longer electron-donating and consequently there is no more intramolecular charge-transfer to the central anthracene core.³⁷ Notably, the addition of $\text{CF}_3\text{CO}_2\text{H}$ results in a hypsochromic shift of the emission maxima of **2.6e** (Figure 2.18e).

In contrast to the full protonation of **2.6e**, one would expect only a partial protonation of **2.6f** owing to the poorer electron donating ability of the NPh_2 groups (relative to NMe_2 in **2.6e**). Considering the steric bulk, it is not surprising that these protonated derivatives of **2.6f** tend to aggregate, which is ultimately reflected as the disappearance (aggregation caused quenching) of the emission maxima of **2.6f** (Figure 2.19c). The attenuation of both the high-energy ($\pi \rightarrow \pi^*$) absorbance maxima ($\lambda_{\text{max}} = 344 \text{ nm}$) (Figure 2.19a) and the low-energy (charge-transfer (CT)) absorbance band (450–550 nm Figure 2.19a) is observed apart from the appearance of a new low-energy CT band (600–700 nm, Figure 2.19a) upon the addition of $\text{CF}_3\text{CO}_2\text{H}$ to the solution of **2.6f** in chloroform. The new CT band is attributed to the increased intramolecular charge transfer (ICT) in the partially protonated **2.6f** which leads to a push–pull electron relay from the electron-donating NPh_2 groups to the electron-withdrawing protonated NPh_2 groups via the anthracene core. Thus, while the full protonation of **2.6e** results in a decreased ICT along with the associated hypsochromic shift of the CT band, the partial protonation of **2.6f** gives rise to a new redshifted CT band owing to the increased ICT. Notably, halochromism is demonstrated as the protonation process that is mostly reversible for **2.6e** (Figure 2.18f) and **2.6f** (Figure 2.19d), respectively, by the addition of Et_3N (TEA). The initial intensity could not be completely recovered owing to the inherent challenges in the complete deprotonation of statistically protonated multiple amine groups.

2.3. Detection of hydrogen by PAHs based electrical sensors

2.3.1. Introduction

The availability of energy sources have a great impact on human life. Nowadays, the demand of energy has increased with increase in human population and industrial revolution. The main sources of energy are petroleum, coal, and natural gas.³⁸ The fossil fuels are non-renewable resources of energy and their combustion results in the emission of greenhouse gasses.³⁹ Over the years, air pollution has been a sensible concern due to the emission of hazardous and poisonous

gases in the atmosphere which causes severe health diseases. Unlike combustion of fossil fuels, in fuel cell only water is produced as the only side product without any CO₂ emission,⁴⁰ in order to convert H₂ to electrical energy.⁴¹ Currently, the researchers are greatly focused on utilization of hydrogen gas as renewable energy source^{40a, 42} for the future due to its abundance,⁴³ high gravimetric energy density,^{42b, 43} and high efficiency of combustion.^{40b} But, it is highly inflammable (lower flammable limit 4%),^{38c} tasteless, odourless and colourless which possess a threat to human health.⁴⁴ Human cannot sense the hydrogen gas and detection of its leakage is very difficult. The production, transport and storage of it is highly risky.^{39, 45} For these reasons, the detection of H₂ with high selectivity as well as sensitivity is desirable.⁴⁴ The hydrogen sensors must be power-efficient, inexpensive and also functional in humidity at room temperature.⁴⁶

In terms of detection method, gas sensors can be categorised as (i) variations on the electrical characteristics, (ii) variations in other characteristics.⁴⁷ In the first category, the sensor is fabricated based on semiconductors and works on electrical properties.⁴⁸ On the other hand, the gas can be measured by other parameters like thermal, optical, gas chromatography-mass spectroscopy, mechanical and acoustic.⁴⁹ Among the detection methods, electrical sensors based on semiconductors have received significant interest owing to their advantage in terms of easy assembly and intrinsic qualities of converting chemical or physical occurrences to the voluntarily observable electrical signal.^{48a, 50} Over the last decades, various types of semiconductors have been reported to detect hydrogen gas like metal oxide semiconducting materials,^{38a, 38c, 46, 50c, 51} carbon-based materials⁵² and conducting polymers.⁵³ The interaction of H₂ with the semiconductor improves the surface electron concentration and enhances the conductivity of the *n*-type semiconductor.^{38a, 48a}

Undoubtedly, mostly metal oxide semiconductors like ZnO, TiO₂, SnO₂, WO₃, and V₂O₅ are used to detect hydrogen gas.^{38a, 54} Metal oxide-based semiconductors have a wide band gap,^{38a, 54b, 55} so it is incapable of exciting them spontaneously at room temperature.⁵⁶ One requires UV light or heating for excitation to overcome this barrier, which is a drawback in their broad application.^{48a} Modification is required to detect hydrogen gas at room temperature by semiconductors-based sensors.⁵⁷ As a result, a semiconductor material with a low band gap is preferable for efficiently detecting hydrogen.

Organic semiconductors are widely used as active materials in electronic devices.^{1-2, 58} Extended-conjugated small organic molecules are promising candidates for fabricating an

electronic device due to their solution processability, light weight, mechanical flexibility, low-cost production, good film-forming ability, room temperature operation, and easily tailored functional group for sensing applications.^{2a} Small organic compounds, to the best of our knowledge, have not been studied for their ability to detect hydrogen gas. Because of its environmental stability, electric conductivity, and intriguing redox properties associated with a nitrogen atom in the chain, polyaniline (PANI) and polypyrrole have been reported as a hydrogen sensor.⁵³ However, the development of hydrogen sensors based on metal-free small organic semiconductors remains a challenge.

The mobility of 2,6,9,10-tetraalkynylatedanthracene was found up to $1.6 \text{ cm}^2/\text{Vs}$ and $I_{\text{on/off}}$ is 10^7 .^{2a} Recently our group reported a library of symmetrical 2,6,9,10-tetraalkynylatedanthracenes compounds.⁵⁹ As anthracene molecule has fused three benzene rigid ring and introduction of alkyne unit to anthracene moiety enhances its thermal stability, planarity and π -conjugation which are essential for intermolecular interaction and charge transport. 2,6,9,10-Tetrakis(phenylethynyl)anthracene (**2.6**, CCDC No 2070944)⁵⁹ and 2,6,9,10-Tetrakis(*p*-tolylethynyl)anthracene (**2.6a**, CCDC No 2070945)⁵⁹ exhibit unsymmetrical T-shaped and symmetrical bifurcate C-H $\cdots$ (C $\equiv$ C) interactions involving both $C_{\text{sp}2}$ -H donors and conjugated π_{alkyne} acceptors in solid state but interactions are absent in the compound **2.6e**. The compound **2.6e** contains $-\text{PhNMe}_2$ group which acts as a donor, acetylene unit present acts as a π -space and anthracene moiety behaves as an acceptor. In addition, **2.6e** shows holochromism in the presence of CF_3COOH and Et_3N .⁵⁹ Molecule **2.6e** exhibits lower band gap up to 1.79 eV ⁵⁹ which can be good organic semiconductor and acetylene unit can form weakly interaction with reducing agent hydrogen, allowing us to make a high-quality sensor under room conditions.

The microfabrication technique is also required for the development of low-cost organic semiconductor-based portable electronic devices.⁶⁰ This technique is widely used in a variety of industries to create small designs for property modification, patterning, subtractive and additive processes, and packaging. Traditional microfabrication technology is insufficient in terms of both money and time. As a result, developing a low-cost sensor will be difficult. Printing, on the other hand, is a relatively new microfabrication technique that has recently been investigated as an alternative to decades-old technology. The primary benefit of this technology is the reduced time required for device manufacturing, which enables rapid prototyping and device testing with minimal material waste. As a result, the cost of producing electronic devices is significantly

reduced. It also ensures that low-volume and high-volume fabrication needs are met simultaneously and high-volume fabrication needs are met at the same cost.⁶¹

As per our knowledge, this is the first time we report the electronic device which is fabricated by using μ G printing technology for small organic semiconductor to gas sensing. The

2.3.2. Fabrication process

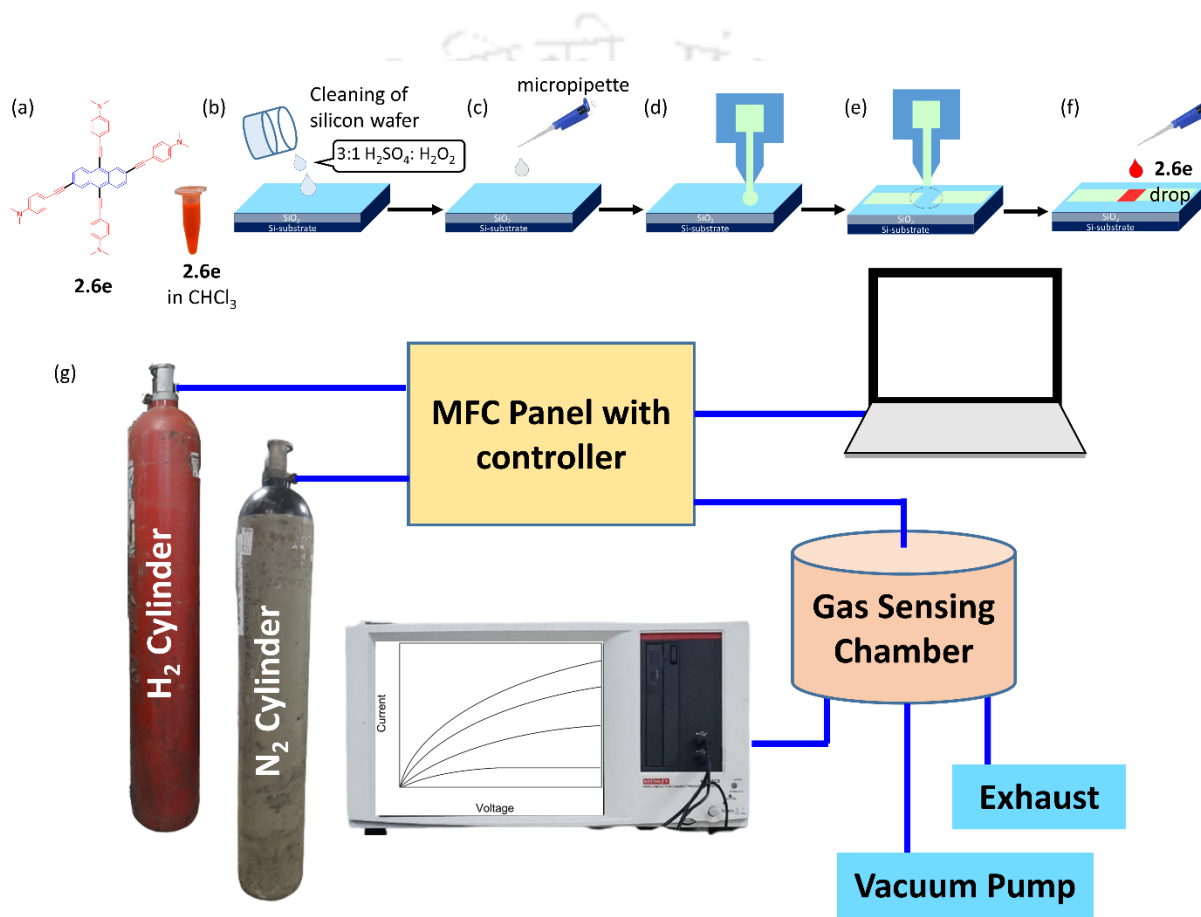


Figure 2.20. Fabrication steps of electrical devices (a) Structure of the 2.6e, (b) Cleaning of silicon wafer by piranha solution, (c) Drop casting the AgNP ink, (d) Placing μ girder, (e) Patterning μ girder, (f) Drop casting of 2.6e, (g) fabricated device connected to Keithly 2600 for sensing experiment.

sensor is developed on an undoped silicon/silicon oxide (Si/SiO_2) substrate that was exposed to UV light for 10 minutes prior to fabrication. A printing system (Make, Model: K-FAB TECH PRIVATE LIMITED, K-FT1PS) is used to control and optimise the fabrication of metal contact pads. The system's printing head includes a stainless-steel micro girder patterning tool through

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which ink flows down to the substrate. The printing was carried out at room temperature and with a relative humidity of approximately 45 percent. Two distinct AgNP ink spots were drop-cast with a 1mm spacing on the SiO₂ substrate. The micro girder's tip is positioned to lightly tap AgNP ink on the upper surface of a spot. To close the gap, AgNP ink is dragged closer to the other spot. The second AgNP spot is then treated in the same manner, with the ink dragged closer to the previously printed electrode to reduce the channel gap to approximately 20 nm. For 20 minutes, the printed electrodes are gently heated at 160°C. The entire electrode fabrication process can be completed in 30 minutes with 2l of AgNP ink. The solution of **2.6e** was prepared in DCM (1 mM). The channel material is then dropped cast over the printed AgNP electrodes, with a drop cast diameter of about 2 mm. After that, the device is annealed for five minutes at 120°C. The schematic of the fabricated device is shown in Figure 2.21.

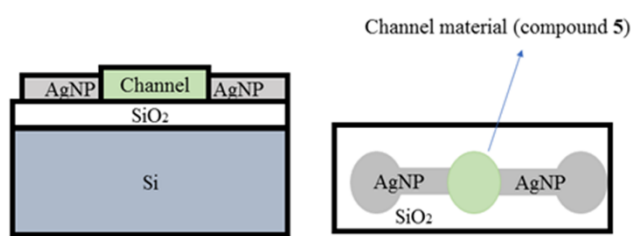


Figure 2.21 Schematic of fabricated device.

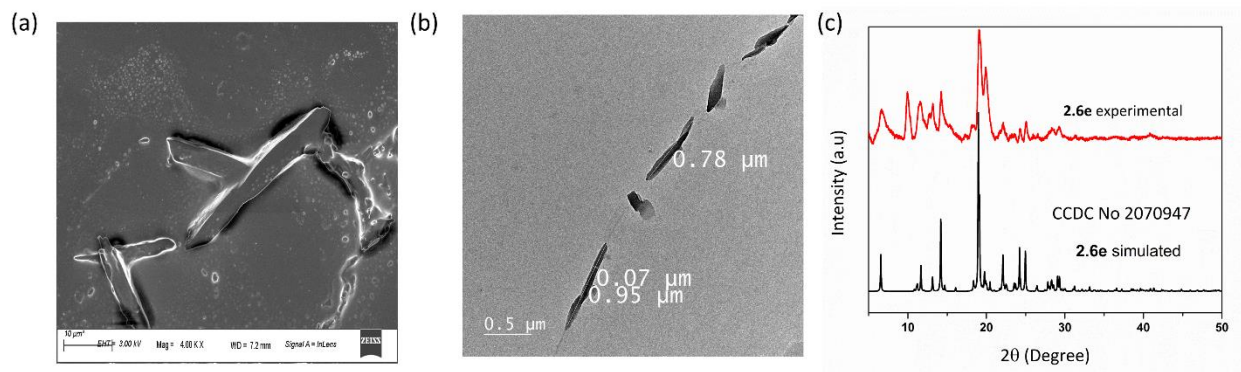


Figure 2.22. (a) Field emission scanning electron microscopy (FESEM) image of **2.6e** (b) Field emission transmission electron microscope (FETEM) image of **2.6e** (c) PXRD pattern of **2.6e**.

Figure 22a and b depicts the morphology of a sub-micron nanowire. Nanostructures, such as nanowires and nanocrystals morphology, provide new and sometimes unique opportunities for sensing biological and chemical species, and thus intuitively represent excellent primary

transducers for signal production. We used Field Emission Transmission Electron Microscopy (FETEM) to examine the aspect ratio of submicron wires with a diameter of 0.07 μm and a single crystal structure. Powder XRD analysis was done to analyse the phase identification of the **2.6e**. Previously, we had reported the SCXRD of the **2.6e** (CCDC No 2070947) and Figure 2.22 confirms that the material peaks are almost same as the simulated XRD pattern. This shows that the crystallinity and phase are intact in crystal as well as powder form Figure 2.22c.

2.3.3. Electrical characteristics

The electrical properties of the fabricated devices were investigated using a Keithly 2600 source metre. A low-noise triaxial cable connects the device to the analyzer. To perform the sensing experiment, an in-house designed gas sensing system (Fabricator: Genrenew India) was connected to the above analyzer via low-noise triaxial cables. To achieve the desired gas concentration, the gas sensing chamber is outfitted with a Mass Flow Controller (MFC) panel composed of three MFCs with varying flow rates. The carrier gas flow is controlled by one MFC, while the other MFCs control the analyte gas flow. The sensing experiment is carried out in two conditions: (a) in nitrogen ambient and (b) in various hydrogen concentrations (H_2).

To avoid cross-contamination, the gas sensing chamber is purged with nitrogen before being vacuumed three times. The baseline readings of the sensors were taken in a nitrogen environment with less than 1% humidity and close to atmospheric pressure. The I-V characteristic of sensing devices is examined by sweeping a voltage from 0 to 5 V. The device exhibits an ohmic response as shown in the figure 2.23a. The gas sensing chamber is purged with nitrogen before being vacuumed three times to avoid cross-contamination. The sensors' baseline readings were taken in a nitrogen ambient, at less than 1% humidity and close to atmospheric pressure. Sweeping a voltage from 0 to 5 V is used to analyse the I-V characteristic of sensing devices. The device shows an ohmic characteristic. Sweeping a voltage from 0 to 5 V is used to analyse the I-V characteristic of sensing devices. A series of experiments are carried out to evaluate the response of the devices by varying the concentration of hydrogen gas from 100 to 9000 ppm. Figure 2.23a depicts the device's I-V characteristics for a sweeping voltage of 0 to 5 Volt with different hydrogen concentrations. The electrical properties confirm an increase in current with increasing hydrogen concentration. The interaction with H_2 gas reduces the device's resistance. Because H_2

is a reducing gas, interacting with it raises the concentration of surface electrons on n type semiconductors. The following equation was used to determine the response of the gas sensors.

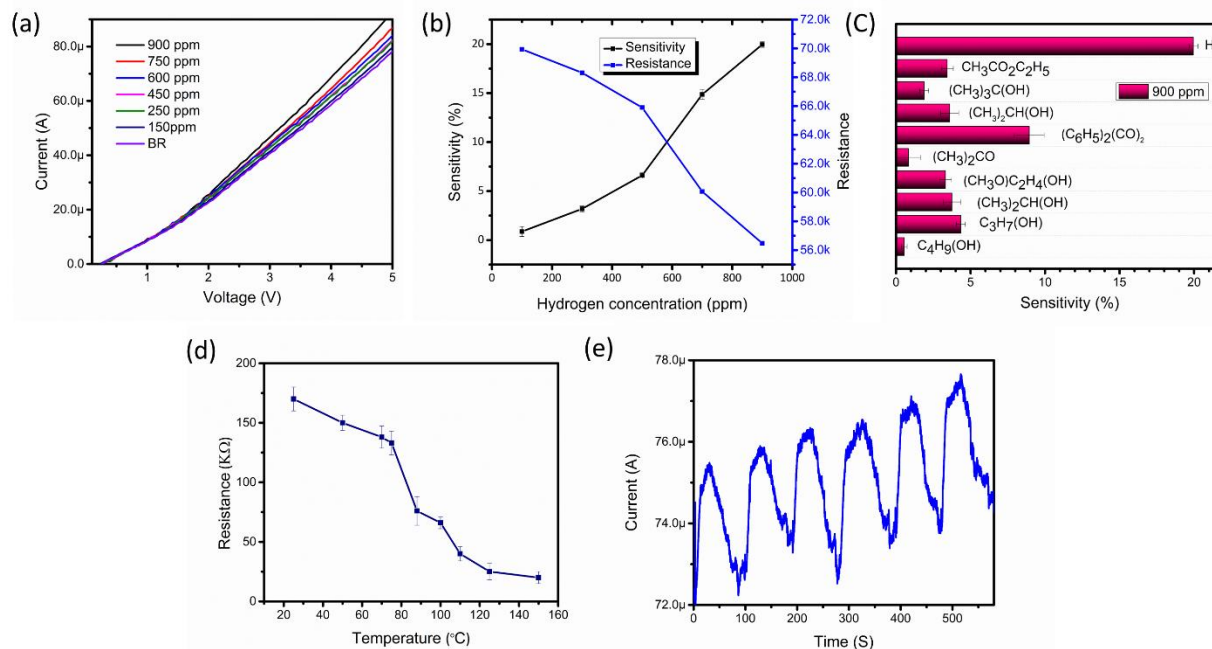


Figure 2.23. (a) The I-V characteristic of sensing devices, (b) Sensors' AER and sensitivity vs. hydrogen concentration, (c) Sensor responses to some VOCs and hydrogen, (d) Temperature response of the sensor, (e) the sensor's transient response.

$$S = ([R_g - R_o] / R_o) \times 100\% \quad (4)$$

Where R_g is the average electrical resistance obtained by sweeping the voltage from 0 to 5V toward varying H₂ concentrations, and R_o is the average electrical resistance of the sensors in the nitrogen atmosphere. Figure 2.23b depicts the sensors' AER and sensitivity vs. H₂ concentration plots. The AER response confirms that a significant shift in the fabricated device. According to the results, the sensor has a high sensitivity of 19.95 percent to 900 ppm and 0.86 percent to 50 ppm.

Figure 2.23c depicts the sensor's sensitivity to various VOCs at 900 ppm concentration. The desired VOC concentrations were achieved by combining it with deionization water and injecting it into the chamber. VOCs exhibit significantly lower responses than H₂ gas at the same concentration. When the sensor's limit of detection (LOD) is calculated using the equation 2, it shows a value of 49 ppm.

$$LOD = |\sigma| / \text{slope} \quad (5)$$

Where slope denotes the average electrical resistance for the various analyte gas concentrations and σ is the standard deviation of the base reading.

For the sensor's response to temperature variation, a tightly sealed chamber was used. Initially, the chamber is kept at 20°C and then heated to 160°C to analyse the sensor characteristics related to resistance variation. Figure 2.23d depicts the variation of resistance with temperature. The resistance decreases significantly in the temperature range of 20 to 160 degrees Celsius. As a result, it is possible to conclude that the device's resistance decreases as the temperature rises. Temperature is an external factor that can affect the sensor.

Figure 2.23e depicts the sensor's transient response. The sensor was continuously flashed to seven pulses of H₂ gas at various concentrations of 100, 250, 400, 550, 700, and 900 ppm, accompanied by a mild evacuation of the gas in the sensing chamber at a constant voltage of 5 V. For different H₂ concentrations, the transient response provides an excellent response time ranging from 0 to 15 s with a good recovery time of 40 to 60 s. The gas in-conditioning process begins when the gas sensing chamber is pressurised to atmospheric pressure, and the gas out-conditioning process begins when the flow of the analyte gas is stopped and evacuated. A mild baseline shift was observed when the sensor shifted back and forth between mild vacuum and test gas environment.

2.4. Detection of nitro-aromatic compounds by polyalkynylatedanthracenes

Explosives detection is a crucial issue in homeland security and counter-terrorism. Due to their ease of production and usage, explosive bombs have by far been the most common form of terrorism. As a result, they have killed tens of thousands of people and caused significant property damage. The increase of international terrorism has prompted the need for stand-off/remote, sensitive, and affordable explosive detection. The analysis of explosives has also been crucial in forensic research, landmine detection, and environmental issues related to explosive leftovers because to the extensive usage of explosive formulations.⁶² Concerns about environmental contamination at the locations where explosives are generated and kept have also been raised due to the extensive use of explosives for military purposes.⁶³ Anemia, cancer, altered liver function, cataract formation, skin irritation, and other serious health risks could be caused by short- or long-term exposure to nitroaromatic explosives in both humans and animals. Rapid, sensitive and selective explosive detection could therefore offer appropriate feedback during the characterization and remediation of contaminated sites, provide rapid warning in the event of

terrorist attacks, assist in tracking and locating explosive materials as well as reduce the ongoing deaths of civilians caused by landmines.⁶⁴ In the comprehensive literature survey, the polyalkynylated polycyclic aromatic hydrocarbons compounds are efficient to detect the explosive nitro-aromatic compounds (NACs) which have been discussed in chapter I, section 1.4.1.^{2b} The

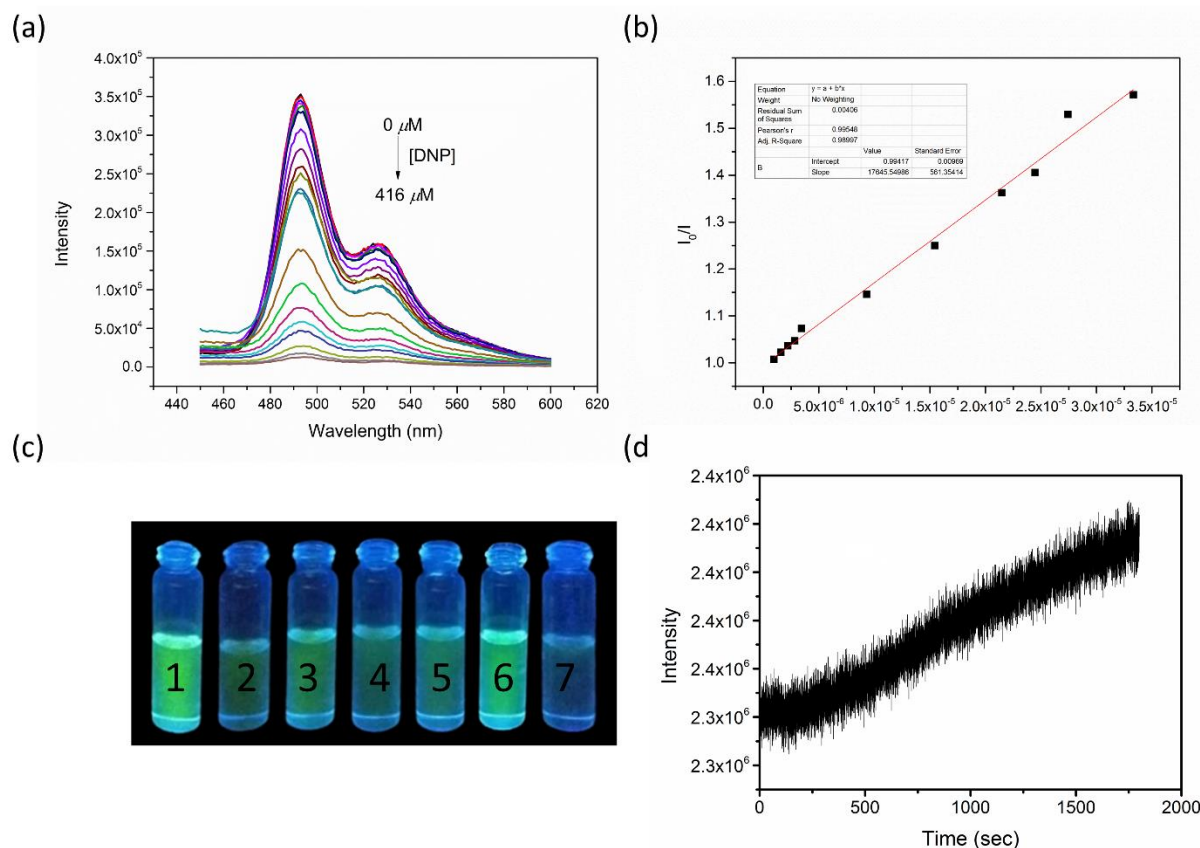


Figure 2.24. (a) Reduction in the emission intensity of 2.6 upon gradual addition of DNP (b) Plot of I_0/I of vs. [DNP] in dioxane (c) The colour after addition of various nitro-aromatic compounds (1 = **2.6** in dioxane, 2 = **2.6** + 2,4-dinitrooluene, 3 = **2.6** + 4-nitrooluene, 4 = **2.6** + 1,3-dinitrobenzene, 5 = **2.6** + nitrooluene, 6 = **2.6** + 2,4,6-trinitrophenol, 7 = **2.6** + 2,4-dinitrophenol) under 365 nm UV light (d) photostability of **2.6** in dioxane.

compounds **2.6-2.6i** are same analogue of previous reported polyalkynylated PAHs which were successfully employed to detect the NACs. To check the response of the compound **2.6** towards NACs different concentration of 2,4-dinitrophenol (2,4-DNP) was added to a solution of **2.6** in dioxane. A gradual decrease in emission intensity ratio of **2.6** was observed with increasing concentration of 2,4-DNP (Figure 2.24a). From the plot of I_0/I vs. concentration of 2,4-DNP the

limit of detection (LOD) was calculated to be 75.5 ppb (Figure 2.24b). Same concentration of the other NACs such as 2,4-dinitrofluorene, 4-nitrofluorene, 1,3-dinitrobenzene, nitrofluorene, 2,4,6-trinitrophenol were also added to the solution of **2.6** in dioxane medium but interestingly no such quenching in the emission intensity as 2,4-DNP was observed (Figure 2.24c). Although, the extent of quenching and LOD value indicated the efficiency of **2.6** towards the selective detection of 2,4-DNP, an abnormal photostability with respect to emission intensity was observed in this medium (Figure 2.24d). The photostability of the **2.6** was also checked in different solvent medium such as THF, MeOH, DMF, dioxane + H₂O, THF + H₂O, DMF + H₂O and MeOH + H₂O, but unfortunately the desired photostability was not found. Similarly, the others synthesized compounds (**2.6a-2.6i**) were not photostable. If the issue related to photostability can be solved, then these compounds could be efficient sensors towards NACs.

2.5. Conclusions

For the first time, a direct single-step one-pot route to tetra-fold Sonogashira coupled products has been formulated to access nine new symmetric tetraalkynylated anthracenes with high yields employing Pd(CH₃CN)₂Cl₂/cataCXium®A as catalyst. Five of these tetraalkynylated anthracenes have been crystallographically characterized, with two of them exhibiting multiple interactions that significantly shorten the inter-planar distances in the solid-state structure. The rich photophysical properties exhibited by these molecules hold immense promise for future applications in sensors and optoelectronic devices. Two of the considered tetraalkynylated anthracenes comprising a D- π -A- π -D motif demonstrate solvatochromism and halochromism, with one of them showing a low bandgap of 1.79 eV. The remaining compounds demonstrate bandgaps in the range of 1.79–2.04 eV. The considered tetraalkynylated anthracenes could be potential candidates as sensors for NACs provided their photostability is improved.

Highly sensitive, selective, low-cost and room temperature hydrogen gas sensors were fabricated based on D- π -A- π -D motif small organic semiconductor. These detect H₂ at concentrations as low as 150 part per million (ppm) at room temperature. Different additive microfabrication techniques are used to fabricate the devices. A precisely controlled fabrication is enabled by employing a μ -gridded printing system. The gas sensor shows excellent sensitivity, fast response, and high recovery to H₂ at room temperature. Moreover after the interaction with H₂, the surface electron of the *N,N*-dimethyl amine containing tetraarylatedanthracene gets enhanced

and shows a decrease in the resistance of the fabricated device. Sensor exhibits a limit of detection of 49 ppb with the highest sensitivity of 19.95% for the detection of 900 ppm of H₂, with a response time of 10 to 20 seconds.

2.6. Experimental section

2.6.1. Materials & methods

All the reactions were carried out under purified argon using a standard double manifold, unless otherwise mentioned. All the chemicals and solvents were purchased from SigmaAldrich, Alfa Aesar, and Merck. HPLC grade solvents were purchased from Merck. The chemicals were used without further purification but solvents were used after either distillation or drying. Tetrahydrofuran (THF), toluene, 1,4-dioxane and triethylamine (Et₃N) were dried via double distillation by using Na/benzophenone and potassium hydroxide. The reactions were monitored by TLC analysis and compounds were purified by column chromatography using Merck Silica gel (60–120 mesh, 100–200 and 400 mesh). To carry out the printing experiments, a silver nanoparticle (AgNP) conductive ink (Product No. 736481), is purchased from Merck-India Pvt. We also purchased a Silicon wafer from university wafers. A calibrated cylinder containing 50000 ppm of H₂ in nitrogen was used for the sensing investigation. Si, SiO₂, Ag were purchased from Sigma-Aldrich, Alfa-aesar. A Field Emission Scanning Electron Microscope (FESEM) [Make: JEOL, Model: JSM-7610F] is used to visualise the physical properties of the material. TEM image was capture by using Field Emission Transmission Electron Microscopy (FETEM) [Make JEOL, Model: JEM 2100F]. A high-resolution Rigaku TTRAX III 18 kW X-ray diffractometer was used to analyse the phase identification of the as-synthesized material.

2.6.2. Physical measurements

NMR spectra were recorded by using either Bruker ASCEND 400 MHz, Bruker ASCEND 500 MHz or Bruker AVANCE 600 MHz for ¹H NMR and 100 MHz (Bruker ASCEND), 125 MHz (Bruker ASCEND), and 150 MHz (Bruker AVANCE) for ¹³C NMR. Peak characterisation: s = singlet, d = doublet, t = triplet, and m = multiplet. MALDI analysis measurements were carried out using a Bruker MALDI-TOF/TOF mass spectrometer employing an α -cyano-hydroxyl cinnamic acid matrix. HRMS was performed on an Agilent Accurate-Mass Q-TOF ESI-MS 6520

spectrometer. FT-IR measurements were performed using a PerkinElmer IR spectrometer. Melting points were recorded using a Buchi melting point B-540 apparatus in an open capillary tube. The photophysical studies of all the compounds were performed in HPLC grade solvents (hexane, toluene, DCM, THF, CHCl_3 , 1,4-dioxane, MeOH, CH_3CN , DMF, and DMSO) and Milli-Q water. UV-Vis spectra in solution as well as in the powder state were obtained by using a PerkinElmer Model Lambda-750 spectrophotometer. Fluorescence emission spectra in solution, thin-film and powder state were recorded by using a Horiba Fluoromax-4 spectrofluorometer. The quantum yield is the ratio between the emitted number of photons and the absorbed number of photons by the fluorophores. The relative fluorescence quantum yield was calculated by the following eqn (1):

$$\phi_F = \phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \left(\frac{\eta}{\eta_R}\right)^2 \quad (8)$$

where ϕ_F and ϕ_R are the relative quantum yields of the analyte and reference, respectively; I and I_R are the area of emission of the analyte and reference; A and A_R are the absorbance of the analyte and reference; and η and η_R are the refractive index of the analyte and reference solutions, respectively. Time resolved lifetime measurements were recorded using the time correlated single photon counter from Horiba Instruments and the LifeSpec-II from Edinburgh Instruments. Cyclic voltammetry studies were carried out using the K-Lyte cyclic voltammetry instrument. The cyclic voltammetry experiments were performed in acetonitrile with 0.1 M tetra *n*-butylammonium hexafluorophosphate (TBFP) as the supporting electrolyte to investigate the HOMO and LUMO energy levels. For this purpose, the chloroform solution of compounds **2.6** & **2.6a–2.6i** was drop-cast on the working electrode (glassy carbon) leading to the corresponding thin layers on the glassy carbon. The HOMO and LUMO energy levels for **2.6** and its derivatives were calculated by using eqn (3) and (4), respectively. As the events involved in the CV analysis were irreversible, a good understanding of the counterpart energy levels could be obtained from the solid-state bandgap (Table 3) using eqn (5):

$$E_{1/2 \text{ ferrocene}} = (E_{\text{oxidation;ferrocene}} + E_{\text{reduction;ferrocene}})/2 \quad (5)$$

$$E_{\text{HOMO}} = - (E_{\text{oxidation}} - E_{1/2 \text{ ferrocene}} + 4.8) \text{ eV} \quad (6)$$

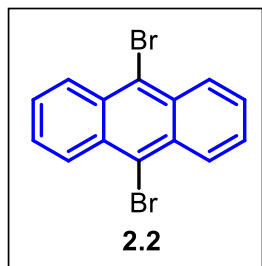
$$E_{\text{LUMO}} = (E_{\text{reduction}} - E_{1/2 \text{ ferrocene}} + 4.8) \text{ eV} \quad (7)$$

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (8)$$

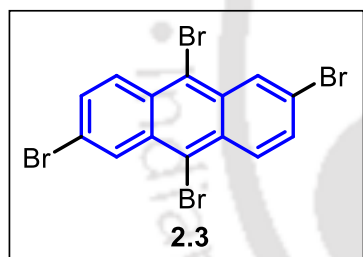
Crystallographic data were collected on a Bruker D8 Venture single-crystal X-ray diffractometer using graphite-monochromated Mo K_α radiation and the crystal structures were solved and further

refined by the full matrix least-squares method using SHELXS-14.⁶⁵ Mercury 4.1.3. for Windows was used to create structural drawings.⁶⁶

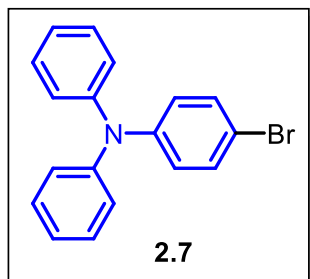
2.6.3. Synthetic procedures



9,10-Dibromoanthracene (2.2). Compound (2.2) was synthesized by modification of the literature procedure.⁶⁷ The solution of bromine (2.8 mL, 56.1 mmol) in distilled chloroform (40 mL) was added dropwise into the suspension of anthracene (5 g, 28.05 mmol) in distilled chloroform (80 mL) and the reaction mixture was stirred at room temperature under dark conditions for 4 h. The reaction was monitored by TLC analysis. After the completion of the reaction, the reaction mixture was filtered and washed with methanol (30 mL $\times$ 3) to remove excess bromine. The product was purified by recrystallization from toluene to obtain yellow needle-like crystals (8.3 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.60 (dd, J = 6.8, 3.2 Hz, 4H), 7.64 (dd, J = 6.8, 3.2 Hz, 4H).¹³C NMR (101 MHz, CDCl₃) δ 131.2, 128.4, 127.6, 123.6.



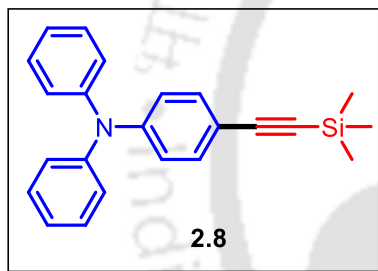
2,6,9,10-Tetrabromoanthracene (2.3). Compound (2.3) was synthesized by modification of the literature procedure.²³ 9,10-Dibromoanthracene (4 g, 11.904 mmol) and nitrobenzene (28 mL) were added into a two-neck round bottom flask. The solution of bromine (1.6 mL) in nitrobenzene (2.8 mL) was added dropwise into a mixture of 9,10-dibromoanthracene at 100 °C and stirred at 180 °C for 6 h. The reaction mixture was then stirred at 200 °C for 30 min. It was subsequently cooled down to room temperature and stirred overnight. The yellow solid precipitate formed was filtered and washed with hot DCM (20 mL $\times$ 3). The yellow solid (3.2 g) obtained was dissolved in toluene (100 mL) at 60–70 °C and cooled down to get a yellow precipitate (2.46 g, 41%). ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, J = 1.9 Hz, 2H), 8.45 (d, J = 9.4 Hz, 2H), 7.69 (dd, J = 9.3, 1.9 Hz, 2H).



4-Bromo-N,N-diphenylaniline (2.7). Compound (2.7) was synthesized according to the literature procedure.⁶⁹ N-bromosuccinamide (720 mg, 4.07 mmol) was added to a stirring solution of triphenylamine (1 g, 4.07 mmol) in tetrachloromethane and the stirring was continued at 76 °C for 4 h under inert conditions. After the completion of the reaction, the bromosuccinamide precipitate was

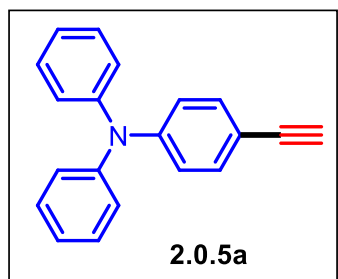
removed by filtration and the organic solvent was evaporated under reduced pressure. The residue was recrystallized from ethanol, affording a white powder (1.2 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.29–7.23 (m, 4H), 7.06 (dd, *J* = 27.3, 7.5 Hz, 6H), 6.95 (d, *J* = 8.4 Hz, 2H). ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 147.3, 132.1, 129.3, 125.1, 124.4, 123.2, 114.7.

N,N-Diphenyl-4-((trimethylsilyl)ethynyl)aniline (2.8). Compound (2.8) was synthesized by



modification of the literature procedure.⁷⁰ A two-neck round bottom flask was taken, evacuated and charged thrice with argon. Triethylamine (dry) and THF (dry) (15 mL 1 : 1) were added into the round bottom flask and the solvent was degassed by the freeze–pump–thaw process. This was followed by the addition of

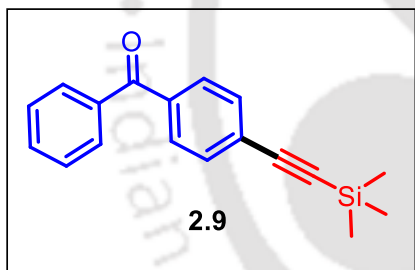
Pd(PPh₃)₂Cl₂ (129 mg 0.18 mmol), CuI (70 mg 0.37 mmol%), **2.7** (1.2 g, 3.7 mmol) and ethynyltrimethylsilane (545 mg, 5.55 mmol) which were then stirred at reflux overnight. After the completion of the reaction, the organic solvent was evaporated. The reaction mixture was extracted with DCM (20 ml × 3) and washed with saturated NH₄Cl (20 ml × 3). The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography by using hexane as the eluent (*R*_f = 0.4 in hexane). The product was obtained as a white solid (700 mg, 67%). ¹H NMR (600 MHz, CDCl₃) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 4H), 7.05 (t, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 0.23 (s, 9H). ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 148.1, 147.2, 133.0, 129.5, 125.0, 123.6, 122.3, 116.0, 105.5, 93.2, 0.2.



4-Ethynyl-N,N-diphenylaniline (2.0.5a). Compound (2.0.5a) was synthesized by modification of the literature procedure.⁷¹ Compound **2.8** (617 mg, 1.8 mmol) was added into the mixture of THF and MeOH (1 : 1, 30 mL) in a round-bottom flask. A solution of KOH (1216 mg, 21.67 mmol) in distilled H₂O (10 ml) was added into the round bottom flask and stirred at room temperature overnight. After

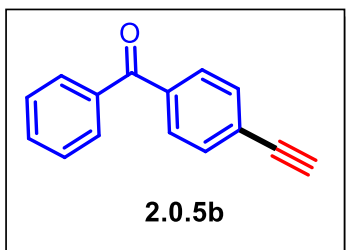
the completion of the reaction, the organic solvent was evaporated, extracted with DCM (20 ml × 3) and washed with saturated NH₄Cl (20 ml × 3). The organic solvent was evaporated under reduced pressure. The product obtained (432 mg, 89%) was used for the next step without purification. ¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, *J* = 8.7 Hz), 7.27 (dd, *J* = 7.2, 6.3 Hz, 4H), 7.10 (dd, *J* = 8.5, 0.9 Hz, 4H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.02 (s, 1H). ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 148.5, 147.2, 133.2, 129.5, 125.1, 123.7, 122.1, 114.8, 84.0, 76.3.

Phenyl(4-((trimethylsilyl)ethynyl)phenyl)methanone (2.9). Compound (2.9) was synthesized



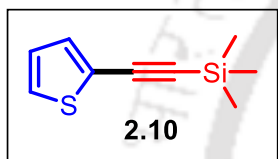
by modification of the literature procedure.⁷² A two-neck round bottom flask was taken, evacuated and charged thrice with argon. Triethylamine (dry) and THF (dry) (15 mL 1 : 1) were added into the round bottom flask and the solvent was degassed by the freeze–pump–thaw process. This was

followed by the addition of Pd(PPh₃)₂Cl₂ (133 mg 0.19 mmol), CuI (72 mg 0.38 mmol%), (4 bromophenyl)(phenyl)methanone (1 g, 3.8 mmol) and ethynyltrimethylsilane (564 mg, 5.7 mmol) which were then stirred overnight at room temperature. After the completion of the reaction, the organic solvent was evaporated. The reaction mixture was extracted with DCM (20 ml × 3), washed with saturated NH₄Cl (20 ml × 3) and the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography by using hexane as the eluent (*R*_f = 0.3 in hexane). The product was obtained as a brown solid (1 g, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 9.6, 7.9 Hz, 4H), 7.58 (dd, *J* = 18.2, 7.9 Hz, 3H), 7.49 (t, *J* = 7.6 Hz, 2H).



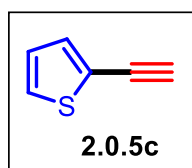
(4-Ethynylphenyl)(phenyl)methanone (2.0.5b). Compound **(2.0.5b)** was synthesized by modification of the literature procedure.⁷³ Compound **2.9** (1 g, 3.68 mmol) and K_2CO_3 (1.3 g, 9.2 mmol) were added into MeOH (20 mL) in a round-bottom flask and stirred at room temperature for 4 h. After the completion of the reaction, the organic solvent was evaporated and extracted

with ethylacetate (20 ml $\times$ 3) and washed with saturated NH_4Cl (20 ml $\times$ 3) and distilled H_2O (20 ml $\times$ 1). The organic layer was evaporated under reduced pressure. The product obtained (703 mg, 95%) was used for the next step without purification. ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, J = 10.1, 7.9 Hz, 4H), 7.61 (dd, J = 19.0, 12.3 Hz, 3H), 7.49 (t, J = 7.7 Hz, 2H), 3.25 (s, 1H).



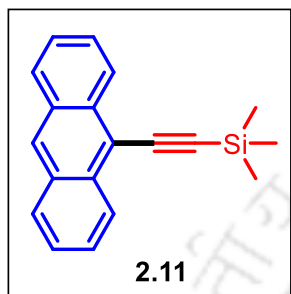
Trimethyl(thiophen-2-ylethynyl)silane (2.10). Compound **(2.10)** was synthesized by modification of the literature procedure.⁷⁴ A two-neck round-bottomed flask was taken, evacuated and charged thrice with argon. Triethylamine (dry) and THF (dry) (15 mL 1 : 1) were added into

the round-bottomed flask and the solvent was degassed by the freeze–pump–thaw process. This was followed by the addition of $Pd(PPh_3)_2Cl_2$ (166 mg 0.23 mmol), CuI (90 mg 0.47 mmol%), 2-iodine thiophene (1 g, 4.75 mmol) and ethynyltrimethylsilane (700 mg, 7.13 mmol) which were then stirred overnight at 60 °C. After the completion of the reaction, the organic solvent was evaporated. The reaction mixture was extracted with DCM (20 ml $\times$ 3) and washed with saturated NH_4Cl (20 ml $\times$ 3) and the organic layer was dried over anhydrous Na_2SO_4 and evaporated out under reduced pressure. The crude product was purified by column chromatography by using hexane as the eluent (R_f = 0.4 in hexane) to yield 533 mg of the product (62%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 4.4 Hz, 2H), 6.96–6.93 (m, 1H), 0.24 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 132.7, 127.4, 126.9, 123.3, 98.8, 97.6, 0.0.

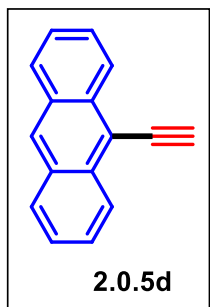


2-Ethynylthiophene (2.0.5c). Compound **(2.0.5c)** was synthesized by modification of the literature procedure.⁷⁵ Compound **2.10** (533 mg, 2.95 mmol) was added into MeOH (10 mL) in a round-bottomed flask. A solution of KOH (182 mg, 3.25 mmol) in distilled H_2O (5 ml) was added to the reaction mixture

and stirred at room temperature for 8 h. After the completion of the reaction, the organic solvent was evaporated and extracted with DCM (20 ml $\times$ 3) and washed with saturated NH_4Cl (20 ml $\times$ 2) and distilled H_2O (20 ml $\times$ 1). The organic layer was evaporated under reduced pressure. The product obtained (102 mg, 32%) was used for the next step without purification. ^1H NMR (600 MHz, CDCl_3) δ 7.30–7.26 (m, 2H), 6.98 (dd, J = 5.1, 3.7 Hz, 1H), 3.34 (s, 1H).



(Anthracen-9-ylethynyl)trimethylsilane (2.11). Compound (2.11) was synthesized by modification of the literature procedure.⁷⁶ A two-neck round bottom flask was taken, evacuated and charged thrice with argon. Triethylamine (dry) (15 mL) was added into the round bottom flask and the solvent was degassed by the freeze–pump–thaw process. This was followed by the addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (133 mg 0.19 mmol), CuI (72 mg 0.38 mmol%), 9-bromoanthracene (1 g, 3.8 mmol) and ethynyltrimethylsilane (559 mg, 5.7 mmol) which were then stirred for 36 h under reflux conditions. After the completion of the reaction, the organic solvent was evaporated. The reaction mixture was extracted with DCM (20 ml $\times$ 3) and washed with saturated NH_4Cl (20 ml $\times$ 3) and the organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography by using hexane as the eluent to yield 594 mg (56%) of the product. ^1H NMR (600 MHz, CDCl_3) δ 8.56 (d, J = 8.7 Hz, 2H), 8.42 (s, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.62–7.56 (m, 2H), 7.53–7.47 (m, 2H), 0.42 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 133.0, 131.1, 128.7, 128.0, 126.9, 126.8, 125.7, 117.2, 106.3, 101.6, 0.4.

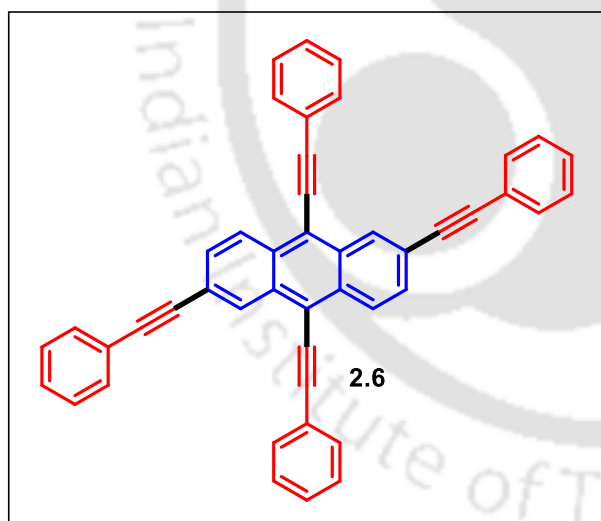


9-Ethynylanthracene (2.0.5d). Compound (2.0.5d) was synthesized by modification of the literature procedure.⁷⁷ Compound **2.11** (594 mg, 2.16 mmol) and K_2CO_3 (2.09 g, 15.16 mmol) were added to MeOH/THF (20 mL, 1 : 1) in a round-bottomed flask and stirred overnight at room temperature. After the completion of reaction, the organic solvent was evaporated and extracted with ethylacetate (20 ml $\times$ 3) and washed with saturated NH_4Cl (20 ml $\times$ 2) and distilled H_2O (20 ml $\times$ 1). The organic layer was evaporated under reduced pressure. The product obtained (350 mg, 80%) was used for the next step without purification. ^1H

NMR (600 MHz, CDCl_3) δ 8.58 (d, J = 8.7 Hz, 2H), 8.46 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.63–7.56 (m, 2H), 7.55–7.48 (m, 2H), 3.99 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 133.3, 131.1, 128.8, 128.3, 126.9, 126.7, 125.8, 116.1, 88.3, 80.4.

General procedure of the Sonogashira reaction for 2.6–2.6i.

A two-neck round bottom flask was taken, evacuated and charged thrice with argon. Anhydrous triethylamine (7 mL) and anhydrous THF (7 mL) were added into the round bottom flask and the solvent was degassed by the freeze–pump–thaw process. This was followed by the addition of 2,6,9,10-tetrabromoanthracene (0.404 mmol), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.0404 mmol), CuI (0.0810 mmol), and alkyl/aryl acetylene (2.43 mmol) which were then stirred under reflux conditions overnight. After the completion of the reaction, the reaction mixture was passed through Celite by using DCM (200 ml $\times$ 3) as the eluent and the filtrate was evaporated under reduced pressure. The NMR yield of the crude product was determined by ^1H NMR by using 1,4-dioxane as the external standard. The crude product was purified by column chromatography (eluent: hexane and DCM).

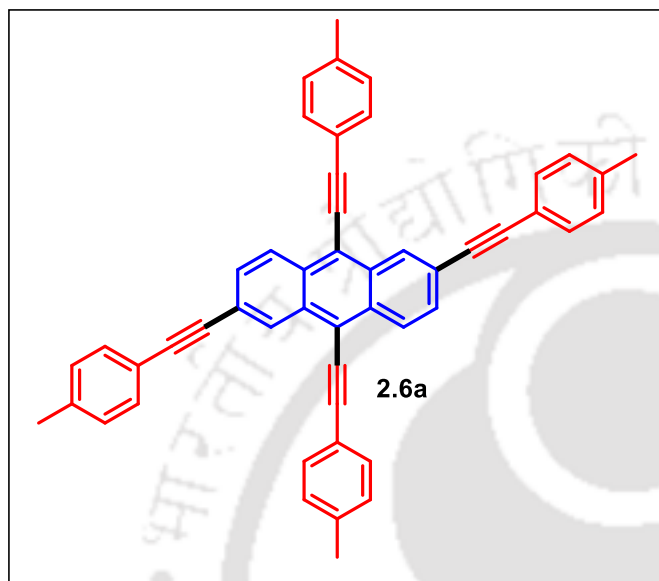


2,6,9,10-Tetrakis(phenylethynyl)anthracene

(**2.6**). Compound **2.6** was synthesized from 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and phenylacetylene (248 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 30% DCM in hexane). The product (205 mg) was obtained as an orange solid (yield = 88%). ^1H NMR (400 MHz, CDCl_3) δ 8.81 (d, J = 0.8

Hz, 2H, H-1 and H-5 of anthracene), 8.61 (d, J = 8.9 Hz, 2H, H-4 and H-8 of anthracene), 7.81 (dd, J = 7.8, 1.6 Hz, 4H, ortho-protons on two of the phenyl groups), 7.69 (dd, J = 8.9, 1.5 Hz, 2H, H-3 and H-7 of anthracene), 7.65 (dd, J = 7.2, 2.3 Hz, 4H, ortho-protons on the other two phenyl groups), 7.50–7.45 (m, 6H, meta- and para-protons on two of the phenyl groups), 7.43–7.37 (m, 6H, meta- and para-protons on the other two phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 132.0, 131.9, 131.9, 131.7, 130.8, 129.6, 129.0, 128.7, 128.7, 128.5, 127.6, 123.2, 123.2, 122.0,

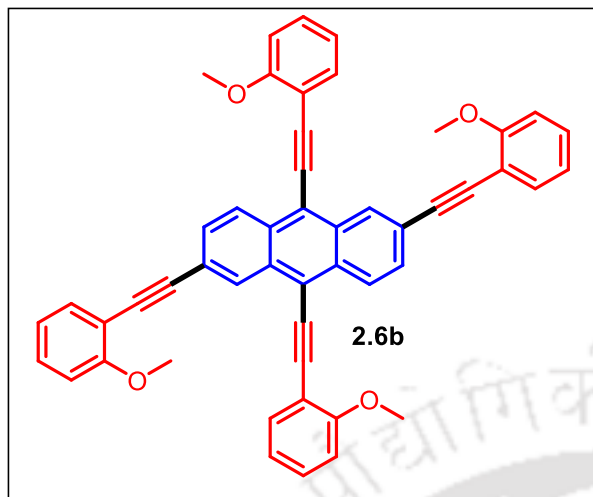
118.4, 103.2 (Ar) ($\text{C}\equiv\text{C}$), 91.7 ($\text{C}\equiv\text{C}$), 90.2 ($\text{C}\equiv\text{C}$), 85.9 ($\text{C}\equiv\text{C}$). MALDI-TOF calculated exact mass for $\text{C}_{46}\text{H}_{26}$ (M^+): 578.20, found: 578.82. HRMS (ESI) m/z [$\text{M} + \text{H}$] $^+$ calculated for $\text{C}_{46}\text{H}_{27}$ 579.2113, found 579.2114. mp = 258-260 °C.



2,6,9,10-Tetrakis(*p*-tolylethynyl)anthracene (2.6a).

Compound **2.6a** was synthesized from 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 1-ethynyl-4-methylbenzene (282 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 35% DCM in hexane). The product (148 mg) was obtained as an orange solid with a yield of 58%. ^1H NMR (600 MHz,

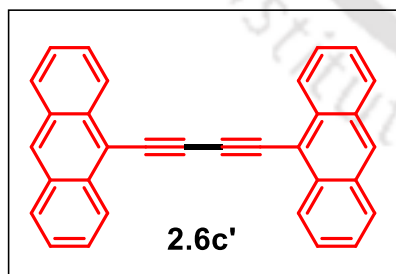
CDCl_3) δ 8.79 (d, J = 0.8 Hz, 2H, H-1 and H-5 of anthracene), 8.60 (d, J = 8.8 Hz, 2H, H-4 and H-8 of anthracene), 7.70 (d, J = 7.9 Hz, 4H, ortho-protons on two of the tolyl groups), 7.67 (dd, J = 8.8, 1.4 Hz, 2H, H-3 and H-7 of anthracene), 7.53 (d, J = 7.9 Hz, 4H, ortho-protons on the other two tolyl groups), 7.28 (d, J = 7.8 Hz, 4H, metaprotons on two of the tolyl groups), 7.20 (d, J = 7.8 Hz, 4H, meta-protons on the other two tolyl groups), 2.44 (s, 6H, Ar- CH_3), 2.40 (s, 6H, Ar- CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 139.3, 138.8, 132.0, 131.8, 131.8, 131.6, 130.7, 129.5, 129.3, 127.6, 122.1, 120.2, 120.1, 118.4 (Ar), 103.3 ($\text{C}\equiv\text{C}$), 91.8 ($\text{C}\equiv\text{C}$), 89.6 ($\text{C}\equiv\text{C}$), 85.5 ($\text{C}\equiv\text{C}$), 21.8 (CH_3), 21.7 (CH_3). MALDI TOF calculated exact mass for $\text{C}_{50}\text{H}_{34}$ (M^+): 634.26, found: 634.91. HRMS (ESI) m/z [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{50}\text{H}_{35}$ 635.2739, found 635.2745. mp = 307–309 °C.



2,6,9,10-Tetrakis((2-methoxyphenyl)ethynyl)anthracene (2.6b).

Compound (2.6b) was synthesized from 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 1-ethynyl-2-methoxybenzene (321 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 40% DCM in hexane). The product (172 mg) was obtained as a red solid with a yield

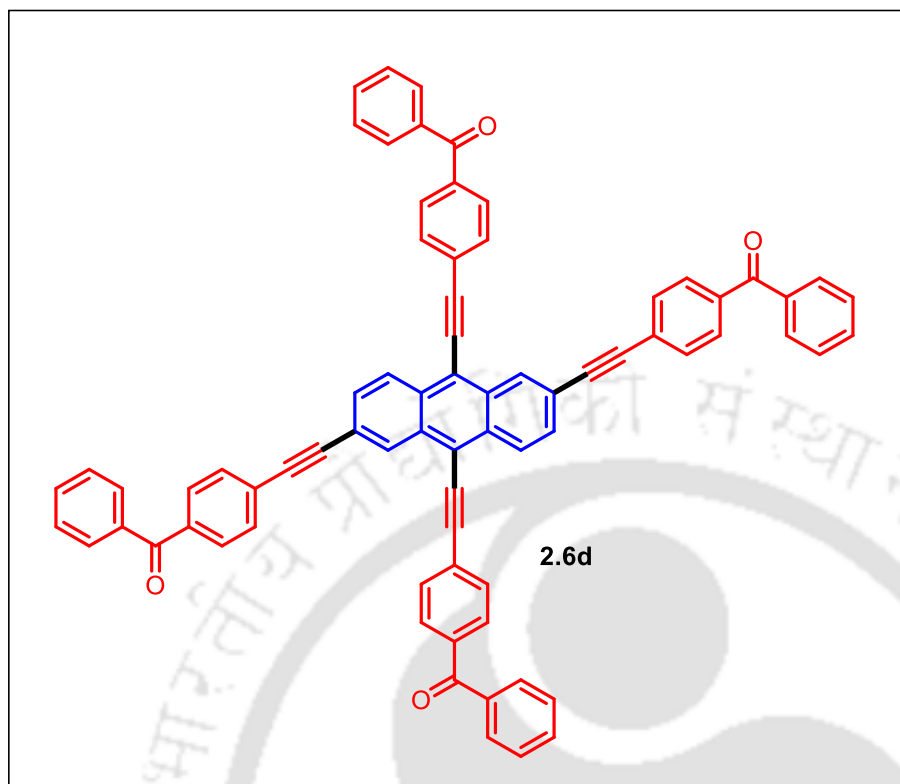
of 61%. ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 2H, H-1 and H-5 of anthracene), 8.74 (d, $J = 8.9$ Hz, 2H, H-4 and H-8 of anthracene), 7.82–7.69 (m, 4H, ortho-protons on the methoxy-phenyl groups), 7.60 (dd, $J = 7.5, 1.6$ Hz, 2H, H-3 and H-7 of anthracene), 7.38 (ddd, $J = 15.6, 8.7, 1.6$ Hz, 4H, para-protons on the methoxy-phenyl groups), 7.01 (ddd, $J = 26.0, 17.0, 8.0$ Hz, 8H, meta-protons on the methoxy-phenyl groups), 4.12 (s, 6H, protons from two of the methoxy groups), 3.97 (s, 6H, protons from the other two methoxy groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 160.7, 160.2, 133.8, 133.0, 132.1, 131.5, 131.3, 130.3, 130.1, 129.5, 127.6, 122.1, 120.7, 118.7, 112.8, 112.6, 110.8, 110.7 (Ar), 99.8 ($\text{C}\equiv\text{C}$), 94.6 ($\text{C}\equiv\text{C}$), 91.0 ($\text{C}\equiv\text{C}$), 87.6 ($\text{C}\equiv\text{C}$), 56.0 (OCH_3), 55.9 (OCH_3). MALDI-TOF calculated exact mass for $\text{C}_{50}\text{H}_{34}\text{O}_4$ (M^+): 698.24, found: 698.65. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{50}\text{H}_{35}\text{O}_4$ 699.2535, found 699.2535. mp = 223–225 °C.



1,4-Di(anthracen-9-yl)buta-1,3-diyne (2.6c').

The reaction of 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 9-ethynylantracene (491 mg, 2.43 mmol) was performed by using the general procedure of the Sonogashira reaction. About 185 mg of the compound 6c' was obtained as homo-coupling product with a yield of 19%. ^1H NMR (500

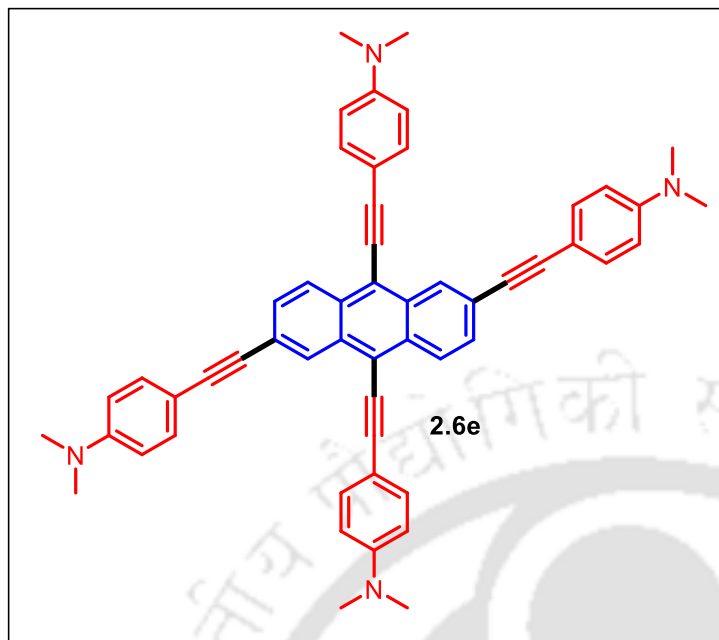
MHz, CDCl_3) δ 8.71 (dd, $J = 9.0, 3.2$ Hz, 4H,), 8.49 (dd, $J = 15.5, J = 5.0$ Hz, 2H,), 8.06 (dd, $J = 8.9, 3.3$ Hz, 4H,), 7.67 (q, $J = 5.8, 3.3$ Hz, 4H,), 7.57 (d, $J = 8.7$ Hz, 4H,).



((Anthracene-
2,6,9,10-

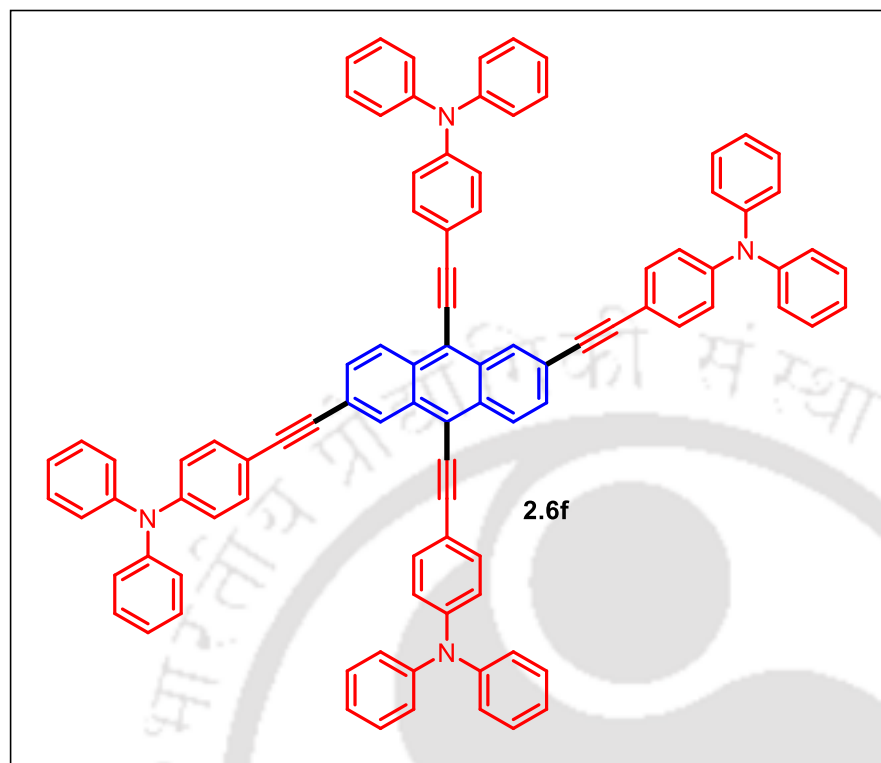
tetrayltetrakis(ethyne-2,1-diyl)tetrakis(benzene-4,1-diyl)tetrakis(phenylmethanone)

(2.6d). Compound **(2.6d)** was synthesized from 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and (4-ethynylphenyl)(phenyl)methanone (501 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 90% DCM in hexane). The product (353 mg) was obtained as a maroon solid with a yield of 88%. ^1H NMR (400 MHz, CDCl_3) δ 8.87 (s, 2H, H-1 and H-5 of anthracene), 8.67 (d, J = 8.9 Hz, 2H, H-4 and H-8 of anthracene), 7.98–7.91 (m, 8H, ortho-protons on the phenyl ring of C(=O)Ph), 7.89–7.72 (m, 18H, H-3 and H-7 of anthracene, ortho and meta-protons of the phenyl group connected to the alkyne), 7.63 (q, J = 7.2 Hz, 4H, para-protons on the phenyl ring of C(=O)Ph), 7.53 (q, J = 7.4 Hz, 8H, meta-protons on the phenyl ring of C(=O)Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.0 (C=O), 195.9 (C=O), 137.7, 137.5, 137.4, 137.3, 132.9, 132.8, 132.2, 132.0, 131.8, 131.8, 131.1, 130.5, 130.3, 130.1, 130.1, 129.8, 128.6, 128.5, 127.7, 127.3, 127.1, 122.1, 118.6 (Ar), 102.8 (C $\equiv$ C), 92.8 (C $\equiv$ C), 91.4 (C $\equiv$ C), 88.6 (C $\equiv$ C). MALDI-TOF calculated exact mass for $\text{C}_{74}\text{H}_{42}\text{O}_4$ (M^+): 994.30, found: 994.86. HRMS (ESI) m/z [$\text{M} + \text{CH}_3\text{CN} + \text{H}_2\text{O} + \text{H}$] $^+$ calcd for $\text{C}_{76}\text{H}_{48}\text{NO}_5$ 1054.3532, found 1054.3798. mp = 259–261 $^\circ\text{C}$.



4,4',4'',4'''-(Anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(N,N-dimethylaniline) (2.6e). Compound (2.6e) was synthesized 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 4-ethynyl-*N,N*-dimethylaniline (353 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 60% DCM in

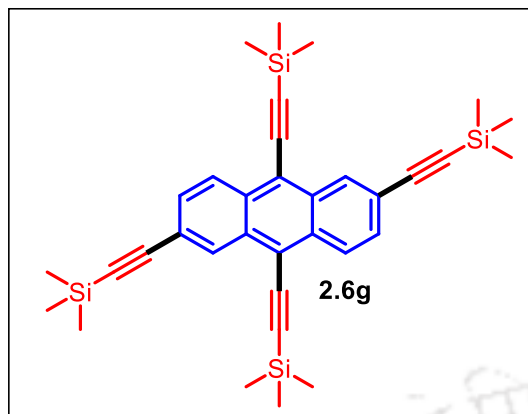
hexane). The product (194 mg) was obtained as a brown solid with a yield of 64%. ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 2H, H-1 and H-5 of anthracene), 8.60 (d, $J = 8.8$ Hz, 2H, H-4 and H-8 of anthracene), 7.68 (d, $J = 8.7$ Hz, 4H, ortho-protons on two of the phenyl groups), 7.64 (d, $J = 8.1$ Hz, 2H, H-3 and H-7 of anthracene), 7.52 (d, $J = 8.7$ Hz, 4H, ortho-protons on the other two phenyl groups), 6.78 (d, $J = 8.9$ Hz, 4H, meta-protons on two of the phenyl groups), 6.70 (d, $J = 8.8$ Hz, 4H, meta-protons on the other two phenyl groups), 3.06 (s, 12H, protons from two of the dimethylamino groups), 3.02 (s, 12H, protons from the other two dimethylamino groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 150.5, 150.3, 133.1, 133.1, 131.8, 131.3, 130.2, 129.2, 127.5, 122.1, 118.1, 112.1, 112.0, 110.3, 110.2 (Ar), 104.3 ($\text{C}\equiv\text{C}$), 92.7 ($\text{C}\equiv\text{C}$), 88.7 ($\text{C}\equiv\text{C}$), 84.8 ($\text{C}\equiv\text{C}$), 40.4 (NCH_3), 40.3 (NCH_3). MALDI-TOF calculated exact mass for $\text{C}_{54}\text{H}_{46}\text{N}_4$ (M^+): 750.37, found: 750.90. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{54}\text{H}_{47}\text{N}_4$ 751.3801, found 751.3802. mp > 410 °C.



4,4',4'',4'''-(Anthracene-2,6,9,10-tetra-yltetrakis(ethyne-2,1-diyl))tetrakis(N,N-diphenylaniline) (2.6f).

Compound **2.6f** was synthesized 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 4-ethynyl-*N,N*-diphenylaniline (654 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction.

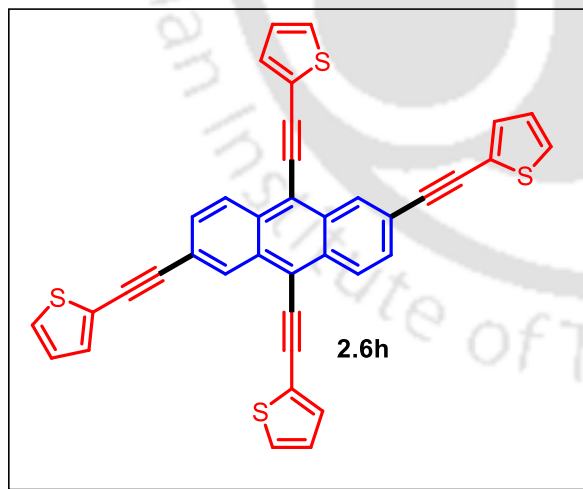
The crude product was purified by column chromatography (eluent: 70% DCM in hexane). The product (156 mg) was obtained as a maroon solid with a yield of 31%. ^1H NMR (400 MHz, CDCl_3) δ 8.76 (d, $J = 0.8$ Hz, 2H, H-1 and H-5 of anthracene), 8.58 (d, $J = 8.9$ Hz, 2H, H-4 and H-8 of anthracene), 7.65 (dd, $J = 5.1, 1.6$ Hz, 2H, H-3 and H-7 of anthracene), 7.62 (d, $J = 6.2$ Hz, 4H, ortho-protons on two of the phenyl groups connected to the alkyne), 7.46 (d, $J = 8.7$ Hz, 4H, orthoprotons on the other two phenyl groups connected to the alkyne), 7.33–7.26 (m, 16H, meta-protons on the phenyl ring of NPh_2), 7.19–7.01 (m, 32H, ortho- and para-protons on the phenyl ring of NPh_2 and meta-protons on the phenyl groups connected to the alkyne). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 148.2, 147.3, 147.2, 132.9, 132.8, 131.9, 131.5, 130.5, 129.6, 129.5, 129.4, 127.6, 125.3, 125.2, 123.9, 123.7, 122.3, 122.1, 118.2, 116.0, 115.9 (Ar), 103.6 ($\text{C}\equiv\text{C}$), 92.0 ($\text{C}\equiv\text{C}$), 89.7 ($\text{C}\equiv\text{C}$), 85.6 ($\text{C}\equiv\text{C}$). MALDI-TOF calculated exact mass for $\text{C}_{94}\text{H}_{62}\text{N}_4$ (M^+): 1247.50, found: 1247.97. HRMS (ESI) m/z [$\text{M} + \text{K}$] $^+$ calcd for $\text{C}_{94}\text{H}_{62}\text{KN}_4$ 1285.4612, found 1285.4508. mp = 407–409 °C.



(Anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(trimethylsilane) (2.6g).

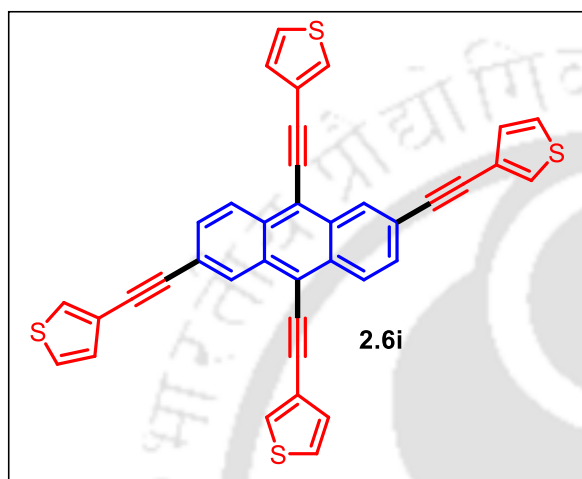
Compound **2.6g** was synthesized 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and ethynyltrimethylsilane (238 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: hexane). The product (188 mg) was obtained as a yellow solid with a yield of 83%. ^1H NMR (600 MHz, CDCl_3) δ 8.66 (s, 2H, H-1 and H-5 of anthracene), 8.44 (d, J = 8.9 Hz, 2H, H-4 and H-8 of anthracene), 7.57 (dd, J = 8.9, 1.3 Hz, 2H, H-3 and H-7 of anthracene), 0.43 (s, 18H, methyl protons on two of the $-\text{Si}(\text{CH}_3)_3$ groups), 0.31 (s, 18H, methyl protons on the other two $-\text{Si}(\text{CH}_3)_3$ groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 132.1, 131.8, 131.7, 129.5, 127.4, 121.9, 118.4 (Ar), 109.4 ($\text{C}\equiv\text{C}$), 105.5 ($\text{C}\equiv\text{C}$), 100.9 ($\text{C}\equiv\text{C}$), 96.8 ($\text{C}\equiv\text{C}$), 0.2 (SiCH_3), 0.1 (SiCH_3). MALDI-TOF calculated exact mass for $\text{C}_{34}\text{H}_{42}\text{Si}_4$ (M^+): 562.23, found: 562.62. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{43}\text{Si}_4$ 563.2442, found 563.2441. mp = 228–230 °C.

2,2',2'',2'''-(Anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrathiophene (2.6h).



Compound **2.6h** was synthesized 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 2-ethynylthiophene (262 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 40% DCM in hexane). The product (143 mg) was obtained as a yellow powder with a yield of 59%. ^1H NMR (600 MHz, CDCl_3) δ 8.73 (s, 2H, H-1 and H-5 of anthracene), 8.55 (d, J = 8.9 Hz, 2H, H-4 and H-8 of anthracene), 7.68 (d, J = 8.9 Hz, 2H, H-3 and H-7 of anthracene), 7.56 (d, J = 3.5 Hz, 2H, H-5 of two of the thiophene linkers), 7.45 (d, J = 5.1 Hz, 2H, H-5 of the other two thiophene linkers), 7.40 (d, J = 3.4 Hz, 2H, H-3 of two of the thiophene linkers), 7.36 (d, J = 5.1 Hz, 2H, H-3 of the other two thiophene linkers), 7.17–7.13 (m,

2H, H-4 of two of the thiophene linkers), 7.08–7.05 (m, 2H, H-4 of the other two thiophene linkers). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 132.9, 132.6, 131.8, 131.6, 130.6, 129.4, 128.5, 127.9, 127.6, 127.6 127.4, 123.2, 123.0, 121.9, 118.3 (Ar), 96.5 ($\text{C}\equiv\text{C}$), 93.8 ($\text{C}\equiv\text{C}$), 89.8 ($\text{C}\equiv\text{C}$), 85.2 ($\text{C}\equiv\text{C}$). MALDI-TOF calculated exact mass for $\text{C}_{38}\text{H}_{18}\text{S}_4$ (M^+): 602.02, found: 602.36. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{19}\text{S}_4$ 603.0370, found 603.0369. mp = 281–283 °C.



3,3',3'',3'''-(Anthracene-2,6,9,10-tetrayltetrakis(ethyne-3,1-diyl))tetrathiophene (2.6i).

Compound **2.6i** was synthesized 2,6,9,10-tetrabromoanthracene (200 mg, 0.404 mmol) and 3-ethynylthiophene (262 mg, 2.43 mmol) by using the general procedure of the Sonogashira reaction. The crude product was purified by column chromatography (eluent: 40% DCM in

hexane). The product (48 mg) was obtained as a brown powder in a yield of 20%. ^1H NMR (400 MHz, CDCl_3) δ 8.78 (d, J = 0.8 Hz, 2H, H-1 and H-5 of anthracene), 8.60 (d, J = 8.5 Hz, 2H, H-4 and H-8 of anthracene), 7.81 (dd, J = 2.7, 1.4 Hz, 2H, H-2 of two of the thiophene linkers), 7.69–7.63 (m, 4H, H-3 and H-7 of anthracene and H-2 of the other two thiophene linkers), 7.47–7.42 (m, 4H, H-5 of the thiophene linkers), 7.35 (dd, J = 5.0, 3.0 Hz, 2H, H-4 of two of the thiophene linkers), 7.30 (dd, J = 5.0, 1.1 Hz, 2H, H-4 of the other two thiophene linkers). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 132.0, 131.7, 130.7, 130.1, 130.0, 129.6, 129.5, 129.3, 127.6, 126.0, 125.7, 122.2, 122.2, 121.9, 118.3 (Ar), 98.1 ($\text{C}\equiv\text{C}$), 89.6 ($\text{C}\equiv\text{C}$), 86.9 ($\text{C}\equiv\text{C}$), 85.4 ($\text{C}\equiv\text{C}$). MALDI-TOF calculated exact mass for $\text{C}_{38}\text{H}_{18}\text{S}_4$ (M^+): 602.02, found: 602.41. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{19}\text{S}_4$ 603.0370, found 603.0364. mp = 279–281 °C.

Supporting information (containing NMR and HRMS spectra of various compounds) for *Chapter II* is available as appendix I and can be found at

https://drive.google.com/file/d/1mAjwzTbJBbfvNoO6xAcVLhDRoMg91NYi/view?usp=share_link

2.7. X-ray crystallographic analysis

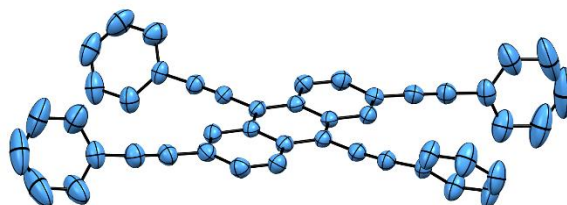


Figure 2.25. ORTEP diagram of **2.6** with the ellipsoids drawn at the 50% probability level..

Table 2.6. Crystal data for **2.6**

Identification code (CCDC No) 2070944			
Bond precision: C-C = 0.0040 Å		Wavelength = 0.71073	
Cell:	a = 9.8457 (7) alpha = 90	b = 19.1932 (16) beta = 101.212 (2)	c = 17.0462 (14) gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	3159.8 (4)	3159.7 (4)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	?	
Moiety formula	C ₄₆ H ₂₆	C ₄₆ H ₂₆	
Sum formula	C ₄₆ H ₂₆	C ₄₆ H ₂₆	
Mr	578.67	578.67	
Dx, g cm ⁻³	1.216	1.216	
Z	4	4	
Mu (mm ⁻¹)	0.069	0.069	
F000	1208.0	1208.0	
F000'	1208.45		
h,k,l _{max}	11,22,20	11,22,20	
Nref	5568	5566	
Tmin,Tmax	0.981,0.984		
Tmin'	0.981		
Correction method = Not given			
Data completeness = 1.000		Theta(max) = 25.000	
R(reflections) = 0.0586(3707)		wR ₂ (reflections) = 0.1746(5566)	
S = 1.056		Npar = 415	

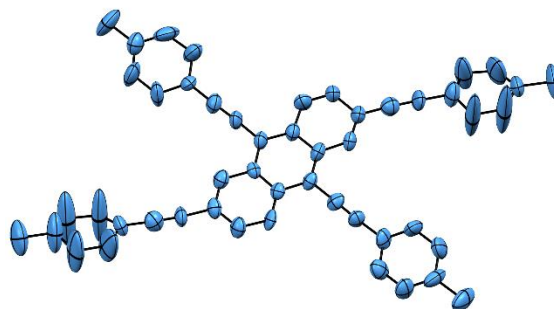


Figure 2.26. ORTEP diagram of **2.6a** with the ellipsoids drawn at the 50% probability level..

Table 2.7. Crystal data for **2.6a**

Identification code (CCDC No) 2070945			
Bond precision:	C-C = 0.0141 Å		Wavelength = 0.71073
Cell:	a = 14.929 (3)	b = 11.922 (3)	c = 10.529 (2)
	alpha = 90	beta = 92.393(7)	gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	1872.4 (7)	1872.3 (7)	
Space group	P c	P c	
Hall group	P -2yc	?	
Moiety formula	C ₅₀ H ₃₄	C ₅₀ H ₃₄	
Sum formula	C ₅₀ H ₃₄	C ₅₀ H ₃₄	
Mr	634.77	634.77	
Dx,g cm ⁻³	1.126	1.126	
Z	2	2	
Mu (mm ⁻¹)	0.064	0.064	
F000	668.0	668.0	
F000'	668.25		
h,k,lmax	17,14,12	17,14,12	
Nref	6596 [3305]	6588	
Tmin,Tmax	0.982,0.985		
Tmin'	0.982		
Correction method = Not given			
Data completeness = 1.99/1.00		Theta(max)= 25.000 R(reflections)= 0.0836(3080)	
wR ₂ (reflections) = 0.2604(6588)			
S = 1.026		Npar = 455	

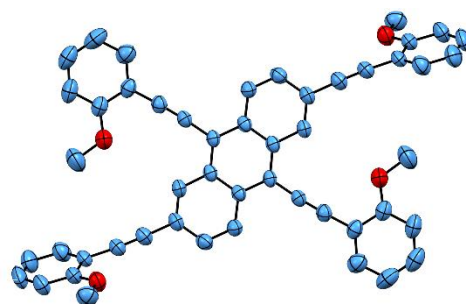


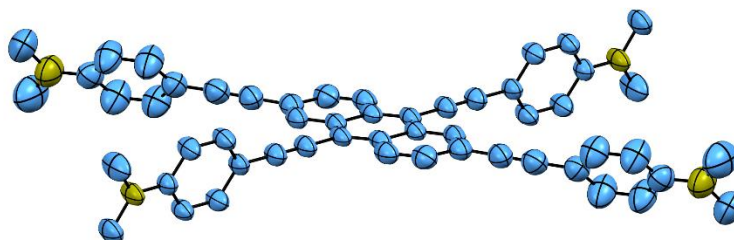
Figure 2.27. ORTEP diagram of **2.6b** with the ellipsoids drawn at the 50% probability level.

Table 2.8. Crystal data for **2.6b**

Identification code (CCDC No) 2070946			
Bond precision: C-C = 0.0038 Å		Wavelength = 0.71073	
Cell:	a = 4.6663 (5)	b = 14.0000 (16)	c = 14.5094 (17)
	alpha = 75.898 (4)	beta = 83.094 (4)	gamma = 83.357 (4)
Temperature:	296 K		
	Calculated	Reported	
Volume	908.96 (18)	908.96 (18)	
Space group	P -1	P -1	
Hall group	-P 1	?	
Moiety formula	C ₅₀ H ₃₄ O ₄	C ₅₀ H ₃₄ O ₄	
Sum formula	C ₅₀ H ₃₄ O ₄	C ₅₀ H ₃₄ O ₄	
Mr	698.77	698.77	
Dx,g cm ⁻³	1.277	1.254	
Z	1	1	
Mu (mm ⁻¹)	0.080	0.079	
F000	366.0	354.0	
F000'	366.16		
h,k,l _{max}	5,16,17	5,16,17	
Nref	3221	3217	
Tmin,Tmax	0.978, 0.982		
Tmin'	0.978		
Correction method = Not given			
Data completeness = 0.999		Theta(max) = 25.000	
R(reflections) = 0.0470(1913)		wR ₂ (reflections) = 0.1609 (3217)	

S = 0.762

Npar = 246

**Figure 2.28.** ORTEP diagram of **2.6e** with the ellipsoids drawn at the 50% probability level.**Table 2.9.** Crystal data for compound **2.6e**

Identification code (CCDC No) 2070947		
Bond precision: C-C = 0.0046 Å		Wavelength = 0.71073
Cell:	A = 9.2771 (9) alpha = 71.119 (3)	B = 9.6139 (8) beta = 86.812 (4)
Temperature:	296 K	C = 14.3349 (14) Gamma = 61.782 (3)
	Calculated	Reported
Volume	1058.66 (18)	1058.66 (17)
Space group	P -1	P -1
Hall group	-P 1	?
Moiety formula	C ₅₄ H ₄₆ N ₄	C ₅₄ H ₄₆ N ₄
Sum formula	C ₅₄ H ₄₆ N ₄	C ₅₄ H ₄₆ N ₄
Mr	750.95	750.95
Dx, g cm ⁻³	1.178	1.200
Z	1	1
Mu (mm ⁻¹)	0.069	0.070
F000	398.0	412.0
F000'	398.14	
h,k,l _{max}	11,11,17	11,11,17
Nref	3732	3727
Tmin,Tmax	0.980, 0.983	
Tmin'	0.980	
Correction method = Not given		
Data completeness = 0.999		Theta(max) = 25.000
R(reflections) = 0.0562(2056)		wR2(reflections) = 0.1939(3727)
S = 0.869		Npar = 266

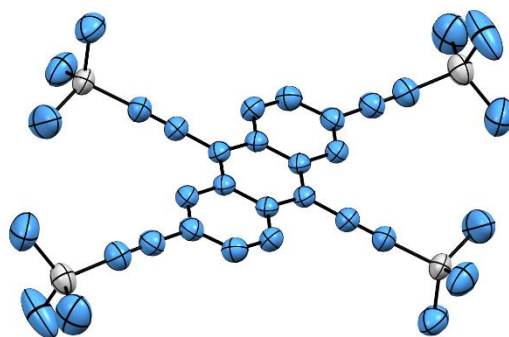


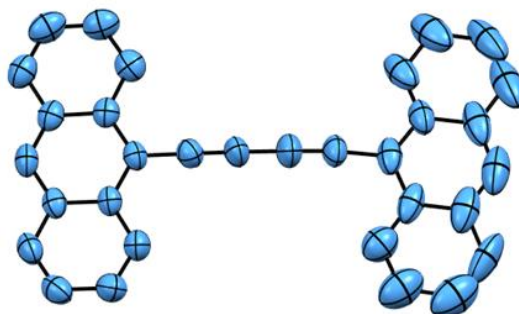
Figure 2.29. ORTEP diagram of **2.6g** with the ellipsoids drawn at the 50% probability level.

Table 2.10. Crystal data for compound **2.6g**

Identification code (CCDC No) 2070948			
Bond precision: C-C = 0.0030 Å		Wavelength = 0.71073	
Cell:	a = 6.0741 (8)	b = 11.2759 (16)	c = 14.146 (2)
	alpha = 99.128 (5)	beta = 96.304 (5)	gamma = 105.017 (4)
Temperature:	296 K		
	Calculated	Reported	
Volume	912.3 (2)	912.3 (2)	
Space group	P -1	P -1	
Hall group	-P 1	?	
Moiety formula	C ₃₄ H ₄₂ Si ₄	C ₃₄ H ₄₂ Si ₄	
Sum formula	C ₃₄ H ₄₂ Si ₄	C ₃₄ H ₄₂ Si ₄	
Mr	563.04	563.04	
Dx,g cm ⁻³	1.025	1.025	
Z	1	1	
Mu (mm ⁻¹)	0.182	0.182	
F000	302.0	302.0	
F000'	302.40		
h,k,l _{max}	7,13,16	7,13,16	
Nref	3214	3212	
Tmin,Tmax	0.950,0.957		
Tmin'	0.950		
Correction method = Not given			
Data completeness = 0.999		Theta(max) = 25.000	
R(reflections) = 0.0436(2273)		wR ₂ (reflections) = 0.1232(3212)	

S = 1.038

Npar = 178

**Figure 2.30.** ORTEP diagram of **2.6c'** with the ellipsoids drawn at the 50% probability level.**Table 2.11.** Crystal data for compound **2.6c'**

Identification code (CCDC No) 2086685			
Bond precision: C-C = 0.0066 Å		Wavelength = 0.71073	
Cell:	a = 11.162 (3)	b = 11.978 (3)	c = 15.916 (4)
	alpha = 90	beta = 90	gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	2127.9 (9)	2128.0 (9)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	?	
Moiety formula	C ₃₂ H ₁₈	C ₃₂ H ₁₈	
Sum formula	C ₃₂ H ₁₈	C ₃₂ H ₁₈	
Mr	402.46	402.46	
Dx,g cm ⁻³	1.256	1.256	
Z	4	4	
Mu (mm ⁻¹)	0.071	0.071	
F000	840.0	924.0	
F000'	840.32		
h,k,lmax	13,14,18	13,14,18	
Nref	3760	3065	
Tmin,Tmax	0.979,0.982		
Tmin'	0.979		
Correction method = Not given			
Data completeness = 0.815		Theta(max) = 25.000	
R(reflections) = 0.0719(1427)		wR2(reflections) = 0.2674(3065)	

S = 0.790

Npar = 289

2.8. References

1. Chen, M.; Yan, L.; Zhao, Y.; Murtaza, I.; Meng, H.; Huang, W., *J. Mater. Chem. C* **2018**, *6*, 7416-7444.
2. Islam, K.; Narjinari, H.; Kumar, A., Polycyclic Aromatic Hydrocarbons Bearing Polyethynyl Bridges: Synthesis, Photophysical Properties, and their Applications. *Asian J. Organic Chemistry* **2021**, *10*, 1544-1566
3. Ehlers, P.; Neubauer, A.; Lochbrunner, S.; Villinger, A.; Langer, P., *Org. Lett.* **2011**, *13*, 1618-1621.
4. Huy Do, H.; Villinger, A.; Lochbrunner, S.; Ehlers, P.; Langer, P., Palladium-Catalyzed Synthesis and Fluorescence Study of Ethynylated Naphthalene Derivatives. *Eur. J. Org. Chem.* **2017**, *2017*, 2238-2244.
5. Slodek, A.; Filapek, M.; Schab-Balcerzak, E.; Grucela, M.; Kotowicz, S.; Janeczek, H.; Smolarek, K.; Mackowski, S.; Malecki, J. G.; Jedrzejowska, A., *Eur. J. Org. Chem.* **2016**, *2016*, 4020-4031.
6. (a) Salunke, J. K.; Sonar, P.; Wong, F.; Roy, V.; Lee, C.; Wadgaonkar, P. P., *Phys. Chem. Chem. Phys.* **2014**, *16*, 23320-23328; (b) Kapf, A.; Eslahi, H.; Blanke, M.; Saccone, M.; Giese, M.; Albrecht, M., *New J. Chem.* **2019**, *43*, 6361-6371.
7. Lee, I. L.; Li, S. R.; Chen, K. F.; Ku, P. J.; Singh, A. S.; Kuo, H. T.; Wen, Y. S.; Chu, C. W.; Sun, S. S., *Eur. J. Org. Chem.* **2012**, *2012*, 2906-2915.
8. Wu, T.-L.; Chou, H.-H.; Huang, P.-Y.; Cheng, C.-H.; Liu, R.-S., *J. Org. Chem.* **2014**, *79*, 267-274.
9. Broggi, A.; Tomasi, I.; Bianchi, L.; Marrocchi, A.; Vaccaro, L., *ChemPlusChem* **2014**, *79*, 486-507.
10. Shanmugaraju, S.; Mukherjee, P. S., *Chem. Commun.* **2015**, *51*, 16014-16032.
11. Kumar, S.; Varshney, S. K., A room-temperature discotic nematic liquid crystal. *Angew. Chem. Int. Ed.* **2000**, *39*, 3140-3142.
12. Lin, S.-H.; Wu, F.-I.; Liu, R.-S., *Chem. Commun.* **2009**, 6961-6963.
13. (a) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C., *Org. Lett.* **2000**, *2*, 1729-1731; (b) Kanwal, I.; Mujahid, A.; Rasool, N.; Rizwan, K.; Malik, A.; Ahmad, G.; Shah, S. A. A.; Rashid, U.; Nasir, N. M., *Catal.* **2020**, *10*, 443; (c) Chinchilla, R.; Nájera, C., *Chem. Rev.* **2007**, *107*, 874-922; (d) Chinchilla, R.; Nájera, C., *Chem. Soc. Rev.* **2011**, *40*, 5084-5121; (e) Yang, Y.; Chew, X.; Johannes, C. W.; Robins, E. G.; Jong, H.; Lim, Y. H., *Eur. J. Org. Chem.* **2014**, *2014*, 7184-7192.
14. García, D.; Cuadro, A. M.; Alvarez-Builla, J.; Vaquero, J. J., *Org. Lett.* **2004**, *6*, 4175-4178.
15. Ehlers, P.; Dang, T. T.; Patonay, T.; Villinger, A.; Langer, P., Synthesis of Alkynylated Selenophenes by Site-Selective Sonogashira Reactions of Tetrabromoselenophene. *Eur. J. Org. Chem.* **2013**, *2013*, 2000-2007.
16. Guan, X.; Jia, T.; Zhang, D.; Zhang, Y.; Ma, H.; Lu, D.; Lai, S.; Lei, Z., *Dyes Pigm.* **2017**, *136*, 873-880.
17. Das, P.; Kumar, A.; Chowdhury, A.; Mukherjee, P. S., *ACS Omega* **2018**, *3*, 13757-13771.

18. Grenz, D. C.; Schmidt, M.; Kratzert, D.; Esser, B., *J. Org. Chem.* **2018**, *83*, 656-663.
19. Ho, M. H.; Balaganesan, B.; Chen, C. H., *Isr. J. Chem.* **2012**, *52*, 484-495.
20. Ehlers, P.; Hakobyan, A.; Neubauer, A.; Lochbrunner, S.; Langer, P., *Adv. Synth. Catal.* **2013**, *355*, 1849-1858.
21. Park, J.-H.; Chung, D. S.; Park, J.-W.; Ahn, T.; Kong, H.; Jung, Y. K.; Lee, J.; Yi, M. H.; Park, C. E.; Kwon, S.-K., *Org. Lett.* **2007**, *9*, 2573-2576.
22. (a) Jung, K. H.; Bae, S. Y.; Kim, K. H.; Cho, M. J.; Lee, K.; Kim, Z. H.; Choi, D. H.; Lee, D. H.; Chung, D. S.; Park, C. E., *Chem. Commun.* **2009**, 5290-5292; (b) Shin, J.; Kang, N. S.; Lee, T. W.; Cho, M. J.; Hong, J. M.; Ju, B.-K.; Choi, D. H., *Org. Electron.* **2014**, *15*, 1521-1530; (c) Jo, S.-Y.; Hur, J.-A.; Kim, K.-H.; Lee, T.-W.; Shin, J.-C.; Hwang, K.-S.; Chin, B.-D.; Choi, D.-H., *Bull. Korean Chem. Soc.* **2012**, *33*, 3061-3070; (d) Hur, J.-A.; Shin, J.-C.; Lee, T.-W.; Kim, K.-H.; Cho, M.-J.; Choi, D.-H., *Bull. Korean Chem. Soc.* **2012**, *33*, 1653-1658; (e) Hur, J. A.; Bae, S. Y.; Kim, K. H.; Lee, T. W.; Cho, M. J.; Choi, D. H., *Org. Lett.* **2011**, *13*, 1948-1951; (f) Lee, H.; Lee, H.; Hur, J. A.; Cho, M. J.; Choi, D. H.; Kang, T. D., *J. Korean Phys. Soc.* **2013**, *62*, 930-936.
23. Del Rosso, P. G.; Almassio, M. F.; Bruno, M.; Garay, R. O., *Tetrahedron Lett.* **2010**, *51* (51), 6730-6733.
24. (a) Das, K.; Nandi, P. G.; Islam, K.; Srivastava, H. K.; Kumar, A., *Eur. J. Org. Chem.* **2019**, *2019*, 6855-6866; (b) Das, K.; Dutta, M.; Das, B.; Srivastava, H. K.; Kumar, A., *Adv. Synth. Catal.* **2019**, *361*, 2965-2980.
25. Dutta, M.; Das, K.; Prathapa, S. J.; Srivastava, H. K.; Kumar, A., *Chem. Commun.* **2020**, *56*, 9886-9889.
26. Das, K.; Yasmin, E.; Das, B.; Srivastava, H. K.; Kumar, A., *Catal. Sci. Technol.* **2020**, *10*, 8347-8358.
27. Raynor, S.; Song, H. H., *ACS Omega* **2020**, *5*, 27546-27555.
- 28 (a) Pati, A. K.; Gharpure, S. J.; Mishra, A. K., *J. Phys. Chem. A* **2015**, *119*, 10481-10493; (b) Bushuk, B.; Rubinov, A.; Stupak, A., *J. Appl. Spectrosc.* **1987**, *47*, 1251-1254.
29. Li, Y.-X.; Yang, X.-F.; Miao, J.-L.; Zhang, Z.-W.; Sun, G.-X., *CrystEngComm* **2016**, *18*, 2098-2104.
30. Makula, P.; Pacia, M.; Macyk, W., ACS Publications: 2018; Vol. 9, pp 6814-6817.
31. Péan, E. V.; Dimitrov, S.; De Castro, C. S.; Davies, M. L., *Phys. Chem. Chem. Phys.* **2020**, *22*, 28345-28358.
32. Iuliano, V.; Talotta, C.; Gaeta, C.; Soriente, A.; De Rosa, M.; Geremia, S.; Hickey, N.; Mennucci, B.; Neri, P., *Org. Lett.* **2019**, *21*, 2704-2707.
33. Reichardt, C., *Chem. Rev.* **1994**, *94*, 2319-2358.
34. Davis, R.; Saleesh Kumar, N.; Abraham, S.; Suresh, C.; Rath, N. P.; Tamaoki, N.; Das, S., *J. Phys. Chem. C* **2008**, *112*, 2137-2146.
35. Singh, A.; Pati, A. K.; Mishra, A. K., *Phys. Chem. Chem. Phys.* **2018**, *20*, 14889-14898.
36. (a) Otal, E.; Kim, M.; Calvo, M. E.; Karvonen, L.; Fabregas, I. O.; Sierra, C.; *Chem. Commun.* **2016**, *52*, 6665-6668; (b) Achelle, S.; Robin-Le Guen, F., *Tetrahedron Lett.* **2013**, *54*, 4491-4496; (c) Achelle, S.; Barsella, A.; Baudequin, C.; Caro, B.; Robin-Le Guen, F., *J. Org. Chem.* **2012**, *77*, 4087-4096; (d) Wink, C.; Detert, H., *J. Phys. Org. Chem.* **2013**, *26*, 137-143.
37. Seliskar, C. J.; Brand, L., *J. Am. Chem. Soc.* **1971**, *93*, 5414-5420.
38. (a) Luo, Y.; Zhang, C.; Zheng, B.; Geng, X.; Debliquy, M., *Int. J. Hydrog. Energy* **2017**, *42*, 20386-20397; (b) Zhang, M.; Zhen, Y.; Sun, F.; Xu, C., *Mater. Sci. Eng. B* **2016**, *209*, 37-44; (c)

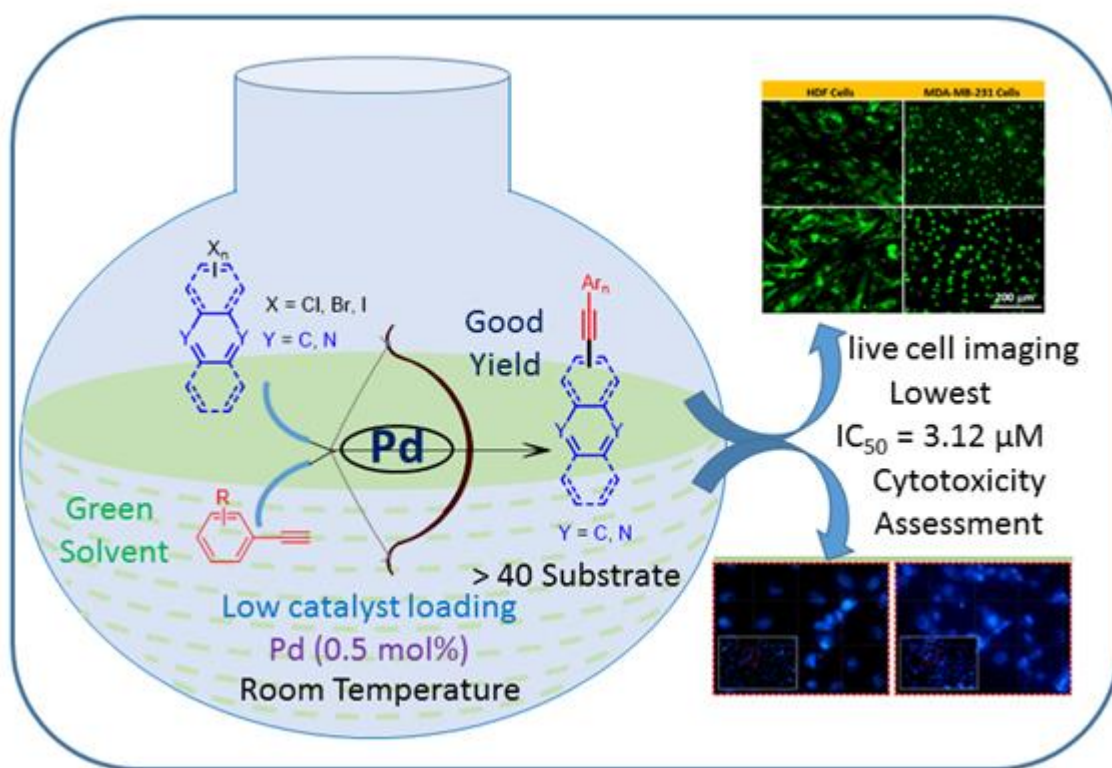
- Chauhan, P. S.; Bhattacharya, S., Hydrogen gas sensing methods, materials, and approach to achieve parts per billion level detection: A review. *Int. J. Hydrog. Energy* **2019**, *44*, 26076-26099.
39. Östergren, I.; Pourrahimi, A. M.; Darmadi, I.; da Silva, R.; Stolaś, A.; Lerch, S.; Berke, B.; Guizar-Sicairos, M.; Liebi, M.; Foli, G., *ACS Appl. Mater. Interfaces* **2021**, *13*, 21724-21732.
40. (a) Lubitz, W.; Tumas, W., *Chem. Rev.* **2007**, *107*, 3900-3903; (b) Urs, K. M.; Sahoo, K.; Bhat, N.; Kamble, V., *ACS Appl. Electron. Mater.* **2022**, *4*, 87-91.
41. (a) Singh, S.; Jain, S.; Venkateswaran, P.; Tiwari, A. K.; Nouni, M. R.; Pandey, J. K.; Goel, S., *Renew. Sust. Energ. Rev.* **2015**, *51*, 623-633; (b) Arnason, B.; Sigfusson, T. I., *Int. J. Hydrog. Energy* **2000**, *25*, 389-394; (c) Korotcenkov, G.; Han, S. D.; Stetter, J. R., *Chem. Rev.* **2009**, *109*, 1402-1433; (d) Sasaki, K., Springer: 2016; pp 3-14; (e) De Vrieze, J.; Verbeeck, K.; Pikaar, I.; Boere, J.; Van Wijk, A.; Rabaey, K.; Verstraete, W., *New biotechnol.* **2020**, *55*, 12-18.
42. (a) Abbasi, T.; Abbasi, S., *Renew. Sust. Energ. Rev.* **2011**, *15*, 3034-3040; (b) Mai, H. D.; Jeong, S.; Nguyen, T. K.; Youn, J.-S.; Ahn, S.; Park, C.-M.; Jeon, K.-J., *ACS Appl. Mater. Interfaces* **2021**, *13*, 14644-14652.
43. Momirlan, M.; Veziroglu, T., Current status of hydrogen energy. *Renew. Sust. Energ. Rev.* **2002**, *6*, 141-179.
44. (a) Hübert, T.; Boon-Brett, L.; Black, G.; Banach, U., Hydrogen sensors—a review. *Sens. Actuators B Chem.* **2011**, *157*, 329-352; (b) Nag, P.; Majumdar, S.; Bumajdad, A.; Devi, P. S., *RSC Adv.* **2014**, *4*, 18512-18521.
45. Dutta, S., A review on production, storage of hydrogen and its utilization as an energy resource. *J. Ind. Eng. Chem.* **2014**, *20*, 1148-1156.
46. Lupan, C.; Khaledialidusti, R.; Mishra, A. K.; Postica, V.; Terasa, M.-I.; Magariu, N.; Pauporté, T.; Viana, B.; Drewes, J.; Vahl, A., *ACS Appl. Mater. Interfaces* **2020**, *12*, 24951-24964.
47. Liu, X.; Cheng, S.; Liu, H.; Hu, S.; Zhang, D.; Ning, H., *Sens.* **2012**, *12* (7), 9635-9665.
48. (a) Daniel, T. T.; Raveesh, S.; Saikia, K.; Paily, R. P., *IEEE Sens. J.* **2021**, *21*, 9038-9045; (b) Daniel, T. T.; Yadav, V. K. S.; *IEEE Sens. J.* **2022**, *22*, 10910-10917.
49. (a) Mahajan, S.; Jagtap, S., *Appl. Mater. Today* **2020**, *18*, 100483; (b) Daniel, T. T.; Majumder, S.; Yadav, V. K. S.; Paily, R., *IEEE Sens. J.* **2020**, *20*, 13341-13348.
50. (a) Chang, S.-J.; Hsueh, T.-J.; Chen, I.-C.; Hsieh, S.-F.; Chang, S.-P.; Hsu, C.-L.; Lin, Y.-R.; Huang, B.-R., *IEEE Trans. Nanotechnol.* **2008**, *7*, 754-759; (b) Varghese, S. S.; Lonkar, S.; *Sens. Actuators B Chem.* **2015**, *218*, 160-183; (c) Nikolic, M. V.; Milovanovic, V.; Vasiljevic, Z. Z.; Stamenkovic, Z., *Sens.* **2020**, *20*, 6694.
51. (a) Phanichphant, S., *Procedia Eng.* **2014**, *87*, 795-802; (b) Zhang, Z.; Zou, X.; Xu, L.; Liao, L.; Liu, W.; Ho, J.; Xiao, X.; Jiang, C.; Li, J., *Nanoscale* **2015**, *7*, 10078-10084.
52. (a) Singla, M.; Jaggi, N., *Sens. Actuators A Phys.* **2021**, *332*, 113118; (b) Kaniyoor, A.; Jafri, R. I.; Arockiadoss, T.; Ramaprabhu, S., *Nanoscale* **2009**, *1*, 382-386; (c) Ilnicka, A.; Lukaszewicz, J. P., *Processes* **2020**, *8*, 633.
53. (a) Zhu, Z.; Liu, C.; Jiang, F.; Liu, J.; Liu, G.; Ma, X.; Liu, P.; Huang, R.; Xu, J.; Wang, L., *J. Hazard. Mater.* **2021**, *411*, 125008; (b) Zou, Y.; Wang, Q.; Xiang, C.; Tang, C.; Chu, H.; Qiu, S.; Yan, E.; Xu, F.; Sun, L., *Int. J. Hydrog. Energy* **2016**, *41*, 5396-5404; (c) Wang, P.-C.; Dan, Y.; Liu, L.-H., *Mater. Chem. Phys.* **2014**, *144*, 155-161; (d) Nasirian, S.; Moghaddam, H. M., *Int. J. Hydrog. Energy* **2014**, *39*, 630-642; (e) Al-Mashat, L.; Debiemme-Chouvy, C.; Borensztajn, S.; Wlodarski, W., *J. Phys. Chem. C* **2012**, *116*, 13388-13394; (f) Al-Hartomy, O. A.; Khasim, S.; Roy, A.; Pasha, A., *Appl. Phys. A* **2019**, *125* (1), 1-9; (g) Shah, S. S. A.; Nasir, H.; Saboor, A., *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 402-411.

54. (a) Ren, Q.; Cao, Y.-Q.; Arulraj, D.; Liu, C.; Wu, D.; Li, W.-M.; Li, A.-D., Resistive-type hydrogen sensors based on zinc oxide nanostructures. *J. Electrochem. Soc.* **2020**, *167*, 067528; (b) Zhao, J.; Wang, W.; Liu, Y.; Ma, J.; Li, X.; Du, Y.; Lu, G., *Sens. Actuators B Chem.* **2011**, *160*, 604-608; (c) Boudiba, A.; Roussel, P.; Zhang, C.; Olivier, M.-G.; Snyders, R.; Debliquy, M., *Sens. Actuators B Chem.* **2013**, *187*, 84-93; (d) Sanger, A.; Kumar, A.; Kumar, A.; Jaiswal, J.; Chandra, R., *Sens. Actuators B Chem.* **2016**, *236*, 16-26.
55. (a) Zhou, W.; Li, W.; Wang, J.-Q.; Qu, Y.; Yang, Y.; Xie, Y.; Zhang, K.; Wang, L.; Fu, H.; Zhao, D., *J. Am. Chem. Soc.* **2014**, *136*, 9280-9283; (b) Boudiba, A.; Zhang, C.; Umek, P.; Bittencourt, C.; Snyders, R.; Olivier, M.-G.; Debliquy, M., *Int. J. Hydrog. Energy* **2013**, *38*, 2565-2577.
56. Daniel, T. T.; Saikia, K.; Raveesh, S.; Paily, R., *IEEE Trans. Nanotechnol.* **2021**, *20*, 669-677.
57. Punetha, D.; Kar, M.; Pandey, S. K., *Sci. Rep.* **2020**, *10*, 1-11.
58. Jhulki, S.; Moorthy, J. N., *J. Mater. Chem. C* **2018**, *6* (31), 8280-8325.
59. Islam, K.; Narjinari, H.; Bisarya, A.; Kumar, A., *Org. Biomol. Chem.* **2021**, *19*, 9692-9704.
60. Daniel, T. T.; Yadav, V. K. S.; Natu, G.; Paily, R., Fully printed inorganic schottky diode. *IEEE Electron Device Letters* **2021**, *42* (8), 1212-1215.
61. Palathinkal, J. R.; Majumder, S.; Daniel, T. T.; Yadav, V. K. S.; Palathinkal, R. P., IEEE: 2022; pp 1-5.
62. (a) Germain, M. E.; Knapp, M. J., *Chem. Soc. Rev.* **2009**, *38*, 2543-2555; (b) Salinas, Y.; Martínez-Máñez, R.; Marcos, M. D.; Sancenón, F.; Costero, A. M.; Parra, M.; Gil, S., *Chem. Soc. Rev.* **2012**, *41*, 1261-1296.
63. Saravanan, N. P.; Venugopalan, S.; Senthilkumar, N.; Santhosh, P.; Kavita, B.; Prabu, H. G., *Talanta* **2006**, *69*, 656-662.
64. Sun, X.; Wang, Y.; Lei, Y., *Chem. Soc. Rev.* **2015**, *44*, 8019-8061.
65. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3-8.
66. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M., *J. Appl. Crystallogr.* **2020**, *53*, 226-235.
67. Zhan, Y.; Cao, K.; Xue, P.; Lu, R., *Tetrahedron Lett.* **2013**, *54*, 594-599.
68. Wang, J.-L.; Zhou, Y.; Li, Y.; Pei, J., *J. Org. Chem.* **2009**, *74*, 7449-7456.
69. Wang, H.-Y.; Chen, G.; Xu, X.-P.; Chen, H.; Ji, S.-J., *Dyes Pigm.* **2011**, *88*, 358-365.
70. Chen, Y.; Zhang, X.; Wang, M.; Peng, J.; Zhou, Y.; Huang, X.; Gao, W.; Liu, M.; Wu, H., *J. Mater. Chem. C* **2019**, *7*, 12580-12587.
71. Wang, L.; Yin, L.; Wang, L.; Xie, B.; Ji, C.; Li, Y., *Dyes Pigm.* **2017**, *140*, 203-211.
72. He, L.; Liu, X.; Liang, J.; Cong, Y.; Weng, Z.; Bu, W., *Chem. Commun.* **2015**, *51*, 7148-7151.
73. Dutta, U.; Lupton, D. W.; Maiti, D., *Org. Lett.* **2016**, *18*, 860-863.
74. Sakai, N.; Komatsu, R.; Uchida, N.; Ikeda, R.; Konakahara, T., *Org. Lett.* **2010**, *12*, 1300-1303.
75. Uttiya, S.; Miozzo, L.; Fumagalli, E. M.; Bergantin, S.; Ruffo, R.; Parravicini, M.; Papagni, A.; Moret, M.; Sassella, A., *J. Mater. Chem. C* **2014**, *2*, 4147-4155.
76. Göstl, R.; Sijbesma, R. P., *Chem. Sci.* **2016**, *7*, 370-375.
77. Li, Q.; Zhu, H.; Huang, F., *J. Am. Chem. Soc.* **2019**, *141*, 13290-13294.



CHAPTER III

Synthesis of Valuable PAHs by Copper and Amine Free Sonogashira Reaction in Green Solvent and In-Vitro Assessment of their Cytotoxicity Potentials.



K. Islam, B. K. Bhunia, G. Mandal, B. Nag, C. Jaiswal, B. B. Mandal, A. Kumar, *ACS Omega* **2023**, 8, 16907-16926

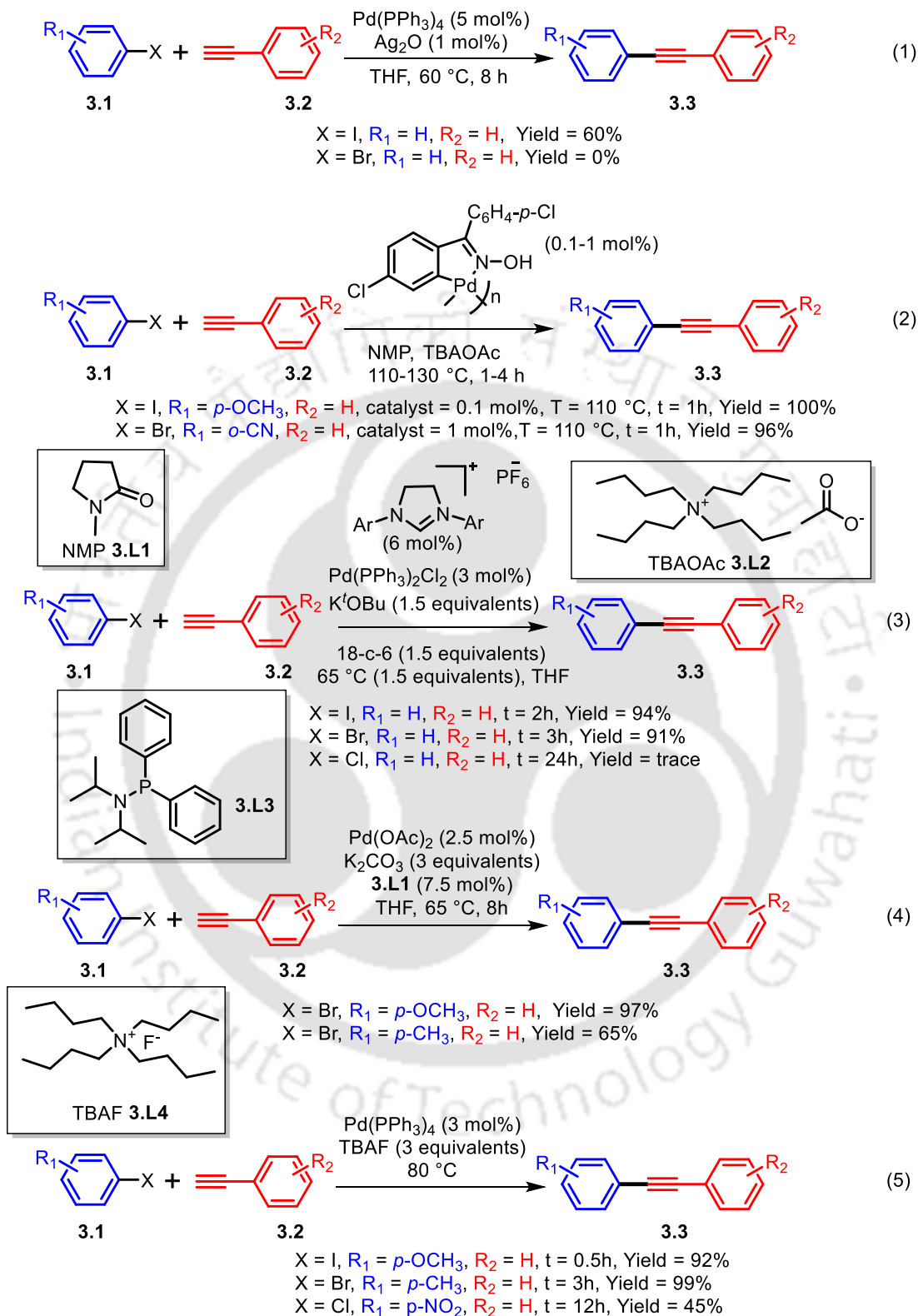


3.1 Introduction

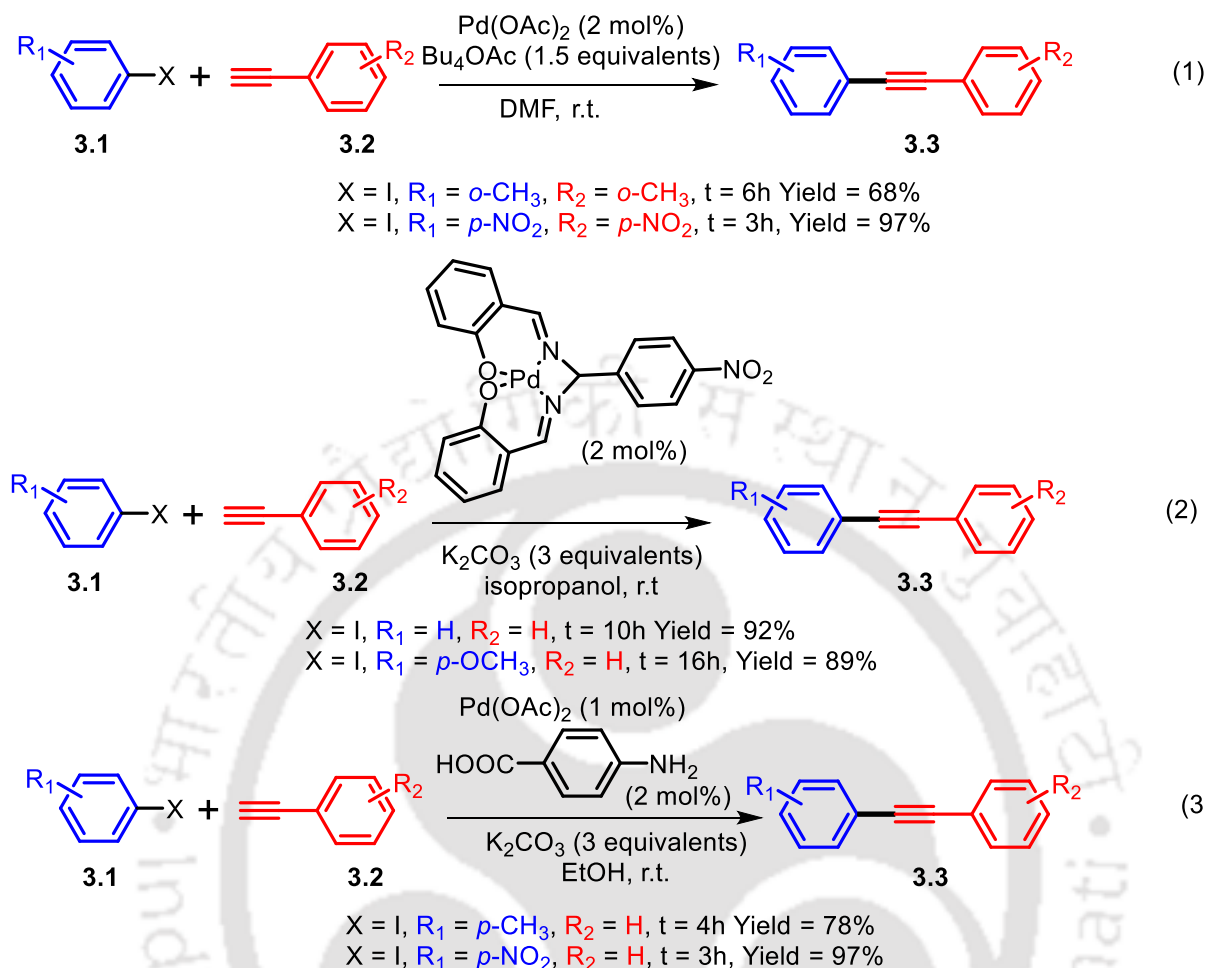
Organic semiconducting materials based on polyethynylated anthracene¹ have attracted global attention due to their versatile applications in solar cells,^{1e, 2} organic light-emitting diodes (OLEDs),^{1b} organic field-effect transistors (OFETs),^{1f, 1h} devices based on nanowire,³ sensors,^{4,1d} liquid-crystal displays⁵ and organic fluorescence.^{1g} The fluorescence efficiency and the electronic properties of the molecules depends on the geometry of the molecules.^{1d} The rigid polycyclic aromatic hydrocarbons (PAHs)^{1d, 6} exhibit high fluorescence efficiency which can be controlled by the addition of electron withdrawing and/or electron donating substituents. Addition of polyethynylated units to the PAHs enhances the π -conjugation which helps to decrease the band-gap, lowering the torsional barrier and enhance the thermal stability, which are favorable for the fabrication of such compounds in optoelectronic devices.^{1d} Polyethynylated unit can be introduced to the PAHs by Sonogashira reaction. The Sonogashira reaction is vital in organic synthetic chemistry for the synthesis of various organic compounds like natural products,⁷ pharmaceutical molecules,⁸ biologically active complexes,⁹ heterocycles,¹⁰ and organic materials.^{1d}

Traditionally, in Sonogashira reaction Pd(II)/Cu(I) catalytic system is required to form the C-C bond from the terminal alkyne and aryl/alkyl/vinyl halide, Cu(I) co-ordinates with alkyne to enhance the acidity of the terminal acetylenic proton, assisting the formation of the acetylide Cu(I), which is involved in the transmetalation step in the catalytic cycle when the alkyne unit is transferred to Pd and subsequently couples with the aryl moiety to form the desired product via reductive elimination.^{1d} However, presence of copper salts can sometimes have deleterious effect on catalysis,¹¹ that include but not limited to participation in Glaser homocoupling of two terminal alkynes to form dialkynes,^{1d, 9, 11a} inhibition of the activity of the Pd-catalyst,^{11a} and oxidation of unsaturated Pd(0) species to halide-bridged dinuclear Pd(I) complexes that accelerate polymerization¹² of the alkyne. Rightly, a lot of research emphasis is devoted on development of copper-free and preferably amine-free Sonogashira catalytic systems.^{9, 11, 13} There are reports that demonstrate that Pd and Cu together are no longer required as catalyst for Sonogashira reaction, instead, simply Pd has proven to be adequate when correctly complexed with the state of art ligands in absence of any amine additives.^{9, 11a, 13c, 13d, 13f, 14}

In 2000, for the first time Mori and co-workers reported the copper-free and amine-free Sonogashira reaction of aryl/alkenyl halide and terminal alkyne by employing the catalyst Pd(PPh₃)₄ in the presence of activator Ag₂O/TBAF/TBAOH (equation 1, Scheme 3.1).¹⁵



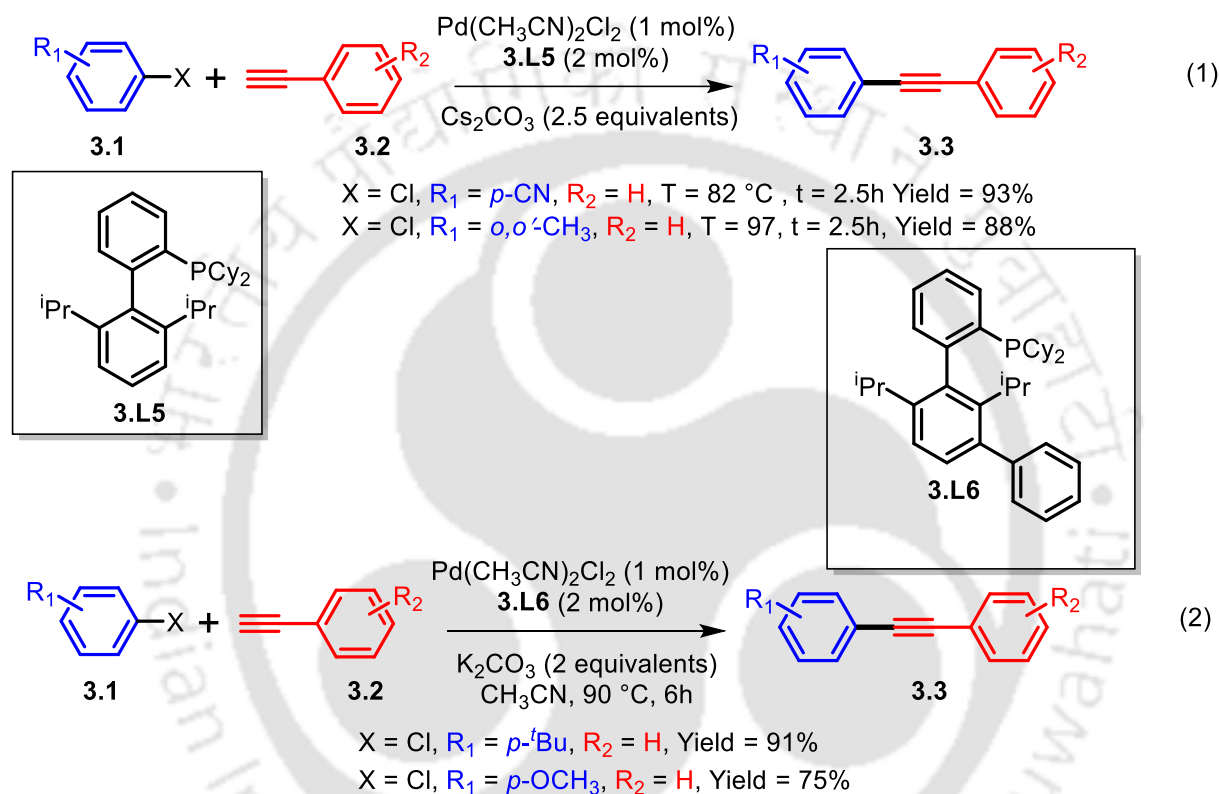
Scheme 3.1. Copper-free and amine-free Sonogashira reaction



Scheme 3.2. Copper-free and amine-free Sonogashira reaction at room temperature

Later, Najera group described the Sonogashira reaction of aryl halides and terminal alkyne in the presence of oxime based palladacycle catalyst and tetrabutylammonium acetate (equation 2, Scheme 3.1).¹⁶ The copper free Sonogashira reaction was investigated by employing the combination of bulky NHC phenanthrylimidazolium carbene ligand and $\text{Pd(PPh}_3)_2\text{Cl}_2$ by Andrus group in 2003 (equation 3, Scheme 3.1).¹⁷ In 2004, Zang and co-workers developed trivalent aminophosphine ligand which accelerates the reactivity of Pd(OAc)_2 towards Sonogashira reaction in absence of copper and amine (equation 4, Scheme 3.1).¹⁸ Li and co-workers investigated copper-free, amine-free and solvent-free Sonogashira reaction in the presence of $\text{Pd(PPh}_3)_2\text{Cl}_2$ and TBAF (equation 5, Scheme 3.1) in 2006.¹⁹ In 2003, Buchwald demonstrated copper-free and amine-free Sonogashira reaction catalyzed by $\text{Pd(CH}_3\text{CN)}_2\text{Cl}_2$ (1 mol%) and X-Phos type ligand (2 mol%) in

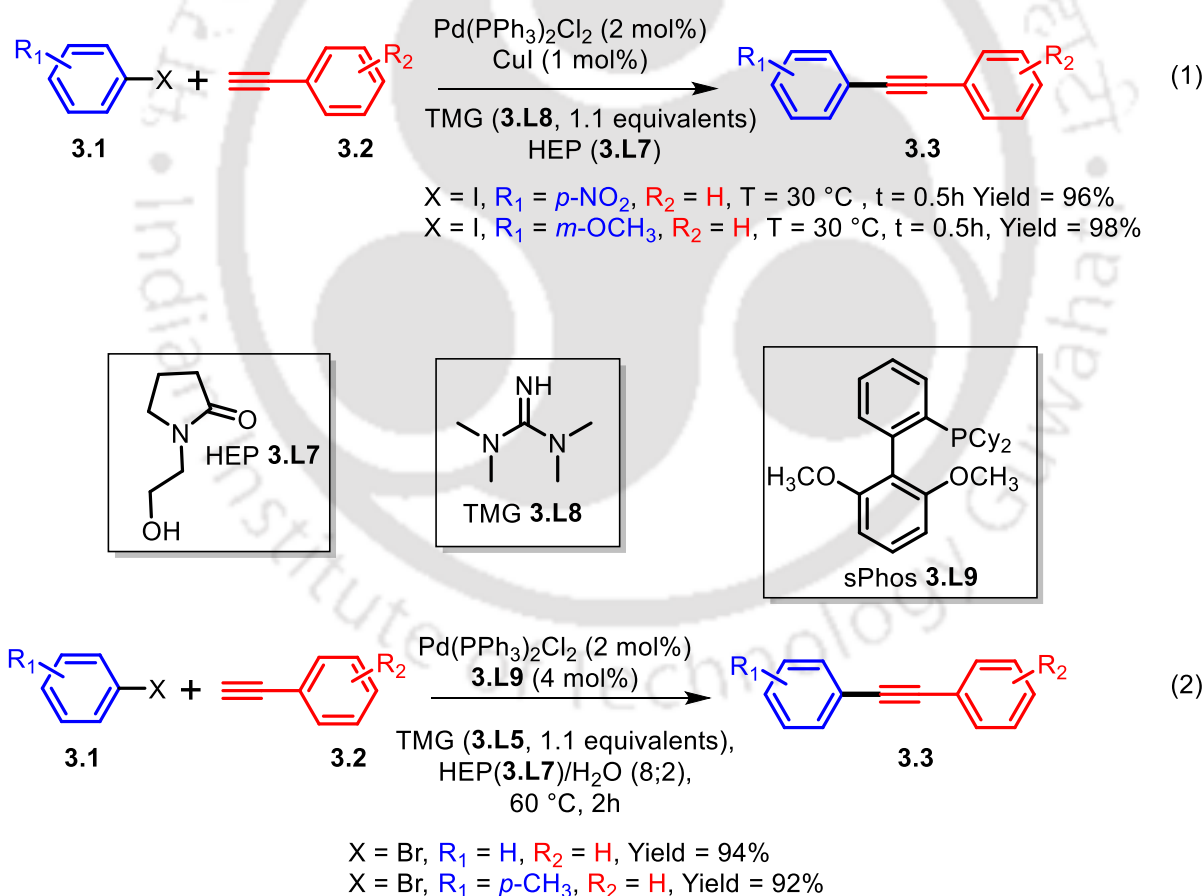
the presence of Cs_2CO_3 (2 equivalents) in CH_3CN at 70-95 °C (equation 1, Scheme 3.3).^{11a} Lim and co-workers reported copper-free and amine-free Sonogashira reaction by employing $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1 mol%) in combination with **3.L6** (2 mol%) using Cs_2CO_3 (2 equivalents) as base in CH_3CN at 90 °C for 6 h (equation 2, Scheme 3.3).^{14b} It is thus evident that while there are a few studies on copper-free and amine-free Sonogashira systems, reports that accomplish these very important reaction at room temperature are very rare (equation 1-3, Scheme 3.2).^{9, 20}



Scheme 3.3. Copper-free and amine-free Sonogashira reaction in the presence of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$.

The waste of chemical industries is mainly from solvent which is about 80-90% of total mass process.²¹ The choice of solvent is very crucial in Pd catalysed cross-coupling reaction owing to the stability of catalyst, selectivity and rate of the reaction.²² As per the literature, more than 40 % reports on Heck-Casser-Sonogashira reactions have been performed in *N,N*-dimethylformamide (DMF) which generates toxic dimethylamine and highly genotoxic nitrosamine.²³ Other solvents like tetrahydrofuran (THF), 1,4-dioxane, dimethoxyethane (DME), dimethylsulfoxide (DMSO) and trimethylamine (TEA) have also been used in Sonogashira reaction.^{23b} Triethylamine is malodorous substance, highly toxic and exhibits bioaccumulation potential.²⁴ Exposure to amine vapors for 0.5 h to several hours may cause glaucopsia, blurr vision, halos around lights.²⁵

Unfortunately, all other solvents have the same drawback like DMF which are threat to environment, human body and ecosystem.²⁵ Recently, the green solvents like dimethylisorbide, γ -valerolactone, cyrene, *tert*-butyl acetate (*t*BuOAc), anisole, *N*-octylpyrrolidone (NOP), *N*-cyclohexylpyrrolidone (NCP), *N*-benzylpyrrolidone (NBnP) and, *N*-hydroxyethylpyrrolidone (HEP) have been reported in Sonogashira reaction. Recently, Cabri, Martelli and co-workers developed the Sonogashira reaction by using the green base as well as solvent *N,N,N,N*-tetramethylguanidine and *N*-hydroxyethyl pyrrolidone (HEP) in the presence of catalytic system Pd(PPh₃)₂Cl₂ (2.0 mol%) and CuI (1 mol%) (equation 1, Scheme 3.4).^{23b} They also demonstrated the reaction under the same reaction condition in presence of monodendate phosphine ligand but in the absence of CuI (equation 2, Scheme 3.4).^{23a}



Scheme 3.4. Sonogashira reaction in the green solvent and base.

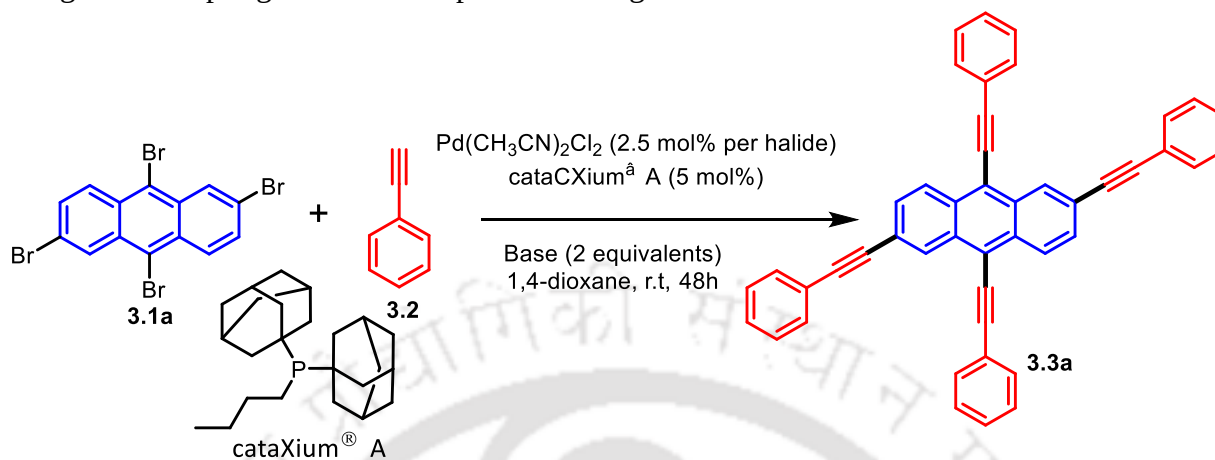
3.1.1 Objectives

The brief survey of the literature above clearly indicates that development of copper-free and amine-free Sonogashira catalytic systems in green solvents at room temperature is still a challenge unaddressed. 2-methyltetrahydrofuran (2-MeTHF) that is readily obtained from renewable biomass cellulose, bagasse and agricultural waste²⁶ has not been explored till now.²³ From the context of PAHs it would thus be valuable to have a Sonogashira catalytic system that could bring about multi-fold coupling in a green solvent such as 2-MeTHF at room temperature under copper-free and amine-free conditions. Anthracene derivatives are suitable candidates for anti-cancer drugs. In this current chapter an attempt is made to address the following question.

- Can one develop a new efficient synthetic methodology for copper-free and amine-free Sonogashira reaction in a green solvent by employing low catalyst loading?
- Is it possible to utilize the new synthetic protocol in multi-fold Sonogashira reaction to arrive at polyethynyl bridged polycyclic aromatic hydrocarbons?
- Is it possible to study the cytotoxicity of synthesized polyethynyl polycyclic aromatic hydrocarbons?

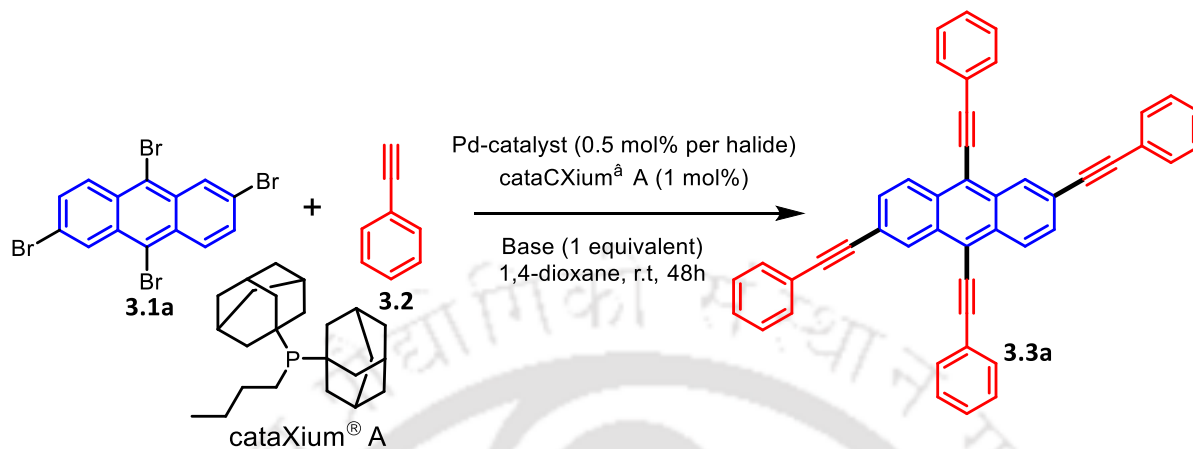
3.2. Results & Discussion

The optimization of the Sonogashira catalytic system was commenced with 2,6,9,10-tetrabromoanthracene (**3.1a**) and phenylacetylene (**3.2**) as model substrates with the best conditions reported earlier at 90°C^{1c} involving Pd(CH₃CN)₂Cl₂ (2.5 mol% per halide) and CataCXium® A (5 mol% per halide) in a 1:1 mixture of 1,4-dioxane and triethyl amine albeit under copper-free conditions at room temperature (entry 1, Table 3.1). Unfortunately, these conditions afforded no products even after stirring for 48 hours (entry 1, Table 3.1). This underlines the importance of copper and the higher temperature for these conditions.^{1c} With an intention to move away from amines,^[23-24] the copper-free Sonogashira reactions at room temperature were repeated with various inorganic bases (entries 2-15, Table 3.1). While moderate yields of **3.3a** was obtained with bases such as K₃PO₄ (52%, entry 2, Table 3.1), K₂CO₃ (44%, entry 3, Table 3.1) and KOH (45%, entry 7, Table 3.1), trace or no yield was observed upon use of other bases derived from potassium and sodium (entries 4-6 and 8-12, Table 3.1). On the other hand, use of two equivalents of Cs₂CO₃ resulted in very high yields of **3.3a** (ca. 98%, entry 13, Table 3.1). The yields were un-

Table 3.1. The Optimization of the Pd Catalyzed Cu-Free and Amine-Free Multi-Fold Sonogashira coupling at Room Temperature Using Various Bases.^a

Entry	Base	Catalyst	Solvent	Yield (%) of 3.3a ^b
1	Et ₃ N	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
2	K ₃ PO ₄	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	52
3	K ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	44
4	Na ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	5
5	KHCO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	9
6	NaHCO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	trace
7	KOH	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	45
8	NaOH	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
9	KO ^t Bu	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
10	NaO ^t Bu	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
11	NaOEt	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
12	NaH	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
13	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	98
14 ^c	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	100
15 ^d	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	100

^aReaction conditions: 0.101 mmol of **3.1a** and 0.606 mmol of **3.2** in the presence of Pd(CH₃CN)₂Cl₂ (2.5 mol% per halide), cataCXium[®] A (5 mol% per halide) in the 1,4-dioxane (5 mL) at room temperature for 48 h. [b] Yield determined from ¹H NMR using toluene as internal standard. ^cCs₂CO₃ (1 equivalent per halide). ^dCs₂CO₃ (0.75 equivalents per halide)

Table 3.2. The Optimization of the Pd Catalyzed Cu-Free and Amine-Free Multi-Fold Sonogashira coupling at Room Temperature Under Various Conditions.^a

Entry	Base	Catalyst	Solvent	Yield (%) of 3.3a
1 ^c	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	100
2 ^{c,d}	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	100
3 ^d	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	83
4	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	98
5 ^e	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	80
6	Cs ₂ CO ₃	Pd(OAc) ₂	Dioxane	32
7	Cs ₂ CO ₃	Pd(dba) ₂	Dioxane	87
8	Cs ₂ CO ₃	Pd(PPh ₃) ₂ Cl ₂	Dioxane	36
9	Cs ₂ CO ₃	Pd(PPh ₃) ₄	Dioxane	24
10 ^f	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Dioxane	0
11 ^f	Cs ₂ CO ₃	Pd(OAc) ₂	Dioxane	0
12 ^f	Cs ₂ CO ₃	Pd(dba) ₂	Dioxane	0
13 ^f	Cs ₂ CO ₃	Pd(PPh ₃) ₂ Cl ₂	Dioxane	34
14 ^f	Cs ₂ CO ₃	Pd(PPh ₃) ₄	Dioxane	3
15	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	Toluene	0
16	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	THF	94
17	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	2-MeTHF	98 ^g
18 ^h	Cs ₂ CO ₃	Pd(CH ₃ CN) ₂ Cl ₂	2-MeTHF	69

^aReaction conditions: 0.101 mmol of **3.1a** and 0.606 mmol of **3.2** in the presence of Pd-catalysts (0.5 mol% per halide), cataCXium[®] A (1.0 mol% per halide) in the 1,4-dioxane (5 mL) at room temperature for 48 h.

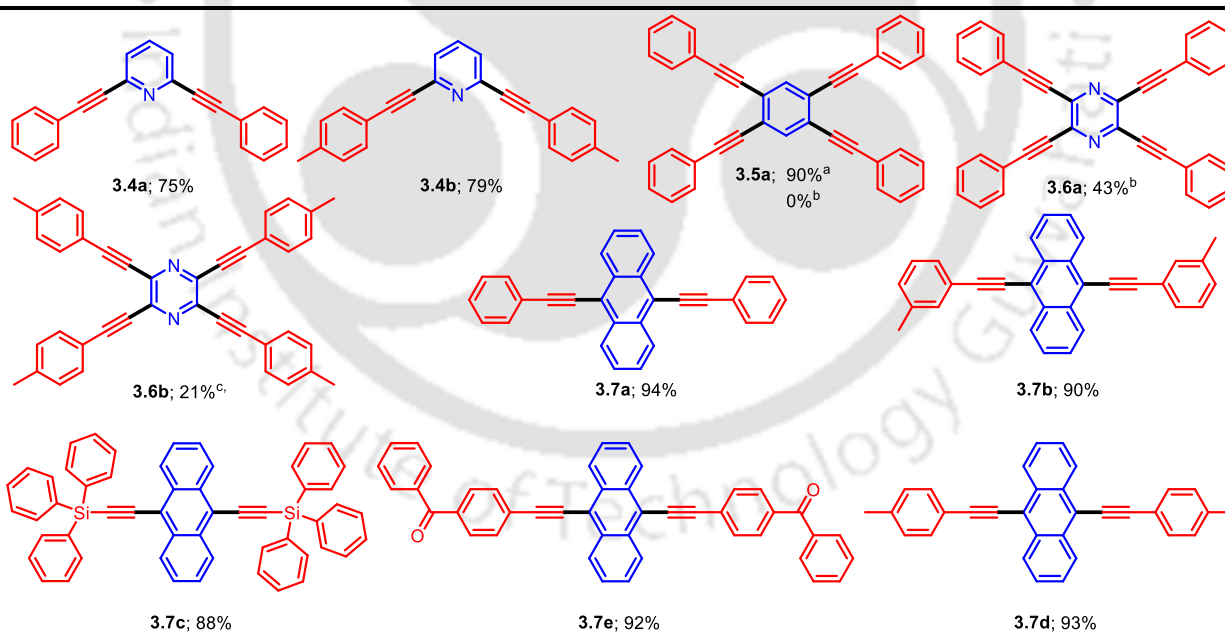
^bYield determined from ¹H NMR using toluene as internal standard. ^cPd-catalyst (2.5 mol% per halide).

^dCs₂CO₃ (0.75 equivalents per halide). ^ePd-catalyst (0.25 mol% per halide). ^fWithout cataCXium[®] A.

^gAverage of two runs. ^hReaction time is 36 h.

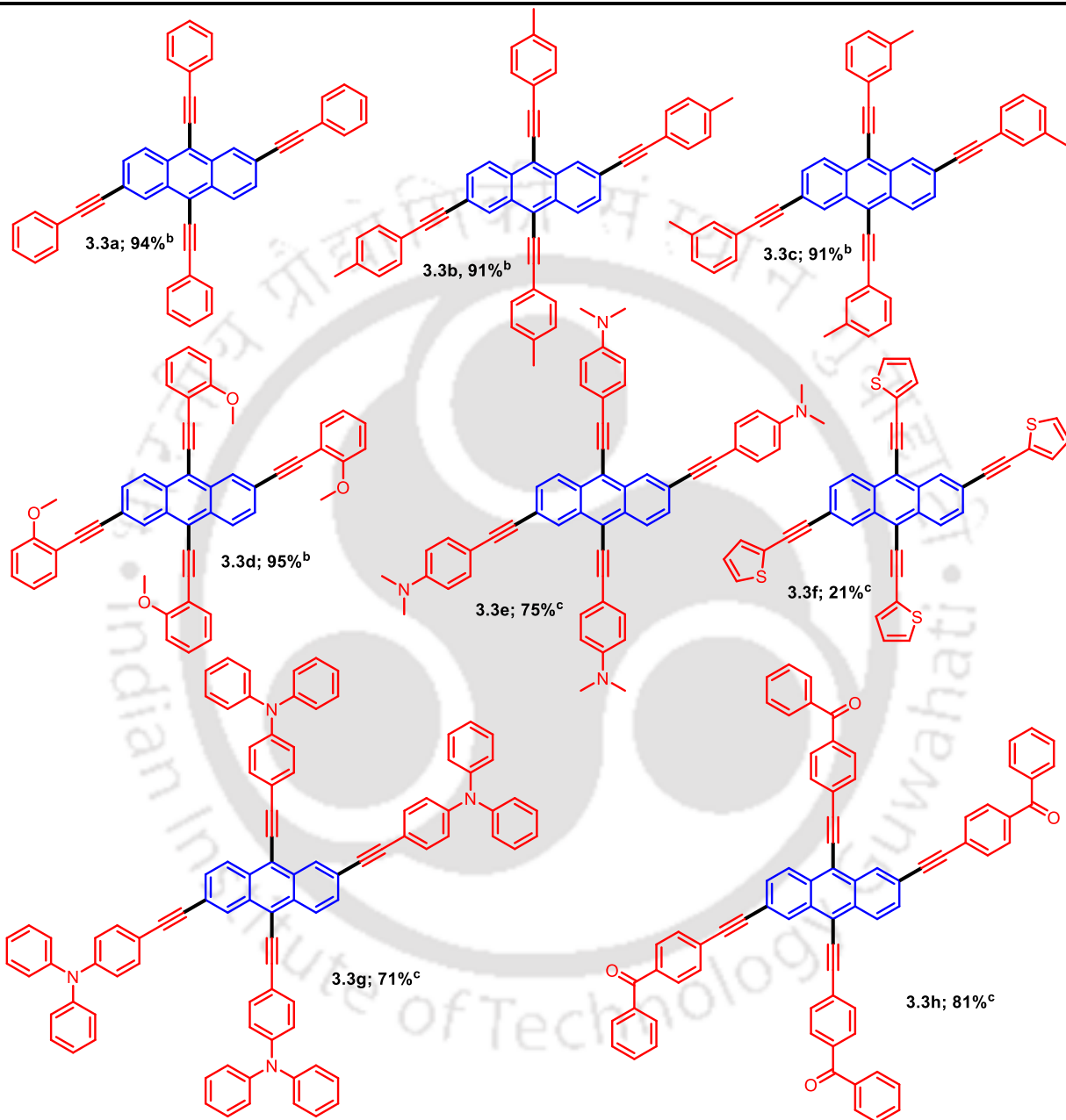
-affected upon lowering the loading of Cs_2CO_3 either to one equivalent (entry 14, Table 3.1 and entry 1, Table 3.2) or to 0.75 equivalents (entry 15, Table 3.1 and entry 2, Table 3.2). In the presence of 0.75 equivalents Cs_2CO_3 when the reaction was performed at a lower loading of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol% per halide) and CataCXium® A (1 mol% per halide) at room temperature, the yield of **3.3a** decreased to 83% (entry 3, Table 3.2). However, a combination of an equivalent Cs_2CO_3 and $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol% per halide) + CataCXium® A (1.0 mol% per halide) resulted in nearly quantitative yield of product **3.3a** (entry 4, Table 3.2). Further decrease in catalyst loading to 0.25 mol% lowered the yield of **3.3a** (entry 5, Table 3.2). the optimized condition (entry 4, Table 3.2) was used to screen a series of Pd catalysts (entry 6-9, Table 3.2). While use of $\text{Pd}(\text{dba})_2$ instead of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ under otherwise similar conditions

Table 3.3. The $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) Catalyzed Cu-Free and Amine-Free Multi-Fold Sonogashira Coupling at Room Temperature in 2-MeTHF Leading to Various PAHs.^a



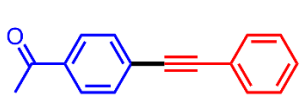
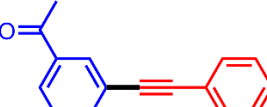
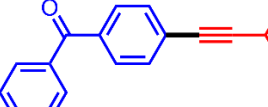
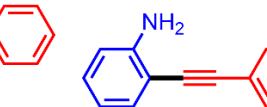
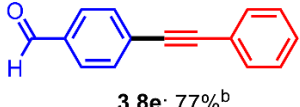
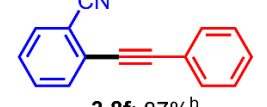
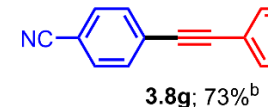
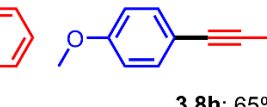
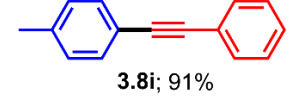
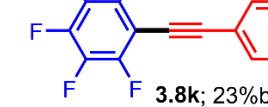
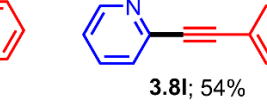
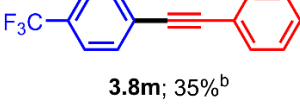
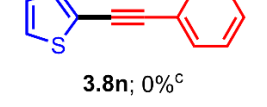
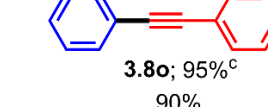
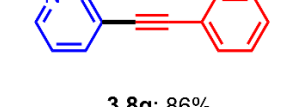
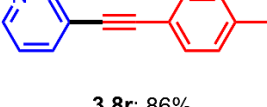
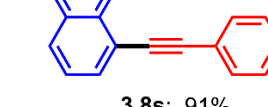
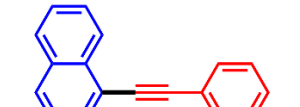
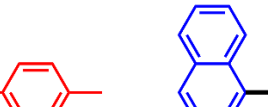
^aReaction conditions: 0.101 mmol of aryl bromide, 0.606 mmol of arylacetylene (1.5 equivalents per halide), 2 mol% of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol% per halide), 4 mol% cataCXium® A (1 mol% per halide), 0.404 mmol Cs_2CO_3 (1 equivalent per halide) in 2-methyltetrahydrofuran (5 mL) at room temperature under argon for 48 h. ^bAryl iodide used. ^cAryl chloride used. ^dIsolated yield.

Table 3.4. The Pd(CH₃CN)₂Cl₂ (0.5 mol%) + CataCXium® A (1 mol%) Catalyzed Cu-Free and Amine-Free Multi-Fold Sonogashira Coupling at Room Temperature in 2-MeTHF Leading to Various PAHs.^a



^aReaction conditions: 0.101 mmol of aryl bromide, 0.606 mmol of arylacetylene (1.5 equivalents per halide), 2 mol% of Pd(CH₃CN)₂Cl₂ (0.5 mol% per halide), 4 mol% cataCXium® A (1 mol% per halide), 0.404 mmol Cs₂CO₃ (1 equivalent per halide) in 2-methyltetrahydrofuran (5 mL) at room temperature under argon for 48 h. ^bIsolated yield ^cYield calculated from ¹H NMR by using toluene as internal standard.

Table 3.5. The Pd(CH₃CN)₂Cl₂ (0.5 mol%) + CataCXium® A (1 mol%) Catalyzed Cu-Free and Amine-Free One-Fold Sonogashira Coupling at Room Temperature in 2-Me-THF.^a

			
3.8a; 96% ^b	3.8b; 80% ^b	3.8c; 93% ^b	3.8d; 22% ^b
			
3.8e; 77% ^b	3.8f; 87% ^b	3.8g; 73% ^b	3.8h; 65%
			
3.8i; 91%	3.8j; 89%	3.8k; 23% ^b	3.8l; 54%
			
3.8m; 35% ^b	3.8n; 0% ^c	3.8o; 95% ^c 90% 12% ^d	3.8p; 88%
			
3.8q; 86%,	3.8r; 86%	3.8s; 91%	3.8t; 92%
			
3.8u; 91%	3.8v; 95%	3.8w; 56%	

^aReaction conditions: 0.5 mmol of aryl bromide, 1.5 mmol of arylacetylene, 0.5 mol% of Pd(CH₃CN)₂Cl₂, 1 mol% of cataCXium® A, 0.5 mmol (1 equivalent) Cs₂CO₃ in 2-methyltetrahydrofuran (5 mL) at room temperature under argon for 48 h. All are isolated yield. ^b1 mol% of Pd(CH₃CN)₂Cl₂ and 2 mol% of cataCXium® A. ^cAryl iodide, ^dAryl chloride.

5, Table 3.2). similar conditions resulted in slightly lowered yield of **3.3a** (ca. 87%, entry 7, Table 3.2), the corresponding yields of **3.3a** upon use of Pd(OAc)₂, Pd(PPh₃)₂Cl₂ and Pd(PPh₃)₄ were poor (entries 6, 8 and 9, Table 3.2). The presence of CataCXium® A is pivotal for obtaining good yields as is evident from the reactions performed in its absence where no product formation was observed (entries 10-12 and 14, Table 3.2) with the reaction catalyzed by Pd(PPh₃)₂Cl₂ as the only

exception where 34% of **3.3a** was observed (entry 13, Table 3.2). The similar yields obtained in the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ catalyzed reactions in the presence and in the absence of CataCXium® A indicates that the latter has no role to play in reactions catalyzed by the former (entry 8 vs. entry 13, Table 3.2). Performing the reaction under the best conditions (entry 4, Table 3.2) but with toluene as solvent resulted in no reactivity (entry 15, table 3.2). Use of THF resulted in comparable reactivity (entry 16, Table 3.2). More importantly, the corresponding reaction in a readily available green solvent 2-MeTHF proceeded smoothly giving rise to **3.3a** in nearly quantitative yields (entry 17, Table 3.2). Reducing the reaction time resulted in lower yields of **3.3a** (entry 18, Table 3.2). Thus entry 17, Table 3.2 depicts the best optimized conditions of the current work where the challenging multi-fold Sonogashira coupling has been accomplished using a catalytic system comprising of an equivalent Cs_2CO_3 and $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) in a green solvent 2-MeTHF at room temperature under copper-free and amine-free conditions.

The applicability of the optimized condition was tested for a series of multi-fold Sonogashira coupling reactions (Table 3.3 and 3.4). The two-fold Sonogashira coupling of 2,6-dibromo pyridine was accomplished with ease to yield the corresponding products **3.4a** and **3.4b** respectively in moderate yields (Table 3). While tetraiodobenzene gave 90% of the corresponding tetraalkynylated product **3.5a**, the reaction with the corresponding chloro analogue resulted in no reactivity (Table 3) which is in accordance with the C-X (X = Cl and I) bond strengths. This points to the involvement of the oxidative addition of C-X bond in the rate-determining step (RDS) (see Scheme 3.5, *vide-infra*). Moderate to poor reactivity (**3.6a** and **3.6b**, Table 3.3) was observed in the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) catalyzed Cu-free and amine-free tetra-fold Sonogashira coupling of tetrachloro pyrazine at room temperature in 2-MeTHF.

On the other hand, very good yields of Sonogashira coupled products **3.7a-e** were obtained in the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) catalyzed two-fold coupling of dibromo anthracene at room temperature in 2-MeTHF. The excellent Sonogashira activity of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) towards formation of **3.3a** was extended with equal success to accomplish the synthesis of several of its derivatives (**3b-e** & **3g-h**) albeit with little success in the case of **3f** that originates from a heterocycle containing acetylene.

With an objective to probe the generic nature of the formulated protocol, the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) + CataCXium® A (1 mol%) catalyzed Sonogashira coupling in the presence of an equivalent of Cs_2CO_3 in 2-MeTHF at room temperature under copper-free and

amine-free conditions was examined for simple substrates involving a one-fold coupling. In general, all substrates gave good to excellent yields of products (Table 3.5). While the poor yields of **3.8d** and **3.8l** can be attributed to the ability of the substrates to form chelates with Pd. Similar to the case discussed for **3.5a**, the yield of **3.8o** was dependent on the halo benzene substrate with the reactivity following the order Ph-I > Ph-Br > Ph-Cl which is again indicative of the involvement of the oxidative addition of C-X bond in the rate-determining step (RDS).

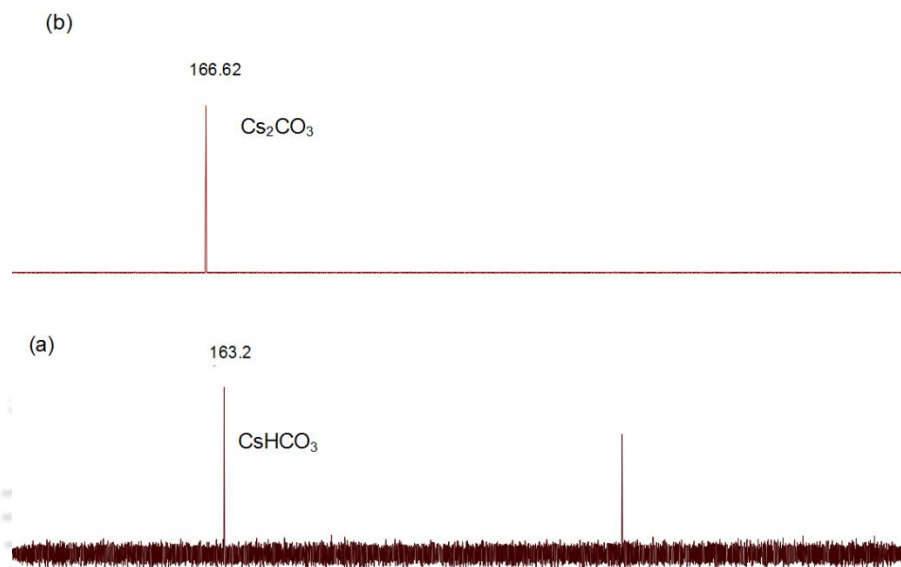
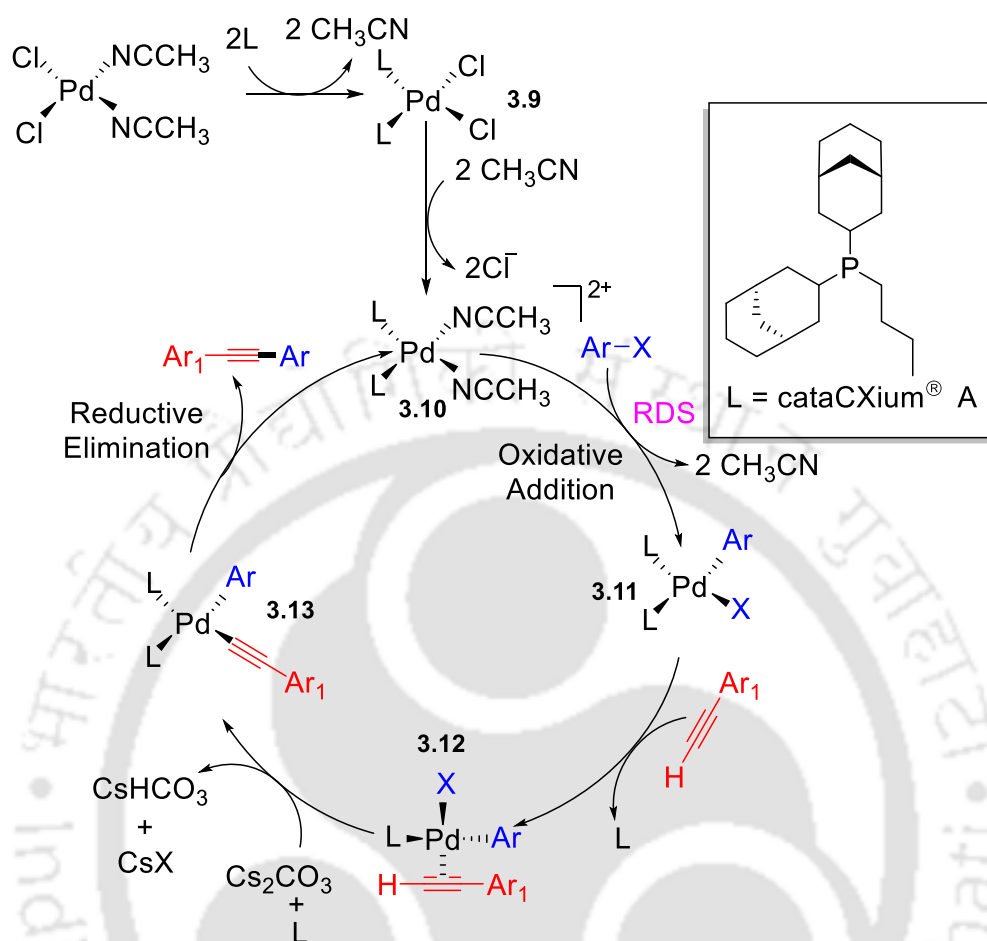


Figure 3.1. (a) Detection of CsHCO₃ in the aqueous fraction by ¹³C NMR in the Pd(CH₃CN)₂Cl₂ and CataCXium® A Catalyzed Sonogashira Coupling reaction after work-up. (b) Carbonate carbon in the ¹³C NMR of Cs₂CO₃.

In 2016, Mak has computed the mechanism for Cu-free Sonogashira at 90 °C using a catalytic system based on Pd(CH₃CN)₂Cl₂ and XPhos-type ligands.²⁷ In accordance to their proposal and in line with the current observations, the plausible mechanism involved in the Pd(CH₃CN)₂Cl₂ and CataCXium® A catalyzed Cu-free and amine-free Sonogashira coupling is depicted in Scheme 3.5. CataCXium® A initiates the dissociation of acetonitrile from Pd(CH₃CN)₂Cl₂ to give **3.9** which is followed by the reduction of Pd(II) in **3.9** to Pd(0) in **3.10**. A subsequent oxidative addition of the aryl halide to the Pd(0) centre in **3.10** results in the Pd(II) species **3.11**. The reactivity of various aryl halides follows the order of C-X (X = Cl, Br and I) bond strengths and demonstrates the trend Ar-I > Ar-Br > Ar-Cl. Considering the fact that the



Scheme 3.5. Plausible Mechanism of the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ and CataCXium[®] A Catalyzed Cu-Free and Amine-Free Sonogashira Coupling

reaction is facile when an aryl iodide is used and that it slows down in the presence of an aryl chloride, it is likely that the oxidative addition is the RDS. The alkyne then coordinates to the Pd(II) centre giving rise to **3.12** from which the Cs_2CO_3 abstracts the proton to give CsHCO_3 and complex **3.13**. Notably CsHCO_3 has been detected by ^{13}C NMR in the reaction after work-up in the aqueous fraction (Figure 3.1). The chemical shift of the bicarbonate carbon is in agreement with A final reductive elimination of the alkynylated arene product from **3.13** leads to the regeneration of the active catalyst **3.10**.

Anthracenes have been classified as ‘Group 3 - non classifiable as carcinogenic to human’ by USEPA (United States Environmental Protection Agency).²⁸ Studies have shown that

anthracene derivatives can be used as potential anti-cancer drugs and chemotherapeutic agents,

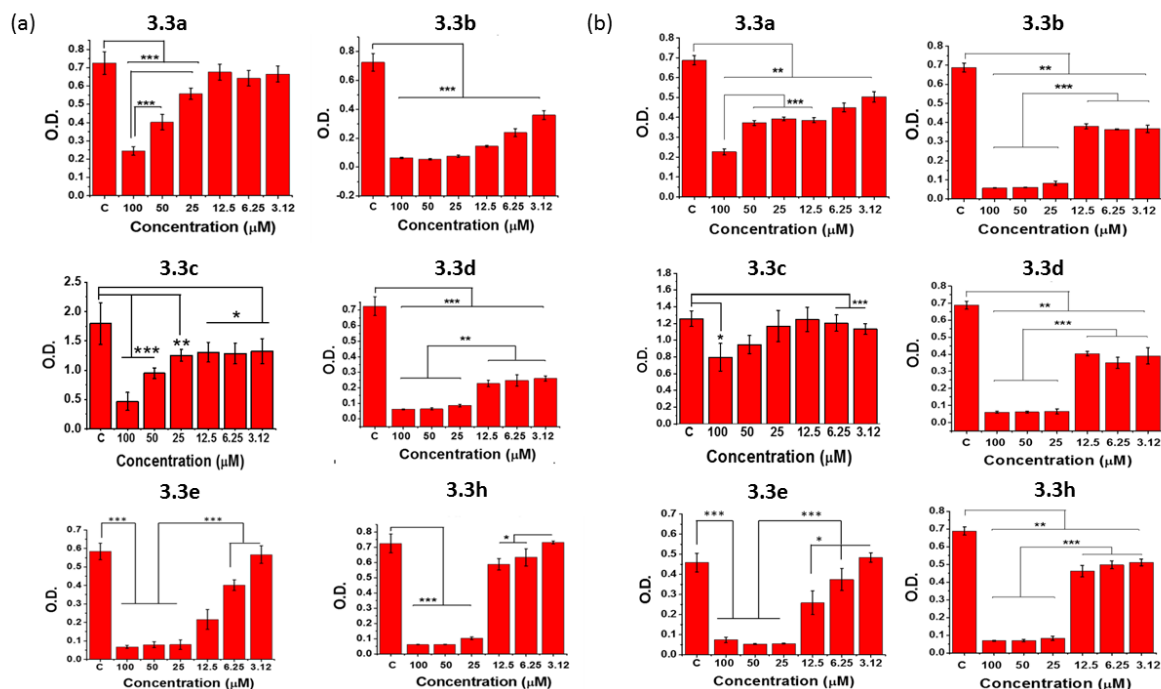


Figure 3.2. (a) Cytotoxicity assessment of tetraalkynylated anthracene derivatives **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e**, **3.3h** against MDA-MB-231 cell line. Data represent mean $\pm$ SD ($n = 3$), where $***p \leq 0.001$, $**p \leq 0.01$, $*p \leq 0.05$ and “ns” = non-significant. (b) Cytotoxicity assessment of tetraalkynylated anthracene derivatives **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e**, **3.3h** against HDF cell line. Data represent mean $\pm$ SD ($n = 3$), where $***p \leq 0.001$, $**p \leq 0.01$, $*p \leq 0.05$ and “ns” = non-significant.

Entry	compound	IC ₅₀ (HDF) μ M	IC ₅₀ (MDA-MB-231) μ M
1	3.3a	>50	50
2	3.3b	~12.5	~3.12
3	3.3c	>100	~50
4	3.3d	~12.5	3.12
5	3.3e	~12.5	~12.5
6	3.3h	>12.5	>12.5

mainly in breast cancer.²⁸⁻²⁹ The most common problem with long-term treatment of cancer is multidrug resistance (MDR) and these anthracene derivatives show promising results in overcoming MDR resistance in cancer treatments.^{29a, 29f} MHY412, a novel anthracene derivative

was successful in arresting breast cancer cells in sub-G1 phase of cell cycle via inhibition of cyclin-dependent kinase 2 (CDK2) and p21 expression in MCF-7/Adr cells.^{29a} HL-37, another anthracene derivative showed potential anti-tumor activity by inducing apoptosis in MDA-MB-435 and MCF-7 cells via Ca^{2+} /caspase pathway.^{29b} Radiotherapy (RT) and photodynamic therapy (PDT) has been performed using anthracene and Ag@anthracene scintillating nanoparticles in colon cancer cell lines. This has shown high singlet oxygen species generation ($^1\text{O}_2$), which in turn promotes cell death and apoptosis.²⁸ 7-Methylbenz(a)anthracene and its derivatives (7-Bromomethyl-12-methylbenz(a)-anthracene, 7-bromomethyl-12-methylbenz(a) anthracene and 4-Chloro-7-bromomethylbenz(a)anthracene) have shown anti-cancer activities against subcutaneous sarcomata in lung and liver in mice.³⁰ Rubiasins- anthracene derivatives isolated from the roots and stems of *Rubia cordifolia* have shown chemotherapeutic activity against colon cancer cell lines.^{29c} Aromatic azo-derivatives of anthracene have shown potential anti-tumor effects against breast cancer and adrenal cancer.^{29d}

All these studies have shown that anthracene and its derivatives can induce cell death via DNA damage and inducing apoptosis. They also show selectivity towards rapidly dividing cancer cells.³¹ Hence, it would be interesting to study the cytotoxic effects of the anthracenes obtained in the current study. Particular emphasis was laid on studying the cytotoxic effect of the new and less explored tetraalkynylated anthracene derivatives on cancer cells based on breast cancer cell lines to estimate the minimum inhibitory concentration and simultaneously compare the corresponding results with healthy Human Dermal Fibroblast (HDF) cells.

The cytotoxicity of various tetraalkynylated anthracene derivatives were tested against MDA-MB-231 cell lines and HDF cells as shown in Figure 3.2. All the tetraalkynylated anthracene derivatives exhibited a concentration dependent anti-proliferative activity with the IC_{50} values in the range of 6-12 μM (**3.3a-h**, Figure 3.2a). Among all the considered tetraalkynylated anthracene derivatives, **3.3d** and **3.3b** (Figure 3.2a) showed relatively higher anticancer effect when tested on MDA-MB-231 cell lines. These two compounds exhibited the anti-proliferative properties even at the lowest concentration (3.12 μM) tested.

In contrast, **3.3a**, **3.3c** and **3.3h** showed the least anti-cancer effect even at concentrations of 12.5 μM (Figure 3.2a). A gradual increase in anti-proliferative effect was also noticed when the concentration of **3.3e** and **3.3c** increased from 6.25 μM to 100 μM (Figure 3.2a). A similar trend in anti-proliferative effect of all the considered tetraalkynylated anthracene derivatives (except

3.3a and **3.3h**) with relatively reduced activity was also observed when tested against HDF cells (Figure 3.2b). It is thus evident that the considered tetraalkynylated anthracene derivatives demonstrated an increased cytotoxic effect and selectivity against MDA-MB-231 cells as compared to the HDF cells under same experimental conditions.

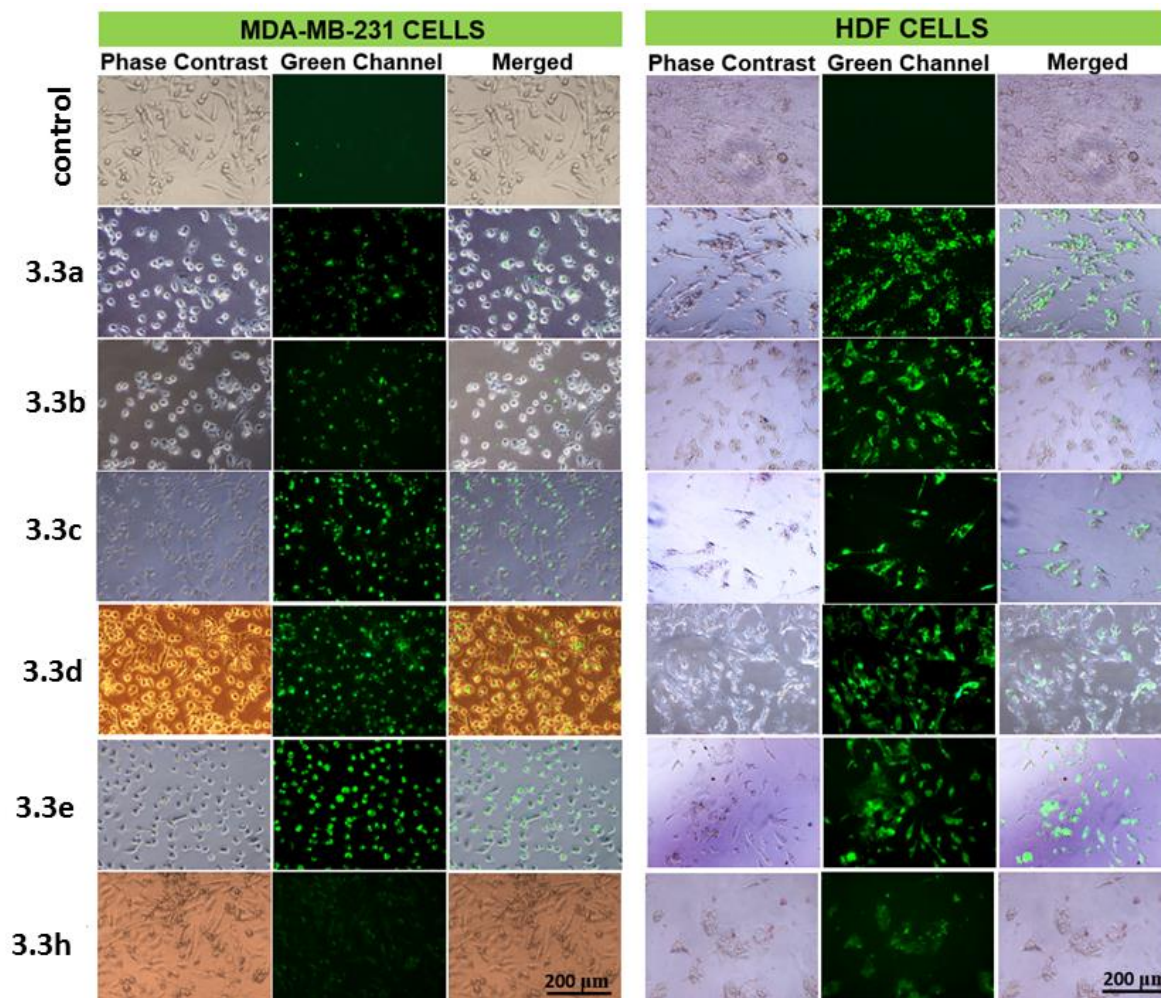


Figure 3.3. Fluorescence imaging of tetraalkynylated anthracene derivatives in the living cells; Images presenting (i) tetraalkynylated anthracene derivatives treated phase contrast microscopic image, and (ii) fluorescent images of tetraalkynylated anthracene derivatives treated cells in green channel, (iii) merged images showing cellular localization of the tetraalkynylated anthracene derivatives.

The live cell imaging experiment was conducted to demonstrate the fluorescence properties of tetraalkynylated anthracene derivatives in the living cells. 10 μ M concentration was chosen for treatment as it lies in the range of the calculated IC_{50} value (Figure 3.3). An intense green

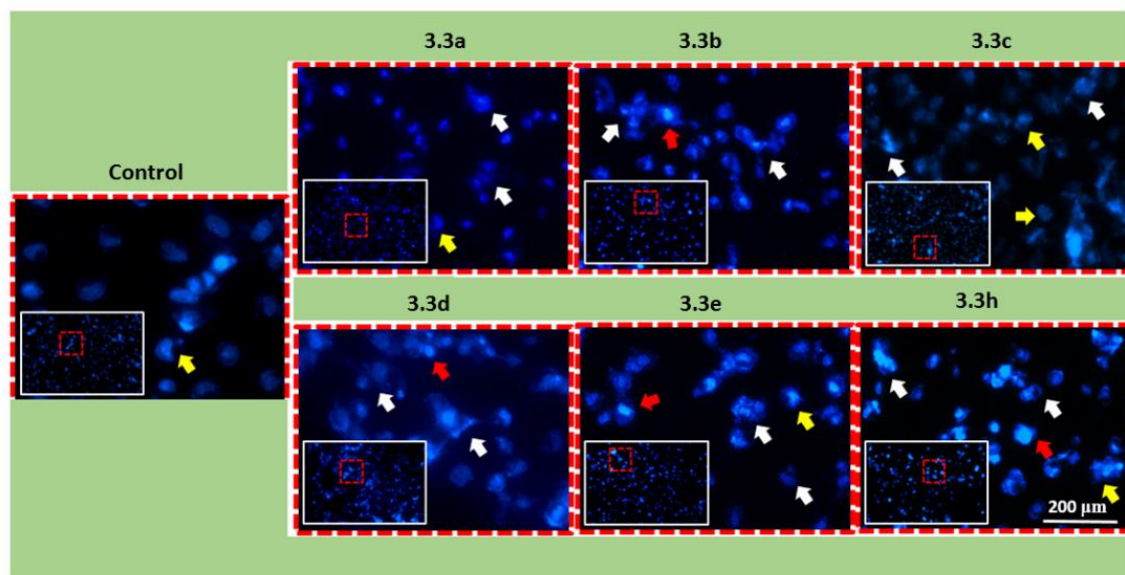


Figure 3.4. DAPI stained cells after treatment with the tetraalkynylated anthracene derivatives **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e** and **3.3h** against MDA-MB-231 cell line. The white arrows represent nuclear fragmentation, yellow arrows represent nuclear blebbing and the red arrows represent nuclear condensation. The green arrows in the control (no chemical treatment was given) show healthy rounded nucleus when stained with DAPI.

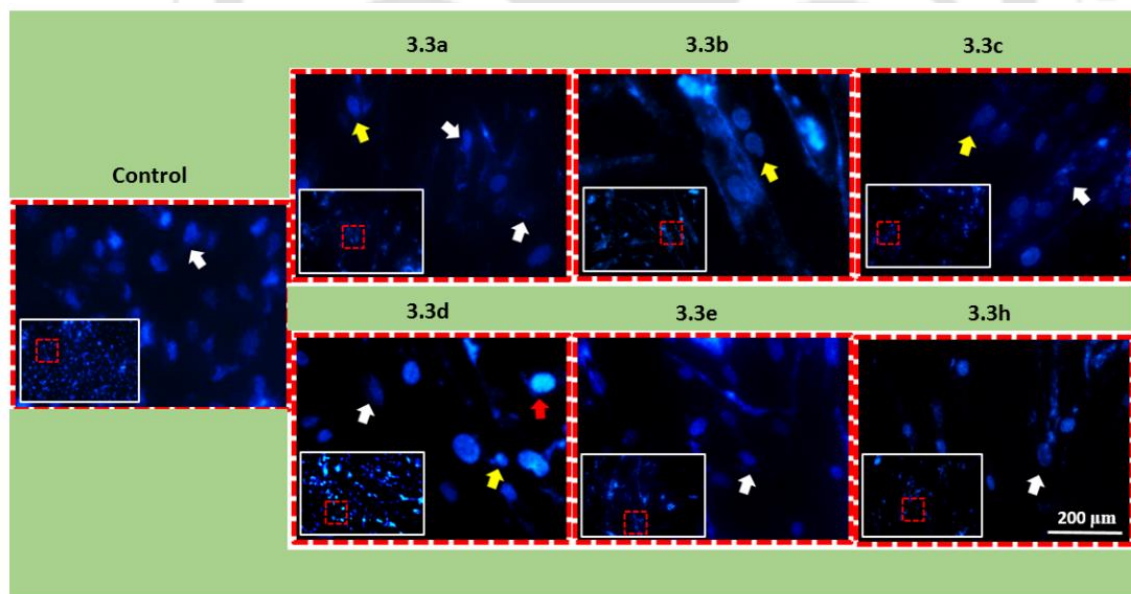


Figure 3.5. DAPI stained cells after treatment with the tetraalkynylated anthracene derivatives: **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e**, and **3.3h** against HDF cell line. The white arrows represent nuclear fragmentation, yellow arrows represent nuclear blebbing and the red arrows represent nuclear condensation.

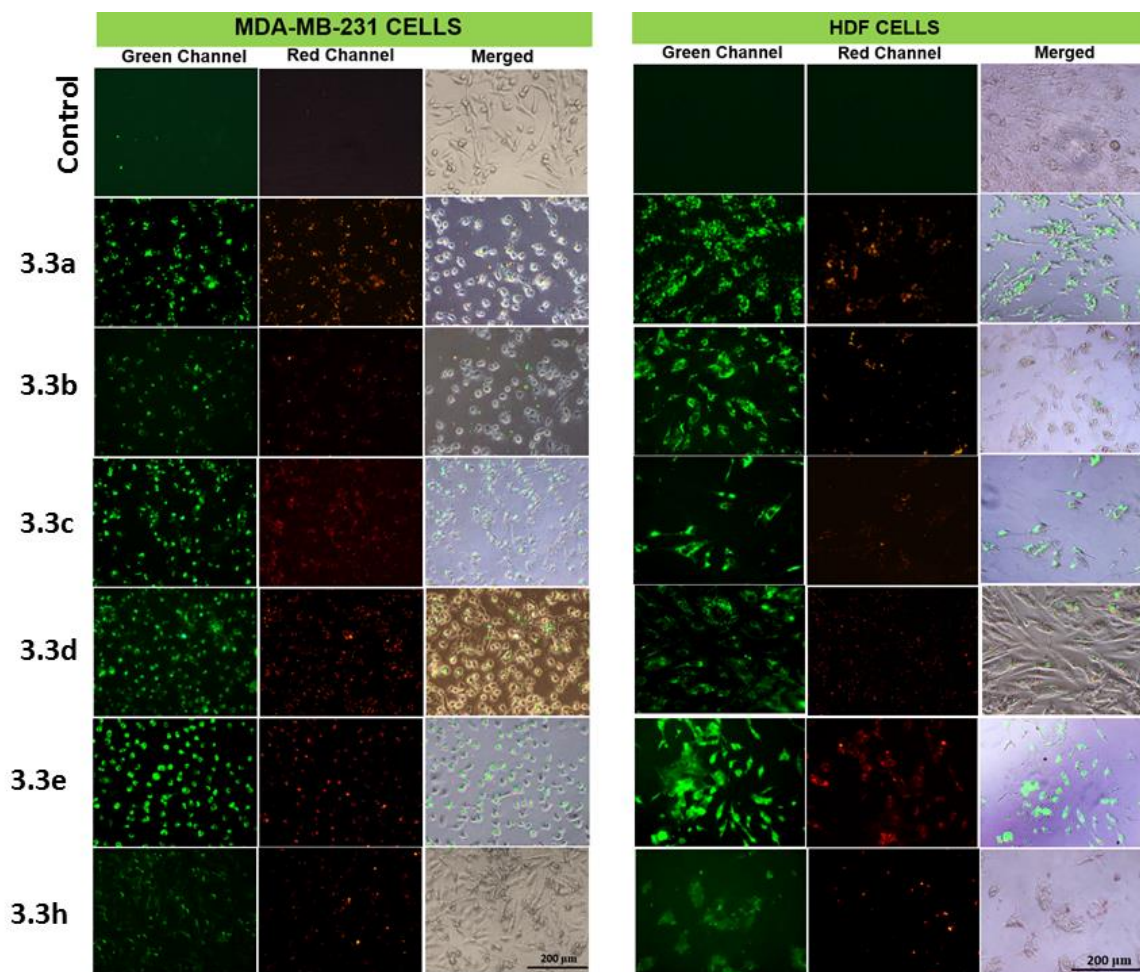


Figure 3.6. (a) PI stained cells after treatment with the tetraalkynylated anthracene derivatives: **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e**, **3.3h** against MDA-MB-231 cell line. Images presenting (i) fluorescent images of compound treated cells in green channel, (ii) fluorescent images of compound treated cells in red channel after PI staining (iii) merged images showing the presence of red PI stain where membrane disruption has occurred due to cellular localisation of the compounds inside the cells. (b) PI stained cells after treatment with the tetraalkynylated anthracene derivatives: **3.3a**, **3.3b**, **3.3c**, **3.3d**, **3.3e**, **3.3h** against HDF cell line. Images presenting (i) fluorescent images of compound treated cells in green channel, (ii) fluorescent images of compound treated cells in red channel after PI staining (iii) merged images showing the presence of red PI stain where membrane disruption has occurred due to cellular localisation of the compounds inside the cells.

fluorescent signal was obtained when both HDF and MDA-MB-231 cells were treated with **3.3c**, **3.3d** and **3.3e** (Figure 3.3). On other hand, in stark contrast to MDA-MB-231 cells treated with **3.3a** and **3.3b**, the corresponding **3.3a** and **3.3b** treated HDF cells showed bright green florescence (Figure 3.3). However,

when treated with **3.3h**, faint live cell fluorescence was observed from both MDA-MB-231 cells and HDF cells (Figure 3.3). While compound **3.3a** had not entered the cells and had localized on the cell surface, the compound **3.3h** showed no cell surface or intracellular localization (Figure 3.3).

DAPI staining was performed to check if treatment with the tetraalkynylated anthracene derivatives resulted in nuclear fragmentation and apoptosis (Figure 3.4). The MDA-MB-231 cells showed increased nuclear fragmentation, nuclear blebbing and nuclear condensation as compared to HDF cells (Figure 3.5) under the identical treatment conditions. This is commensurable with the results of the MTT assay which clearly shows that the tetraalkynylated anthracene derivatives are displaying increased cytotoxicity and selectivity against the MDA-MB-231 cell line. DAPI staining in HDF cell lines show the presence of numerous healthy rounded cells in each case as compared to MDA-MB-231 cells under the same experimental conditions, supporting the results obtained in MTT Assay (Figure 3.5).

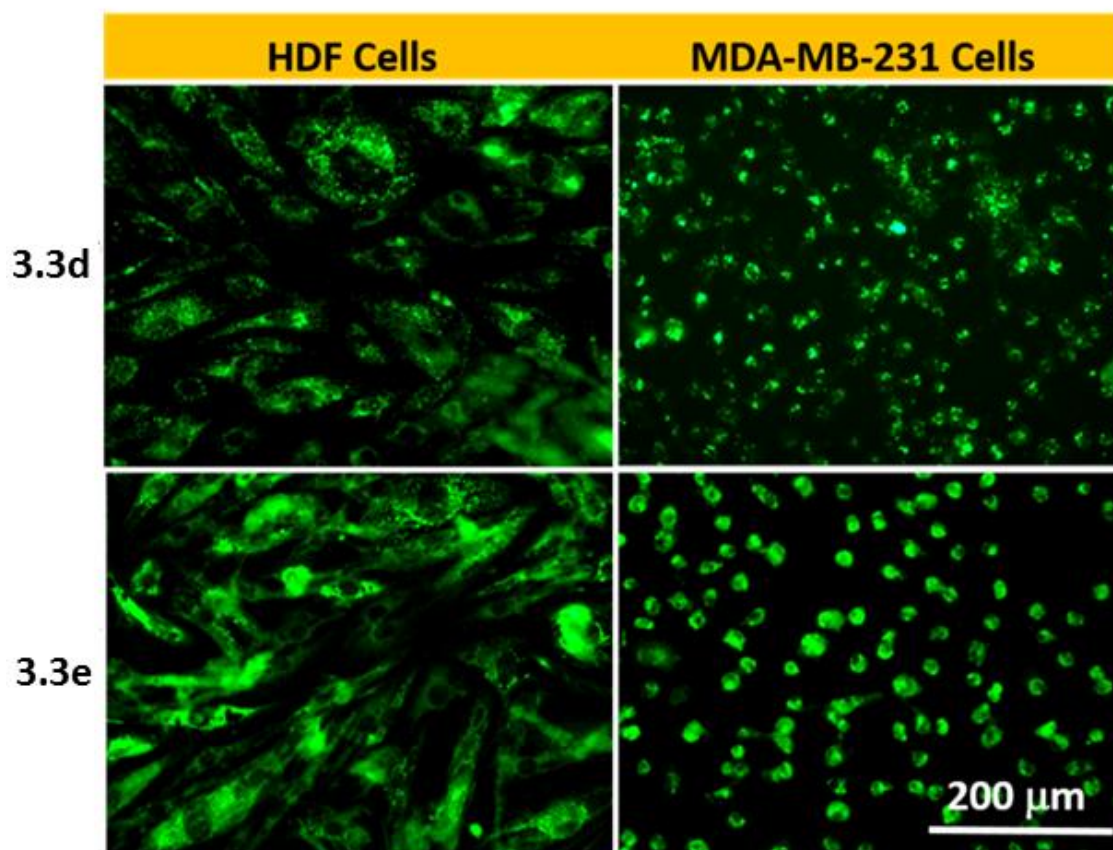


Figure 3.7. HDF cells and MDA-MB-231 cells stained with compounds **3.3d** and **3.3e**, showing intense green fluorescence which can be potential fluorescent dyes for bioimaging purposes.

PI staining was done to check whether the treatment with the tetraalkynylated anthracene derivatives resulted in membrane integration and necrosis. The MDA-MB-231 cells showed increased membrane disintegration (Figure 3.6) as compared to HDF cells under the same treatment conditions (Figure 3.6). This is commensurable with the results of the MTT Assay which shows clearly that the tetraalkynylated anthracene derivatives are displaying increased cytotoxicity and selectivity against the MDA-MB-231 cell line. The results obtained by PI staining clearly makes it evident that the tetraalkynylated anthracene derivatives are more cytotoxic against the MDA-MB-231 cell line as compared to HDF cells. They have an inherent selectivity towards the rapidly proliferating cancer cells.

It is now evident that compound **3.3d** (Figure 3.7) has the maximum cytotoxic effect as compared to the other compounds and is also selective towards the breast cancer cell line. It displays extensive cellular localization at $10\mu\text{M}$. Compound **3.3e** (Figure 3.7) is not cytotoxic at low concentrations of $10\mu\text{M}$ in either MDA-MB-231 or HDF cells. Interestingly it shows beautiful cellular localization at $10\mu\text{M}$ (Figure 3.7). In both the compounds, the cytoplasm gets stained while the nucleus remains unstained. Compound **3.3d** and **3.3e** can be potential anti-cancer agents, which can be further used for bioimaging and diagnostic purposes (to detect cancer cells in a biopsy sample).

3.3. Conclusions

An efficient method for the multi-fold Sonogashira coupling of a variety of aryl halides with aryl acetylene has been formulated using a catalytic system comprising of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) and CataCXium® A (1 mol%) in the presence of an equivalent of Cs_2CO_3 at room temperature under copper-free and amine-free conditions in a readily available green solvent. The reaction is tolerant to various substrates and the coupled products were obtained in good to excellent yields. The reactivity of various aryl halide substrate was in accordance to the C-X (X = Cl, Br and I) bond strength and followed the order $\text{Ar-I} > \text{Ar-Br} > \text{Ar-Cl}$. This is indicative of the fact that the oxidative addition of Ar-X is involved in the RDS of the overall catalytic cycle. The generic nature of the protocol was exhibited by accomplishing the Sonogashira coupling not only in one-fold but also in a multi-fold fashion thereby obtaining access to various valuable polycyclic aromatic hydrocarbons (PAHs).

The application of one such class of PAHs that involves the tetraalkynylated anthracenes towards investigation of their cytotoxic potentials was attempted. This led to an exciting set of observations that provided conclusive evidence for the possibility of two of the considered anthracene derivatives as potential candidates for anticancer therapy. Interestingly, the most efficient anthracene derivatives show cytotoxicity even at concentrations as low as $3.12 \mu\text{M}$. The anthracene derivatives induced apoptosis via nuclear fragmentation and membrane disruption as inferred from DAPI and PI staining. A more pronounced nuclear fragmentation and membrane disruption has been noticed in case of the MDA-MB-231 cells as compared to the HDF cells. This clearly is indicative of the probability of the anthracene derivatives being selective towards the TNBC cell lines. Gratifyingly the anthracene derivatives which were not so cytotoxic are still valuable considering their exciting fluorescence properties which renders them as potentially promising fluorescent dyes for bio-imaging purposes. The future scope of this study lies in the fact that being strongly fluorescent, these compounds can be used for bio-imaging purposes.

3.4. Experimental section

3.4.1. Materials and methods

A Constant supply of purified argon using a standard double manifold was used to perform all the reactions, unless otherwise mentioned. Avra, Sigma-Aldrich, SRL, and Merck Chemicals were the principle suppliers for the chemicals such as arylacetylene, aryl halides, anthracene, bromine, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{dba})_2$, $\text{Pd}(\text{OAc})_2$, NaOEt , NaOH , KOH , Na^tOBu , K^tOBu , K_2CO_3 , Cs_2CO_3 , NaHCO_3 , KHCO_3 , and K_3PO_4 were used without an additional purification. Along with this the solvents used in the experiments like 1,4-dioxane, toluene, and tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-Me-THF) were procured from Merck and were used without purification. All the reactions were performed under inert atmosphere and closed system, unless otherwise mentioned. The reactions were monitored using TLC analysis and column chromatography was done to purify the required product by means of Merck silica gel (100–200) mesh as the stationary phase. The reactions were monitored using TLC analysis and column chromatography was done to purify the required product by means of Merck silica gel (100–200) mesh as the stationary phase. The purified products were characterized via NMR analysis recorded by Bruker AVANCE 400, Bruker AVANCE 500, and Bruker AVANCE 600 operating at 400 MHz, 500 MHz and 600 MHz for ^1H NMR, 110 MHz (Bruker AVANCE 400),

126 MHz (Bruker AVANCE 500), and 151 MHz (Bruker AVANCE 600) for $^{13}\text{C}\{^1\text{H}\}$ NMR, 377 MHz (Bruker AVANCE 400) and 471 MHz (Bruker AVANCE 500) for ^{19}F NMR. Peak characterisation: s = singlet, d = doublet, t = triplet, and m = multiplet. High resolution mass spectra (HRMS) along with fast atom bombardment (FAB) analysis were acquired using Agilent technologies model G6564 QTOF and a double focusing magnetic sector mass spectrometer respectively in addition to electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). FT-IR measurements were documented using PerkinElmer IR spectrometer. The melting points were recorded in an open capillary tube with the usage of Buchi melting point B-540 apparatus.

3.4.2. Synthetic procedures

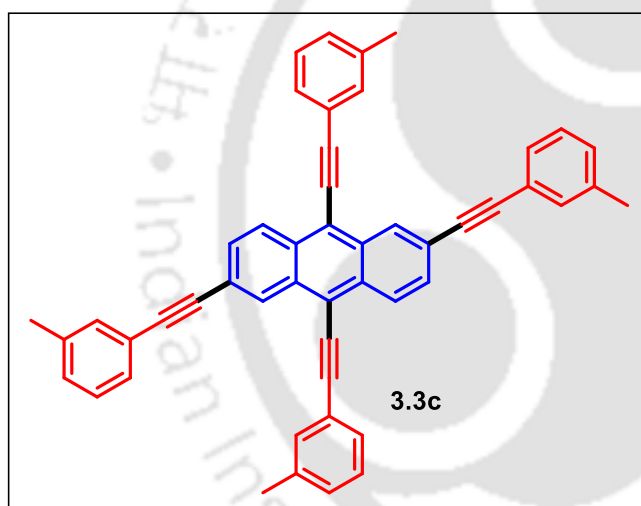
3.4.2.1. General synthetic protocol for Sonogashira coupling

A 10 mL Schlenk flask was taken, evacuated and charged with argon for three times. Aryl halide (1 equivalent), aryl acetylene (1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 or 1.0 mol% per halide), cataCXium[®] A (1.0 or 2.0 mol% per halide), Cs_2CO_3 (1 equivalent per halide) and, 2-MeTHF (5 ml) were added and stirred at room temperature for 48 h. The reaction was monitored by TLC analysis. After completion of the reaction, the organic solvent was evaporated under reduced pressure. The reaction mixture was extracted by DCM/EtOAc and washed with distilled H_2O (20 ml x 3). The organic phase was dried over anhydrous Na_2SO_4 , filtered and then solvent was evaporated under reduced pressure. The yield of the product (wherever applicable) was calculated by recording ^1H NMR of the crude product using toluene as internal standard. The crude product was purified by silica gel (100-200 mesh) column chromatography using a mixture of DCM/EtOAc and hexane as eluent prior to determining the isolated yield.

2,6,9,10-tetrakis(phenylethynyl)anthracene (3.3a).^{1c} Compound (3.3a) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), phenylacetylene (62 mg, 0.606 mmol, 1.0 equivalent per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium[®] A (1.4 mg, 0.00404 mmol, 1 mol% per halide) and Cs_2CO_3 (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was pass through 100-200 mesh size silica by using 50% DCM in Hexane as eluent and precipitate was obtained by slow evaporation of solvent at room temperature. The product (55 mg)

was obtained as orange solid with 94% isolated yield. Characterization described in **Chapter II** as **2.6** Page No 124-125.

2,6,9,10-tetrakis(*p*-tolylethynyl)anthracene (3.3b).^{1c} Compound (**3.3b**) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), *p*-ethynyltoluene (70 mg, 0.606 mmol, 1.0 equivalent per halide), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium® A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was pass through 100-200 mesh size silica by using 50% DCM in Hexane as eluent and precipitate was obtained by slow evaporation of solvent at room temperature. The product (58 mg) was obtained as orange solid with 91% isolated yield. Characterization described in **Chapter II** as **2.6a** Page No 125.



2,6,9,10-tetrakis(*m*-tolylethynyl)anthracene (3.3c). Compound (**3.3c**) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), *m*-ethynyltoluene (70 mg, 0.606 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium® A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0

equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was pass through 100-200 mesh size silica by using 50% DCM in Hexane as eluent and precipitate was obtained by slow evaporation of solvent at room temperature. The product (58 mg) was obtained as red solid with 91% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.82 (s, 2H, H-1 and H-5 of anthracene), 8.63 (d, *J* = 8.8 Hz, 2H, H-4 and H-8 of anthracene), 7.69 (dd, *J* = 8.9, 1.6 Hz, 2H, H-3 and H-7 of anthracene), 7.66 – 7.60 (m, 4H, *ortho*-protons of the tolyl groups), 7.48 (s, 2H, *ortho*-protons on two of the tolyl groups), 7.45 (d, *J* = 7.7 Hz, 2H, *ortho*-protons on two of the tolyl groups), 7.37 (t, *J* = 7.6 Hz, 2H, *para*-protons on two of the tolyl groups), 7.31 – 7.26 (m, 4H, *ortho*-protons on two of the tolyl groups and *meta*-protons on two of the tolyl groups), 7.19

(d, $J = 7.7$ Hz, 2H, *meta*-protons on two of the tolyl groups), 2.46 (s, 6H, Ar-CH₃), 2.39 (s, 6H, Ar-CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.5, 138.2, 132.5, 132.5, 132.0, 131.7, 130.8, 130.0, 129.6, 129.6, 129.1, 129.0, 128.6, 128.4, 127.6, 123.1, 123.0, 122.1, 118.5 (Ar), 103.4 (C≡C), 91.9 (C≡C), 89.9 (C≡C), 85.7 (C≡C), 21.5 (Ar-CH₃), 21.4 (Ar-CH₃). FT-IR (KBr, cm⁻¹) 3057 (Aromatic, C-H str), 3023 (Aromatic, C-H str), 2951 (Aromatic, C-H str), 2918 (Aromatic, C-H str), 2853 (-CH₃, C-H str), 2190 (C≡C str), 1613 (Aromatic, C=C str), 1598 (Aromatic, C=C str), 1576 (Aromatic, C=C str), 1484 (Aromatic, C=C str). HRMS (ESI) m/z [M+ H]⁺ calcd for C₅₀H₃₅ 635.2739, found 635.2706. mp = 222-224 °C.

2,6,9,10-tetrakis((2-methoxyphenyl)ethynyl)anthracene (3.3d).^{1c} Compound (3.3d) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), *o*-ethynylanisole (80 mg, 0.606 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium® A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was pass through 100-200 mesh size silica by using 50% DCM in Hexane as eluent and precipitate was obtained by slow evaporation of solvent at room temperature. The product (67 mg) was obtained as red solid with 95% isolated yield. Characterization described in **Chapter II** as **2.6b** Page No. 126.

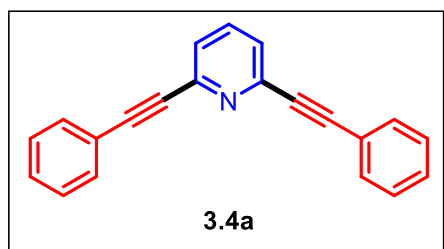
4,4',4'',4'''-(anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(N,N-dimethylaniline) (3.3e).^{1c} Compound (3.3e) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), *p*-ethynyl-*N,N*-dimethylaniline (88 mg, 0.606 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium® A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 60% DCM in hexane as eluent. Yield 75%; brown solid; calculated by ¹H NMR. Characterization described in **Chapter II** as **2.6e** Page No. 128.

2,2',2'',2'''-(anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrathiophene (3.3f).^{1c} Compound (3.3f) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1

equivalent), *o*-ethynylthiophene (66 mg, 0.606 mmol, 1.5 equivalent per halide), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium[®] A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 40% DCM in hexane as eluent. Yield 21%; yellow powder; calculated by ¹H NMR. Characterization described in **Chapter II** as **2.6h** Page No. 130-131.

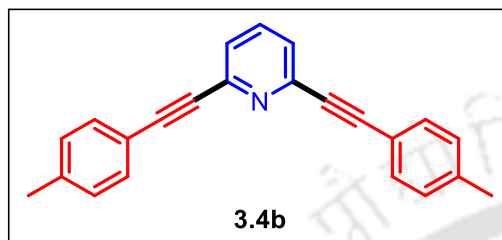
4,4',4'',4'''-(anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(N,N-diphenylaniline) (3.3g).^{1c} Compound (3.3g) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), *p*-ethynyl-*N,N*-diphenylaniline (163 mg, 0.606 mmol, 6.0 equivalent), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium[®] A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 70% DCM in hexane as eluent. Yield 71%; maroon solid; calculated by ¹H NMR. Characterization described in **Chapter II** as **2.6f** Page No. 129.

((anthracene-2,6,9,10-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(benzene-4,1-diyl))tetrakis(phenylmethanone) (3.3h).^{1c} Compound (3.3h) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent), (*p*-ethynylphenyl)(phenyl)methanone (125 mg, 0.606 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.00202 mmol, 0.5 mol% per halide), cataCXium[®] A (1.4 mg, 0.00404 mmol, 1.0 mol% per halide) and Cs₂CO₃ (131 mg, 0.404 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 90% DCM in hexane as eluent. Yield 81%; maroon solid; calculated by ¹H NMR. Characterization described in **Chapter II** as **2.6d** Page No. 127.



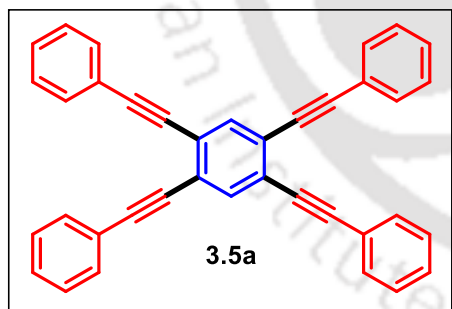
2,6-bis(phenylethynyl)pyridine (3.4a).³² Compound (3.4a) was synthesized from 2,6-dibromopyridine (100 mg, 0.42 mmol, 1 equivalent), phenylacetylene (129 mg, 1.26 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (1.1 mg, 0.00422 mmol, 0.5 mol% per halide), cataCXium[®] A (3 mg, 0.00844 mmol, 1.0 mol% per halide) and Cs₂CO₃ (274 mg, 0.844 mmol, 1.0 equivalent per halide)

by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 30% DCM in hexane as eluent. The product (88 mg) was obtained as white colour solid with 75% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.69 (t, J = 7.8 Hz, 1H), 7.61 (d, J = 5.0 Hz, 4H), 7.48 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 5.9 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 143.9, 136.6, 132.2, 129.2, 128.5, 126.3, 122.2, 89.9, 88.3.



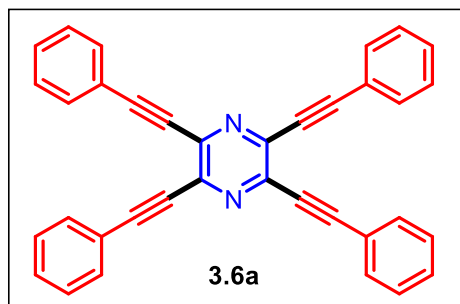
2,6-bis(*p*-tolylethynyl)pyridine (3.4b).³³ Compound (3.4b) was synthesized from 2,6-dibromopyridine (100 mg, 0.42 mmol, 1 equivalent), *p*-ethynyltoluene (146 mg, 1.26 mmol, 1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.09 mg, 0.00422 mmol, 1.0 mol%),

cataCXium[®] A (3 mg, 0.00844 mmol, 2.0 mol%), and Cs_2CO_3 (274 mg, 0.844 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 30% DCM in hexane as eluent. The product (102 mg) was obtained as white colour solid with 79% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.66 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 4H), 7.45 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 4H), 2.38 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 144.0, 139.5, 136.5, 132.1, 129.3, 126.1, 119.2, 90.2, 87.9, 21.7.

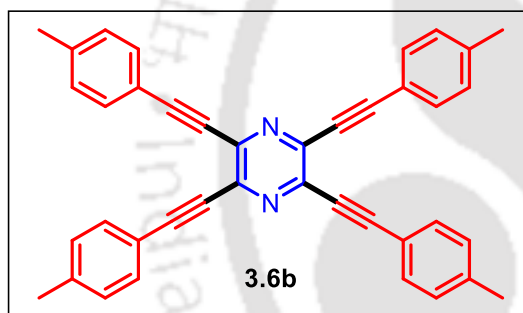


1,2,4,5-tetrakis(phenylethynyl)benzene (3.5a).³⁴

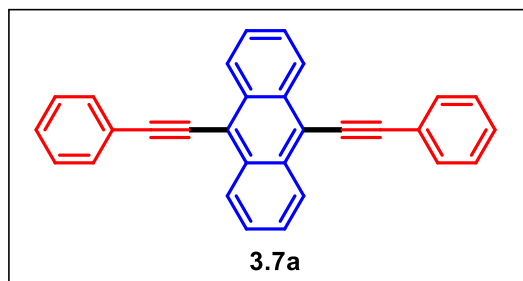
Compound (3.5a) was synthesized from 1,2,4,5-tetraiodobenzene (100 mg, 0.17 mmol, 1 equivalent), phenylacetylene (105 mg, 1.03 mmol, 1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.9 mg, 0.0034 mmol, 0.5 mol% per halide) and cataCXium[®] A (2.5 mg, 0.0070 mmol 1.0 mol% per halide) and Cs_2CO_3 (228 mg, 0.7 mmol, 1 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (73 mg) was obtained as white solid with 90% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.77 (s, 2H), 7.62 – 7.54 (m, 8H), 7.37 (d, J = 2.8 Hz, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 135.0, 131.9, 128.9, 128.6, 125.5, 123.1, 95.6, 87.6.

**2,3,5,6-tetrakis(phenylethynyl)pyrazine (3.6a).³⁵**

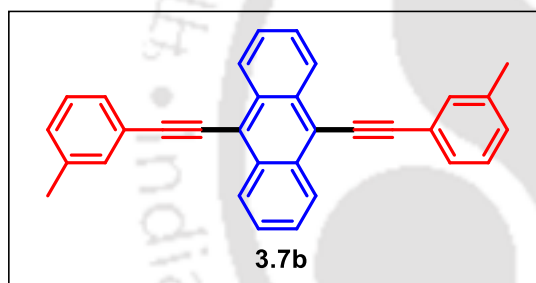
Compound **(3.6a)** was synthesized from tetrachloropyrazine (100 mg, 0.46 mmol, 1 equivalent), phenylacetylene (281 mg, 2.76 mmol, 1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (2.4 mg, 0.00918 mmol, 0.5 mol% per halide), cataCXium[®] A (6.6 mg, 0.01836 mmol 1.0 mol% per halide) and Cs_2CO_3 (598 mg, 1.836 mmol, 1 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 30% DCM in hexane as eluent. The product (95 mg) was obtained as orange solid with 43% isolated yield. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (dd, $J = 7.9, 1.8$ Hz, 8H), 7.50 – 7.33 (m, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.2, 132.4, 130.0, 128.7, 121.8, 97.9, 86.2.

**2,3,5,6-tetrakis(p-tolyethynyl)pyrazine (3.6b).³⁵**

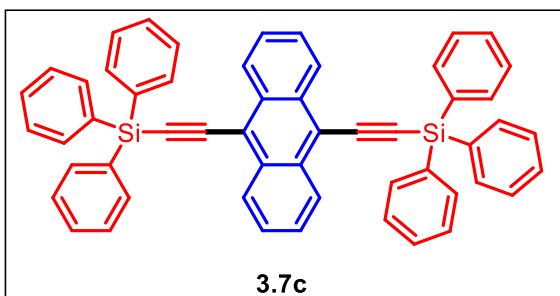
Compound **(3.6b)** was synthesized from tetrachloropyrazine (100 mg, 0.46 mmol, 1 equivalent), *p*-ethynyltoluene (281 mg, 2.76 mmol, 1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (2.4 mg, 0.00918 mmol, 0.5 mol% per halide) and cataCXium[®] A (6.6 mg, 0.01836 mmol 1.0 mol% per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (52 mg) was obtained as white solid with 21% isolated yield. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.9$ Hz, 8H), 7.20 (d, $J = 7.8$ Hz, 7H), 2.40 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 140.4, 139.1, 132.3, 129.5, 118.8, 98.1, 85.9, 21.8.

**9,10-bis(phenylethynyl)anthracene (3.7a).**³⁶

Compound (3.7a) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent), phenylacetylene (92 mg, 0.9 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.003 mmol, 0.5 mol% per halide), cataCXium® A (2.1 mg, 0.006 mmol, 1.0 mol% per halide) and Cs₂CO₃ (193 mg, 0.6 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (107 mg) was obtained as brown colour solid with 94% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.70 (dd, *J* = 6.6, 3.3 Hz, 4H), 7.82 – 7.75 (m, 4H), 7.65 (dd, *J* = 6.7, 3.2 Hz, 4H), 7.53 – 7.39 (m, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 132.2, 131.8, 128.8, 128.7, 127.4, 126.9, 123.5, 118.6, 102.5, 86.6.

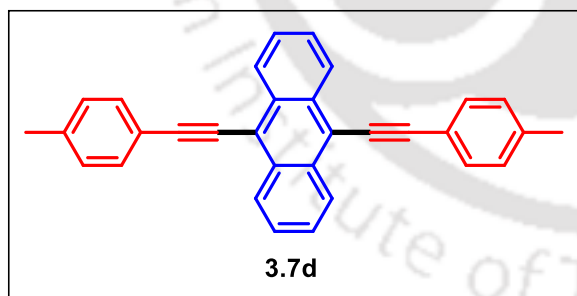
**9,10-bis(*m*-tolyethynyl)anthracene (3.7b).**

Compound (3.7b) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent), *m*-ethynyltoluene (104 mg, 0.90 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.003 mmol, 0.5 mol% per halide), cataCXium® A (2.1 mg, 0.006 mmol, 1.0 mol% per halide) and Cs₂CO₃ (193 mg, 0.6 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (110 mg) was obtained as orange colour solid with 90% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.70 (dd, *J* = 6.6, 3.3 Hz, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.65 (dd, *J* = 6.7, 3.2 Hz, 4H, H-2, H-3, H-6 and H-7 of anthracene), 7.62 – 7.55 (m, 4H, *ortho*-protons of the tolyl groups), 7.35 (t, *J* = 7.6 Hz, 2H, *para*-protons of the tolyl groups), 7.26 – 7.22 (m, 2H, *meta*-protons of the tolyl groups), 2.45 (s, 6H, Ar-CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.4, 132.3, 132.2, 129.7, 128.9, 128.6, 127.4, 126.9, 123.3, 118.6 (Ar), 102.7 (C≡C), 86.3 (C≡C), 21.4 (Ar-CH₃). FT-IR (KBr, cm⁻¹) 3055 (Aromatic, C-H str), 2950 (Aromatic, C-H str), 2916 (Aromatic, C-H str), 2845 (-CH₃ C-H str), 2190 (C≡C str), 1598 (Aromatic, C=C str), 1575 (Aromatic, C=C str), 1486 (Aromatic, C=C str). HRMS (ESI) *m/z* [M+ H]⁺ calcd for C₃₂H₂₃ 407.1800, found 407.1789. mp = 182-184 °C.

**9,10-bis((triphenylsilyl)ethynyl)anthracene**

(3.7c): Compound (3.7c) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent), ethynyltriphenylsilane (256 mg, 0.90 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.003 mmol, 0.5 mol%

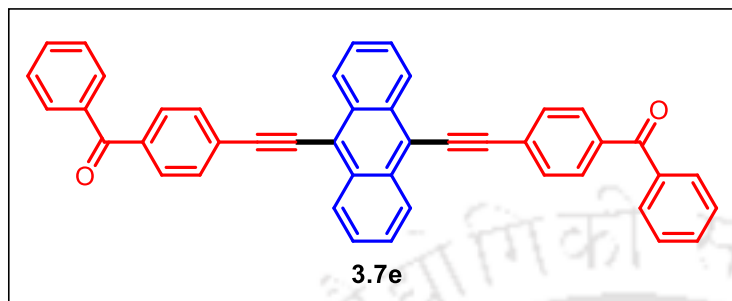
per halide), cataCXium[®] A (2.1 mg, 0.006 mmol, 1.0 mol% per halide) and Cs₂CO₃ (193 mg, 0.6 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (194 mg) was obtained as brown colour solid with 88% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.65 (dd, *J* = 6.7, 3.3 Hz, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.93 – 7.78 (m, 12H, Ar-H), 7.65 (dd, *J* = 6.7, 3.2 Hz, 4H, H-2, H-3, H-6 and H-7 of anthracene), 7.59 (dd, *J* = 6.8, 3.3 Hz, 4H, Ar-H), 7.46 (dt, *J* = 14.3, 7.0 Hz, 18H, Ar-H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 135.8, 133.5, 132.8, 130.2, 128.3, 127.4, 118.6 (Ar), 106.1 (C≡C), 103.4 (C≡C). FT-IR (KBr, cm⁻¹) 3067 (Aromatic, C-H str), 3049 (Aromatic, C-H str), 2916 (Aromatic, C-H str), 2955 (Aromatic, C-H str), 2916 (Aromatic, C-H str), 2127 (C≡C str), 1427 (Aromatic, C=C str), 1374 (Aromatic, C=C str). HRMS (ESI) *m/z* [M+ H]⁺ calcd for C₅₄H₃₉Si₂ 743.2590, found 743.2575. mp = 249-251 °C.

**9,10-bis(*p*-ethynylphenyl)anthracene (3.7d).**³⁷

Compound (3.7d) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent), *p*-ethynyltoluene (104 mg, 0.90 mmol, 1.5 equivalents per halide), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.003 mmol, 0.5 mol%

per halide), cataCXium[®] A (2.1 mg, 0.006 mmol, 1.0 mol% per halide) and Cs₂CO₃ (193 mg, 0.6 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (113 mg) was obtained as brown colour solid with 93% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.69 (dd, *J* = 6.7, 3.3 Hz, 4H), 7.67 (d, *J* = 7.7 Hz, 4H), 7.63 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.27 (d, *J*

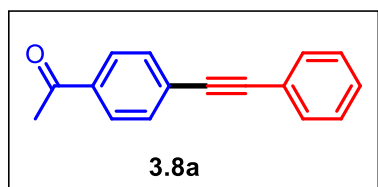
= 8.1 Hz, 4H), 2.44 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 139.0, 132.2, 131.7, 129.4, 127.4, 126.8, 120.5, 118.6, 102.7, 86.0, 21.7.



((anthracene-9,10-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(phenylmethanone)

(3.7e): Compound (3.7e) was synthesized from 9,10-dibromoanthracene (50 mg, 0.15

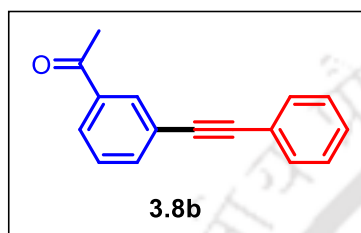
mmol, 1 equivalent), (*p*-ethynylphenyl)(phenyl)methanone (92 mg, 0.45 mmol, 1.5 equivalents per halide), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.4 mg, 0.0015 mmol, 0.5 mol% per halide), cataCXium[®] A (1.0 mg, 0.006 mmol, 1.0 mol% per halide), and Cs_2CO_3 (193 mg, 0.003 mmol, 1.0 equivalent per halide) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 60% DCM in hexane as eluent. The product (80 mg) was obtained as orange colour solid with 92% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.71 (ddd, J = 6.7, 3.3, 1.7 Hz, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.91 (q, J = 7.4, 6.7 Hz, 8H, *ortho*-protons of the phenyl group connected to COPh and *meta*-protons of the phenyl group connected to the alkyne), 7.85 (d, J = 8.1 Hz, 4H, H-2, H-3, H-6 and H-7 of anthracene), 7.72 – 7.67 (m, 4H, *ortho*-protons of the phenyl group connected to the alkyne), 7.64 (t, J = 7.3 Hz, 2H, *para*-protons of the phenyl group connected to the COPh), 7.53 (t, J = 7.6 Hz, 4H, *meta*-protons of the phenyl group connected to the COPh). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.0 (C=O), 137.5, 137.3, 132.8, 132.3, 131.6, 130.4, 130.1, 128.5, 127.6, 127.3, 127.3, 118.6 (Ar), 102.0 ($\text{C}\equiv\text{C}$), 89.5 ($\text{C}\equiv\text{C}$). FT-IR (KBr, cm^{-1}) 3055 (Aromatic, C-H str), 3045 (Aromatic, C-H str), 2196 ($\text{C}\equiv\text{C}$ str), 1650 (C=O str) 1596 (Aromatic, C=C str). HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{44}\text{H}_{27}\text{O}_2$ 587.2011, found 587.2004. mp = 249-251 °C.



1-(4-(phenylethynyl)phenyl)ethan-1-one (3.8a):³⁸ Compound (3.8a) was synthesized from *p*-bromoacetophenone (100 mg, 0.5 mmol, 1 equivalent), phenylacetylene (77 mg, 0.75 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.3 mg, 0.005 mmol, 1.0 mol%),

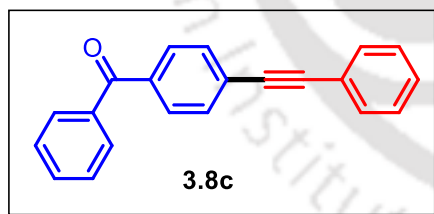
cataCXium[®] A (3.6 mg, 0.010 mmol, 2.0 mol%) and Cs_2CO_3 (162 mg, 0.5 mmol, 1.0 equivalent)

by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 2% ethyl acetate in hexane as eluent. The product (106 mg) was obtained as white solid with 96% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 3.9 Hz, 2H), 7.37 (d, J = 3.3 Hz, 3H), 2.62 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 197.5, 136.3, 131.8, 131.8, 128.9, 128.5, 128.4, 128.3, 122.7, 92.8, 88.7, 26.7.



1-(3-(phenylethynyl)phenyl)ethan-1-one (8b).³⁹ Compound (8b) was synthesized from *m*-bromoacetophenone (100 mg, 0.5 mmol, 1 equivalent), phenylacetylene (77 mg, 0.75 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.3 mg, 0.005 mmol, 1.0 mol%), cataCXium[®] A (3.6 mg, 0.010 mmol, 2.0 mol%) and Cs_2CO_3 (162

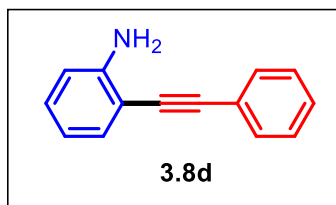
mg, 0.5 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 2% ethyl acetate in hexane as eluent. The product (88 mg) was obtained as brown liquid with 80% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.11 (s, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 3.9 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.36 (s, 3H), 2.63 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 197.5, 137.3, 135.9, 131.8, 131.7, 128.8, 128.7, 128.5, 127.9, 124.0, 122.9, 90.5, 88.4, 26.7.



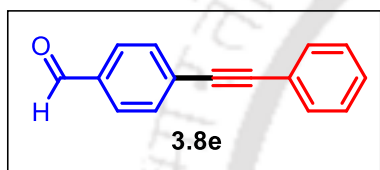
phenyl(4-(phenylethynyl)phenyl)methanone (3.8c).⁴⁰

Compound (3.8c) was synthesized from *p*-bromobenzophenone (100 mg, 0.38 mmol, 1 equivalent), phenylacetylene (58 mg, 0.57 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1 mg, 0.0038 mmol, 1.0 mol%),

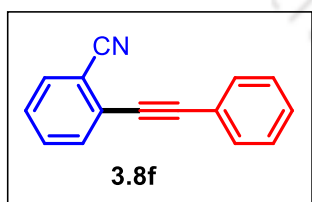
cataCXium[®] A (2.7 mg, 0.0076 mmol, 2.0 mol%) and Cs_2CO_3 (124 mg, 0.38 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 5% ethyl acetate in hexane as eluent. The product (101 mg) was obtained as off white solid with 93% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, J = 7.4 Hz, 4H), 7.62 (dd, J = 21.1, 7.7 Hz, 3H), 7.56 (d, J = 3.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 3.8 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.1, 137.6, 136.9, 132.6, 131.9, 131.5, 130.2, 130.1, 128.9, 128.6, 128.5, 127.7, 122.8, 92.6, 88.8.



2-(phenylethynyl)aniline (8d).⁴¹ Compound (8d) was synthesized from *o*-bromoaniline (100 mg, 0.58 mmol, 1 equivalent), phenylacetylene (89 mg, 0.87 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (1.5 mg, 1.0 mol%), cataCXium[®] A (4.1 mg, 2.0 mol%) and Cs₂CO₃ (188 mg, 0.58 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 30% ethyl acetate in hexane as eluent. The product (25 mg) was obtained as brown solid with 22% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, *J* = 6.1 Hz, 2H), 7.36 (dd, *J* = 14.0, 6.7 Hz, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 4.28 (s, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.9, 132.2, 131.6, 129.8, 128.5, 128.3, 123.4, 118.1, 114.4, 108.0, 94.8, 86.0.

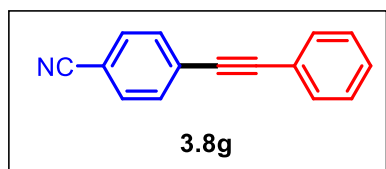


***p*-(phenylethynyl)benzaldehyde (3.8e).**⁴² Compound (3.8e) was synthesized from *p*-bromobenzaldehyde (100 mg, 0.54 mmol, 1 equivalent), phenylacetylene (83 mg, 0.81 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (1.4 mg, 0.0054 mmol, 1.0 mol%) cataCXium[®] A (3.9 mg, 0.0108 mmol, 2.0 mol%) and Cs₂CO₃ (0.81 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (86 mg) was obtained as brown liquid with 77% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 10.02 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.56 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.43 – 7.33 (m, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 191.6, 135.5, 132.2, 131.9, 129.7, 129.7, 129.1, 128.6, 122.6, 93.6, 88.6.

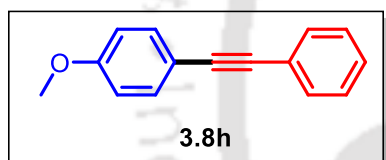


***o*-(phenylethynyl)benzonitrile (3.8f).**⁴³ Compound (3.8f) was synthesized from *o*-bromobenzonitrile (100 mg, 0.55 mmol, 1 equivalent), phenylacetylene (84 mg, 0.82 mmol, 1.5 equiv.), Pd(CH₃CN)₂Cl₂ (1.4 mg, 0.0055 mmol, 1.0 mol%), cataCXium[®] A (3.9 mg, 0.011 mmol, 2.0 mol%) and Cs₂CO₃ (178 mg, 0.55 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 5% ethyl acetate in hexane as eluent. The product (97 mg) was obtained as brown liquid with 87% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.67 (d, *J* = 7.8 Hz, 1H),

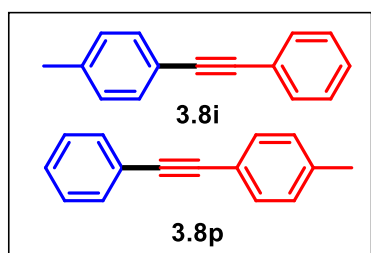
7.62 (s, 3H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.44 – 7.36 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 132.7, 132.5, 132.2, 132.1, 129.3, 128.5, 128.3, 127.3, 122.1, 117.6, 115.4, 96.1, 85.7.



***p*-(phenylethynyl)benzonitrile (3.8g).**⁴³ Compound (3.8g) was synthesized from *p*-bromobenzonitrile (100 mg, 0.55 mmol, 1 equivalent), phenylacetylene (84 mg, 0.82 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.4 mg, 0.0055 mmol, 1.0 mol%), cataCXium® A (3.94 mg, 0.011 mmol, 2.0 mol%) and Cs_2CO_3 (178 mg, 0.55 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (81 mg) was obtained as white solid with 73% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.64 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.55 (dd, $J = 6.4, 2.7$ Hz, 2H), 7.38 (d, $J = 5.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 132.2, 132.2, 131.9, 129.2, 128.6, 128.4, 122.3, 118.6, 111.6, 93.9, 87.8.

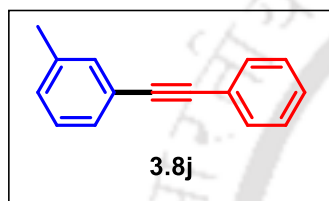


1-methoxy-4-(phenylethynyl)benzene (3.8h).³⁸ Compound (3.8h) was synthesized from *p*-bromoanisole (100 mg, 0.53 mmol, 1 equivalent), phenylacetylene (82 mg, 0.80 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.7 mg, 0.0027 mmol 0.5 mol%), cataCXium® A (1.9 mg, 0.0053 1.0 mol%) and Cs_2CO_3 (173 mg, 0.53 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (72 mg) was obtained as off white solid with 65% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.54 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.29 (m, 3H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.7, 133.2, 131.5, 128.4, 128.0, 123.7, 115.5, 114.1, 89.5, 88.2, 55.4.



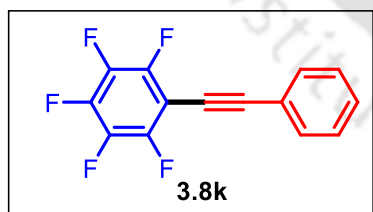
1-methyl-4-(phenylethynyl)benzene (3.8i & 3.8p).⁴⁴ Compound (3.8i) was synthesized from *p*-bromotoluene (100 mg, 0.58 mmol, 1 equivalent), phenylacetylene (89 mg, 0.87 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.8 mg, 0.0029 mmol, 0.5 mol%), cataCXium® A (2 mg, 0.0058 mmol, 1.0 mol%) and Cs_2CO_3 (189 mg, 0.58 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The

crude product was purified by column chromatography by using hexane as eluent. Compound (**3.8p**) was synthesized from bromobenzene (100 mg, 0.64 mmol, 1 equivalent), *p*-ethynyltoluene (112 mg, 0.96 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.0032 mmol, 0.5 mol%), cataCXium[®] A (2.3 mg, 0.0064 mmol, 1.0 mol%) and Cs₂CO₃ (207 mg, 0.64 mmol, 1 equivalent) by using general synthetic protocol of Sonogashira reaction. The product (**3.8i** = 102 mg and **3.8p** = 108 mg) were obtained as white solid with 91% (**3.8i**) and 88% (**3.8p**) isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, *J* = 5.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.5, 131.6, 131.6, 129.2, 128.4, 128.2, 123.6, 120.3, 89.6, 88.8, 21.6.



1-methyl-3-(phenylethynyl)benzene (3.8j).⁴⁴ Compound (**3.8j**) was synthesized from *m*-bromotoluene (100 mg, 0.58 mmol, 1 equivalent), phenylacetylene (89 mg, 0.87 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.8 mg, 0.0029 mmol, 0.5 mol%), cataCXium[®] A (2

mg, 0.0058 mmol, 1.0 mol%) and Cs₂CO₃ (189 mg, 0.58 mmol,) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (X = 100 mg) were obtained as colorless liquid with 89% isolated yield. ¹H NMR (600 MHz, CHCl₃) δ 7.57 – 7.50 (m, 2H), 7.40 – 7.29 (m, 5H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 2.36 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.1, 132.3, 131.7, 129.3, 128.8, 128.4, 128.3, 128.3, 123.5, 123.2, 89.7, 89.1, 21.3.

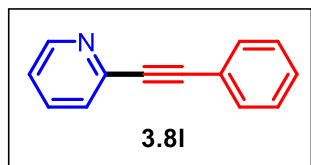


1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene (3.8k).⁴⁵

Compound (**3.8k**) was synthesized from pentafluoriodobenzene (293 mg, 1 mmol, 1 equivalent), phenylacetylene (153 mg, 1.5 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (2.6 mg, 0.01 mmol, 1.0 mol%), cataCXium[®] A (7.2 mg, 0.02 mmol, 2.0 mol%) and

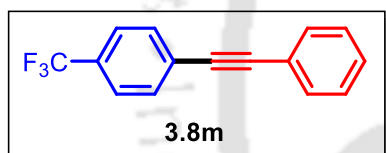
Cs₂CO₃ (325 mg, 1 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (61 mg) was obtained as white solid with 23% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.35 (m, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -136.49 (d, *J* =

14.4 Hz, 2F), -153.74 – -156.76 (m, 1F), -162.89 (dd, $J = 21.0, 14.8$ Hz, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 132.6, 129.3, 128.5, 121.9, 81.7, 74.0.



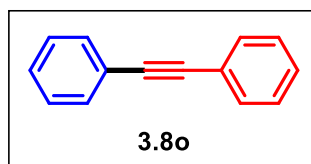
2-(phenylethynyl)pyridine (3.8l).⁴⁶ Compound (3.8l) was synthesized from *o*-bromopyridine (100 mg, 0.63 mmol, 1 equiv.), phenylacetylene (97 mg, 0.95 mmol, 1.5 equiv.), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.8 mg, 0.032 mmol, 0.5 mol%), cataCXium[®] A (2.3 mg, 0.0063 mmol, 1.0 mol%) and Cs_2CO_3 (205 mg, 0.63 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 2% ethyl acetate in hexane as eluent. The product (61 mg) was obtained as colorless liquid with 54% isolated yield.

^1H NMR (600 MHz, CDCl_3) δ 8.62 (d, $J = 4.9$ Hz, 1H), 7.71 – 7.67 (m, 1H), 7.61 (dd, $J = 6.3, 2.7$ Hz, 2H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 5.3$ Hz, 3H), 7.24 (d, $J = 6.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 150.0, 143.4, 136.4, 132.2, 129.1, 128.5, 127.3, 122.9, 122.3, 89.7, 88.5.



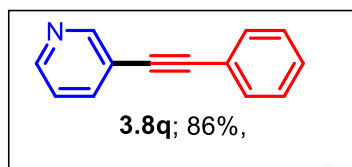
1-(phenylethynyl)-4-(trifluoromethyl)benzene (3.8m).³⁸

Compound (3.8m) was synthesized from 1-iodo-4-(trifluoromethyl)benzene (100 mg, 0.37 mmol, 1 equivalent), phenylacetylene (56 mg, 0.55 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.9 mg, 0.0036 mmol, 1.0 mol%), cataCXium[®] A (2.6 mg, 0.0073 mmol, 2.0 mol%) and Cs_2CO_3 (120 mg, 0.37 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (31 mg) was obtained as white solid with 35% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.62 (q, $J = 8.3$ Hz, 4H), 7.57 – 7.50 (m, 2H), 7.37 (q, $J = 3.1, 2.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 131.95, 131.89, 130.17, 129.95, 128.98, 128.60, 127.27, 125.43 (d, $J = 3.9$ Hz), 125.00, 123.19, 122.70, 91.89, 88.10. ^{19}F NMR (471 MHz, CDCl_3) δ -62.8.

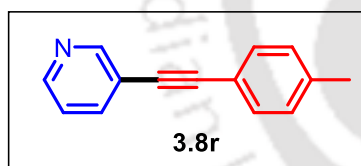


1,2-diphenylethyne (3.8o).⁴⁷ Compound (3.8o) was synthesized from bromobenzene (100 mg, 0.64 mmol, 1 equivalent), phenylacetylene (98 mg, 0.96 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.8 mg, 0.0032 mmol, 0.5 mol%), cataCXium[®] A (2.3 mg, 0.0064 mmol, 1.0 mol%) and Cs_2CO_3 (207 mg, 0.64 mmol, 1.0 equivalent) by using general synthetic protocol of

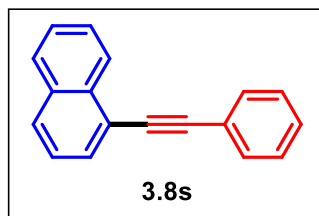
Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (104 mg) was obtained as colourless liquid with 91% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.57 (d, J = 7.8 Hz, 4H), 7.38 (d, J = 7.3 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 131.7, 128.4, 123.4, 89.5.



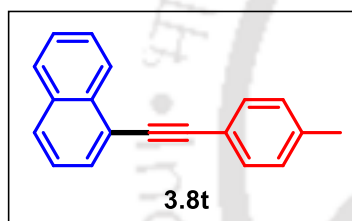
3-(phenylethynyl)pyridine (3.8q).³⁸ Compound (**3.8q**) was synthesized from 3-bromopyridine (100 mg, 0.63 mmol, 1.0 equivalent), phenylacetylene (97 mg, 0.95 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.8 mg, 0.0032 mmol, 0.5 mol%), cataCXium[®] A (2.3 mg, 0.0063 mmol, 1.0 mol%) and Cs_2CO_3 (205 mg, 0.63 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 2 % ethyl acetate in hexane as eluent. The product (97 mg) was obtained as brown colour solid with 86% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.78 (s, 1H), 8.56 (d, J = 4.9 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.55 (dd, J = 6.5, 3.0 Hz, 2H), 7.38 (d, J = 3.0 Hz, 3H), 7.33 (dd, J = 7.9, 5.0 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 151.7, 148.0, 139.1, 131.8, 129.0, 128.6, 123.4, 122.5, 120.9, 93.2, 85.7.



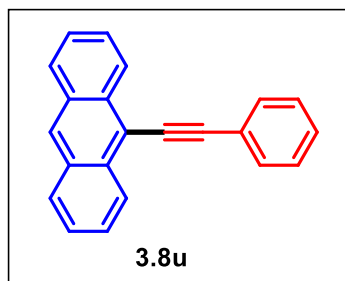
3-(p-tolyethynyl)pyridine (3.8r).⁴⁸ Compound (**3.8r**) was synthesized from 3-bromopyridine (100 mg, 0.63 mmol, 1 equivalent), *p*-ethynyltoluene (110 mg, 0.94 mmol, 1.5 equivalents), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.8 mg, 0.0032 mmol, 0.5 mol%), cataCXium[®] A (2.3 mg, 0.0063 mmol, 1.0 mol%) and Cs_2CO_3 (205 mg, 0.63 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 2% ethyl acetate hexane as eluent. The product (105 mg) was obtained as white solid with 86% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.75 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 4.8, 1.7 Hz, 1H), 7.79 (dt, J = 7.9, 1.9 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.27 (dd, J = 7.8, 4.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 152.3, 148.5, 139.2, 138.5, 131.7, 129.3, 123.1, 120.8, 119.5, 93.0, 85.4, 21.7.



1-(phenylethynyl)naphthalene (3.8s).⁴⁹ Compound (3.8s) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent), phenylacetylene (74 mg, 0.72 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.6 mg, 0.0024 mmol, 0.5 mol%), cataCXium[®] A (1.7 mg, 0.0048 mmol, 1.0 mol%) and Cs₂CO₃ (156 mg, 0.48 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (100 mg) was obtained as colorless liquid with 91% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 14.6, 8.2 Hz, 2H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 6.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.35 (m, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 133.4, 133.3, 131.8, 130.5, 128.9, 128.5, 128.5, 128.4, 126.9, 126.5, 126.3, 125.4, 123.5, 121.0, 94.4, 87.6.

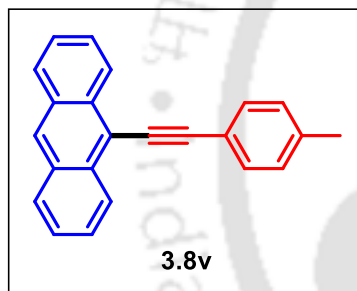


1-(p-tolyethynyl)naphthalene (3.8t).⁴⁹ Compound (3.8t) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent), *p*-ethynyltoluene (84 mg, 0.72 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.6 mg, 0.0024 mmol, 0.5 mol%), cataCXium[®] A (1.7 mg, 1.0 mol%) and Cs₂CO₃ (156 mg, 0.48 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (107 mg) was obtained as white solid with 92% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.46 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.54 (dd, *J* = 13.8, 7.5 Hz, 3H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.7, 133.4, 133.3, 131.7, 130.3, 129.3, 128.7, 128.4, 126.8, 126.5, 126.4, 125.4, 121.2, 120.4, 94.6, 87.0, 21.7.



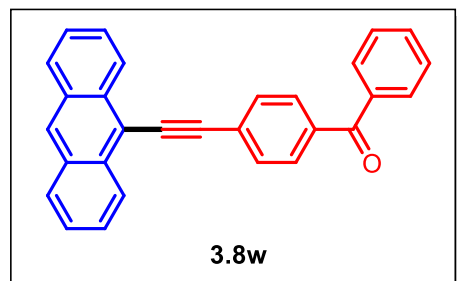
9-(phenylethynyl)anthracene (3.8u).⁵⁰ Compound (3.8u) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equiv.), phenylacetylene (59 mg, 0.58 mmol, 1.5 equiv.), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.0019 mmol, 0.5 mol%), cataCXium[®] A (1.4 mg, 0.0039 mmol, 1.0 mol%) and Cs₂CO₃ (127 mg, 0.39 mmol, 1.0 equivalent) by using general synthetic protocol of Sonogashira

reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (98 mg) was obtained as white solid with 91% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.66 (d, *J* = 8.7 Hz, 2H), 8.45 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 1H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 132.7, 131.8, 131.3, 128.8, 128.6, 128.6, 127.8, 126.9, 126.7, 125.8, 123.7, 117.4, 100.8, 86.4.



9-(p-tolylethynyl)anthracene (3.8v).⁵¹ Compound (3.8v) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent), *p*-ethynyltoluene (67 mg, 0.58 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.5 mg, 0.0019 mmol, 0.5 mol%), cataCXium[®] A (1.4 mg, 0.0039 mmol, 1.0 mol%) and Cs₂CO₃ (127 mg, 0.39 mmol, 1.0 equivalent) by using general synthetic protocol of

Sonogashira reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (108 mg) was obtained as white solid with 95% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.66 (d, *J* = 8.7 Hz, 2H), 8.43 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 5.9 Hz, 2H), 2.43 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.8, 132.6, 131.7, 131.3, 129.4, 128.8, 127.6, 126.9, 126.6, 125.8, 120.7, 117.7, 101.1, 85.7, 21.7.



(4-(anthracen-9-ylethynyl)phenyl)(phenyl)methanone (3.8w). Compound (3.8w) was synthesized from 9-bromoanthracene (50 mg, 0.19 mmol, 1 equivalent), (*p*-ethynylphenyl)(phenyl)methanone (60 mg, 0.29 mmol, 1.5 equivalents), Pd(CH₃CN)₂Cl₂ (0.3 mg, 0.00095 mmol, 0.5 mol%), cataCXium[®] A (0.7 mg, 0.0019 mmol, 1.0 mol%)

and Cs₂CO₃ (62 mg, 0.19 mmol, 1 equivalent) by using general synthetic protocol of Sonogashira reaction. The crude product was purified by column chromatography by using 5% DCM in hexane as eluent. The product (41 mg) was obtained as green solid with 56% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.65 (d, *J* = 8.7 Hz, 2H, H-1 and H-8 of anthracene), 8.49 (s, 1H, H-10 of anthracene), 8.05 (d, *J* = 8.4 Hz, 2H, H-4 and H-5 of anthracene), 7.91 (d, *J* = 8.0 Hz, 2H, H-2 and H-7 of anthracene), 7.90 – 7.82 (m, 4H, H-3 and H-6 of anthracene and *ortho*-protons of phenyl group connected to C(=O)), 7.66 – 7.60 (m, 3H, *para*-proton of phenyl group connected to C(=O) and *meta*-protons of phenyl group connected to alkyne), 7.54 (q, *J* = 7.6 Hz, 4H, *ortho*-protons of both phenyl groups). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 196.1 (C=O), 137.6, 137.0, 132.9, 132.7, 131.5, 131.3, 130.4, 130.1, 128.9, 128.6, 128.5, 128.0, 127.0, 126.7, 125.9, 116.7 (Ar), 100.0 (C≡C), 89.6 (C≡C). FT-IR (KBr, cm⁻¹) 3052 (Aromatic, C-H str), 2923 (Aromatic, C-H str), 2853 (Aromatic, C-H str), 2198 (C≡C str), 1654 (C=O str), 1594 (Aromatic, C=C str), 1445 (Aromatic, C=C str). HRMS (ESI) *m/z* [M+ H]⁺ calcd for C₂₉H₁₉O 383.1436, found 383.1436. mp = 150-152 °C.

Supporting information (containing NMR and HRMS spectra of various compounds) for Chapter III is available as *appendix II* and can be found at

https://drive.google.com/file/d/1mAjwzTbJBbfvNoO6xAcVLhDRoMg91NYi/view?usp=share_link

Cell culture and maintenance.

Human triple-negative breast cancer (TNBC) cell line MDA-MB-231 (procured from National Centre for Cell Science NCCS, Pune, India) and human dermal fibroblasts (HDF; procured from Himedia, India) were cultured and maintained separately in high glucose Dulbecco's Modified Eagle's Medium (DMEM; Gibco, Life Technologies, U.S.A.) supplemented with 10% fetal bovine

serum (FBS; Gibco, Life Technologies, U.S.A.) and 1% streptomycin–penicillin (Sigma, U.S.A.). Cells were seeded in tissue culture flasks (T25; ThermoFisher, U.S.A.) and placed at 37 °C in a humidified (85%) incubator (ThermoFisher Scientific, U.S.A.) with 5% CO₂. The medium was replenished every alternate day.

Cytotoxicity assay

The cytotoxicity of chemical compounds **3**, **3a**, **3b**, **3c**, **3d** and **3g** was tested *in vitro* on human TNBC cell line MDA-MB-231 and HDF cells by the virtue of MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide) tetrazolium reduction assay as described in previous report⁵². Briefly, 1×10⁴ cells per well were seeded into 96-well plate and incubated at 37 °C for 24 h in a CO₂ incubator. Post incubation, used medium was replaced with 200 µl fresh medium containing different concentrations (3.12 µM, 6.25 µM, 12.5 µM, 25 µM, 50 µM, and 100 µM) of chemical compounds. Treated cells along with control (phosphate buffered saline (PBS, pH 7.4) treatment) were then incubated for 72 h in a similar condition as described. Post 72 h, used medium was replaced with 180 µl fresh medium and 20 µl MTT (5 mg/ml) was added to each well followed by incubation at 37 °C for 4 h. Plates were then centrifuged at 1,000 rpm for 5 min and 200 µl dimethyl sulfoxide (DMSO, Sigma, U.S.A.) was added to each well to dissolve the purple pellets (formazan crystals). Absorbance was recorded at 570 nm using a multiplate reader (Multiskan Sky, ThermoFisher, U.S.A.).

Live cells fluorescence imaging

Fluorescence of chemical compounds inside the live cells were checked with both MDA-MB-231 and HDF cells. In brief, both type of cells were seeded (1×10⁴ cells per well) in a 96-well plate separately and incubated at 37 °C for 24 h in a CO₂ incubator. Post incubation, cells were treated with various chemical compounds at a concentration of 10 µM in complete DMEM and incubated for next 72 h. Thereafter, cells were thoroughly washed with PBS (pH 7.4) and images were captured using a fluorescence microscope (EVOSFL, Life Technologies, U.S.A.).

PI Staining

PI staining was performed in both MDA-MB-231 cells and HDF cells to check if the treatment with the chemical compounds resulted in membrane disintegration and cellular uptake of the dye.

The dead cells whose membrane undergoes disintegration takes up PI stain and shows bright orange-red fluorescence (λ_{Ex} : 493 nm, and λ_{Em} : 636 nm). Both types of cells were seeded (1×10^4 cells per well) in a 96-well plate separately and incubated at 37 °C for 24 h in a CO₂ incubator. Post incubation, the cells were treated with various chemical compounds at a concentration of 10 μM in complete DMEM and incubated for next 72 h. Thereafter, cells were thoroughly washed with PBS (pH 7.4) and PI at the concentration of 10 $\mu\text{g/ml}$ was added followed by incubation at 37 °C for 15 minutes. After incubation, PI was removed and washed thoroughly with PBS. Images were captured using a fluorescence microscope (EVOSFL, Life Technologies, U.S.A.)

DAPI Staining

Post treatment of MDA-MB-231 and HDF cells with the compounds for 72 hours, the cells were washed thoroughly with PBS and then fixed with 10% NBF for 30 min. Post fixation, NBF was removed and cells were washed with PBS and then stained with DAPI for 15 min. After 15 min of staining, DAPI was removed and washed with PBS to remove excess stain. Images were captured in fluorescence microscope (NIKON Eclipse Ti2, Japan).

3.5. References

1. (a) Gao, Y.; Feng, C.; Seo, T.; Kubota, K.; Ito, H., *Chem. Sci.* **2022**, *13*, 430-438; (b) Slodek, A.; Filapek, M.; Schab-Balcerzak, E.; Grucela, M.; Kotowicz, S.; Janeczek, H.; Smolarek, K.; Mackowski, S.; Malecki, J. G.; Jedrzejowska, A., *Eur. J. Org. Chem.* **2016**, *2016*, 4020-4031; (c) Islam, K.; Narjinari, H.; Bisarya, A.; Kumar, A., *Org. Biomol. Chem.* **2021**, *19*, 9692-9704; (d) Islam, K.; Narjinari, H.; Kumar, A., *Asian J. Org. Chem.* **2021**, *10*, 1544-1566 (e) Teng, C.; Yang, X.; Yang, C.; Li, S.; Cheng, M.; Hagfeldt, A.; Sun, L., *J. Phys. Chem. C* **2010**, *114* (19), 9101-9110; (f) Chen, M.; Yan, L.; Zhao, Y.; Murtaza, I.; Meng, H.; Huang, W., *J. Mater. Chem. C* **2018**, *6*, 7416-7444; (g) Yamada, S.; Morita, M.; Konno, T., *J. Fluor. Chem.* **2017**, *202*, 54-64; (h) Liu, J.; Liu, J.; Zhang, Z.; Xu, C.; Li, Q.; Zhou, K.; Dong, H.; Zhang, X.; Hu, W., *J. Mater. Chem. C* **2017**, *5*, 2519-2523; (i) Goudappagouda; Wakchaure, V. C.; Ranjeesh, K. C.; Abhai, C. A. R.; Babu, S. S., *Chem. Commun.* **2017**, *53*, 7072-7075.
2. Seri, M.; Marrocchi, A., *J. Mater. Chem. C* **2021**, *9*, 16164-16186.
3. Briseno, A. L.; Mannsfeld, S. C.; Jenekhe, S. A.; Bao, Z.; Xia, Y., *Mater. Today* **2008**, *11*, 38-47.
4. Shanmugaraju, S.; Mukherjee, P. S., *Chem. Commun.* **2015**, *51*, 16014-16032;
5. Sagara, Y.; Yamane, S.; Mutai, T.; Araki, K.; Kato, T., *Adv. Funct. Mater.* **2009**, *19*, 1869-1875.
6. Islam, K.; Arora, V.; Vikas, V.; Nag, B.; Kumar, A., *ChemCatChem* **2022**, e202200440
7. Wang, D.; Gao, S., *Org. Chem. Front.* **2014**, *1*, 556-566.
8. Leyva-Pérez, A.; Cabrero-Antonino, J. R.; Rubio-Marqués, P.; Al-Resayes, S. I.; Corma, A., *ACS Catal.* **2014**, *4*, 722-731.

9. Mohajer, F.; Heravi, M. M.; Zadsirjan, V.; Poormohammad, N., *RSC Adv.* **2021**, *11*, 6885-6925.
10. (a) Albano, G.; Aronica, L. A., *Catal.* **2019**, *10*, 25; (b) Heravi, M. M.; Sadjadi, S., *Tetrahedron* **2009**, *65*, 7761-7775.
11. (a) Gelman, D.; Buchwald, S. L., *Angew. Chem.* **2003**, *115*, 6175-6178; (b) Pu, X.; Li, H.; Colacot, T. J., *J. Org. Chem.* **2013**, *78*, 568-581; (c) Ljungdahl, T.; Pettersson, K.; Albinsson, B.; Mårtensson, J., *J. Org. Chem.* **2006**, *71*, 1677-1687.
12. Aufiero, M.; Proutiere, F.; Schoenebeck, F., *Angew. Chem. Int. Ed.* **2012**, *51*, 7226-7230.
13. (a) Hooshmand, S. E.; Heidari, B.; Sedghi, R.; Varma, R. S., *Green Chem.* **2019**, *21*, 381-405; (b) Amatore, C.; Bensalem, S.; Ghalem, S.; Jutand, A.; Medjour, Y., *Eur. J. Org. Chem.* **2004**, *2004*, 366-371; (c) Mak, A. M.; Lim, Y. H.; Jong, H.; Yang, Y.; Johannes, C. W.; Robins, E. G.; Sullivan, M. B., *Organometallics* **2016**, *35*, 1036-1045; (d) Zhu, J.; Lindsay, V. N., *ACS Catal.* **2019**, *9*, 6993-6998; (e) Monguchi, Y.; Wakayama, F.; Ueda, S.; Ito, R.; Takada, H.; Inoue, H.; Nakamura, A.; Sawama, Y.; Sajiki, H., *RSC Adv.* **2017**, *7*, 1833-1840; (f) Reddy, A. G. K.; Satyanarayana, G., *Synth.* **2017**, *49*, 5149-5158.
14. (a) Chinchilla, R.; Nájera, C., *Chem. Soc. Rev.* **2011**, *40*, 5084-5121; (b) Yang, Y.; Chew, X.; Johannes, C. W.; Robins, E. G.; Jong, H.; Lim, Y. H., *Eur. J. Org. Chem.* **2014**, *2014*, 7184-7192; (c) Singh, J.; Verma, A. K., *J. Chem. Sci.* **2011**, *123*, 937-942; (d) Ruiz, J.; Cutillas, N.; Lopez, F.; Lopez, G.; Bautista, D., *Organometallics* **2006**, *25*, 5768-5773; (e) Reddy, A. S.; Laali, K. K., *Tetrahedron Lett.* **2015**, *56*, 4807-4810; (f) Sabounchei, S. J.; Ahmadi, M., *Catal. Commun.* **2013**, *37*, 114-121; (g) Nikoshvili, L. Z.; Tupikina, E. P.; Kiwi-Minsker, L., *Chem. Eng. Trans.* **2021**, *88*, 271-276; (h) Yang, Y.; Lim, J. F. Y.; Chew, X.; Robins, E. G.; Johannes, C. W.; Lim, Y. H.; Jong, H., *Catal. Sci. Technol.* **2015**, *5*, 3501-3506; (i) Patil, P. H.; Fernandes, R. A., *RSC adv.* **2015**, *5*, 54037-54045; (j) Yang, Y.; Lim, Y. H.; Robins, E. G.; Johannes, C. W., *RSC Adv.* **2016**, *6* (76), 72810-72814.
15. Mori, A.; Kawashima, J.; Shimada, T.; Suguro, M.; Hirabayashi, K.; Nishihara, Y., *Org. Lett.* **2000**, *2*, 2935-2937.
16. Alonso, D. A.; Nájera, C.; Pacheco, M. C., *Tetrahedron Lett.* **2002**, *43*, 9365-9368.
17. Ma, Y.; Song, C.; Jiang, W.; Wu, Q.; Wang, Y.; Liu, X.; Andrus, M. B., *Org. Lett.* **2003**, *5*, 3317-3319.
18. Cheng, J.; Sun, Y.; Wang, F.; Guo, M.; Xu, J.-H.; Pan, Y.; Zhang, Z., *J. Org. Chem.* **2004**, *69*, 5428-5432.
19. Liang, Y.; Xie, Y.-X.; Li, J.-H., *J. Org. Chem.* **2006**, *71*, 379-381.
20. (a) Das, S. K.; Sarmah, M.; Bora, U., *Tetrahedron Lett.* **2017**, *58*, 2094-2097; (b) Gogoi, A.; Dewan, A.; Borah, G.; Bora, U., *New J. Chem.* **2015**, *39*, 3341-3344; (c) Urgaonkar, S.; Verkade, J. G., *J. Org. Chem.* **2004**, *69*, 5752-5755; (d) Kozell, V.; McLaughlin, M.; Strappaveccia, G.; Santoro, S.; Bivona, L. A.; Aprile, C.; Gruttadauria, M.; Vaccaro, L., *ACS Sustain. Chem. Eng.* **2016**, *4*, 7209-7216.
21. Clarke, C. J.; Tu, W.-C.; Levers, O.; Brohl, A.; Hallett, J. P., *Chem. Rev.* **2018**, *118*, 747-800.
22. Sherwood, J.; Clark, J. H.; Fairlamb, I. J.; Slattery, J. M., *Green Chem.* **2019**, *21* (9), 2164-2213.
23. (a) Fantoni, T.; Bernardoni, S.; Mattellone, A.; Martelli, G.; Ferrazzano, L.; Cantelmi, P.; Corbisiero, D.; Tolomelli, A.; Cabri, W.; Vacondio, F., *ChemSusChem* **2021**, *14*, 2591-2600; (b) Ferrazzano, L.; Martelli, G.; Fantoni, T.; Daka, A.; Corbisiero, D.; Viola, A.; Ricci, A.; Cabri, W.; Tolomelli, A., *Org. Lett.* **2020**, *22*, 3969-3973.
24. Zha, L.; Bai, J.; Zhou, C.; Zhang, Y.; Li, J.; Wang, P.; Zhang, B.; Zhou, B., *Chemosphere* **2022**, *289*, 133119.

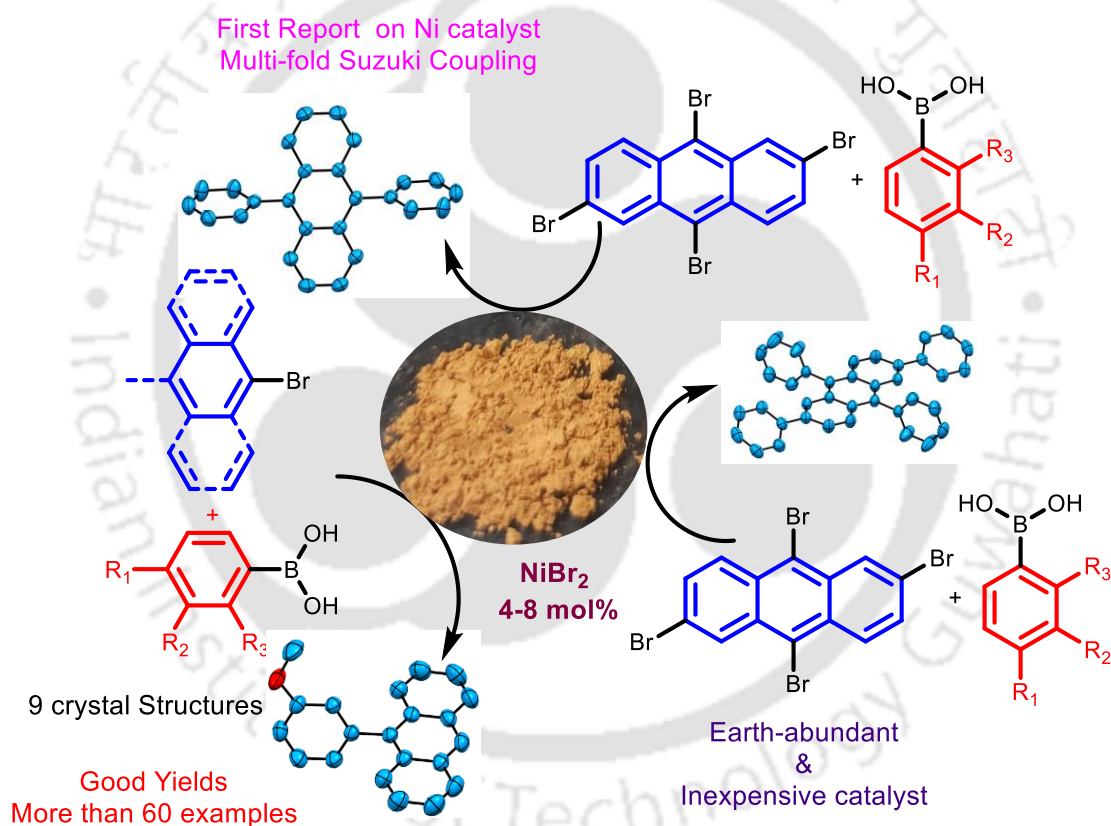
25. Jang, J.-K., Amines as occupational hazards for visual disturbance. *Ind. Health* **2015**, *54*, 101-115.
26. McKillip, W. J.; Collin, G.; Höke, H.; Zeitsch, K. J., Furan and derivatives. *Ullmann's encycl. Ind. Chem.* **2000**.
27. Mak, A. M.; Lim, Y. H.; Jong, H.; Yang, Y.; Johannes, C. W.; Robins, E. G.; Sullivan, M. B., *Organometallics* **2016**, *35*, 1036-1045.
28. Oliveira, J. d. S.; Guidelli, E. J. J. M. S.; C, E., *Mater. Sci. Eng.* **2021**, *126*, 112122.
29. (a) De, U.; Chun, P.; Choi, W. S.; Lee, B. M.; Kim, N. D.; Moon, H. R.; Jung, J. H.; Kim, H. S. J. I. J. o. O., *Int. J. Oncol.* **2014**, *44*, 167-176; (b) Xie, S.-Q.; Zhang, Z.-Q.; Hu, G.-Q.; Xu, M.; Ji, B.-S. J. T., *Toxicology* **2008**, *254*, 68-74; (c) Chang, L. C.; Chávez, D.; Gills, J. J.; Fong, H. H.; Pezzuto, J. M.; Kinghorn, A. D. J. T. I., *Tetrahedron Lett.* **2000**, *41*, 7157-7162; (d) Huggins, C.; Pataki, J. J. P. o. t. N. A. o. S., *Proc. Natl. Acad. Sci.* **1965**, *53*, 791-796; (e) Sugiyama, T. J. G. J. J. o. C. R., *Jpn. J. Cancer Res.* **1973**, *64*, 637-639; (f) Sangthong, S.; Ha, H.; Teerawattananon, T.; Ngamrojanavanich, N.; Neamati, N.; Muangsin, N. J. B.; letters, m. c., Overcoming doxorubicin-resistance in the NCI/ADR-RES model cancer cell line by novel anthracene-9, 10-dione derivatives. *Biorg. Med. Chem. Lett.* **2013**, *23*, 6156-6160; (g) Sangthong, S.; Sangphech, N.; Palaga, T.; Ngamrojanavanich, N.; Puthong, S.; Vilaivan, T.; Muangsin, N. J. E. J. o. M. C., Anthracene-9, 10-dione derivatives induced apoptosis in human cervical cancer cell line (CaSki) by interfering with HPV E6 expression. *Eur. J. Med. Chem.* **2014**, *77*, 334-342.
30. Roe, F.; Dipple, A.; Mitchley, B. J. B. J. o. C., *J. Cancer* **1972**, *26*, 461-465.
31. Somashekar, M.; Chetana, P., *Rev. J. Chem.* **2016**, *3*, 45-52.
32. Pena, M. A.; Sestelo, J. P.; Sarandeses, L. A., *Synth.* **2005**, *2005*, 485-492.
33. Carvalho, J. o. F.; Louvel, J.; Doornbos, M. L.; Klaasse, E.; Yu, Z.; Brussee, J.; IJzerman, A. P., *J. Med. Chem.* **2013**, *56*, 2828-2840.
34. Ehlers, P.; Hakobyan, A.; Neubauer, A.; Lochbrunner, S.; Langer, P., *Adv. Synth. Catal.* **2013**, *355*, 1849-1858.
35. Petrosyan, A.; Ehlers, P.; Surkus, A.-E.; Ghochikyan, T. V.; Saghyian, A. S.; Lochbrunner, S.; Langer, P., *Org. Biomol. Chem.* **2016**, *14*, 1442-1449.
36. Bauch, M.; Klaper, M.; Linker, T., *J. Phys. Org. Chem.* **2017**, *30*, e3607.
37. Nguyen, P.; Todd, S.; Van den Biggelaar, D.; Taylor, N. J.; Marder, T. B.; Wittmann, F.; Friend, R. H., *Synlett* **1994**, *1994*, 299-301.
38. Liang, B.; Dai, M.; Chen, J.; Yang, Z., *J. Org. Chem.* **2005**, *70*, 391-393.
39. Qu, X.; Li, T.; Sun, P.; Zhu, Y.; Yang, H.; Mao, J., *Org. Biomol. Chem.* **2011**, *9*, 6938-6942.
40. Fürstner, A.; Seidel, G., *Tetrahedron* **1995**, *51*, 11165-11176.
41. Hiroya, K.; Itoh, S.; Sakamoto, T., *J. Org. Chem.* **2004**, *69*, 1126-1136.
42. Elangovan, A.; Wang, Y.-H.; Ho, T.-I., *Org. Lett.* **2003**, *5*, 1841-1844.
43. Huang, H.; Liu, H.; Jiang, H.; Chen, K., *J. Org. Chem.* **2008**, *73*, 6037-6040.
44. Fukuyama, T.; Shinmen, M.; Nishitani, S.; Sato, M.; Ryu, I., A copper-free Sonogashira coupling reaction in ionic liquids and its application to a microflow system for efficient catalyst recycling. *Org. Lett.* **2002**, *4*, 1691-1694.
45. Liu, Z.; Budiman, Y. P.; Tian, Y. M.; Friedrich, A.; Huang, M.; Westcott, S. A.; Radius, U.; Marder, T. B., *Chem. Eur. J.* **2020**, *26*, 17267-17274.
46. Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G., *Org. Lett.* **2005**, *7*, 3163-3166.

47. Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K., Indole Synthesis via Rhodium Catalyzed Oxidative Coupling of Acetanilides and Internal Alkynes. *J. Am. Chem. Soc.* **2008**, *130*, 16474-16475.
48. Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S., *J. Org. Chem.* **2010**, *75*, 6244-6251.
49. Cheng, J.; Sun, Y.; Wang, F.; Guo, M.; Xu, J.-H.; Pan, Y.; Zhang, Z., *J. Org. Chem.* **2004**, *69*, 5428-5432.
50. Wan, C. W.; Burghart, A.; Chen, J.; Bergström, F.; Johansson, L. B. Å.; Welford, M. F.; Kim, T. G.; Topp, M. R.; Hochstrasser, R. M.; Burgess, K., Anthracene–BODIPY cassettes: syntheses and energy transfer. *Chem. Eur. J.* **2003**, *9*, 4430-4441.
51. Muthiah, C.; Kumar, K. P.; Mani, C. A.; Kumara Swamy, K. C., *J. Org. Chem.* **2000**, *65*, 3733-3737.
52. Kumar, J. P.; Alam, S.; Jain, A. K.; Ansari, K. M.; Mandal, B. B., Protective activity of silk sericin against UV radiation-induced skin damage by downregulating oxidative stress. *ACS Appl. Bio Mater.* **2018**, *1*, 2120-2132.



CHAPTER IV

Single and Multi-Fold Suzuki Cross Coupling Reaction by Ligand-Free and Activator-Less Metal Salt NiBr_2



K. Islam; V. Arora; Vikas; B. Nag; A. Kumar, *ChemCatChem* **2022**, e202200440



4.1 Introduction

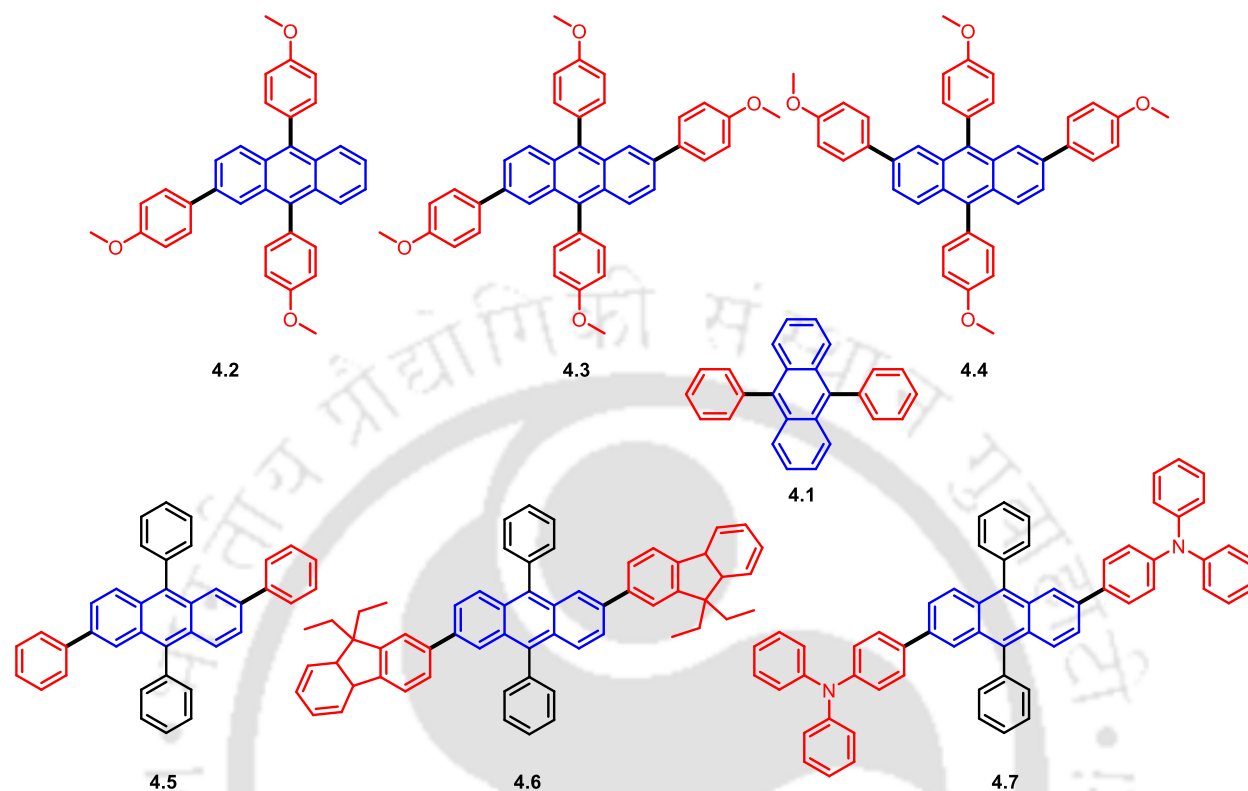
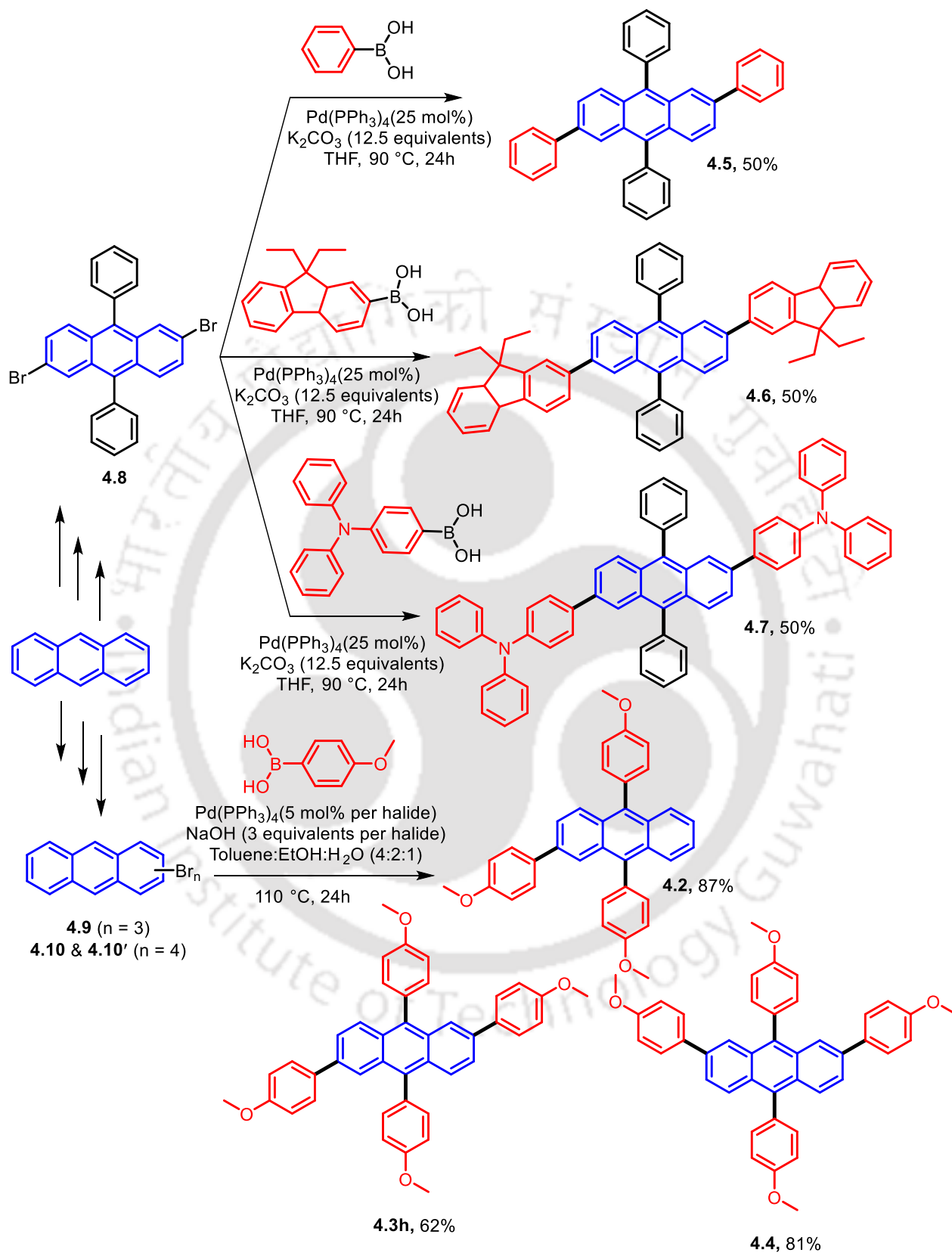
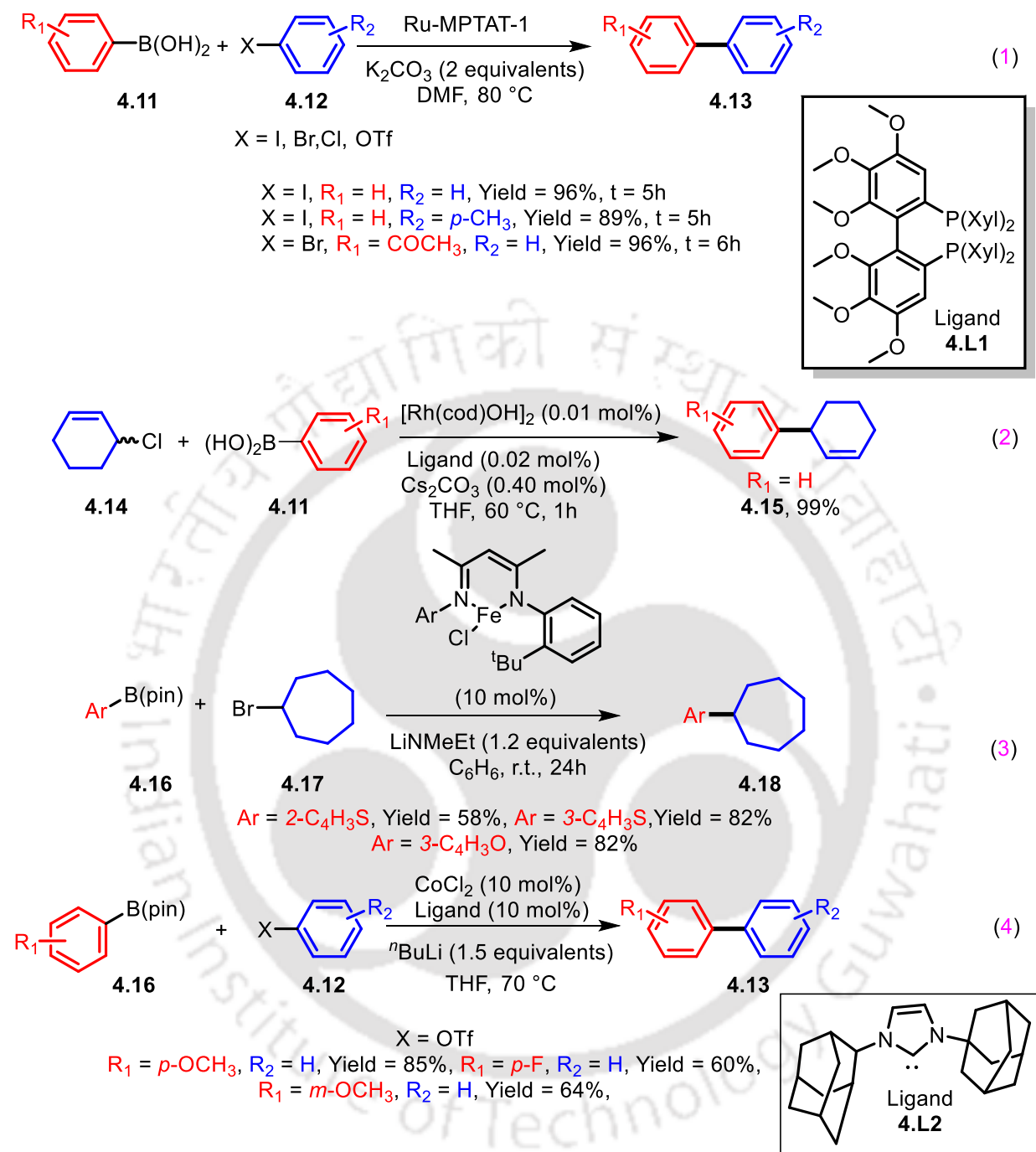


Figure 4.1. Arylatedanthracene molecules that have been utilized in OLEDs devices¹

Polyarylated polycyclic aromatic hydrocarbons (PAHs) are highly fluorescent and have diverse applications as fluorescence sensors,² laser dyes,³ artificial light harvesters⁴ and organic light emitting diodes (OLEDs) materials.^{1b, 1c, 5} The tricyclic anthracene has rigid ring which diminishes the vibronic energy levels and emit the color with high efficiency and purity.⁶ Anthracene also contains aromaticity, which provides well-defined electrochemical and thermal properties.⁶ 9,10-diphenylanthracene (**4.1**, Figure 4.1), one of the blue fluorescent materials, has a fluorescence quantum efficiency that is nearly unity in diluted solution and is also quite fluorescent in solid form.^{1a} Individually, Kwon and Moorthy reported polyarylatedanthracenes (**4.2-4.7**, Figure 4.1) which exhibit blue-emission in OLEDs with high efficiency and act as fluorescence host materials.^{1b, 1c} The polyarylatedanthracene compounds can be synthesized by construction of C-C bonds (Scheme 4.1).



Scheme 4.1. Synthesis of valuable tetraarylated anthracene in the presence of $\text{Pd}(\text{PPh}_3)_4^{1b, 1c}$



Scheme 4.2. Suzuki cross-coupling reaction employing Ru, Rh, Fe and Co as catalyst.⁷

The study of C-C bond formation is an evergreen branch of synthetic organic chemistry that finds immense applications in routes that lead to complex molecules such as natural products,⁸ drugs,⁸⁻⁹ pharmaceutical,⁹ and biological active compounds.¹⁰ Suzuki¹¹ cross-coupling has been one of the most favorite and efficient tool for the construction of C-C bonds leading to valuable

molecules.⁸⁻⁹ The Suzuki coupling has been reported with catalysts mostly based on palladium (Scheme 4.1).¹² Recently, researchers are more focused to develop Suzuki coupling reaction employing metals others than palladium.

Salam and co-workers developed Ru-based catalyst Ru-MPTAT-1 and successfully performed the Suzuki coupling reaction of aryl halide and boronic acid with good to excellent yields (equation 1, Scheme 4.2).^{7a} The Suzuki coupling reaction of phenylboronic acids and racemic halides (cyclohexenylchloride) occurred in the presence of $[\text{Rh}(\text{cod})(\text{OH})]_2$ as catalyst and (S)-Xyl-P-Phos as ligand (equation 2, Scheme 4.2).^{7b} The enantioselectivity of the reaction is controlled by the reductive elimination step, which results in the C-C coupling between the Rh-cyclohexenyl and phenyl moieties. The DFT analysis showed that the *R*-enantiomer reacts more quickly than the *S*-enantiomer. Byers and co-workers formulated a synthetic protocol for Suzuki coupling reaction of alkyl halide and arylboronicester employing the iron based catalyst (equation 3, Scheme 4.2).^{7c} This reaction was found to be most effective at conditions that prevented the development of iron aggregates. The utilisation of amide bases and anionic ligands, which facilitate the transmetalation of boron to iron, were minor but crucial factors in the success of these reactions. Later, Duong developed cobalt based catalyst system ($\text{CoCl}_2/\text{ligand}$) which is most effective towards the Suzuki coupling reaction of aryl triflates and arylboronic esters that are activated by *n*-butyllithium (equation 4, Scheme 4.2).^{7d}

Conventionally, palladium catalyzed Suzuki reaction involves phosphine ligands that are often air- and water-sensitive (Figure 4.2).¹³ Modifications to generate air and moisture stable ligands suffer from tedious synthetic procedures and high cost.¹⁴ Rightly, development of ligand-free (Scheme 4.3)¹⁵ and more preferably Pd-free (equation 1-4, Scheme 4.2)^{7, 12c, 16, 15c, 17} catalytic systems for Suzuki reactions has been a fertile field of research. It is therefore no surprise that the last two decades have witnessed rapid progress in the Suzuki cross-coupling reactions where highly abundant and inexpensive nickel (Scheme 4.4-4.7 & 4.9)^{10c, 16, 18 17a, 19} has steadily replaced its precious metal sibling palladium.^{16c, 20, 21} Early reports on Suzuki reactions catalyzed by Ni(0)-based catalysts were dominated by $\text{Ni}(\text{cod})_2$ (Scheme 4.5)^{16c, 22} in combination with various ligands (Scheme 4.4).

In 2004, Hu and co-workers demonstrated that of $\text{Ni}(\text{PCy}_3)_2\text{Cl}_2$ and $\text{Ni}(\text{PCy}_3)_2\text{Cl}_2/\text{Zn}$ catalysts were unproductive towards Suzuki cross-coupling reaction.²³ This was most likely beca-

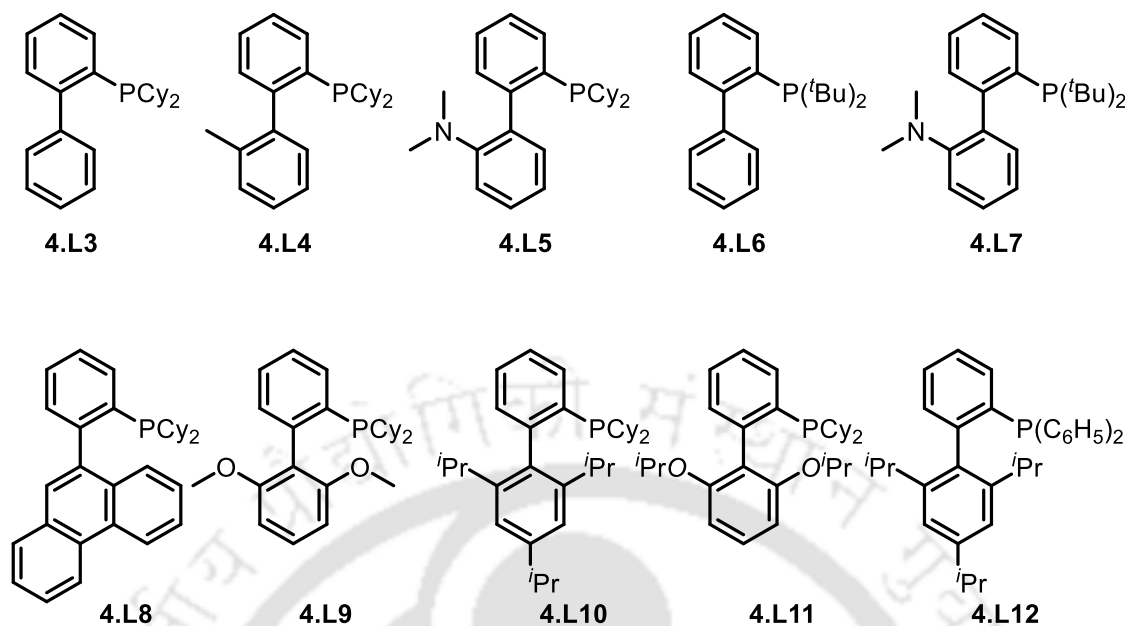
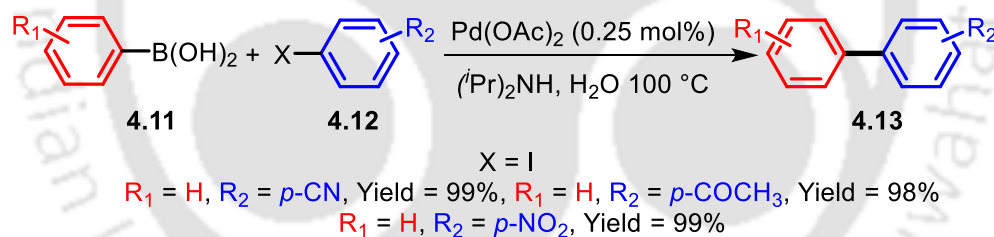


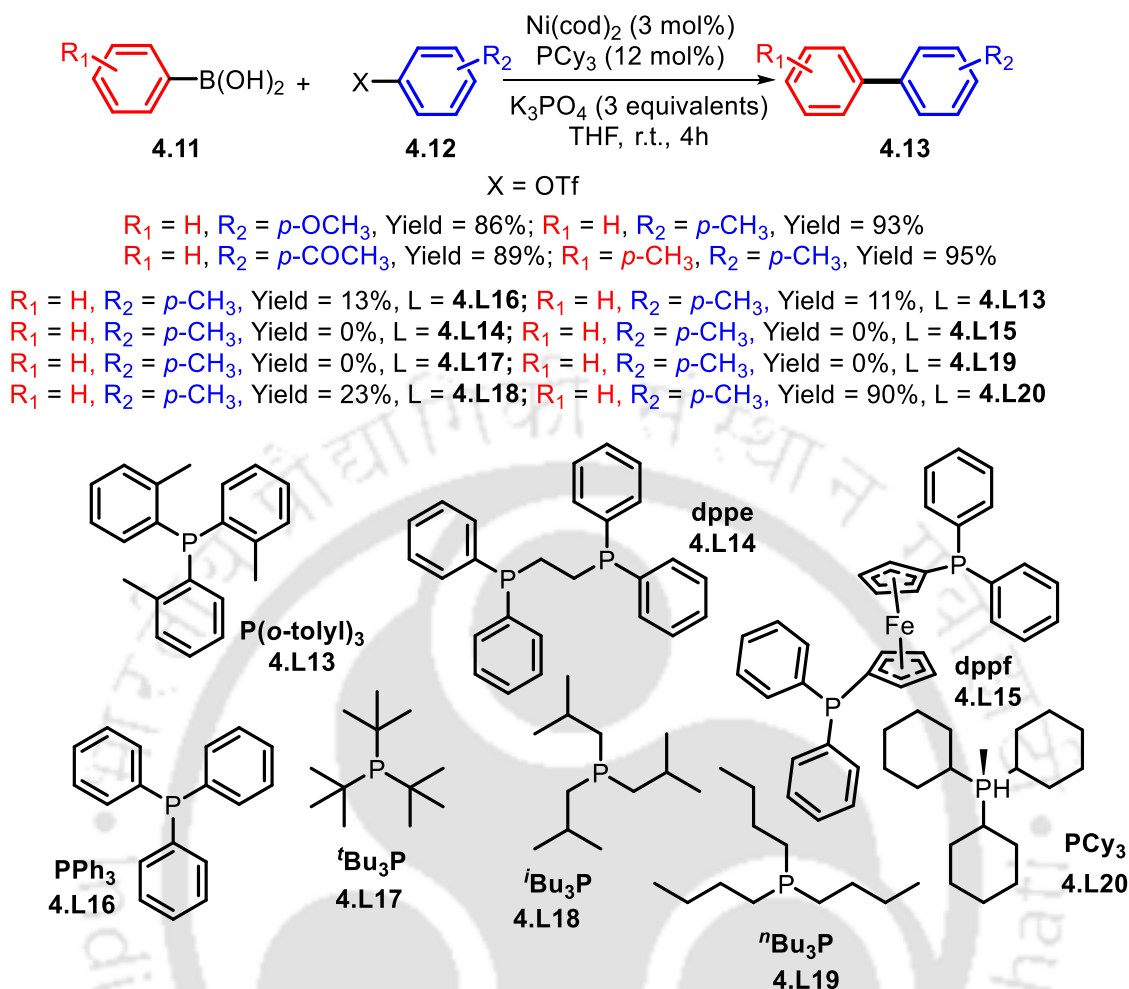
Figure 4.2. Few phosphine based ligands which are highly active towards Suzuki coupling in the presence of Pd-catalysts.^{13, 15}



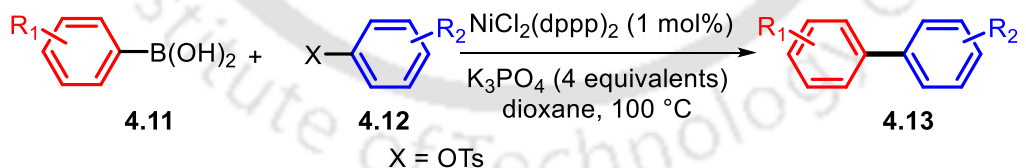
Scheme 4.3. Ligand-free Suzuki cross-coupling reaction in the presence of Pd-catalyst.

-use they failed to produce catalytically active Ni(0) species under the reaction conditions.²³ Suzuki cross-coupling reaction of phenylboronic acid and *p*-tolyltosylate at the room temperature was successful in the presence of Ni(cod)₂. Ni(cod)₂ is less effective towards this reaction in the presence of sterically bulky electron rich or electronically poor phosphine ligands (PPh₃, P(*o*-tolyl)₃, dppf, dppe and ^tBu₃P, Scheme 4.4) but it is highly efficient in the presence of less sterically hindered electron rich phosphine ligands (*tri*-cyclohexylphosphine (Scheme 4.4)).²³

In contrast to related Ni(II) precursors, Ni(cod)₂ is less preferred as it is highly expensive

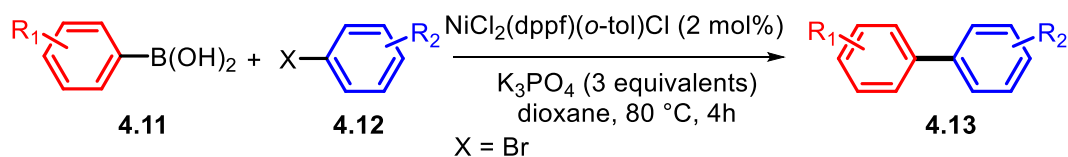


Scheme 4.4. Nickel(0) catalyzed Suzuki-Miyaura cross-coupling reaction in the presence of various phosphine ligands.²³



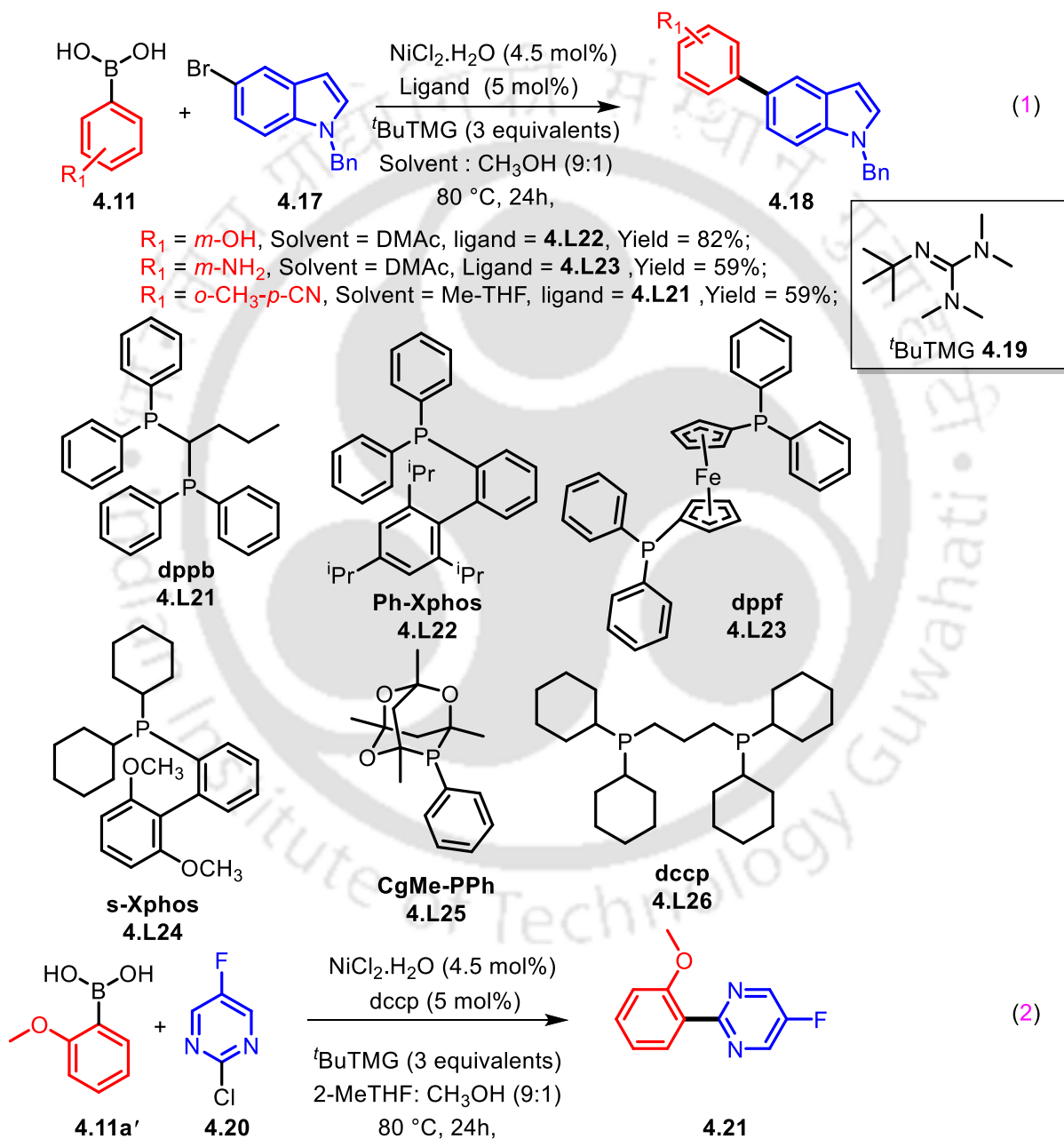
Scheme 4.5. Nickel(II) catalyzed Suzuki-Miyaura cross-coupling reaction.²⁴

apart from being air and moisture sensitive.¹⁸ Recently, there has been significant advancement in the use of Ni(II)^{16a, 16b, 26} based complexes as catalysts for Suzuki reactions under mild conditions with vast substrate scope and high yields. In 2011, Lin and Han group demonstrated the Suzuki



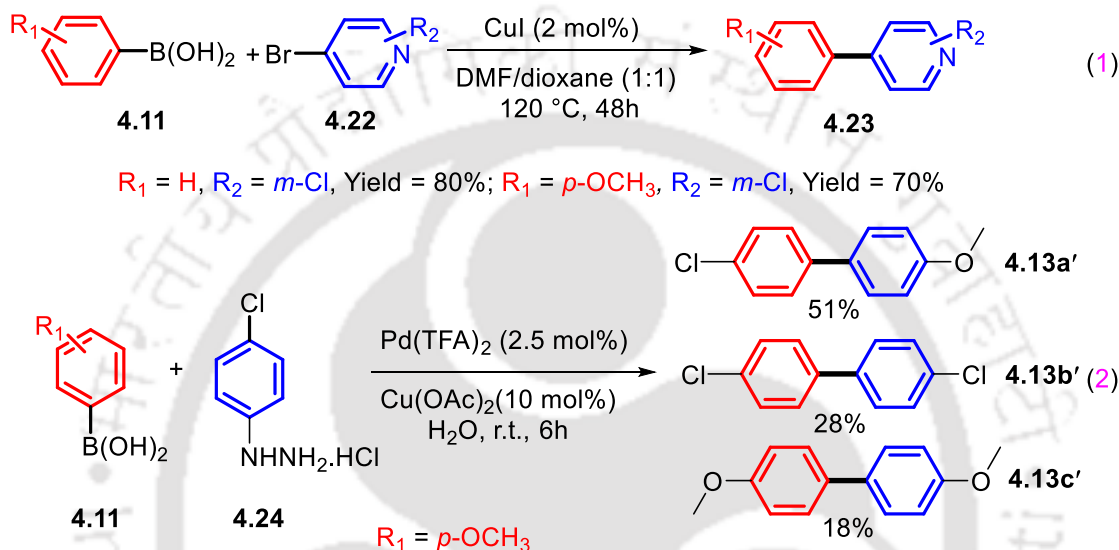
$\text{R}_1 = \text{H}, \text{R}_2 = \textit{p}\text{-F}$, Yield = 98%; $\text{R}_1 = \text{H}, \text{R}_2 = \textit{m}\text{-COCH}_3$, Yield = 91%
 $\text{R}_1 = \text{H}, \text{R}_2 = \textit{o}\text{-CN}$, Yield = 100%; $\text{R}_1 = \text{H}, \text{R}_2 = \textit{o}\text{-OCH}_3$, Yield = 83%

Scheme 4.6. Suzuki-Miyaura cross-coupling reaction in the presence of $\text{NiCl}_2(\text{dppf})(\text{o-tol})\text{Cl}$ ²⁵



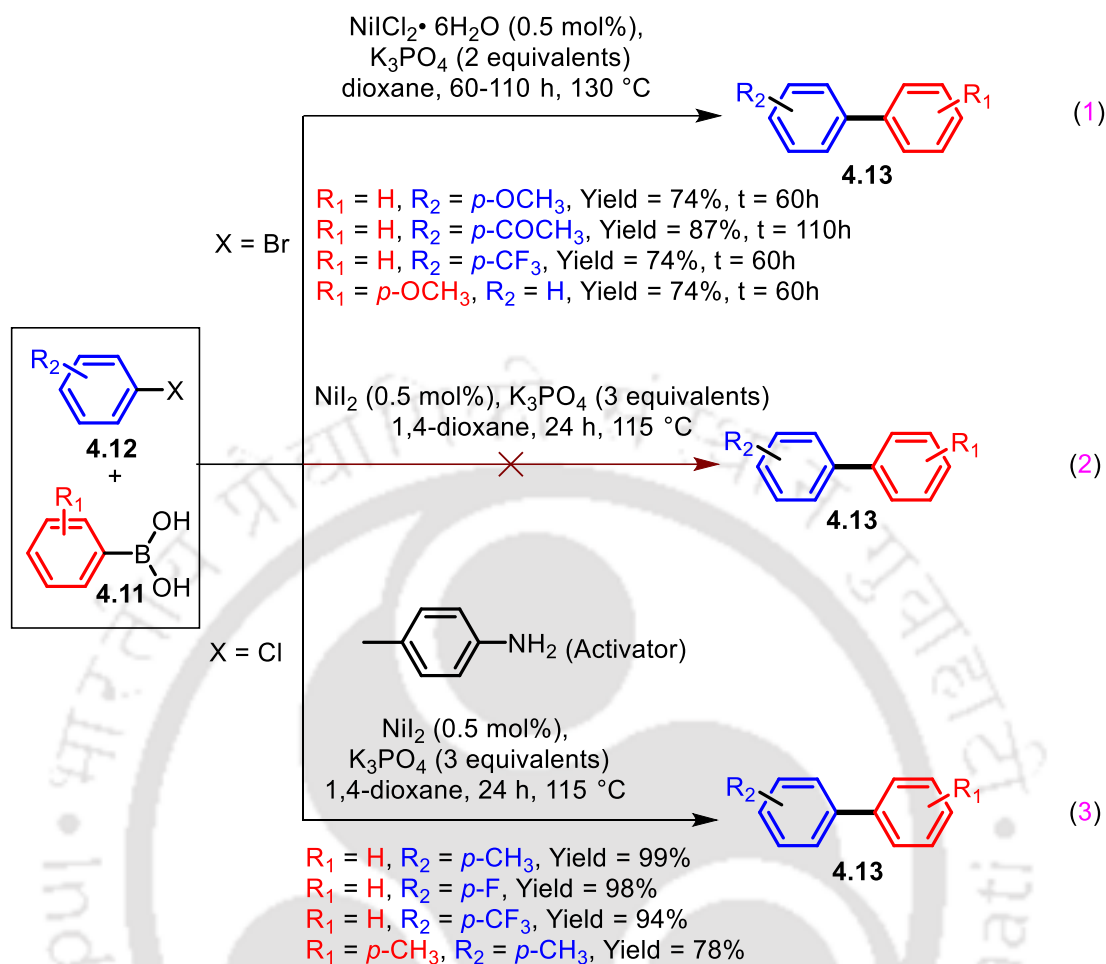
Scheme 4.7. Suzuki-Miyaura cross-coupling reaction in the presence of $\text{NiCl}_2\cdot\text{H}_2\text{O/Ligand}$.^{21a}

coupling reaction by using low cost, stable and highly efficient catalyst $\text{NiCl}_2(\text{dppp})_2$ (Scheme 4.6).²⁴ The catalyst was not only cost effective and reactive, its low loading (up to 1.0 mol% per halide) is sufficient to perform the reaction with aryl halide/aryl tosylates and arylboronic acid in absence of any external ligand. The reaction protocol is applicable to synthesize heteroaromatic and sterically hindered vast substrates with moderate to excellent yield.



Scheme 4.8. Suzuki cross-coupling reaction in the presence Cu(I) and Cu(II) as catalyst.^{11c}

Later, Watson and co-workers described Suzuki coupling reaction of aryl halide and aryl boronic acid in the presence of air stable and highly reactive catalyst $\text{Ni}(\text{ddppf})(o\text{-tol})\text{Cl}$ (Scheme 4.6).²⁵ Recently, Goldfogel and co-workers reported the Suzuki coupling reaction of aryl halide and aryl boronic acid employing the base metal salt $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ in presence of phosphine based ligand (Scheme 4.7). They screened various ligands such as PPh_3 , dppb , CgMe-PPh , Ph-Xphos , dppf , $s\text{-Phos}$, dccp and the most effective ligand was dccp (Scheme 4.7).^{21a} While ligand-free Suzuki coupling have been reported with metal salts based on Pd(II) (equation 2, Scheme 4.3),^{15c, 27} and Cu(I) (equation 1, Scheme 4.8),^{15c, 17b}, the corresponding reports with Ni(II) (Scheme 4.9) salts^{17a, 19, 7f, 15c} are rare. Recent research by Gurung and co-workers described a flexible method for the ligand-free cross-coupling of aryl and heteroarylboronates with arylheteroaryl iodides, which produced the desired products in good to outstanding yields (Scheme 4.8).^{11c} Monteiro and co-workers demonstrated ten examples of cross coupling reaction of aryl halides with phenyl



Scheme 4.9. Suzuki cross-coupling reaction catalyzed by Ni(II) salts under ligand-free conditions.^{17a, 19}

boronic acids using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst (equation 1, Scheme 4.9).^{17a} Yamada observed that the Suzuki reaction of aryl chlorides with phenylboronic acid was unsuccessful when NiI_2 was used as a catalyst, in the presence of K_3PO_4 with dioxane as solvent (equation 2, Scheme 4.9).¹⁹ However, repeating the NiI_2 catalyzed reaction in the presence of *p*-toluidine as an activator in stoichiometric amounts, good yields of Suzuki coupled product was observed (equation 3, Scheme 4.9).¹⁹

4.1.1. Objectives

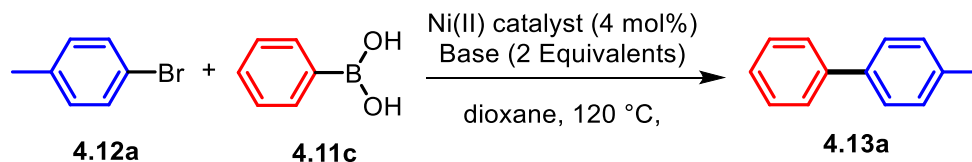
Considering the literature studies, multi-fold Suzuki coupling reaction is known in the presence of palladium catalyst but multi-fold Suzuki cross coupling reaction in a single step with high yield

employing Ni(II)-catalysed reactions under ligand-free and activator-less conditions remains a challenge unaddressed. The current chapter attempts to address the following questions.

- Is it possible to formulate the efficient synthetic protocol for single as well as multi-fold Suzuki cross-coupling reaction in single step employing commercially available and inexpensive nickel (II) salt in absence of a ligand and an activator?
- Would it be possible to synthesize valuable polyarylated polycyclic aromatic hydrocarbons employing the newly developed multi-fold Suzuki coupling reaction protocol?

4.2. Results & Discussion

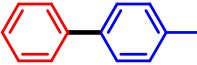
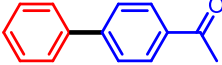
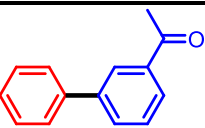
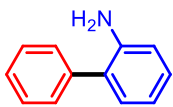
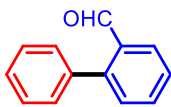
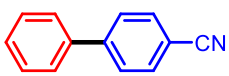
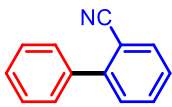
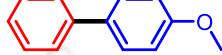
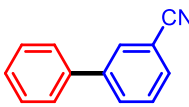
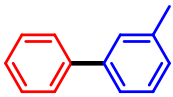
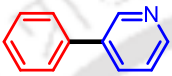
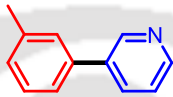
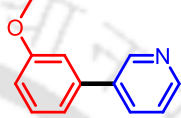
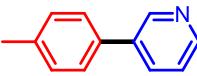
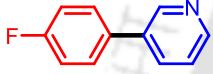
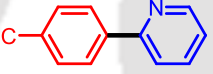
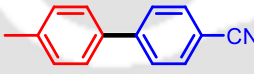
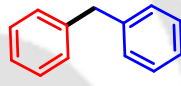
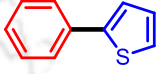
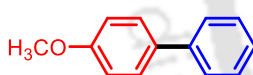
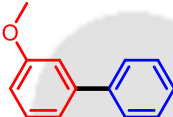
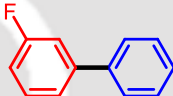
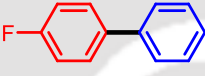
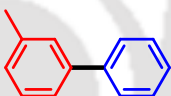
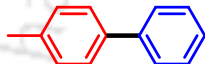
The optimization of Suzuki coupling was commenced by choosing 4-bromotoluene (**4.12a**) and phenylboronic acid (**4.11a**) as the model substrates with NiBr₂ (4 mol%) as catalyst in the presence of two equivalents of a variety of bases (Table 4.1). The NiBr₂ catalyzed reaction of **4.12a** with **4.11a** in the presence of K₃PO₄ in dioxane at 120 °C for 36 h, afforded the desired product **4.13a** with 28% yield (entry 1, Table 4.1). Further, various bases were screened under identical conditions (entries 2-11, Table 4.1) and K₃PO₄ proved to be the best among the bases employed (entry 1, Table 4.1). Performing the reaction in a closed vessel to prevent the homocoupling of phenylboronic acid,²⁸ increased the yield to 45% (entry 12, Table 4.1) and all the subsequent optimizations were performed under closed vessel conditions. The Suzuki coupling reaction gave higher yields when the reaction was increased from 36 h to 48 h (entry 13, Table 4.1). Lower yields were obtained when NiBr₂ was replaced with other nickel salts such as Ni(NO₃)₂·6H₂O (entry 14, Table 1), NiCl₂(DME) (entry 15, Table 1), NiCl₂ (entry 16, Table 1) and, NiCl₂·6H₂O (entry 17, Table 1). The use of different solvents like THF and toluene, lead to a drop in the yield of 4-methyl-1,1'-biphenyl (**4.13a**) (entries 18-19, Table 1). The yield of the desired product (**4.13a**) was enhanced up to 65%, when the catalyst loading was increased to 8 mol% (entry 20, Table 4.1). Under identical conditions, no further improvement in yields were observed when the equivalents of phenyl boronic acid (**4.11a**) were decreased (entries 21-22, Table 4.1). Similar yield of the cross-coupled product was obtained at higher temperature of 140 °C (entry 23, Table 4.1), while a major drop in the yield was observed when reaction was performed with one equivalent of K₃PO₄

Table 4.1. NiBr₂ catalyzed Suzuki-Miyaura cross-coupling of 4-Bromotoluene with Phenylboronic Acid^a

entry	Time (t h)	Ni	Base	Yield of 4.13a , ^b %
1	36	NiBr ₂	K ₃ PO ₄	28
2	36	NiBr ₂	KOH	5
3	36	NiBr ₂	NaOH	13
4	36	NiBr ₂	Na ₂ CO ₃	11
5	36	NiBr ₂	K ₂ CO ₃	5
6	36	NiBr ₂	NaHCO ₃	8
7	36	NiBr ₂	KHCO ₃	0
8	36	NiBr ₂	NaOEt	3
9	36	NiBr ₂	Na ^t BuO	7
10	36	NiBr ₂	K ^t BuO	0
11	36	NiBr ₂	Cs ₂ CO ₃	0
12 ^c	36	NiBr ₂	K ₃ PO ₄	45
13 ^c	48	NiBr ₂	K ₃ PO ₄	60
14 ^c	48	Ni(NO ₃) ₂ ·6H ₂ O	K ₃ PO ₄	10
15 ^c	48	NiCl ₂ (DME)	K ₃ PO ₄	30
16 ^c	48	NiCl ₂	K ₃ PO ₄	18
17 ^c	48	NiCl ₂ ·6H ₂ O	K ₃ PO ₄	18
18 ^{c,d}	48	NiBr ₂	K ₃ PO ₄	28
19 ^{c,e}	48	NiBr ₂	K ₃ PO ₄	28
20 ^{c,j}	48	NiBr ₂	K ₃ PO ₄	65
21 ^{c,f,j}	48	NiBr ₂	K ₃ PO ₄	51
22 ^{c,g,j}	48	NiBr ₂	K ₃ PO ₄	63
23 ^{c,h,j}	48	NiBr ₂	K ₃ PO ₄	65
24 ^{c,i,j}	48	NiBr ₂	K ₃ PO ₄	8

^aReaction conditions: 1 mmol of **4.12a**, 1.5 mmol of **4.11a**, 4 mol% of Ni-catalyst, 2 equivalents of base in dioxane (3 mL) at 120 °C under argon. ^bYield was determined from ¹H NMR using 1,2,4,5-tetramethylbenzene as an internal standard, ^cReaction was performed in closed vessel. ^dToluene was used as solvent. ^eTHF was used as solvent. ^f1 mmol of **4.11a** was used. ^g1.25 mmol of **4.11a** was used. ^hThe reaction was performed at 140 °C. ⁱ1 equivalent of K₃PO₄ was used. ^j8 mol% of NiBr₂ was used.

Table 4.2. NiBr₂ catalyzed Suzuki cross coupling reaction of aryl halide and aryl boronic acid^a

				
4.13a ; 65%	4.13b ; 90%	4.13c ; 66%	4.13d ; 18% ^b	4.13e ; 23%
				
4.13f ; 60%	4.13g ; Trace	4.13h ; 49%	4.13i ; 45%	4.13j ; 63%
				
4.13k ; 0%	4.13l ; 92%	4.13m ; 84%	4.13n ; 77%	4.13o ; 86%
				
4.13p ; 66%	4.13q ; 37% ^b	4.13r ; 85%	4.13s ; 0%	4.13t ; 0%
				
4.13u ; 66% ^c 44% 42% ^d	4.13v ; 72% ^c	4.13w ; 39% ^{b,c}	4.13z ; 20% ^{b,c}	4.13x ; 78% ^c
				4.13y ; 88% ^c

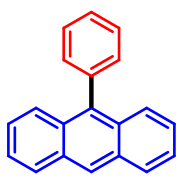
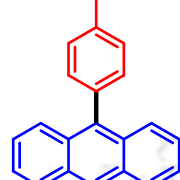
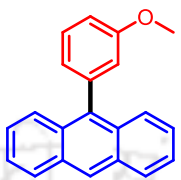
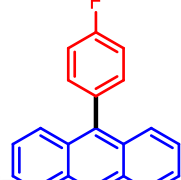
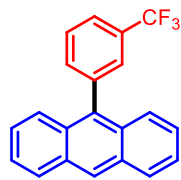
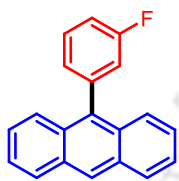
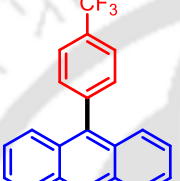
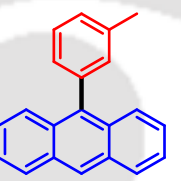
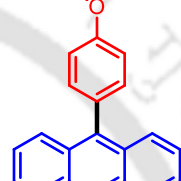
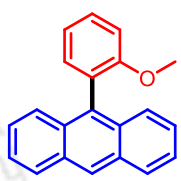
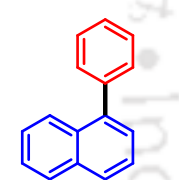
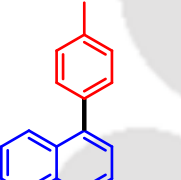
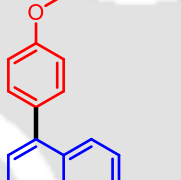
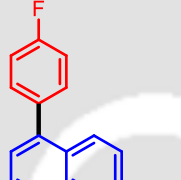
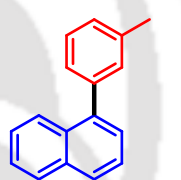
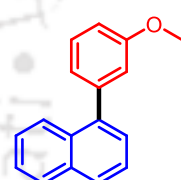
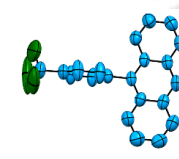
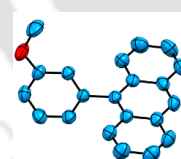
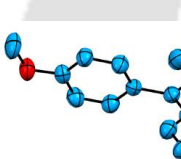
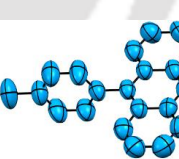
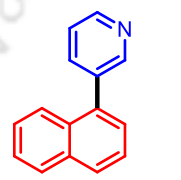
^aReaction conditions: 1 mmol of aryl bromide, 1.5 mmol of aryl boronic acid, 8 mol% of NiBr₂, 2 equivalents of K₃PO₄ in dioxane (3 mL) at 120 °C under argon for 48h. Yield was determined from ¹H NMR using 1,2,4,5 tetramethylbenzene as an internal standard. ^bIsolated yields. ^cAryl iodide was used. ^dAryl chloride was used.

(entry 24, Table 4.1).

The optimized NiBr₂ catalyzed protocol was successfully applied to the Suzuki coupling of various boronic acids with aryl bromides (**4.13a-4.13j**, Table 4.2), aryl iodides (**4.13u-4.13y**, Table 4.2), heteroaryl bromides (**4.13l-q** and **4.13zp**, Table 4.2 & 4.3), bromoanthracene (**4.13z**

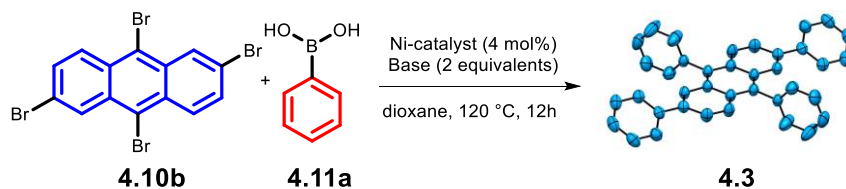
and **4.13za-4.13zi**, Table 4.3) and bromonaphthalene (**4.13zj-4.13zo**, Table 4.3). The poor efficiency with *ortho*-substituted substrates (**4.13d**, **4.13e**, **4.13g**, **4.13zj**, **4.3i** and **4.20d**, Table 4.2,

Table 4.3. NiBr₂ catalyzed Suzuki cross coupling reaction of aryl halide and aryl boronic acid^a

				
4.13za ; 92%	4.13zb ; 85%	4.13zc ; 81%	4.13zd ; 83%	4.13ze ; 65%
				
4.13zf ; 79%	4.13zg ; 68%	4.13zh ; 71%	4.13zi ; 78%	4.13zj ; 5%
				
4.13zk ; 55%	4.13zl ; 49%	4.13zm ; 62%	4.13zn ; 72%	4.13zo ; 61%
				
				
4.13zg CCDC2131726	4.13zc CCDC2131724	4.13zi CCDC2150840	4.13zb CCDC2131725	
				4.13zq ; 92%

^aReaction conditions: 1 mmol of aryl bromide, 1.5 mmol of aryl boronic acid, 8 mol% of NiBr₂, 2 equivalents of K₃PO₄ in dioxane (3 mL) at 120 °C under argon for 12h. All are isolated yields.

4.3 and 4.6) is not surprising as substituents at the *ortho*-position are reported to hinder the cross-coupling of alkyl halides using Pd based catalysts.^{12d-f} The reactivity of nickel bromide towards Suzuki coupling was enhanced for bicyclic (naphthalene) and tricyclic (anthracene) halides, as it got completed within 12h instead of 48 h for the halobenzenes (Table 4.3). The reaction of 1-brom-

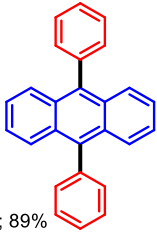
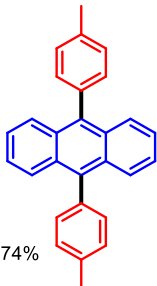
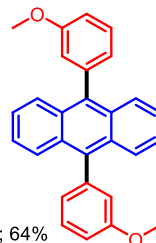
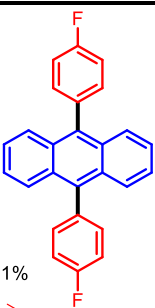
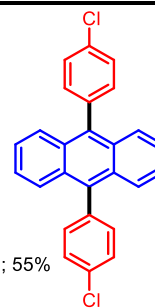
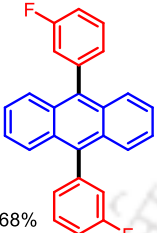
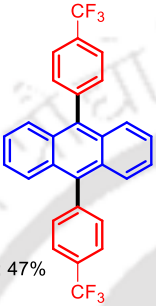
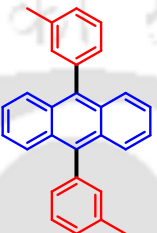
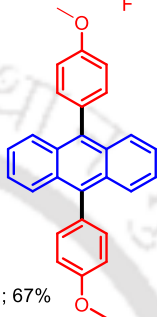
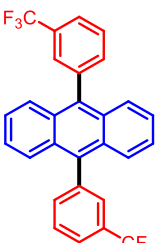
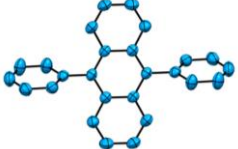
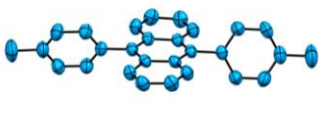
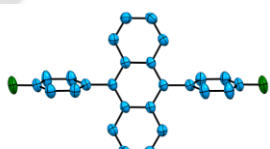
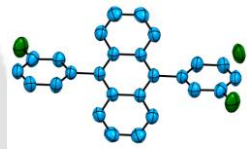
Table 4.4. Optimization of the Ni(II) catalyzed tetra-fold Suzuki coupling of tetrabromoanthracene with PhB(OH)₂^a

entry	Catalyst	Base	Yield ^b of 4.19a , %
1	NiCl ₂	K ₃ PO ₄	40
2	NiCl ₂ ·6H ₂ O	K ₃ PO ₄	trace
3	Ni(DME)Cl ₂	K ₃ PO ₄	4
4	Ni(NO ₃) ₂ ·6H ₂ O	K ₃ PO ₄	17
5	NiBr ₂	K ₃ PO ₄	74
6	NiBr ₂	KOH	31
7	NiBr ₂	KHCO ₃	33
8	NiBr ₂	K ₂ CO ₃	35
9	NiBr ₂	KO ^t Bu	29
10	NiBr ₂	NaOH	10
11	NiBr ₂	NaHCO ₃	11
12	NiBr ₂	Na ₂ CO ₃	18
13	NiBr ₂	NaO ^t Bu	6
14	NiBr ₂	NaOEt	6
15	NiBr ₂	Cs ₂ CO ₃	0
16 ^c	NiBr ₂	K ₃ PO ₄	35
17 ^d	NiBr ₂	K ₃ PO ₄	81
18 ^{d,e}	NiBr ₂	K ₃ PO ₄	42
19 ^{d,f}	NiBr ₂	K ₃ PO ₄	33
20 ^{d,g}	NiBr ₂	K ₃ PO ₄	15
21 ^{d,h}	NiBr ₂	K ₃ PO ₄	27
22 ^{d,i}	NiBr ₂	K ₃ PO ₄	88
23 ^{d,i}	NiI ₂	K ₃ PO ₄	71

^aReaction conditions: 0.101 mmol of **4.10b**, 0.606 mmol of **4.11a**, 4 mol% of Ni-catalyst per halide, 2 equivalents of base per halide in solvent (10mL) at 120 °C conditions. ^bIsolated yield, ^cCatalyst loading 2 mol% per halide, ^dCatalyst loading 8 mol% per halide, ^ebase 1 equivalent per halide, ^fBase 3 equivalents per halide, ^gToluene as solvent, ^hTHF as solvent, ⁱclosed system and solvent used 5mL.

-onaphthalene and 9-bromoanthracene with various arylboronic acids by applying the present synthetic protocol afforded the products aryl-naphthalene (49-84%) and arylanthracene (5- 92%)

Table 4.5. NiBr₂ catalyzed multi-fold Suzuki cross coupling reaction of aryl halide and aryl boronic acid^a

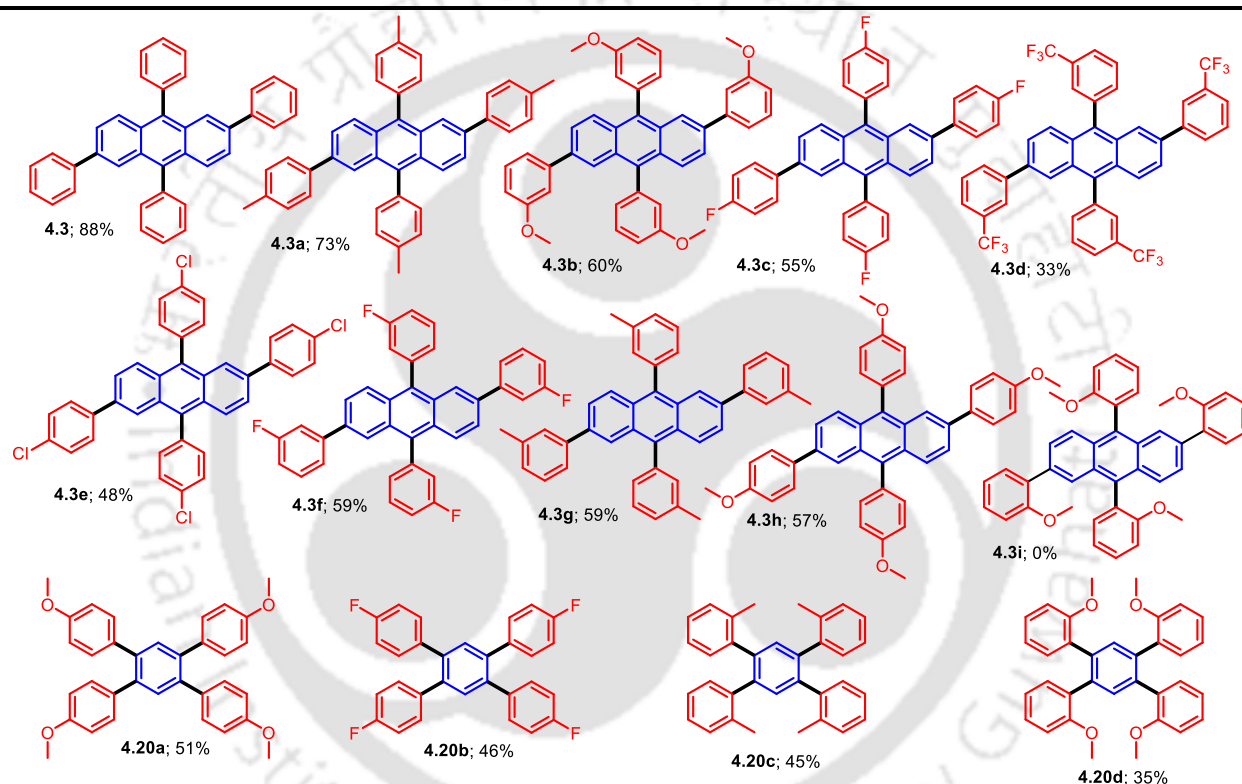
^aReaction conditions: 0.101 mmol of aryl halide, 0.606 mmol of aryl boronic acids, 8 mol% of NiBr₂ per halide, 2 equivalents of base per bromide in dioxane (5 mL) at 120 °C under argon for 12h. All are isolated yields.

with moderate to good yields (Table 4.3). Some of the arylatedanthracene compounds were recrystallized from organic solvent by slow solvent evaporation (**4.13zb** (Figure 4.5), **4.13zc** (Figure 4.6), **4.13zg** (Figure 4.7) and **4.13zi** (Figure 4.8)). Interestingly, the reactivity of various aryl halides follows the order Ar-I > ArBr > Ar-Cl which is in line with the corresponding C-X (X= I, Br and Cl) bond strength. Furthermore, the coupling of aryl boronic acids with benzyl bromides, iodothiophenes and 2-bromo pyridines were not successful (**4.13s-4.13t**, and **4.13k**, Table 4.2).

Considering the importance of polycyclic aromatic hydrocarbon compounds (PAHs)^{1b, 29, 6} that have great application in optoelectronic devices,^{1b, 29a, 29b, 30} we wished to synthesize the derivatives of 2,6,9,10-tetrabromoanthracene (**4.10**). Interestingly while Kwon and co-workers^{1b}

reported a four-step synthetic route to tetrabromoanthracene derivatives using $\text{Pd}(\text{PPh}_3)_4$ as catalyst with an overall yield of 13.4%, the Moorthy group used the same catalyst to synthesize similar derivatives in five steps with an overall yield of 14.2%.^{29b} With an objective to formulate a cost-effective high-yield route to several new 2,6,9,10-tetrabromoanthracenes, we set out to explore the Ni(II) salt catalyzed tetra-fold Suzuki coupling of tetrabromoanthracene^{29c} with phenyl boronic acid (Table 4.4).

Table 4.6. NiBr_2 catalyzed multi-fold Suzuki cross coupling reaction of aryl halide and aryl boronic acid^a



^aReaction conditions: 0.101 mmol of aryl halide, 0.606 mmol of aryl boronic acids, 8 mol% of NiBr_2 per halide, 2 equivalents of K_3PO_4 per bromide in dioxane (5 mL) at 120 °C under argon for 12h. All are isolated yields.

Compound **4.10** when reacted with phenylboronic acid (**4.11a**) (1.5 equivalent with respect to each bromide) in the presence of K_3PO_4 (2 equivalents with respect to each bromide) and nickel chloride (4 mol% with respect to each bromide) in dioxane at 120 °C for 12 h, afforded the desired product **4.3** with 40% isolated yield (entry 1, Table 4.4). Various nickel salts were tested as catalysts under

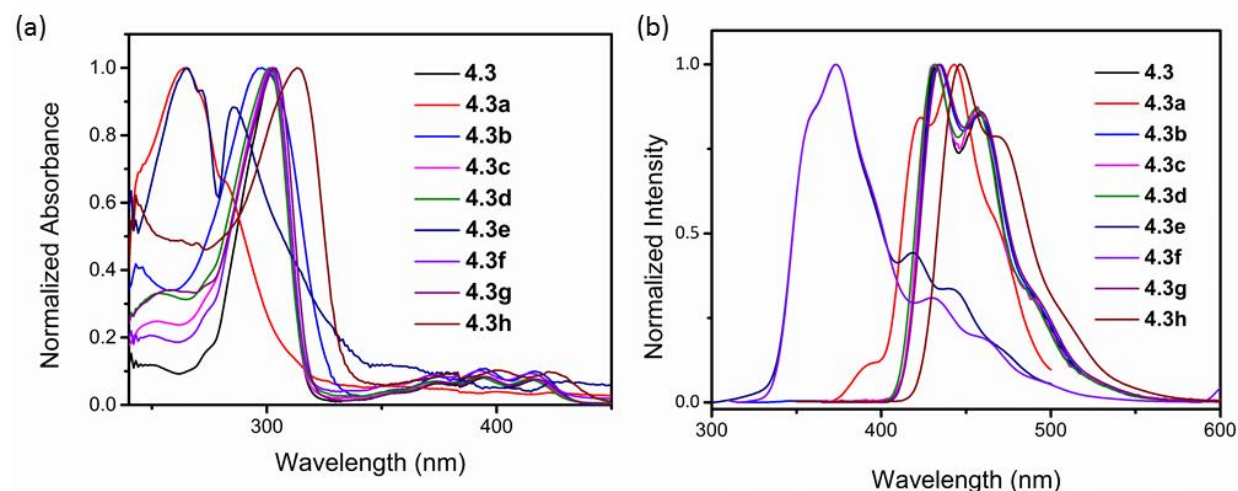


Figure 4.3. (a) Normalized absorption spectra for **4.3** & **4.3a-h** (b) Normalized emission spectra for **4.3** & **4.3a-h**

Table 4.7. Photophysical properties of **4.3** & **4.3-h**

Entry	compound	$\lambda_{\text{max}}^{\text{a}}$ (nm)	$\lambda_{\text{em}}^{\text{a}}$ (nm)	$\phi_{\text{F}}^{\text{b}}$ (%)	E_{g} (eV) ^c
1	4.3	303	432	49	3.9
2	4.3a	264	423	04	3.9
3	4.3b	298	434	37	3.8
4	4.3c	302	432	45	3.8
5	4.3d	301	431	40	3.8
6	4.3e	265	373	08	3.4
7	4.3f	302	373	45	3.8
8	4.3g	303	435	46	3.8
9	4.3h	313	447	90	3.7

^aThe absorption (3×10^{-5} M) as well as emission (6×10^{-6} M) spectra recorded in CHCl_3 . ^b Quantum yield were calculated with respect to quinine sulfate in 0.1 (M) H_2SO_4 as standard ($\phi = 54\%$). ^cThe bandgaps were calculated from Tauc plot.

identical conditions (entries 1-5, Table 4.4) and amongst them, the best yield (ca. 74%) was obtained with NiBr_2 as catalyst (entry 5, Table 4.4). Several bases were employed under the same reaction conditions (entries 5-15, Table 4.4) and K_3PO_4 was found to be very efficient (entry 5, Table 4.4). The yield of the product decreased (ca. 35%) upon lowering the NiBr_2 loading to 2 mol% per bromide (entry 16, Table 4.4), while it increased to 81% in the case of 8 mol% (per

bromide) NiBr_2 loading (entry 17, Table 4.4). Among the varying amounts of K_3PO_4 used (entries 5, 18-19, Table 4.4), the best results were obtained with 2 equivalents of base per bromide (entry 5, Table 4.4). Solvents like THF and toluene, resulted in lower yields (entries 20-21, Table 4.4). The yield of the compound (**4.3**) was enhanced up to 88%, when the reaction was performed in a closed system (entry 22, Table 4.4). The NiBr_2 catalyzed multi-fold Suzuki coupling was then successfully applied to the reaction of tetra- /di-bromoanthracene and tetraiodobenzene with a variety of aryl boronic acids (Table 4.5 & Table 4.6). 9,10-dibromoanthracene with both electron-donating and electron-withdrawing substituents were well tolerated under the optimized conditions resulting in moderate to good yield (37-89%). Four of them (**4.19a** (Figure 4.10), **4.19b** (Figure 4.11), **4.19d** (Figure 4.12), **4.19f** (Figure 4.13)) were recrystallized from dichloromethane by slow evaporation at room temperature.

The current optimized reaction conditions (entry 22, Table 4.4) are efficient to access tetraarylatedbenzene (35-51%) and tetraarylatedanthracene (up to 88%) with moderate to good yields. The single crystal of 2,6,9,10-tetraphenylanthracene was obtained from DCM as shown in Figure 4.9. The tetraarylated anthracenes **4.3** & **4.3a-h** demonstrate exciting photophysical properties (Figure 4.3, Table 4.7). The newly synthesized tetraalkylated anthracene compounds (**4.3a-h**) emit blue light with moderate to good quantum yield. Highly efficient blue emissive electroluminescent materials are the most significant among the three primary colors namely green, red and blue in the manufacturing of affordable and long lasting displays based on OLEDs.^{1b, 29b, 31 32} They can also serve as host material in addition to being more energy efficient than red and green for cascade energy transfer to red and green dopants for the manufacturing of full color displays based on single host matrix.^{29b, 33} Recently, Kwon and Moorthy fabricated 2,6,9,10-tetraarylatedanthracene in OLED devices and they observed that it emits blue-light with high efficiency. Similarly compounds (**4.3a-h**) offer great promise for the fabrication of OLEDs devices.

Negligible effect on the yield of **4.3** (Scheme 4.11) in the presence of radical scavenger TEMPO demonstrates the absence of any radical species. The reaction described in entry 22, Table 4.4 was followed by EPR analysis at 0h, 1h and 3h. The reaction mixture was EPR silent which is indicative of the absence of square-planar Ni(I) , Ni(III) and any radical species (Figure 4.4). This points to the presence of square-planar Ni(0) and Ni(II) species in the catalytic cycle. Addition of COD (16 mol%) lowered the yield of the NiBr_2 (8 mol%) catalysed Suzuki coupling of 4-bromo-

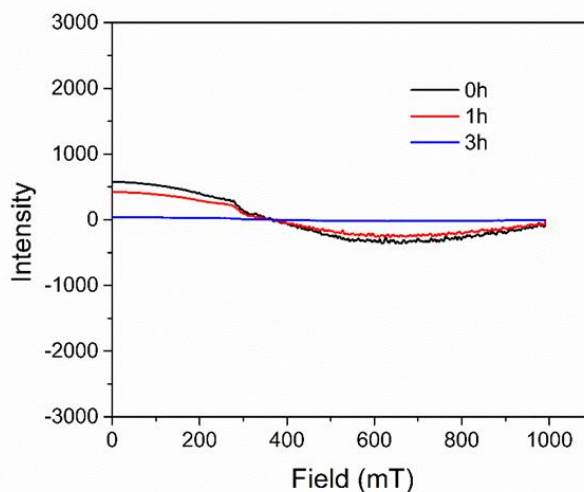
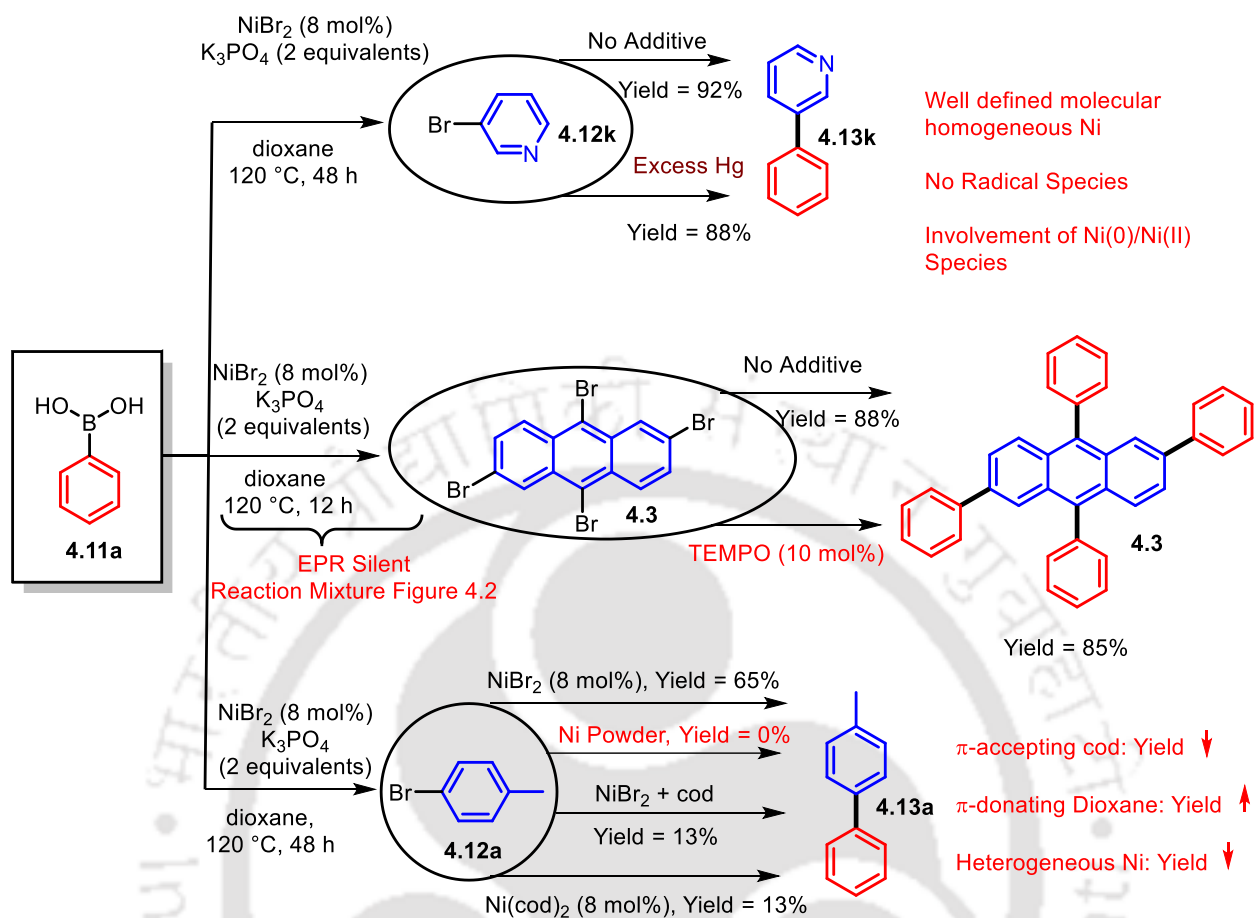
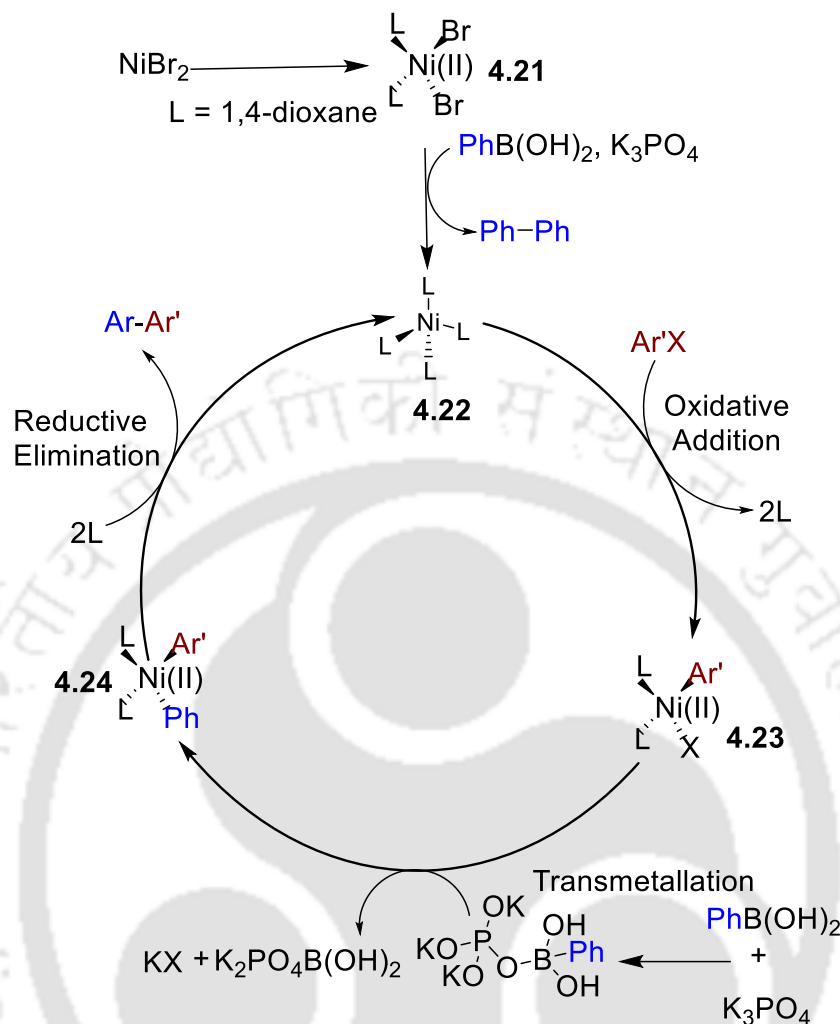


Figure 4.4. X-band EPR spectra of the reaction mixture (entry 16, Table 4.4) at 0 h (Black line), 1 h (red line), 3 h (blue line) at 77K.



Scheme 4.11. Proposed Mechanism

toluene with phenyl boronic acid (Scheme 4.10). The yield remained same (ca. 13%) when NiBr_2 (8 mol%) + COD (16 mol%) was replaced by Ni(COD)_2 (8 mol%) which is indicative of the involvement of a common intermediate such as **4.22** (Scheme 4.11, L = double bond of COD). It has been reported that Ni(0) systems with π -accepting ligands give poor yield of Suzuki coupled products.^{16c, 26a, 34} Using Ni powder as source of Ni(0) also lead to poor yield of **4.3** which is very similar to the reports by Tran³⁵ where good yields are obtained only when additives such as PEG are used. Furthermore, the yield of **4.13k** was unaffected when excess mercury was used to quench any heterogeneous Ni species (Scheme 4.10). These observations indicate the complete homogeneous nature of the reaction which proceeds via well-defined molecular intermediates as shown in Scheme 4.11 which is in line with mechanism proposed with other Ni complexes.^{16c, 26a,}

^{34, 34b, 36} The first step involves the salt metathesis of Ni(II) species **4.21** with the boronic acid and K_3PO_4 ³⁶ followed by reductive elimination of biphenyl to yield the Ni(0) species **4.22**. Interestingly the solvent dioxane stabilizes the Ni(0) in **4.22** and its strong π -donating ability results in a facile oxidative addition of the aryl halide to **4.22** to give the Ni(II) species **4.23**. Not surprisingly, Ni(0) species with π -acceptors such as COD (Scheme 4.10) and phosphines^{16c, 26a, 34} are less reactive. This also indicates that oxidative addition is the RDS of the NiBr₂ catalyzed Suzuki coupling reaction. The salt metathesis of Ni(II) species **4.23** with the boronic acid and K_3PO_4 leads to Ni(II) species **4.24**. A subsequent reductive elimination of the product biaryl from **4.24** yields the desired product along with the regeneration of the active Ni(0) species **4.22**.

4.3. Conclusions

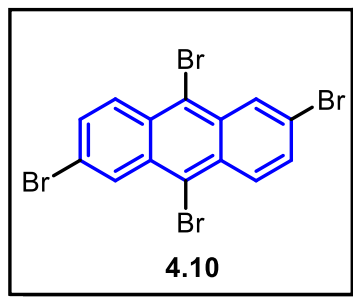
Under ambient conditions, readily available and inexpensive NiBr₂ accomplishes the catalytic Suzuki coupling of a variety (ca. 37 examples) of aryl halides with aryl boronic acids in high yields and good functional group tolerance. In accordance with the C-X (X= I, Br and Cl) bond strength, the reactivity follows the order Ar-I > Ar-Br > Ar-Cl which indicates that the oxidative addition may be the slowest step in the catalytic cycle. The reaction mixture was EPR silent and there was no effect on reaction in the presence of radical scavenger TEMPO which shows that radical species is absent in the catalytic cycle. The NiBr₂ catalyzed Suzuki reaction is likely to proceed via a pure organometallic pathway involving well-defined molecular Ni(0)/Ni(II) species in the catalytic cycle as inferred from EPR analysis and from reaction in the presence of Hg and TEMPO. The yield of the product was drastically decreased in the presence of π -accepting ligand such as 1,5-cyclooctadiene (cod). The π -donating solvent dioxane favors a facile oxidative addition of the aryl halide on Ni(0) species which is likely to be the rate-determining-step (RDS). For the first time, this NiBr₂ based catalytic system has been successfully applied to the multi-fold Suzuki coupling (ca. 23 examples) of tetra-/dibromoanthracene and tetraiodo benzene with several aryl boronic acids leading to valuable new PAHs.

4.4. Experimental section

4.4.1. Materials & methods

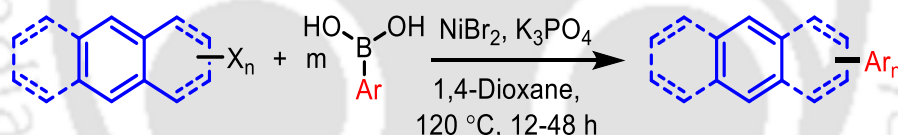
All the reactions were performed under purified argon using a standard double manifold, unless otherwise mentioned. Chemicals such as arylboronic acids, aryl halides, anthracene, bromine, NiBr_2 , NiI_2 , NiCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, K_3PO_4 , NaOH , KOH , Na^tOBu , K^tOBu , CS_2CO_3 , K_2CO_3 , NaHCO_3 , KHCO_3 , and NaOEt were purchased from Avra, Sigma-Aldrich, SRL, and Merck. The chemicals were used without further purification. Solvents such as dioxane, toluene, and tetrahydrofuran (THF) were purchased from Merck and dried via double distillation by using Na/benzophenone .³⁷ HPLC grade Chloroform solvent was used for studies of UV-Vis and fluorescence. TLC analysis was used to monitor the reactions and the desired products were purified by column chromatography using Merck silica gel (100–200) mesh as stationary phase. NMR spectra were recorded by using Bruker AVANCE 400, Bruker AVANCE 500, and Bruker AVANCE 600 operating at 400 MHz, 500 MHz and 600 MHz for ^1H NMR, 110 MHz (Bruker AVANCE 400), 126 MHz (Bruker AVANCE 500), and 151 MHz (Bruker AVANCE 600) for $^{13}\text{C}\{^1\text{H}\}$ NMR, 377 MHz (Bruker AVANCE 400) and 471 MHz (Bruker AVANCE 500) for ^{19}F NMR. Peak characterisation: s = singlet, d = doublet, t = triplet, and m = multiplet. High resolution mass spectra (HRMS) were acquired using Agilent technologies model G6564 QTOF and fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). The samples were ionized in positive ion mode using a MALDI or ESI ionization sources. The X-band EPR spectra were obtained on a JES-FA200 ESR spectrometer, at 77K with microwave power of 0.998 mW and microwave frequency of 9.14 GHz. FT-IR measurements were recorded using PerkinElmer IR spectrometer. UV-Vis spectra were recorded by using a PerkinElmer Model Lambda-750 spectrophotometer and Fluorescence emission spectra were obtained by using a Horiba Fluoromax-4 spectrofluorometer. Buchi melting point B-540 apparatus was used to record melting points in an open capillary tube. Single Crystal X-ray analysis was carried out on a Bruker D8 Venture single-crystal X-ray diffractometer using graphite-monochromated Mo K_α radiation. The structure of crystals were solved and refined by the full matrix least-squares method by using SHELXS-14.27.^{38c} The structures of the crystals were drawn by using Mercury 4.1.3 for Windows.³⁹

4.4.2. Synthetic procedures



2,6,9,10-tetrabromoanthracene (4.10) : Compound (4.10) was synthesized according to literature procedure.^{29c} 9,10-Dibromoanthracene (4 g, 11.904 mmol) and nitrobenzene (28 mL) were added into a two-neck round bottom flask. The solution of bromine (1.6 mL) in nitrobenzene (2.8 mL) was added dropwise into a mixture of 9,10-dibromoanthracene at 100 °C and stirred at 180 °C for 6 h. The reaction mixture was then stirred at 200 °C for 30 min. It was subsequently cooled down to room temperature and stirred overnight. The yellow solid precipitate formed was filtered and washed with hot DCM (20 ml × 3). The yellow solid (3.2 g) obtained was dissolved in toluene (100 ml) at 60–70 °C and cooled down to get a yellow precipitate (2.46 g, 41%). ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, J = 1.9 Hz, 2H, H-1 and H-5 of anthracene), 8.45 (d, J = 9.4 Hz, 2H, H-4 and H-8 of anthracene), 7.69 (dd, J = 9.3, 1.9 Hz, 2H, H-3 and H-7 of anthracene). MALDI-TOF calculated exact mass for C₁₄H₆Br₄ (M⁺): 493.71, found: 493.69.

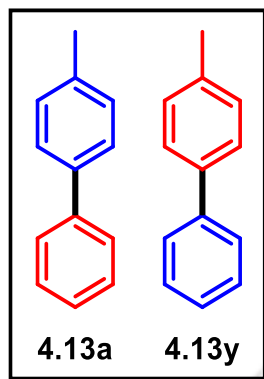
General Scheme of Suzuki Reaction:



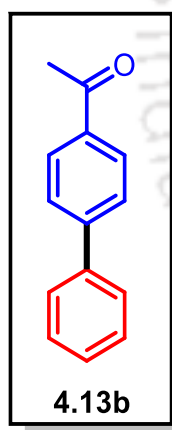
General Synthetic Protocol of Suzuki.

A 10 mL Schlenk flask was taken, evacuated and charged with argon for three times. Aryl halide (1 equivalent), arylboronic acid (1.5 equivalent per halide), NiBr₂ (8 mol% per halide), K₃PO₄ (2 equivalents per halide) and, dioxane (5 ml) were added and stirred at 120 °C for 12-48 h. The reaction was monitored by TLC analysis. After completion of the reaction, the organic solvent was evaporated under reduced pressure. The yield of the product (wherever applicable) was calculated by recording ¹H NMR of the reaction mixture using 1,2,4,5-tetramethylbenzene or toluene as an internal standard. The reaction mixture was extracted by DCM and washed with brine solution (20 ml × 3). The organic phase was dried over anhydrous Na₂SO₄, filtered and then solvent was evaporated under reduced pressure. The crude product was purified by silica gel (100-200 mesh)

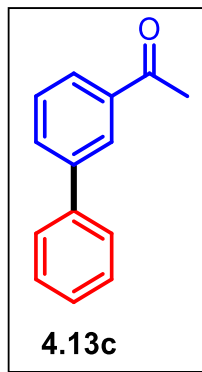
column chromatography using a mixture of DCM and hexane as eluent prior to determining the isolated yield.



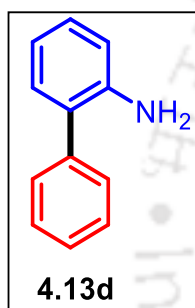
***p*-methyl-1,1'-biphenyl (4.13a/4.13y).**⁴⁰ Compound (**4.13a**) was synthesized from 4-bromotoluene (171 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using hexane as eluent. Compound (**4.13y**) was synthesized from iodobenzene (204 mg, 1 mmol, 1 equivalent) and *p*-tolylboronic acid (204 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. Yield (**4.13a**: 65 %; **4.13y**: 88 %; white solid; Yield calculated by ¹H NMR. ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 8.2, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H).



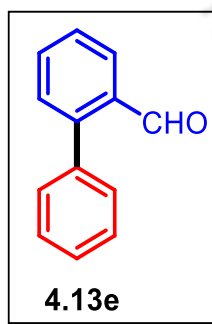
1-([1,1'-biphenyl]-4-yl)ethan-1-one (4.13b).⁴⁰ Compound (**4.13b**) was synthesized from 4-bromoacetophenone (199 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using hexane as eluent. Yield (90 %; white solid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.41 (dd, *J* = 8.3, 6.3 Hz, 1H), 2.64 (d, *J* = 1.5 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 197.96, 145.93, 140.01, 135.98, 129.10, 129.06, 128.38, 127.42, 127.37, 26.82.



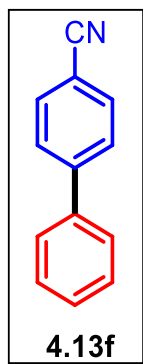
1-([1,1'-biphenyl]-3-yl)ethan-1-one (4.13c).⁴¹ Compound (4.13c) was synthesized from 3'-bromoacetophenone (171 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using hexane as eluent. Yield (66 %; colourless oil; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.19 (t, J = 1.8 Hz, 1H), 7.94 (dt, J = 8.0, 1.4 Hz, 1H), 7.80 (ddd, J = 7.7, 1.9, 1.1 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.41 – 7.38 (m, 1H), 2.66 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 198.25, 141.90, 140.35, 137.81, 131.90, 129.20, 129.08, 127.97, 127.36, 127.13, 26.92.



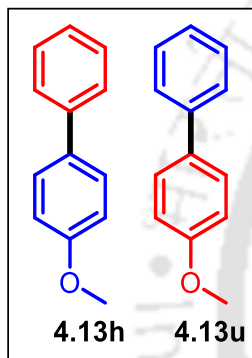
[1,1'-biphenyl]-o-amine (4.13d).⁴² Compound (4.13d) was synthesized from 2-bromoaniline (172 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using hexane as eluent. The product (31 mg) was obtained as white solid with 18% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.47 – 7.43 (m, 4H), 7.36 – 7.33 (m, 1H), 7.18 – 7.12 (m, 2H), 6.83 (td, J = 7.4, 1.2 Hz, 1H), 6.77 (dd, J = 8.0, 1.2 Hz, 1H), 3.76 (br, s, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 143.62, 139.65, 130.58, 129.22, 128.94, 128.62, 127.78, 127.29, 118.78, 115.73.



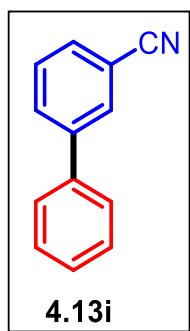
[1,1'-biphenyl]-o-carbaldehyde (4.13e).⁴³ Compound (4.13e) was synthesized from 2-bromobenzaldehyde (185 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 5 % (v/v) ethyl acetate/hexane as eluent. Yield (23 %; colourless oil; Yield calculated by ¹H NMR). ¹H NMR (600 MHz, CDCl₃) δ 9.99 (d, J = 0.9 Hz, 1H), 8.03 (dd, J = 7.8, 1.4 Hz, 1H), 7.65 (td, J = 7.5, 1.4 Hz, 1H), 7.52 – 7.45 (m, 5H), 7.40 – 7.38 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 192.67, 146.13, 137.89, 133.85, 133.73, 130.93, 130.25, 128.58, 128.27, 127.93, 127.71.



[1,1'-biphenyl]-p-carbonitrile (4.13f).⁴¹ Compound (4.13f) was synthesized from 4-bromobenzonitrile (182 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 2 % (v/v) ethyl acetate/hexane as eluent. Yield (60 %; white solid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 145.82, 139.31, 132.74, 129.25, 128.80, 127.87, 127.37, 119.09, 111.04.

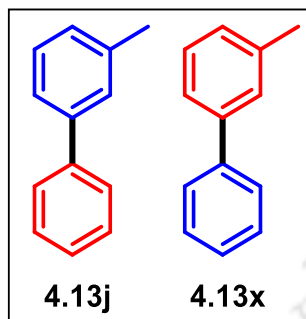


p-methoxy-1,1'-biphenyl (4.13h/4.13u).⁴⁰ Compound (4.13h) was synthesized from *p*-bromoanisole (187 mg 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. Compound (4.13u) was synthesized from arylhalide (1 mmol, 1 equivalent) and (*p*-methoxyphenyl)boronic acid (1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. Yield (3g: 49%; 3s: 66% for X = I, 44% for X = Br, 42% for X = Cl; colourless liquid; Yield calculated by ¹H NMR). ¹H NMR (600 MHz, CDCl₃) δ 7.54 (ddd, J = 12.3, 7.5, 1.8 Hz, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 6.98 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 159.2, 140.9, 133.9, 128.8, 128.3, 126.8, 126.8, 114.3, 55.5.



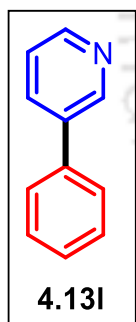
[1,1'-biphenyl]-m-carbonitrile (4.13i).⁴⁴ Compound (4.13i) was synthesized from 3-bromobenzonitrile (182 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 2 % (v/v) ethyl acetate/hexane as eluent. Yield (45 %; colourless liquid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.55

(t, $J = 5.5$ Hz, 3H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 142.52, 138.94, 131.59, 130.79, 129.70, 129.22, 128.49, 127.17, 118.96, 113.02.



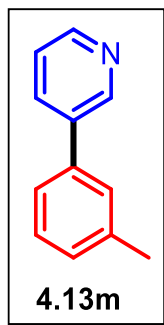
***m*-methyl-1,1'-biphenyl (4.13j/4.13x).**⁴⁰ Compound (**4.13j**) was synthesized from 3-bromotoluene (171 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. Compound (**4.13x**) was synthesized from iodobenzene (204 mg, 1 mmol, 1 equivalents) and *m*-tolylboronic acid (204 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction

mixture product was purified by column chromatography by using hexane as eluent. Yield (3i: 63 %; 3w: 78 %; colourless liquid; Yield calculated by ^1H NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 7.2$ Hz, 2H), 7.40 (q, $J = 11.2, 9.2$ Hz, 4H), 7.34 – 7.29 (m, 2H), 7.15 (d, $J = 7.5$ Hz, 1H), 2.41 (s, 3H).

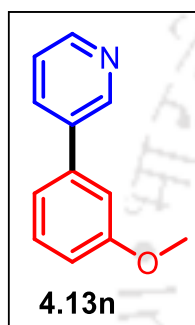


***m*-phenylpyridine (4.13l).**⁴¹ Compound (**4.13l**) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and phenylboronic acid (182 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 10 % (v/v) ethyl acetate/hexane as eluent. Yield (92 %; colourless liquid; Yield calculated by ^1H NMR). ^1H NMR (500 MHz, CDCl_3) δ 8.85 (d, $J = 2.3$ Hz, 1H), 8.59 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.88 (dt, $J = 7.9, 2.1$ Hz, 1H), 7.58 (dd, $J = 7.4,$

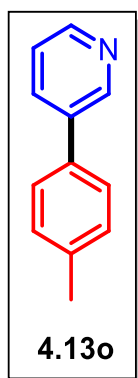
1.7 Hz, 2H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.37 (dd, $J = 7.9, 4.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 148.55, 148.43, 137.95, 136.79, 134.52, 129.21, 128.23, 127.28, 123.69.



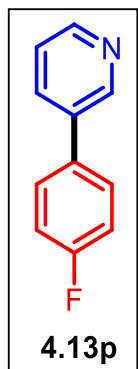
***m*-(*m*-tolyl)pyridine (4.13m).**⁴⁵ Compound (4.13m) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and *m*-tolylboronic acid (204 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 10-15 % (v/v) ethyl acetate/hexane as eluent. Yield (84 %; colourless liquid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.85 – 8.81 (m, 1H), 8.57 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.86 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.22 (dt, *J* = 6.5, 2.0 Hz, 1H), 2.43 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 148.33, 138.84, 137.83, 136.88, 134.53, 129.07, 128.95, 127.98, 124.33, 123.62, 21.60.



***m*-(*m*-methoxyphenyl)pyridine (4.13n).**⁴⁶ Compound (4.13n) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and 3-methoxyphenylboronic acid (228 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 15-18 % (v/v) ethyl acetate/hexane as eluent. Yield (77 %; light yellow liquid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.84 (d, *J* = 2.4 Hz, 1H), 8.59 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.43 – 7.34 (m, 2H), 7.18 – 7.15 (m, 1H), 7.10 (t, *J* = 2.1 Hz, 1H), 6.95 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.87 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 160.25, 148.69, 148.44, 139.41, 136.68, 134.59, 130.28, 123.68, 119.72, 113.55, 113.07, 55.49.

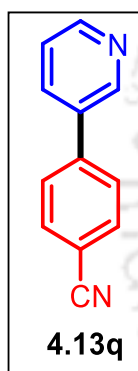


***m*-(*p*-tolyl)pyridine (4.13o).**⁴⁷ Compound (4.13o) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and *p*-tolylboronic acid (204 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 15-18 % (v/v) ethyl acetate/hexane as eluent. Yield (86%; colourless liquid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.83 (d, *J* = 2.3 Hz, 1H), 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.86 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 148.25, 148.22, 138.18, 136.73, 135.01, 134.32, 129.93, 127.09, 123.66, 21.27.



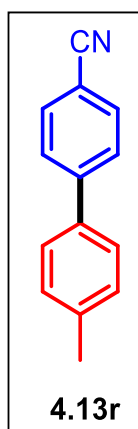
***m*-(*p*-fluorophenyl)pyridine (4.13p).**⁴⁷ Compound (4.13p) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and 4-fluorophenylboronic acid (210 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 15-18 % (v/v) ethyl acetate/hexane as eluent. Yield (66 %; colourless liquid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 8.79 (d, *J* = 2.5 Hz, 1H), 8.57 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.82 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.35 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.16 (t, *J* = 8.8 Hz, 2H).

¹⁹F NMR (377 MHz, CDCl₃) δ -114.17. ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.07 (d, *J* = 247.8 Hz), 148.59, 148.26, 135.89, 134.41, 134.07 (d, *J* = 3.3 Hz), 128.96 (d, *J* = 8.2 Hz), 123.73, 116.22 (d, *J* = 21.7 Hz).



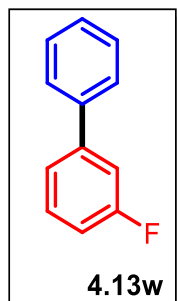
***p*-(pyridin-3-yl)benzonitrile (4.13q).**⁴⁸ Compound (4.13q) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and *p*-cyanophenylboronic acid (220 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 15-20 % (v/v) ethyl acetate/hexane as eluent. The product (66 mg) was obtained as white solid with 37% isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J* = 2.4 Hz, 1H), 8.67 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.89 (dt, *J* = 7.9, 2.1 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.71 – 7.68 (m, 2H), 7.44 – 7.40 (m, 1H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 149.88, 148.37, 142.46, 134.94, 134.65, 133.03, 127.94, 123.95, 118.69, 112.09.

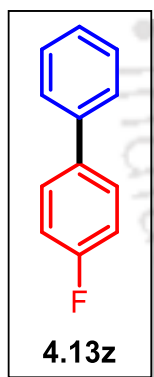


4'-methyl-[1,1'-biphenyl]-4-carbonitrile (4.13r).⁴⁹ Compound (4.13r) was synthesized from 4-bromobenzonitrile (182 mg, 1 mmol, 1 equivalent) and *p*-tolylboronic acid (203 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 5% (v/v) ethyl acetate/hexane as eluent. Yield (85 %; white solid; Yield calculated by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.29

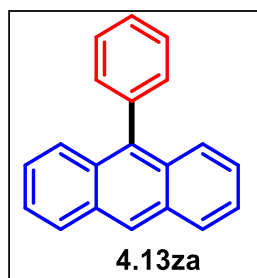
(d, $J = 7.8$ Hz, 2H), 2.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 145.74, 138.89, 136.39, 132.70, 129.97, 127.59, 127.19, 119.18, 110.65, 21.31.



***m*-fluoro-1,1'-biphenyl (4.13w).**⁵⁰ Compound (4.13w) was synthesized from iodobenzene (89 mg, 0.44 mmol, 1 equivalent) and (*m*-fluorophenyl)boronic acid (92 mg, 0.66 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (29 mg) was obtained as colourless liquid 39% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.56 (m, 2H), 7.46 (dd, $J = 8.4, 6.9$ Hz, 2H), 7.44 – 7.35 (m, 3H), 7.31 (ddd, $J = 10.2, 2.6, 1.6$ Hz, 1H), 7.10 – 7.02 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 164.1, 162.5, 143.6 (d, $J = 7.6$ Hz), 140.0 (d, $J = 2.3$ Hz), 130.5 (d, $J = 8.5$ Hz), 130.3 (d, $J = 8.4$ Hz), 129.0, 127.9, 127.2, 114.8 (d, $J = 21.1$ Hz), 114.2 (d, $J = 2.1$ Hz), 114.0 (d, $J = 2.7$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -113.1.

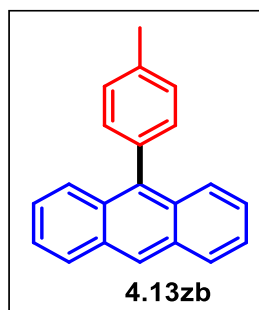


***p*-fluoro-1,1'-biphenyl (4.13z).**⁴¹ Compound (4.13z) was synthesized from iodobenzene (204 mg, 1 mmol, 1 equivalent) and *p*-fluorophenylboronic acid (203 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The product (31 mg) was obtained as white solid with 20 % isolated yield. ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.53 (m, 4H), 7.47 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H), 7.16 – 7.11 (m, 2H). ^{19}F NMR (377 MHz, CDCl_3) δ -115.86. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 162.60 (d, $J = 246.3$ Hz), 140.40, 137.49, 128.96, 128.83 (d, $J = 8.1$ Hz), 127.40, 127.16, 115.75 (d, $J = 21.4$ Hz).

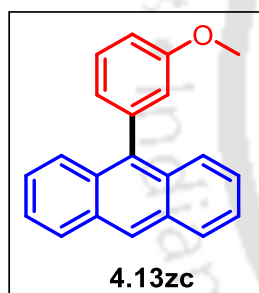


9-phenylanthracene (4.13za).⁵¹ Compound (4.13za) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and phenylboronic acid (71 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (91 mg) was obtained as white solid with 92% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.50 (s, 1H), 8.05 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.8$ Hz, 2H), 7.58 (t, $J = 7.3$ Hz, 2H),

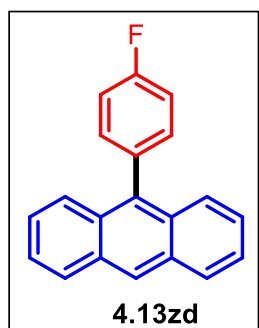
7.53 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.43 (m, 4H), 7.37 – 7.32 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 138.92, 137.17, 131.50, 131.38, 130.34, 128.50, 128.46, 127.59, 126.98, 126.68, 125.45, 125.23.



9-(*p*-tolyl)anthracene (4.13zb).⁵¹ Compound (4.13zb) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and *p*-tolylboronic acid (78 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (88 mg) was obtained as white solid with 85% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.48 (s, 1H), 8.04 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.48 – 7.43 (m, 2H), 7.39 (d, $J = 7.7$ Hz, 2H), 7.36 – 7.31 (m, 4H), 2.53 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 137.29, 137.20, 135.80, 131.53, 131.25, 130.46, 129.20, 128.45, 127.08, 126.50, 125.34, 125.19, 21.53.

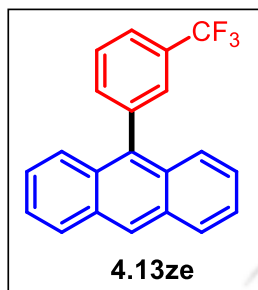


9-(*m*-methoxyphenyl)anthracene (4.13zc).⁵¹ Compound (4.13zc) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (*m*-methoxyphenyl)boronic acid (89 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (89 mg) was obtained as white solid with 81% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 8.51 (s, 1H), 8.06 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.8$ Hz, 2H), 7.55 – 7.44 (m, 3H), 7.40 – 7.35 (m, 2H), 7.10 (d, $J = 8.4$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 7.02 (s, 1H), 3.86 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.7, 140.3, 136.9, 131.4, 130.2, 129.5, 128.4, 126.9, 126.6, 125.4, 125.2, 123.8, 116.6, 113.3, 55.4.



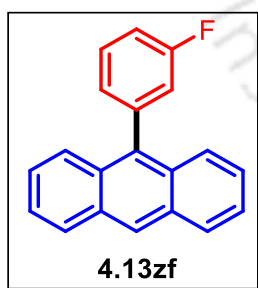
9-(*p*-fluorophenyl)anthracene (4.13zd).⁵¹ Compound (4.13zd) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (*p*-fluorophenyl)boronic acid (82 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (88 mg) was obtained as white solid with 83% isolated yield. ^1H NMR (600

MHz, CDCl₃) δ 8.51 (s, 1H), 8.05 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.41 – 7.32 (m, 4H), 7.28 (t, J = 8.8 Hz, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.2, 161.5, 135.7, 134.5 (d, J = 3.4 Hz), 132.8 (d, J = 7.7 Hz), 131.3, 130.3, 128.4, 126.8, 126.5, 125.5, 125.1, 115.4 (d, J = 21.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -115.0.



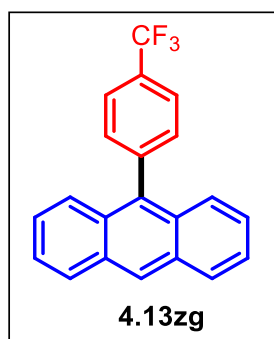
9-(*m*-(trifluoromethyl)phenyl)anthracene (4.13ze).⁵¹ Compound (4.13ze) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (*m*-(trifluoromethyl)phenyl)boronic acid (112 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (81 mg) was obtained as white solid

with 65% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (s, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.52 – 7.47 (m, 2H), 7.40 (ddd, J = 8.7, 6.5, 1.2 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 139.86, 135.12, 134.84, 131.44, 130.97, 130.25, 129.10, 128.65, 128.12 (d, J = 3.8 Hz), 127.46, 126.33, 126.02, 125.38, 124.59 (q, J = 3.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.4.

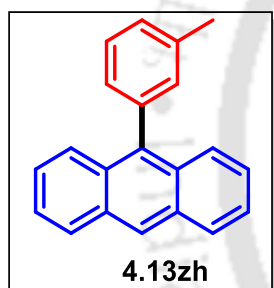


9-(*m*-fluorophenyl)anthracene (4.13zf).⁵¹ Compound (4.13zf) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (*m*-fluorophenyl)boronic acid (82 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (84 mg) was obtained as white solid with 79% isolated yield. ¹H NMR (600

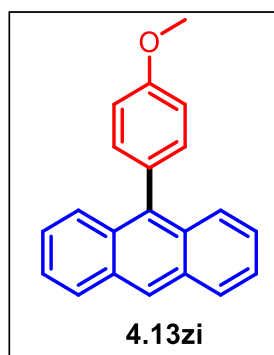
MHz, CDCl₃) δ 8.52 (s, 1H), 8.06 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.41 – 7.34 (m, 2H), 7.25 – 7.21 (m, 2H), 7.17 (dt, J = 9.4, 2.0 Hz, 1H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.7, 162.0, 141.0 (d, J = 7.8 Hz), 135.4, 131.2, 130.8 – 129.5 (m), 128.4, 127.3 – 126.8 (m), 126.4, 125.6, 125.1, 118.3 (d, J = 21.0 Hz), 114.4 (d, J = 21.0 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -113.3.



9-(p-(trifluoromethyl)phenyl)anthracene (4.13zg).³ Compound (4.13zg) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (p-(trifluoromethyl)phenyl)boronic acid (112 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (85 mg) was obtained as white solid with 68% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (s, 1H), 8.11 – 8.02 (m, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.52 – 7.45 (m, 2H), 7.38 (ddd, J = 8.9, 6.4, 1.3 Hz, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 142.8, 135.1, 131.7, 131.2, 129.9, 128.5, 128.1, 127.2, 126.2, 125.8, 125.4 (dt, J = 7.2, 3.7 Hz), 125.2, 123.4. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.3.

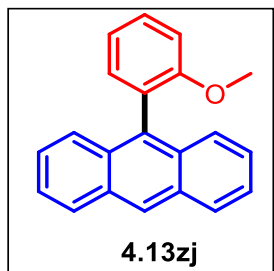


9-(m-tolyl)anthracene (4.13zh).¹⁵ Compound (4.13zh) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and m-tolylboronic acid (78mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (73 mg) was obtained as white solid with 71% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (s, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.41 – 7.32 (m, 3H), 7.29 – 7.22 (m, 2H), 2.47 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 138.8, 138.0, 137.4, 132.0, 131.5, 130.3, 128.4, 128.3, 128.2, 127.0, 126.5, 125.3, 125.1, 21.6.

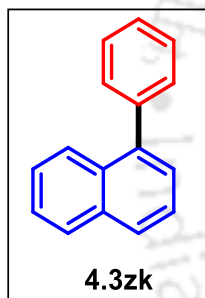


9-(p-methoxyphenyl)anthracene (4.13zi).⁵¹ Compound (4.13zi) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (p-methoxyphenyl)boronic acid (89 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (86 mg) was obtained as white solid with 78% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 8.49 (s, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 9.5 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.36 (d, J = 8.6 Hz, 4H), 7.13 (d, J = 8.6 Hz, 2H), 3.96 (s,

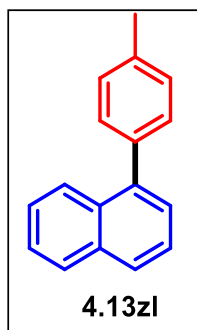
3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.1, 136.9, 132.4, 131.5, 130.9, 130.6, 128.4, 127.0, 126.5, 125.3, 125.2, 113.9, 55.5.



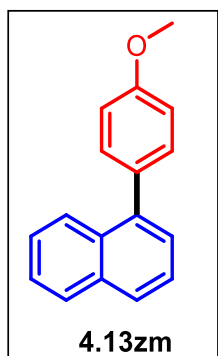
9-(*o*-methoxyphenyl)anthracene (4.13zj).³ Compound (4.13zj) was synthesized from 9-bromoanthracene (100 mg, 0.39 mmol, 1 equivalent) and (*o*-methoxyphenyl)boronic acid (89 mg, 0.59 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (6 mg) was obtained as white solid with 5% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.53 (ddt, J = 8.2, 7.3, 2.1 Hz, 1H), 7.45 (tdd, J = 8.3, 7.1, 1.3 Hz, 2H), 7.33 (ddd, J = 8.8, 6.5, 1.3 Hz, 2H), 7.16 (dddd, J = 11.6, 8.3, 3.7, 1.2 Hz, 3H), 3.61 (s, 3H).



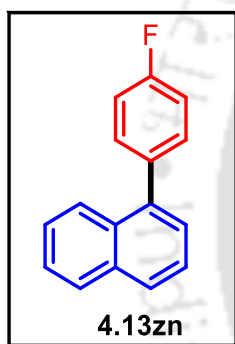
1-phenylnaphthalene (4.13zk).⁵² Compound (4.13zk) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and phenylboronic acid (88 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (54 mg) was obtained as colourless liquid with 55% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.91 (ddt, J = 7.7, 3.2, 1.2 Hz, 2H), 7.87 (dt, J = 8.2, 1.1 Hz, 1H), 7.56 – 7.48 (m, 6H), 7.44 (dddd, J = 7.1, 5.5, 3.5, 2.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 140.9, 140.4, 133.9, 131.7, 128.3, 127.7, 127.3, 127.0, 126.1, 126.1, 125.9, 125.5.



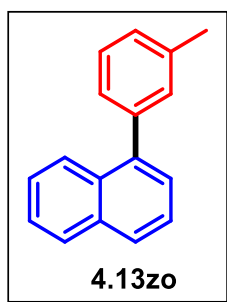
1-(*p*-tolyl)naphthalene (4.13zl).⁵² Compound (4.13zl) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and *p*-tolylphenylboronic acid (100 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (51 mg) was obtained as colourless liquid with 49% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.93 (ddd, J = 15.9, 8.3, 1.4 Hz, 2H), 7.86 (dt, J = 8.3, 1.1 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.46 – 7.40 (m, 4H), 7.32 (d, J = 7.7 Hz, 2H), 2.48 (s, 3H).



1-(p-methoxyphenyl)naphthalene (4.13zm).⁵² Compound (4.13zm) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and (p-methoxyphenyl)boronic acid (100 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (69 mg) was obtained as colourless liquid with 62 % isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.88 (m, 2H), 7.84 (dt, J = 8.2, 1.1 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.46 – 7.38 (m, 4H), 7.08 – 7.01 (m, 2H), 3.90 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 159.0, 140.0, 133.9, 133.2, 131.9, 131.2, 128.4, 127.4, 127.0, 126.2, 126.0, 125.8, 125.5, 113.8, 55.5.

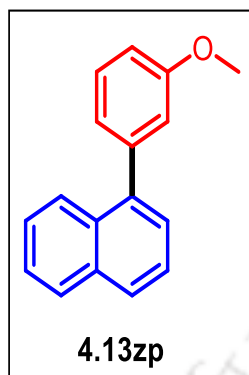


1-(p-fluorophenyl)naphthalene (4.13zn).⁵² Compound (4.13zn) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and (p-fluorophenyl)boronic acid (100 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (76 mg) was obtained as colourless liquid with 72% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.96 – 7.89 (m, 1H), 7.86 (dd, J = 12.1, 8.4 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.47 – 7.44 (m, 3H), 7.40 (dd, J = 7.0, 1.3 Hz, 1H), 7.22 – 7.09 (m, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.2, 161.6, 139.3, 136.8 (d, J = 3.3 Hz), 133.9, 131.8 – 131.6 (m), 128.4, 127.9, 127.1, 126.3, 125.9, 125.9, 125.4, 115.3 (d, J = 21.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -115.4.



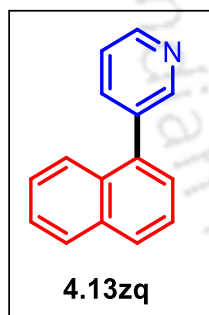
1-(m-tolyl)naphthalene (4.13 zo).⁵² Compound (4.13zo) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and *m*-tolylboronic acid (98 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (64 mg) was obtained as colourless liquid with 61% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (t, J = 8.4 Hz, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.49 (dt, J = 15.4, 7.9 Hz, 2H), 7.40

(dt, $J = 21.9, 7.4$ Hz, 3H), 7.30 (dd, $J = 8.2, 4.4$ Hz, 2H), 7.26 – 7.21 (m, 1H), 2.44 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 140.8, 140.5, 137.9, 133.9, 131.8, 130.9, 128.3, 128.2, 128.0, 127.6, 127.3, 126.9, 126.2, 126.0, 125.8, 125.5, 21.6.



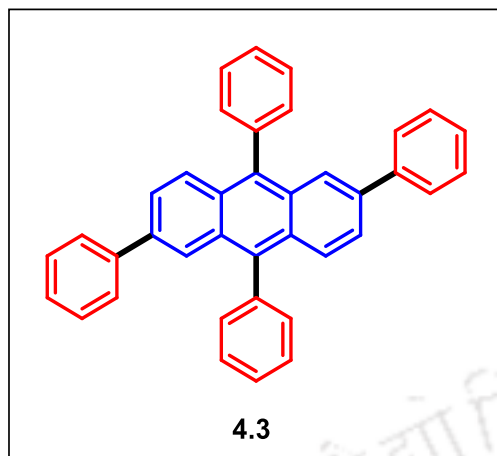
1-(*m*-methoxyphenyl)naphthalene (4.13zp).⁵² Compound (4.13zp) was synthesized from 1-bromonaphthalene (100 mg, 0.48 mmol, 1 equivalent) and (*p*-methoxyphenyl)boronic acid (109 mg, 0.72 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (94 mg) was obtained as colourless liquid with 84% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ 7.99 – 7.90 (m, 2H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.57 –

7.48 (m, 2H), 7.47 – 7.39 (m, 3H), 7.10 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.05 (t, $J = 2.1$ Hz, 1H), 6.99 (dd, $J = 8.3, 2.6$ Hz, 1H), 3.87 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.6, 142.3, 140.2, 133.9, 131.7, 129.3, 128.3, 127.8, 126.9, 126.1, 126.1, 125.9, 125.4, 122.7, 115.7, 113.0, 55.4.



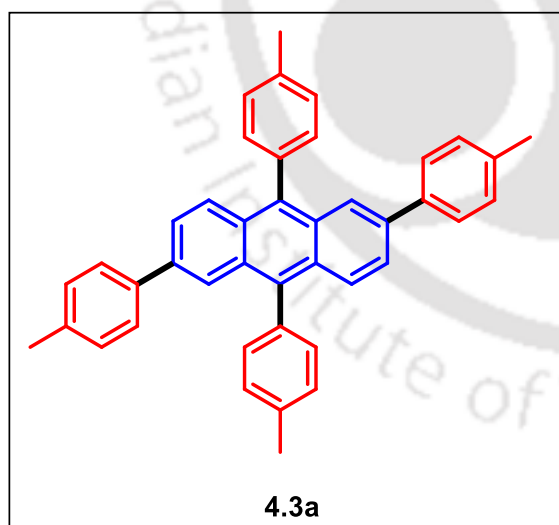
***m*-(naphthalen-1-yl)pyridine (4.13zq).**⁵³ Compound (4.13zq) was synthesized from 3-bromopyridine (158 mg, 1 mmol, 1 equivalent) and 1-naphthylboronic acid (258 mg, 1.5 mmol, 1.5 equivalents) by using general synthetic protocol of Suzuki reaction. The crude reaction mixture product was purified by column chromatography by using 20-25 % (v/v) ethyl acetate/hexane as eluent. Yield (92 %; colourless liquid; Yield calculated by

^1H NMR). ^1H NMR (500 MHz, CDCl_3) δ 8.76 (d, $J = 2.2$ Hz, 1H), 8.69 (dd, $J = 4.9, 1.7$ Hz, 1H), 7.93 (t, $J = 8.4$ Hz, 2H), 7.85 – 7.79 (m, 2H), 7.54 (ddd, $J = 13.6, 8.2, 7.0$ Hz, 2H), 7.49 – 7.41 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 150.64, 148.63, 137.56, 136.55, 136.41, 133.92, 131.59, 128.68, 128.61, 127.53, 126.68, 126.23, 125.52, 125.40, 123.32.



2,6,9,10-tetraphenylanthracene (4.3). Compound (4.3) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and phenylboronic acid (73 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (42 mg) was obtained as yellowish green solid with 88% isolated

yield. ^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 1.5$ Hz, 2H, H-1 and H-5 of anthracene), 7.79 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene), 7.66 – 7.61 (m, 6H, protons of phenyl groups), 7.60 – 7.53 (m, 10H, H-3 and H-7 of anthracene and others protons of phenyl groups), 7.41 (t, $J = 7.7$ Hz, 4H, protons of phenyl groups), 7.32 (t, $J = 7.4$ Hz, 2H, protons of phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 141.1, 138.8, 137.3, 131.3, 130.1, 129.5, 128.8, 128.5, 127.6, 127.6, 127.3, 127.3, 125.2, 124.6 (Ar). FT-IR (KBr, cm^{-1}): 2924 (aromatic C–H str), 1458 (aromatic C = C str). HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{27}$ 483.2113, found 483.2114. mp = 325–327 °C

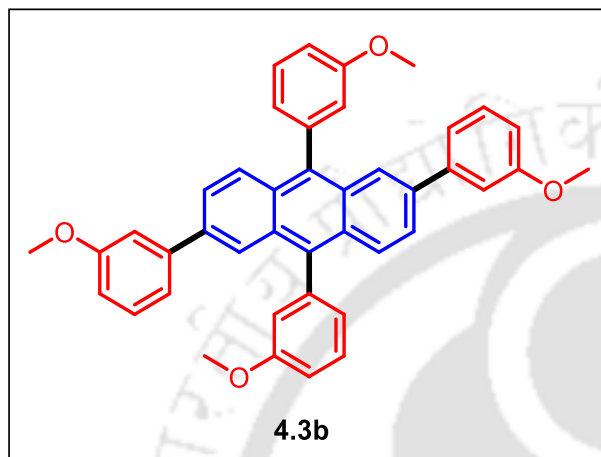


2,6,9,10-tetra-p-tolylanthracene (4.3a).

Compound (4.3a) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and *p*-tolylboronic acid (82 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (40 mg) was obtained as yellow solid with 73% isolated

yield. ^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, $J = 2.0$ Hz, 2H, H-1 and H-5 of anthracene), 7.79 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene), 7.58 (dd, $J = 9.1, 1.9$ Hz, 2H, H-3 and H-7 of anthracene), 7.46 (d, $J = 8.0$ Hz, 4H, protons of phenyl groups), 7.41 (s, 8H, protons of phenyl groups), 7.22 (d, $J = 7.8$ Hz, 4H, protons of phenyl groups), 2.55 (s, 6H, protons of Ar- CH_3), 2.36 (d, $J = 14.2$ Hz, 6H, protons of Ar- CH_3). $^{13}\text{C}\{^1\text{H}\}$

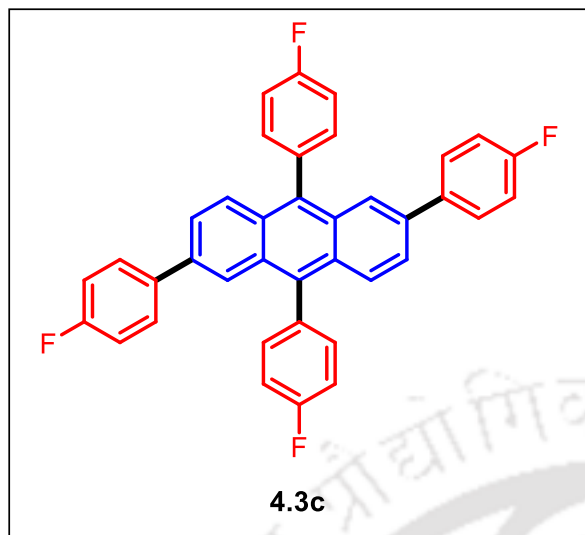
NMR (151 MHz, CDCl_3) δ 138.5, 137.3, 137.2, 137.2, 137.2, 135.9, 131.3, 130.4, 129.6, 129.6, 129.3, 127.7, 127.3, 125.2, 124.4 (Ar), 21.5 (Ar- CH_3), 21.2 (Ar- CH_3). FT-IR (KBr, cm^{-1}): 2922 (aromatic C-H str), 2911 (aliphatic C-H str), 1458 (aromatic C = C str), str), 1381 (CH_3 bend) HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{42}\text{H}_{34}\text{Na}$ 561.2553, found 561.2542. mp = 269-271 $^\circ\text{C}$



2,6,9,10-tetrakis(*m*-methoxyphenyl)anthracene (4.3b).

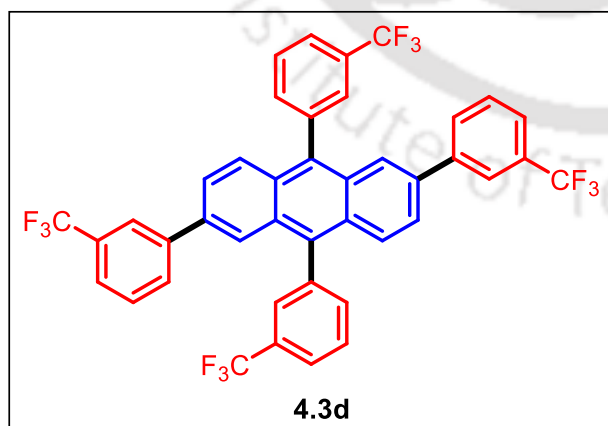
Compound (4.3b) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (*m*-methoxyphenyl)boronic acid (92 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by

using 30% (v/v) DCM: hexane as eluent. The product (36 mg) was obtained as greenish yellow solid with 60% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.94 (s, 2H, H-1 and H-5 of anthracene), 7.82 (d, J = 9.0 Hz, 2H, H-4 and H-8 of anthracene), 7.62 (d, J = 9.0 Hz, 2H, H-3 and H-7 of anthracene), 7.55 (t, J = 7.8 Hz, 2H, protons of phenyl groups), 7.34 (t, J = 7.8 Hz, 2H, protons of phenyl groups), 7.22 – 7.06 (m, 10H, protons of phenyl groups), 6.89 (d, J = 8.1 Hz, 2H, protons of phenyl groups), 3.89 (s, 6H, protons of Ar- OCH_3), 3.84 (s, 6H, protons of Ar- OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 160.0, 159.8, 142.7, 140.3, 137.4, 137.3, 130.1, 129.9, 129.7, 129.5, 127.7, 125.4, 124.8, 123.9, 123.9, 120.0, 116.7, 113.6, 113.6, 113.4, 112.6 (Ar), 55.4 (Ar- OCH_3), 55.4 (Ar- OCH_3). FT-IR (KBr, cm^{-1}): 2925 (aromatic C-H str), 2855 (aliphatic C-H str), 1462 (aromatic C = C str), 1256 (O-C str). HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{42}\text{H}_{34}\text{NaO}_4$ 625.2349, found 625.2318. mp = 315-317 $^\circ\text{C}$



2,6,9,10-tetrakis(*p*-fluorophenyl)anthracene (4.3c). Compound (4.3c) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (*p*-fluorophenyl)boronic acid (84 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (31 mg) was obtained as yellow solid with 55% isolated yield.

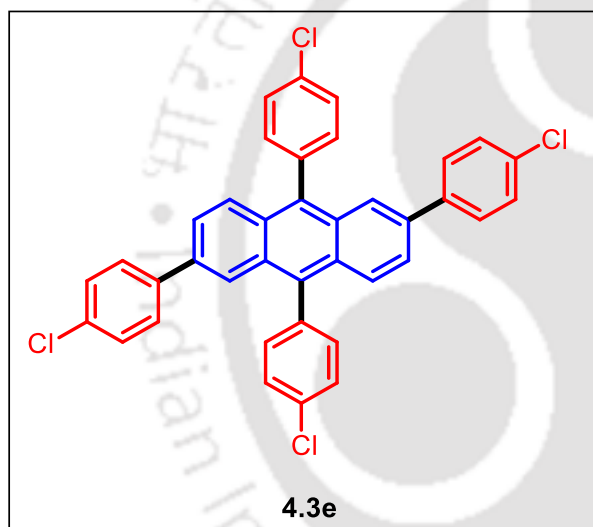
^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, J = 1.9 Hz, 2H, H-1 and H-5 of anthracene), 7.75 (d, J = 9.1 Hz, 2H, H-4 and H-8 of anthracene), 7.60 (dd, J = 9.1, 1.9 Hz, 2H, H-3 and H-7 of anthracene), 7.51 (dtd, J = 11.5, 5.5, 2.0 Hz, 8H, protons of phenyl groups), 7.38 – 7.32 (m, 4H, protons of phenyl groups), 7.11 (t, J = 8.6 Hz, 4H, protons of phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 163.51 (d, J = 12.6 Hz), 161.87 (d, J = 12.1 Hz), 137.05 (d, J = 3.2 Hz), 136.84, 136.50, 134.60 (d, J = 3.4 Hz), 133.00 (d, J = 8.0 Hz), 130.44, 129.75, 128.98 (d, J = 7.8 Hz), 127.74, 125.46, 124.24, 115.99 (d, J = 9.6 Hz), 115.85 (d, J = 9.4 Hz) (Ar). ^{19}F NMR (471 MHz, CDCl_3) δ -114.3, -115.0. FT-IR (KBr, cm^{-1}): 2925 (aromatic C–H str), 1337 (aromatic C = C str), 1124 (C–F str). HRMS (ESI) m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{38}\text{H}_{22}\text{F}_4\text{K}$ 593.1289, found 593.1265. mp = 289–291 °C.



2,6,9,10-tetrakis(3-(trifluoromethyl)phenyl)anthracene (4.3d). Compound (4.3d) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (3-(trifluoromethyl)phenyl)boronic acid (115 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The

crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent.

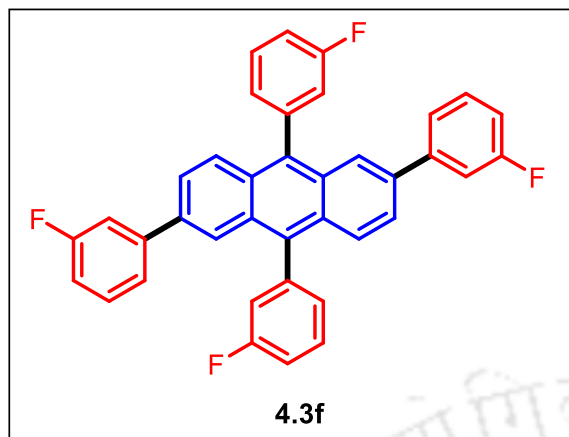
The product (25 mg) was obtained as greenish yellow solid with 33% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, $J = 7.9$ Hz, 2H, H-1 and H-5 of anthracene), 7.85 (d, $J = 5.0$ Hz, 2H, H-4 and H-8 of anthracene), 7.83 – 7.74 (m, 10H, protons of phenyl groups), 7.70 (d, $J = 7.7$ Hz, 2H, protons of phenyl groups), 7.67 (dd, $J = 9.1, 1.8$ Hz, 2H, H-3 and H-7 of anthracene), 7.61 (d, $J = 7.8$ Hz, 2H, protons of phenyl groups), 7.55 (t, $J = 7.7$ Hz, 2H, protons of phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 141.4, 139.1, 136.9, 136.3, 134.6 (d, $J = 7.0$ Hz), 131.4, 131.2, 130.5, 130.1, 129.7 – 128.8 (m), 128.3 – 127.9 (m), 127.7, 125.6, 125.2 – 124.8 (m), 124.5, 124.3 (d, $J = 3.8$ Hz), 124.2 – 123.9 (m) (Ar). ^{19}F NMR (471 MHz, CDCl_3) δ -62.5, -62.7, -62.8, -62.8. FT-IR (KBr, cm^{-1}): 2926 (aromatic C–H str), 1337 (aromatic C = C str), 1125 (C–F str). HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{42}\text{H}_{22}\text{F}_{12}\text{K}$ 793.1161, found 793.1180. mp = 287–289 °C.



2,6,9,10-tetrakis(*p*-chlorophenyl)anthracene

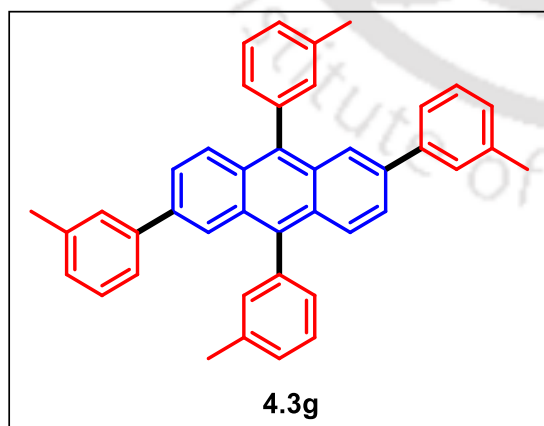
(**4.3e**). Compound (**4.3e**) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (*p*-chlorophenyl)boronic acid (95 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (30 mg) was obtained as green solid

with 48% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 1.9$ Hz, 2H, H-1 and H-5 of anthracene), 7.74 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene), 7.63 (d, $J = 8.3$ Hz, 4H, protons of phenyl groups), 7.60 (dd, $J = 9.1, 1.9$ Hz, 2H, H-3 and H-7 of anthracene), 7.47 (dd, $J = 12.0, 8.4$ Hz, 8H, protons of phenyl groups), 7.40 (d, $J = 8.4$ Hz, 4H, protons of phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 139.2, 137.1, 136.8, 136.4, 134.1, 133.9, 132.7, 130.2, 129.6, 129.2, 129.1, 128.6, 127.7, 125.4, 124.3 (Ar). FT-IR (KBr, cm^{-1}): 2925 (aromatic C–H str), 1465 (aromatic C = C str), 813 (C–Cl str). HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{23}\text{Cl}_4$ 619.0548, found 619.0481. mp = 283–285 °C.

**2,6,9,10-tetrakis(*m*-fluorophenyl)anthracene (4.3f).**

Compound (4.3f) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (*m*-fluorophenyl)boronic acid (84 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (35 mg) was obtained as

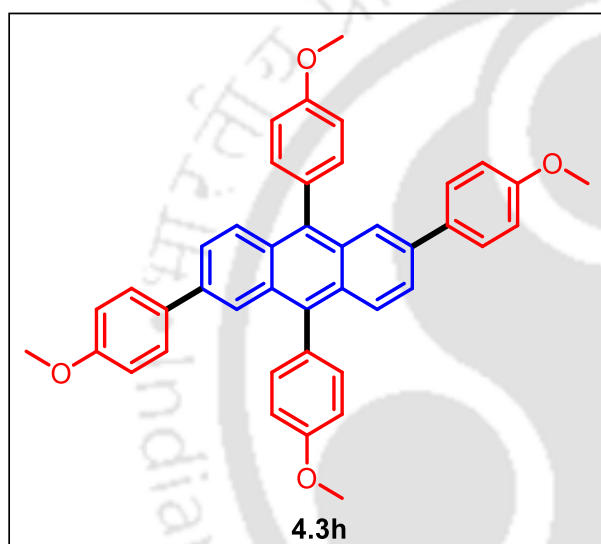
greenish yellow solid with 63% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 1.4$ Hz, 2H, H-1 and H-5 of anthracene), 7.76 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene), 7.65 – 7.61 (m, 4H, H-3 and H-7 of anthracene and protons of phenyl groups), 7.41 – 7.36 (m, 2H, protons of phenyl groups), 7.35 – 7.29 (m, 4H, protons of phenyl groups), 7.28 – 7.23 (m, 6H, protons of phenyl groups), 7.04 (td, $J = 8.2, 2.1$ Hz, 2H, protons of phenyl groups). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 164.0 (d, $J = 31.0$ Hz), 162.4 (d, $J = 33.0$ Hz), 143.1 (d, $J = 7.4$ Hz), 140.8 (d, $J = 7.8$ Hz), 136.8 (d, $J = 2.3$ Hz), 136.5, 130.5 (d, $J = 8.4$ Hz), 130.0, 129.5, 127.7, 127.2 (d, $J = 3.4$ Hz), 125.5, 124.6, 123.1 (d, $J = 2.6$ Hz), 118.4 (dd, $J = 21.0, 4.0$ Hz), 115.1 (d, $J = 20.8$ Hz), 114.4 (dd, $J = 31.7, 21.7$ Hz) (Ar). ^{19}F NMR (377 MHz, CDCl_3) δ -110.6, -112.6, -112.6, -112.7, -112.7. FT-IR (KBr, cm^{-1}): 2926 (aromatic C–H str), 1322 (aromatic C = C str), 1119 (C–F str). HRMS (ESI) m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{38}\text{H}_{22}\text{F}_4\text{K}$ 593.1289, found 593.1247. mp = 275–277 °C.

**2,6,9,10-tetrakis(*m*-tolyl)anthracene (4.3g).**

Compound (4.3g) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and *m*-tolylboronic acid (82mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5% (v/v) DCM: hexane as eluent. The product (32 mg)

was obtained as greenish yellow solid with 59% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 1.9$ Hz, 2H, H-1 and H-5 of anthracene), 7.78 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene),

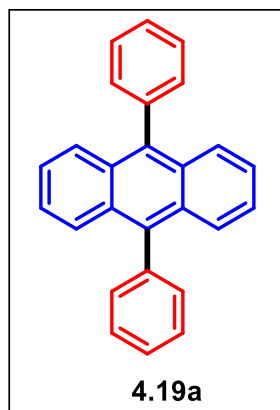
7.60 (dd, $J = 9.1, 1.9$ Hz, 2H, H-3 and H-7 of anthracene), 7.52 (t, $J = 7.8$ Hz, 2H, protons of phenyl groups), 7.42 – 7.33 (m, 10H, protons of phenyl groups), 7.30 (t, $J = 7.5$ Hz, 2H, protons of phenyl groups), 7.14 (d, $J = 7.4$ Hz, 2H, protons of phenyl groups), 2.50 (s, 6H, Ar-CH₃), 2.39 (s, 6H, Ar-CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 141.4, 138.9, 138.4, 138.1, 137.5, 132.1, 130.2, 129.6, 128.8, 128.5, 128.4, 128.4, 128.3, 128.1, 127.7, 125.3, 124.7, 124.6 (Ar), 21.7 (Ar-CH₃), 21.7 (Ar-CH₃). FT-IR (KBr, cm⁻¹): 2923 (aromatic C–H str), 1460 (aromatic C = C str), 2855 (aliphatic C–H str), 1376 (C–H str, CH₃ bend) HRMS (ESI) m/z [M+H]⁺ calcd for C₄₂H₃₅ 539.2733, found 539.2692. mp = 273–275



2,6,9,10-tetrakis(*p*-methoxyphenyl)anthracene (4.3h).

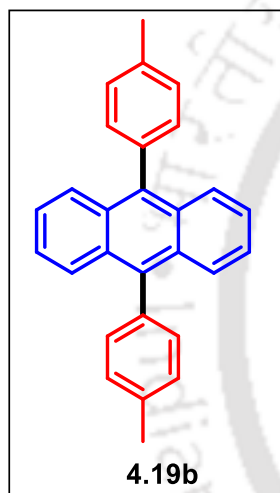
Compound (4.3h) was synthesized from 2,6,9,10-tetrabromoanthracene (50 mg, 0.101 mmol, 1 equivalent) and (*p*-methoxyphenyl)boronic acid (92 mg, 0.606 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 30% (v/v) DCM: hexane as eluent. The product (35 mg) was obtained as yellow solid

with 57% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, $J = 1.5$ Hz, 2H, H-1 and H-5 of anthracene), 7.79 (d, $J = 9.1$ Hz, 2H, H-4 and H-8 of anthracene), 7.59 (dd, $J = 9.1, 1.8$ Hz, 2H, H-3 and H-7 of anthracene), 7.51 (d, $J = 8.8$ Hz, 4H, protons of phenyl groups), 7.45 (d, $J = 8.6$ Hz, 4H, protons of phenyl groups), 7.16 (d, $J = 8.6$ Hz, 4H, protons of phenyl groups), 6.96 (d, $J = 8.8$ Hz, 4H, protons of phenyl groups), 3.98 (s, 6H, Ar-OCH₃), 3.84 (s, 6H, Ar-OCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 159.3, 159.1, 136.8, 133.8, 132.5, 131.2, 130.6, 129.8, 128.4, 127.7, 125.1, 123.8, 114.4, 114.1 (Ar), 55.5 (Ar-OCH₃), 55.5 (Ar-OCH₃). FT-IR (KBr, cm⁻¹): 2925 (aromatic C–H str), 2836 (aliphatic C–H str), 1516 (aromatic C = C str), 1251 (O–C str). HRMS (ESI) m/z [M+H]⁺ calcd for C₄₂H₃₅O₄ 603.253, found 603.2595. mp = 284–286°C

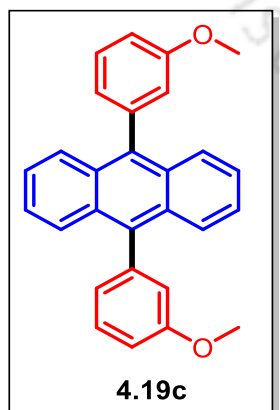


9,10-diphenylanthracene (4.19a).⁵⁴ Compound (4.19a) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and phenylboronic acid (109 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (88 mg) was obtained as white solid with 89% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.70 (dd, J = 6.8, 3.3 Hz, 4H), 7.61 (t, J = 7.3 Hz, 4H), 7.56 (t, J = 7.4 Hz, 2H), 7.49 (d, J = 6.8 Hz, 4H), 7.33 (dd, J = 6.9, 3.2 Hz, 4H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 139.2, 137.2, 131.4, 130.0, 128.5, 127.6, 127.1, 125.1.



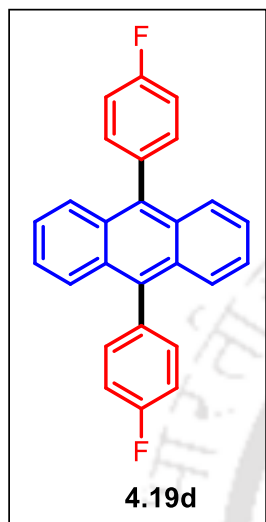
9,10-di-*p*-tolylanthracene (4.19b).⁵⁵ Compound (4.19b) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and *p*-tolylboronic acid (122 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (79 mg) was obtained as white solid with 74% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (dd, J = 6.8, 3.3 Hz, 4H), 7.44 (d, J = 7.8 Hz, 4H), 7.40 (d, J = 6.5 Hz, 4H), 7.35 (dd, J = 6.9, 3.3 Hz, 4H), 2.57 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 137.1, 136.1, 131.3, 130.1, 129.2, 127.1, 125.0, 21.5.



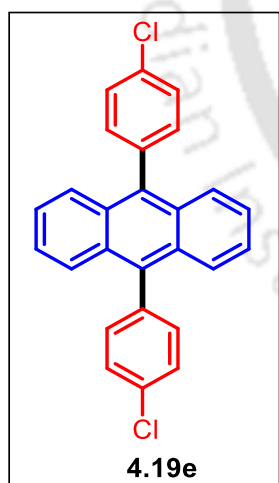
9,10-bis(*m*-methoxyphenyl)anthracene (4.19c). Compound (4.19c) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) (5c) and (*m*-methoxyphenyl)boronic acid (136 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 15% (v/v) DCM: hexane as eluent. The product (74 mg) was obtained as white solid with 64% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.79 – 7.66 (m, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.52

(t, J = 7.8 Hz, 2H, protons of phenyl groups), 7.34 (dd, J = 6.9, 3.2 Hz, 4H, H-2, H-3, H-6 and H-7 of anthracene), 7.12 – 7.06 (m, 4H, protons of phenyl groups), 7.04 (s, 2H, protons of phenyl

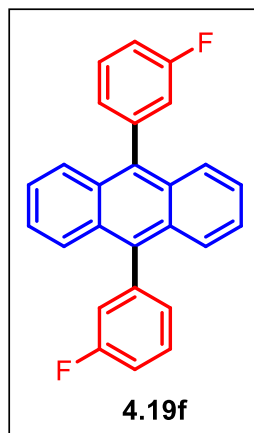
groups), 3.87 (s, 6H, Ar-OCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 159.7, 140.6, 137.0, 129.8, 129.5, 127.1, 125.1, 123.9, 116.7, 113.4 (Ar), 55.4 (Ar-OCH₃). FT-IR (KBr, cm⁻¹): 2927 (aromatic C-H str), 2853 (aliphatic C-H str) 1459 (aromatic C = C str), 1253 (O-C str). HRMS (ESI) m/z [M+H]⁺ calcd for C₂₈H₂₃O₂ 391.1693, found 391.1719. mp = 216-218 °C.



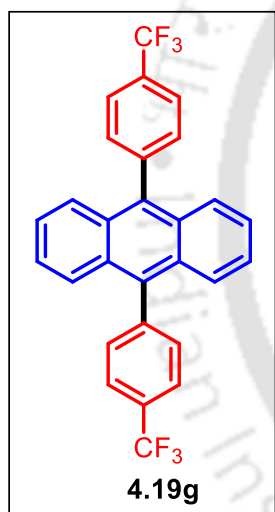
9,10-bis(*p*-fluorophenyl)anthracene (4.19d).⁵⁶ Compound (4.19d) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*p*-fluorophenyl)boronic acid (125 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (77 mg) was obtained as white solid with 71% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.67 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.44 (dd, *J* = 8.1, 5.8 Hz, 4H), 7.36 (dd, *J* = 6.9, 3.2 Hz, 4H), 7.31 (t, *J* = 8.6 Hz, 4H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.3, 161.7, 136.3, 134.8 (d, *J* = 3.5 Hz), 132.9 (d, *J* = 7.9 Hz), 130.1, 126.9, 125.3, 115.6 (d, *J* = 21.3 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -114.8.



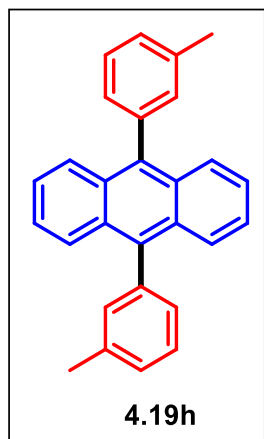
9,10-bis(*p*-chlorophenyl)anthracene (4.19e).⁵⁷ Compound (4.19e) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*p*-chlorophenyl)boronic acid (140 mg, 0.90 mmol, 3 equivalents) using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (65 mg) was obtained as white solid with 55% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.66 (dd, *J* = 6.8, 3.3 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 4H), 7.36 (dd, *J* = 6.9, 3.2 Hz, 4H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 137.5, 136.1, 133.8, 132.7, 129.9, 128.9, 126.8, 125.5.



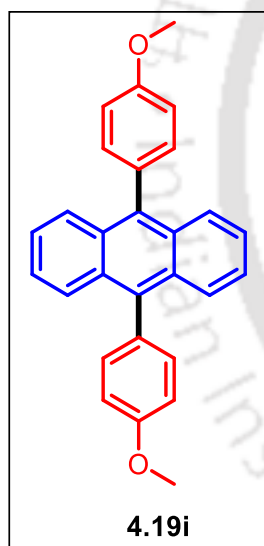
9,10-bis(*m*-fluorophenyl)anthracene (4.19f).⁵⁸ Compound (4.19f) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*m*-fluorophenyl)boronic acid (125 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (74 mg) was obtained as white solid with 68% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.69 (dd, *J* = 6.8, 3.3 Hz, 4H), 7.59 (q, *J* = 7.3 Hz, 2H), 7.38 (dd, *J* = 6.9, 3.2 Hz, 4H), 7.30 – 7.27 (m, 4H), 7.25 – 7.20 (m, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.8, 162.2, 141.3 (d, *J* = 7.5 Hz), 136.0 (d, *J* = 1.8 Hz), 131.0 – 128.5 (m), 128.1 – 126.0 (m), 125.5, 118.4 (dd, *J* = 21.0, 4.1 Hz), 114.7 (d, *J* = 20.8 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -113.1, -113.2.



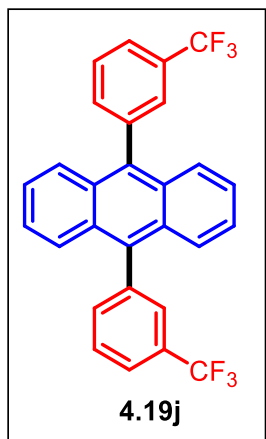
9,10-bis(*p*-(trifluoromethyl)phenyl)anthracene (4.19g). Compound (4.19g) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*p*-(trifluoromethyl)phenyl)boronic acid (170 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (66 mg) was obtained as white solid with 47% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, *J* = 7.9 Hz, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.64 – 7.59 (m, 8H, H-2, H-3, H-6 and H-7 of anthracene), 7.38 (dd, *J* = 6.9, 3.1 Hz, 4H, protons of phenyl groups). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 143.0, 136.1, 131.8, 130.2, 130.0, 129.7, 129.2, 128.9, 128.6, 127.4, 127.3, 127.1, 126.6, 126.3, 125.9, 125.7, 125.7, 125.6, 125.6, 125.6, 125.3, 125.3, 123.5 (Ar). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.3. FT-IR (KBr, cm⁻¹): 2926 (aromatic C–H str), 1322 (aromatic C = C str), 1120 (C–F str). HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₈H₂₃O₂ 467.1229, found 467.1230. mp = 328–330 °C.



9,10-bis(*m*-(trifluoromethyl)phenyl)anthracene (4.19h).⁵⁹ Compound (4.19h) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and *m*-tolylboronic acid (122 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (67 mg) was obtained as white solid with 63% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.71 (dd, J = 6.8, 3.3 Hz, 4H, H-1, H-4, H-5 and H-8 of anthracene), 7.49 (d, J = 15.0 Hz, 2H, protons of phenyl groups), 7.36 (d, J = 7.6 Hz, 2H, protons of phenyl groups), 7.33 (dd, J = 6.9, 3.2 Hz, 4H, H-2, H-3, H-6 and H-7 of anthracene), 7.29 (d, J = 8.8 Hz, 4H, protons of phenyl groups), 2.49 (s, 6H, Ar-CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 139.1, 138.1, 137.3, 132.1, 129.9, 128.5, 128.3, 128.2, 127.1, 125.0 (Ar), 21.7 (Ar-CH₃).

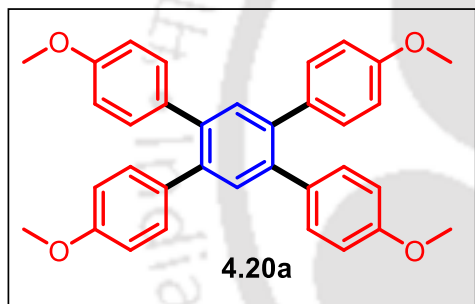


9,10-bis(*p*-methoxyphenyl)anthracene (4.19i).⁶⁰ Compound (4.19i) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*p*-methoxyphenyl)boronic acid (136 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 15% (v/v) DCM: hexane as eluent. The product (78 mg) was obtained as white solid with 67% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.74 (dd, J = 6.8, 3.3 Hz, 4H), 7.39 (d, J = 8.5 Hz, 4H), 7.33 (dd, J = 6.9, 3.2 Hz, 4H), 7.15 (d, J = 8.5 Hz, 4H), 3.97 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 159.1, 136.8, 132.5, 131.3, 130.4, 127.1, 125.0, 114.0, 55.5.



9,10-bis(*m*-(trifluoromethyl)phenyl)anthracene (4.19j).⁵⁶ Compound (4.18j) was synthesized from 9,10-dibromoanthracene (100 mg, 0.30 mmol, 1 equivalent) and (*m*-(trifluoromethyl)phenyl)boronic acid (170 mg, 0.90 mmol, 3 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using hexane as eluent. The product (52 mg) was obtained as white solid with 37% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 4H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.60 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.39 (dd, *J* = 6.9, 3.2 Hz, 4H).

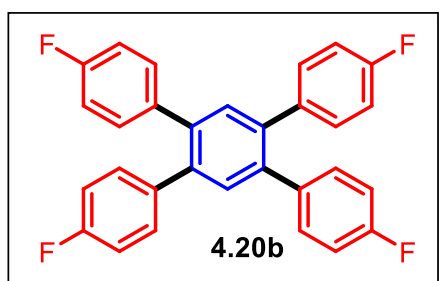
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 139.9, 135.9, 134.8 (d, *J* = 7.1 Hz), 131.3 (d, *J* = 6.5 Hz), 131.1 (d, *J* = 6.5 Hz), 129.9, 129.2 (d, *J* = 5.7 Hz), 128.1 (d, *J* = 5.0 Hz), 126.6, 125.8, 124.7 (d, *J* = 3.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4.



4,4''-dimethoxy-4',5'-bis(4-methoxyphenyl)-1,1':2',1''-terphenyl (4.20a).⁶¹ Compound (4.20a) was synthesized from 1,2,4,5-tetraiodobenzene (64 mg, 0.11 mmol, 1 equivalent) and (*p*-fluorophenyl)boronic acid (100 mg, 0.66 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product

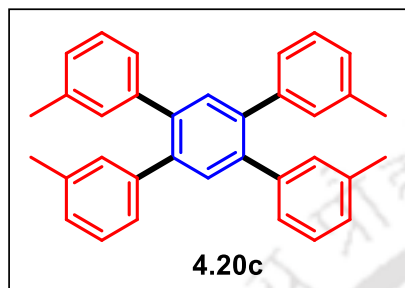
was

purified by column chromatography by using 30% (v/v) DCM: hexane as eluent. The product (28 mg) was obtained as white solid with 51% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (s, 2H), 7.14 (d, *J* = 8.6 Hz, 8H), 6.79 (d, *J* = 8.6 Hz, 8H), 3.79 (s, 12H).



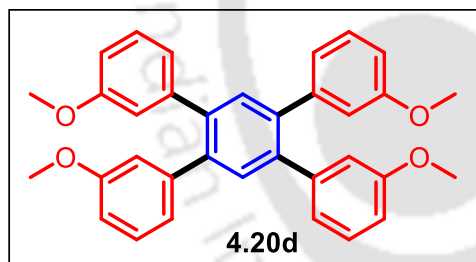
4,4''-difluoro-4',5'-bis(4-fluorophenyl)-1,1':2',1''-terphenyl (4.20b).⁶² Compound (4.20b) was synthesized from 1,2,4,5-tetraiodobenzene (64 mg, 0.11 mmol, 1 equivalent) and (*p*-fluorophenyl)boronic acid (92 mg, 0.66 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column

chromatography by using 5% (v/v) DCM: hexane as eluent. The product (22 mg) was obtained as white solid with 46% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.43 (s, 2H), 7.21 – 7.12 (m, 8H), 7.03 – 6.91 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 162.9, 161.2, 138.9, 136.6 (d, J = 3.3 Hz), 132.9, 131.4 (d, J = 7.8 Hz), 115.2 (d, J = 21.5 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -115.4.



3,3''-dimethyl-4',5'-di-m-tolyl-1,1':2',1''-terphenyl (4.20c).⁶³ Compound (4.20c) was synthesized from 1,2,4,5-tetraiodobenzene (64 mg, 0.11 mmol, 1 equivalent) and *m*-tolylboronic acid (89 mg, 0.66 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product was purified by column chromatography by using 5%

(v/v) DCM: hexane as eluent. The product (21 mg) was obtained as white solid with 45% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.50 (s, 2H), 7.13 – 7.06 (m, 8H), 7.03 (dt, J = 8.1, 1.4 Hz, 4H), 6.96 (dt, J = 7.6, 1.6 Hz, 4H), 2.27 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 141.1, 139.6, 137.6, 132.9, 130.6, 127.7, 127.3, 127.2, 21.5.



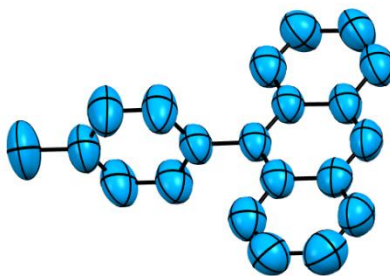
3,3''-dimethoxy-4',5'-bis(3-methoxyphenyl)-1,1':2',1''-terphenyl (4.20d).⁶¹ Compound (4.20d) was synthesized from 1,2,4,5-tetraiodobenzene (64 mg, 0.11 mmol, 1 equivalent) and (*m*-methoxyphenyl)boronic acid (100 mg, 0.66 mmol, 6 equivalents) by using general synthetic protocol of Suzuki reaction. The crude product

was purified by column chromatography by using 30% (v/v) DCM: hexane as eluent. The product (19 mg) was obtained as white solid with 35% isolated yield. ^1H NMR (600 MHz, CDCl_3) δ 7.56 (s, 2H), 7.17 (t, J = 7.9 Hz, 4H), 6.89 – 6.82 (m, 4H), 6.80 – 6.74 (m, 8H), 3.63 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.3, 142.3, 139.7, 132.6, 129.1, 122.4, 115.1, 113.0, 55.3.

Supporting information (containing NMR spectra of various compounds) for Chapter IV is available as *appendix III* and can be found at

https://drive.google.com/file/d/1mAjwzTbJBbfvNoO6xAcVLhDRoMg91NYi/view?usp=share_link

4.5. X-ray crystallographic analysis

**Figure 4.5.** ORTEP diagram of **4.13z** with the ellipsoids drawn at the 50% probability level..**Table 4.6.** Crystal data for **4.13zb**

Identification code (CCDC No)	2131725	
Bond precision:	C-C = 0.0072 Å	Wavelength=0.71073
Cell:	a = 16.625(13) alpha = 90	b = 7.900(7) c = 23.732(19) beta = 100.44(2) gamma = 90
Temperature:	293 K	
Volume	Calculated 3065(4)	Reported 3065(4)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	?
Moiety formula	C ₂₁ H ₁₆	?
Sum formula	C ₂₁ H ₁₆	C ₂₁ H ₁₆
Mr	268.34	268.34
Dx, g cm ⁻³	1.163	1.163
Z	8	8
Mu (mm ⁻¹)	0.066	0.066
F000	1136.0	1136.0
F000'	1136.41	
h,k,l _{max}	19,9,27	19,9,27
Nref	2614	2565
Tmin, Tmax		
Tmin'		
Correction method	=Not given	
Data completeness	= 0.981	Theta(max) = 24.740
R(reflections) = 0.1188(1336)		wR ₂ (reflections) = 0.3841(2565)
S = 2.716		Npar = 192

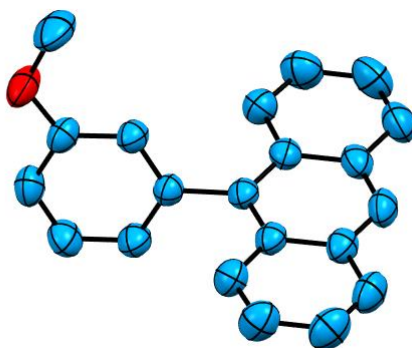


Figure 4.6. ORTEP diagram of **4.13zc** with the ellipsoids drawn at the 50% probability level..

Table 4.7. Crystal data for **4.13zc**

Identification code (CCDC No) 2131724			
Bond precision:	C-C = 0.0034 Å	Wavelength=0.71073	
Cell:	a = 8.850(1)	b = 9.6041(10)	c = 10.3092(13)
	alpha = 67.687 (4)	beta = 69.720(4)	gamma = 85.761(4)
Temperature:	296 K		
	Calculated	Reported	
Volume	758.70(15)	758.70(15)	
Space group	P -1	P -1	
Hall group	-P 1	?	
Moiety formula	C ₂₁ H ₁₆ O	?	
Sum formula	C ₂₁ H ₁₆ O	C ₂₁ H ₁₆ O	
Mr	284.34	284.34	
Dx,g cm ⁻³	1.245	1.245	
Z	2	2	
Mu (mm ⁻¹)	0.075	0.075	
F000	300.0	300.0	
F000'	300.12		
h,k,l _{max}	10,11,12	10,11,12	
Nref	2678	2678	
Tmin, Tmax			
Tmin'			
Correction method = Not given			
Data completeness = 0.999		Theta(max) = 25.000	
R(reflections) = 0.0503 (1881)		wR ₂ (reflections) = 0.1692 (2676)	
S = 0.846		Npar = 200	

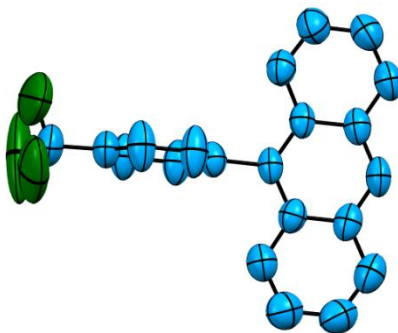


Figure 4.7. ORTEP diagram of **4.13zg** with the ellipsoids drawn at the 50% probability level..

Table 4.8. Crystal data for **4.13zg**

Identification code (CCDC No) 2131726			
Bond precision:	C-C = 0.0070 Å		Wavelength = 0.71073
Cell:	a = 17.075 (15)	b = 8.002 (6)	c = 23.546 (16)
	alpha = 90	beta = 101.44(4)	gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	3153 (4)	3153 (4)	
Space group	C 2/c	C 2/c	
Hall group	-C 2yc	?	
Moiety formula	C ₂₁ H ₁₃ F ₃	?	
Sum formula	C ₂₁ H ₁₃ F ₃	C ₂₁ H ₁₃ F ₃	
Mr	322.31	322.31	
Dx,g cm ⁻³	1.358	1.358	
Z	8	8	
Mu (mm ⁻¹)	0.103	0.103	
F000	1328.0	1328.0	
F000'	1328.81		
h,k,l _{max}	20,9,18	20,9,18	
Nref	2783	2777	
Tmin, Tmax			
Tmin'			
Correction method = Not given			
Data completeness = 0.998		Theta(max) = 25.000	
R(reflections) = 0.1381 (1560)		wR ₂ (reflections) = 0.3878 (2777)	
S = 1.326		Npar = 218	

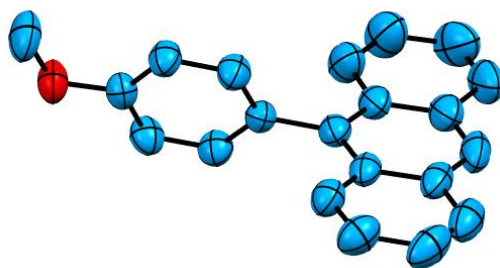


Figure 4.8: ORTEP diagram of **4.13zi** with the ellipsoids drawn at the 50% probability level..

Table 4.9. Crystal data for **4.13zi**

Identification code (CCDC No) 2150840			
Bond precision:	C-C = 0.0057 Å		Wavelength = 0.71073
Cell:	a = 13.564 (4)	b = 15.059 (5)	c = 7.6088 (15)
	alpha = 90	beta = 99.167 (12)	gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	1534.3 (7)	1534.3 (7)	
Space group	P 21/c	P2(1)/c	
Hall group	-P 2ybc	?	
Moiety formula	C ₂₁ H ₁₆ O	C ₂₁ H ₁₆ O	
Sum formula	C ₂₁ H ₁₆ O	C ₂₁ H ₁₆ O	
Mr	284.34	284.34	
Dx,g cm ⁻³	1.231	1.231	
Z	4	4	
Mu (mm ⁻¹)	0.074	0.074	
F000	600.0	868.0	
F000'	600.25		
h,k,l _{max}	15,17,8	15,17,8	
Nref	2546	2546	
Tmin, Tmax			
Tmin'			
Correction method = Not given			
Data completeness = 0.964		Theta(max) = 24.500	
R(reflections) = 0.0660 (1302)		wR ₂ (reflections) = 0.2133 (2454)	
S = 1.056		Npar = 200	

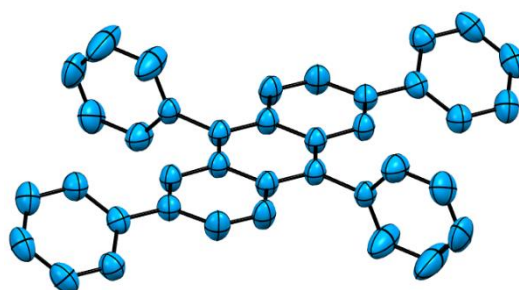


Figure 4.9. ORTEP diagram of **4.3** with the ellipsoids drawn at the 50% probability level.

Table 4.10. Crystal data for **4.3**

Identification code (CCDC No) 2111305			
Bond precision:	C-C = 0.0022 Å	Wavelength=0.71073	
Cell:	a = 5.6845 (5)	b = 9.2629 (9)	c = 12.7180 (12)
	alpha = 92.487 (4)	beta = 98.383 (3)	gamma = 98.773 (3)
Temperature:	296 K		
	Calculated	Reported	
Volume	653.28 (15)	653.28 (11)	
Space group	P -1	P -1	
Hall group	-P 1	?	
Moiety formula	C ₃₈ H ₂₆	C ₃₈ H ₂₆	
Sum formula	C ₃₈ H ₂₆	C ₃₈ H ₂₆	
Mr	482.59	482.59	
Dx,g cm ⁻³	1.227	1.227	
Z	1	1	
Mu (mm ⁻¹)	0.069	0.069	
F000	254.0	254.0	
F000'	254.09		
h,k,l _{max}	7,12,16	7,12,16	
Nref	3257	3250	
Tmin, Tmax	0.982, 0.983		
Tmin'	0.982		
Correction method = Not given			
Data completeness = 0.998		Theta(max) = 28.300	
R(reflections) = 0.0522 (2396)		wR ₂ (reflections) = 0.1548 (3250)	
S = 1.043		Npar = 172	

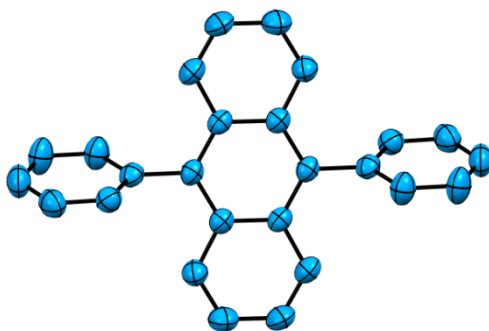


Figure 4.10. ORTEP diagram of **4.19a** with the ellipsoids drawn at the 50% probability level.

Table 4.11. Crystal data for **4.19a**

Identification code (CCDC No) 2150842			
Bond precision:	C-C = 0.0025 Å		Wavelength=0.71073
Cell:	a = 10.6853 (19)	b = 13.5512 (19)	c = 12.2614 (13)
	alpha = 90	beta = 90.652 (7)	gamma = 90
Temperature:	296 K		
	Calculated	Reported	
Volume	1775.3 (4)	1775.3 (4)	
Space group	C 2/c	C2/c	
Hall group	-C 2yc	?	
Moiety formula	C ₂₆ H ₁₈	C ₂₆ H ₁₈	
Sum formula	C ₂₆ H ₁₈	C ₂₆ H ₁₈	
Mr	330.40	330.40	
Dx,g cm ⁻³	1.236	1.236	
Z	4	4	
Mu (mm ⁻¹)	0.070	0.070	
F000	696.0	880.0	
F000'	696.26		
h,k,l _{max}	12,16,14	12,16,14	
Nref	1570	1557	
Tmin, Tmax			
Tmin'			
Correction method = Not given			
Data completeness = 0.992		Theta(max) = 24.990	
R(reflections) = 0.0393 (1235)		wR ₂ (reflections) = 0.1525 (1557)	
S = 1.039		Npar = 119	

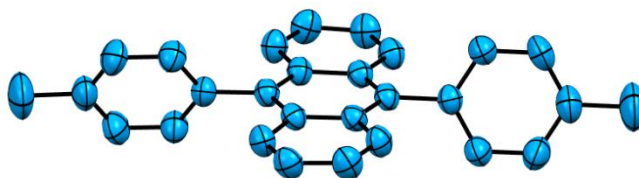


Figure 4.11. ORTEP diagram of **4.19b** with the ellipsoids drawn at the 50% probability level.

Table 4.12. Crystal data for **4.19b**

Identification code (CCDC No) 2150841			
Bond precision:	C-C = 0.0044 Å		Wavelength=0.71073
Cell:	a = 7.832 (9)	b = 7.871 (9)	c = 17.309 (17)
	alpha = 77.62 (4)	beta = 77.35 (4)	gamma = 73.90 (4)
Temperature:	296 K		
	Calculated	Reported	
Volume	986.8 (19)	986.7 (19)	
Space group	P -1	P -1	
Hall group	-P 1	?	
Moiety formula	C ₂₈ H ₂₂	C ₂₈ H ₂₂	
Sum formula	C ₂₈ H ₂₂	C ₂₈ H ₂₂	
Mr	358.46	358.46	
Dx,g cm ⁻³	1.206	1.206	
Z	2	2	
Mu (mm ⁻¹)	0.068	0.068	
F000	380.0	392.0	
F000'	380.14		
h,k,l _{max}	9,9,20	9,9,20	
Nref	3482	3482	
Tmin, Tmax			
Tmin'			
Correction method = Not given			
Data completeness = 0.998		Theta(max) = 25.000	
R(reflections) = 0.0672 (2139)		wR ₂ (reflections) = 0.2044 (3474)	
S = 0.824		Npar = 256	

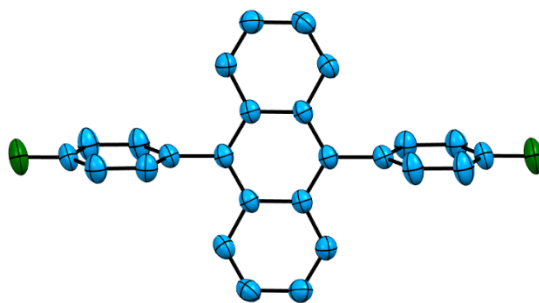


Figure 4.12. ORTEP diagram of **4.19d** with the ellipsoids drawn at the 50% probability level.

Table 4.13. Crystal data for **4.19d**

Identification code (CCDC No)	2156605		
Bond precision:	C-C = 0.0020 Å	Wavelength=0.71073	
Cell:	a = 6.0748 (3)	b = 19.7805 (11)	c = 7.6325 (4)
	alpha = 90	beta = 97.433 (1)	gamma = 90
Temperature:	273 K		
Volume	Calculated 909.43 (8)	Reported 909.43 (8)	
Space group	P 2 ₁ /n	P 1 2 ₁ /n	
Hall group	-P 2 ₁ yn	-P 2 ₁ yn	
Moiety formula	C ₂₆ H ₁₆ F ₂	C ₂₆ H ₁₆ F ₂	
Sum formula	C ₂₆ H ₁₆ F ₂	C ₂₆ H ₁₆ F ₂	
Mr	366.39	366.39	
Dx, g cm ⁻³	1.338	1.338	
Z	2	2	
Mu (mm ⁻¹)	0.091	0.091	
F000	380.0	380.0	
F000'	380.19		
h,k,l _{max}	7, 25, 10	7, 25, 10	
Nref	2140	2120	
Tmin, Tmax	0.937, 0.956	0.581, 0.746	
Tmin'			
Correction method = #	Reported T limits : Tmin = 0.581 Tmax = 0.746		
Correction method = Not given			
Data completeness = 0.991		Theta(max) = 27.801	
R(reflections) = 0.0482 (1795)		wR ₂ (reflections) = 0.1414 (2120)	
S = 1.079		Npar = 127	

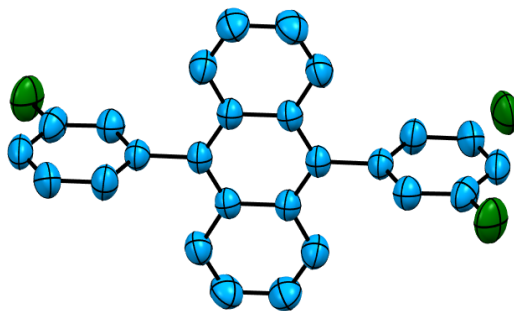


Figure 4.13. ORTEP diagram of **4.19f** with the ellipsoids drawn at the 50% probability level. F atom is disordered over two meta positions of benzene ring.

Table 4.14. Crystal data for **4.19f**

Identification code (CCDC No)	2156606		
Bond precision:	C-C = 0.0023 Å	Wavelength=	0.71073
Cell:	a = 11.3507 (9)	b = 9.5595 (7)	c = 8.6305 (6)
	alpha = 90	beta = 103.204 (2)	gamma = 90
Temperature:	273 K		
Volume	Calculated	Reported	
	911.71 (12)	911.71 (12)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C ₂₆ H _{15.18} F _{2.08}	C ₂₆ H _{15.18} F _{2.08}	
Sum formula	C ₂₆ H _{15.18} F _{2.08}	C ₂₆ H ₁₆ F _{1.98}	
Mr	367.12	365.91	
Dx, g cm ⁻³	1.337	1.333	
Z	2	2	
Mu (mm ⁻¹)	0.091	0.090	
F000	379.8	380.0	
F000'	380.03		
h,k,l _{max}	14, 11, 10	14, 11, 10	
Nref	1853	1835	
Tmin, Tmax	0.947, 0.956	0.708, 0.745	
Tmin'			
Correction method = #	Reported T limits : Tmin = 0.708 Tmax = 0.745		
Correction method = Not given			
Data completeness = 0.990	Theta(max) = 26.336		
R(reflections) = 0.0501 (1566)	wR ₂ (reflections) = 0.1361 (1835)		
S = 1.072	Npar = 143		

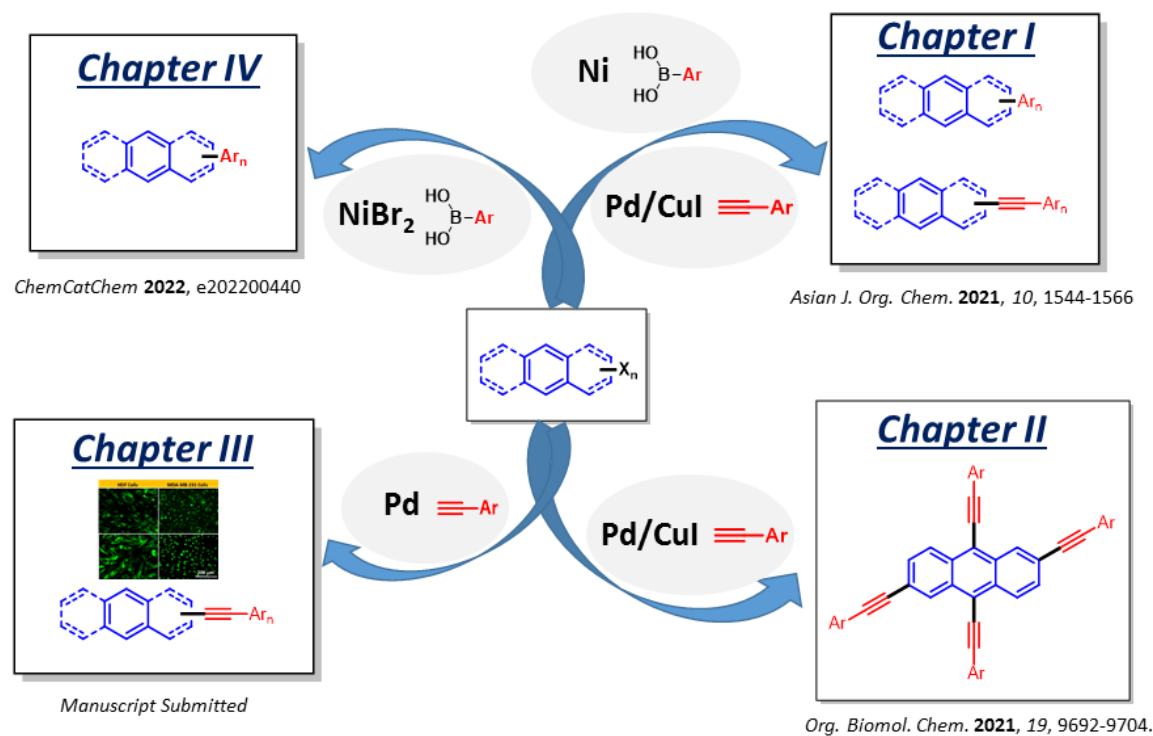
4.6. Reference

1. (a) Zhu, M.; Yang, C., *Chem. Soc. Rev.* **2013**, 42, 4963-4976; (b) Jo, W. J.; Kim, K.-H.; No, H. C.; Shin, D.-Y.; Oh, S.-J.; Son, J.-H.; Kim, Y.-H.; Cho, Y.-K.; Zhao, Q.-H.; Lee, K.-H., *Synth. Met.* **2009**, 159, 1359-1364; (c) Jhulki, S.; Bajpai, A.; Nagarajaiah, H.; Chow, T. J.; Moorthy, J. N., *New J. Chem.* **2017**, 41, 4510-4517.
2. Lakshmi, V.; Rao, M. R.; Ravikanth, M., *Org. Biomol. Chem.* **2015**, 13, 2501-2517.
3. Avellanal-Zaballa, E.; Gartzia-Rivero, L.; Arbeloa, T.; Bañuelos, J., *Int. Rev. Phys. Chem.* **2022**, 41, 177-203.
4. Aratani, N.; Kim, D.; Osuka, A., *Acc. Chem. Res.* **2009**, 42, 1922-1934.
5. Lakshmi, V.; Ravikanth, M., *J. Org. Chem.* **2011**, 76, 8466-8471; (b) Loudet, A.; Burgess, K., *Chem. Rev.* **2007**, 107, 4891-4932.
6. Islam, K.; Narjinari, H.; Kumar, A., *Asian J. Org. Chem.* **2021**, 10, 1544-1566.
7. (a) Salam, N.; Kundu, S. K.; Roy, A. S.; Mondal, P.; Ghosh, K.; Bhaumik, A.; Islam, S., *Dalton Trans.* **2014**, 43, 7057-7068; (b) Pareek, M.; Sunoj, R. B., *ACS Catal.* **2020**, 10, 4349-4360; (c) Crockett, M. P.; Tyrol, C. C.; Wong, A. S.; Li, B.; Byers, J. A., *Org. Lett.* **2018**, 20, 5233-5237; (d) Duong, H. A.; Yeow, Z.-H.; Tiong, Y.-L.; Mohamad Kamal, N. H. B.; Wu, W., *J. Org. Chem.* **2019**, 84, 12686-12691.
8. Maluenda, I.; Navarro, O., *Molecules* **2015**, 20, 7528-7557.
9. Magano, J.; Dunetz, J. R., *Chem. Rev.* **2011**, 111, 2177-2250.
10. Selepe, M. A.; *Molecules* **2013**, 18, 4739-4765.
11. (a) Wu, X. F.; Anbarasan, P.; Neumann, H.; Beller, M., *Angew. Chem. Int. Ed.* **2010**, 49, 9047-9050; (b) Suzuki, A., *Angew. Chem. Int. Ed.* **2011**, 50, 6722-6737.
12. (a) Taheri Kal Koshvandi, A.; Heravi, M. M.; Momeni, T., *Appl. Organomet. Chem.* **2018**, 32, e4210; (b) Li, C.; Chen, D.; Tang, W., *Synlett* **2016**, 27, 2183-2200; (c) Kadu, B. S., *Catal. Sci. Technol.* **2021**, 11, 1186-1221; (d) Sun, L.; He, P.; Xu, B.; Xu, X.; *RSC Adv.* **2013**, 3, 5819-5823; (e) Hoffmann, I.; Blumenröder, B.; neé Thumann, S. O.; Dommer, S.; Schatz, J., *Green Chem.* **2015**, 17, 3844-3857; (f) Fernández, F.; Cordero, B.; Durand, J.; Muller, G.; Malbosc, F.; Kihn, Y.; Teuma, E.; Gómez, M., *Dalton Trans.* **2007**, 5572-5581.
13. (a) Miyaura, N.; Yanagi, T.; Suzuki, A., *Synth. Commun.* **1981**, 11, 513-519; (b) Martin, R.; Buchwald, S. L., *Acc. Chem. Res.* **2008**, 41, 1461-1473.
14. (a) Kostas, I. D.; Andreadaki, F. J.; Kovala-Demertzi, D.; Prentjas, C.; Demertzis, M. A., *Tetrahedron Lett.* **2005**, 46, 1967-1970; (b) Shin, J.; Bertoia, J.; Czerwinski, K. R.; Bae, C., *Green Chem.* **2009**, 11, 1576-1580; (c) Marziale, A. N.; Faul, S. H.; Reiner, T.; Schneider, S.; Eppinger, J., *Green Chem.* **2010**, 12, 35-38; (d) Islam, S.; Mondal, P.; Roy, A. S.; Mondal, S.; Hossain, D., *Tetrahedron Lett.* **2010**, 51, 2067-2070; (e) Conelly-Espinosa, P.; Morales-Morales, D., *Inorganica Chim. Acta* **2010**, 363, 1311-1315.
15. (a) Saha, D.; Chattopadhyay, K.; Ranu, B. C., *Tetrahedron Lett.* **2009**, 50, 1003-1006; (b) Liu, W.-J.; Xie, Y.-X.; Liang, Y.; Li, J.-H., *Synth.* **2006**, 2006, 860-864; (c) Hussain, I.; Capricho, J.; Yawer, M. A., *Adv. Synth. Catal.* **2016**, 358, 3320-3349; (d) Mondal, M.; Bora, U., *Green Chem.* **2012**, 14, 1873-1876.
16. (a) Arora, V.; Narjinari, H.; Nandi, P. G.; Kumar, A., *Dalton Trans.* **2021**, 50, 3394-3428; (b) Beletskaya, I. P.; Alonso, F.; Tyurin, V., *Coord. Chem. Rev.* **2019**, 385, 137-173; (c) Han, F.-S., *Chem. Soc. Rev.* **2013**, 42, 5270-5298.
17. (a) Zim, D.; Monteiro, A. L., *Tetrahedron Lett.* **2002**, 43, 4009-4011; (b) Gurung, S. K.; Thapa, S.; Kafle, A.; Dickie, D. A.; Giri, R., *Org. Lett.* **2014**, 16 (4), 1264-1267.

18. Hazari, N.; Melvin, P. R.; Beromi, M. M., *Nat. Rev. Chem.* **2017**, *1*, 1-16.
19. Dhital, R. N.; Sen, A.; Sato, T.; Hu, H.; Ishii, R.; Hashizume, D.; Takaya, H.; Uozumi, Y.; Yamada, Y. M., *Org. Lett.* **2020**, *22*, 4797-4801.
20. Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V., *Chem. Rev.* **2011**, *111*, 1346-1416.
21. (a) Goldfogel, M. J.; Guo, X.; Meléndez Matos, J. L.; Gurak Jr, J. A.; Joannou, M. V.; Moffat, W. B.; Simmons, E. M.; Wisniewski, S. R., *Org. Process Res. Dev.* **2021**, *26*, 785-794; (b) Hanley, P. S.; Ober, M. S.; Krasovskiy, A. L.; Whiteker, G. T.; Kruper, W. J., *ACS Catal.* **2015**, *5*, 5041-5046; (c) Percec, V.; Bae, J.-Y.; Hill, D. H., *J. Org. Chem.* **1995**, *60*, 1060-1065; (d) Saito, S.; Sakai, M.; Miyaura, N., *Tetrahedron Lett.* **1996**, *37*, 2993-2996.
22. Malapit, C. A.; Bour, J. R.; Brigham, C. E.; Sanford, M. S., *Nature* **2018**, *563*, 100-104.
23. (a) Tang, Z.-Y.; Hu, Q.-S., *J. Am. Chem. Soc.* **2004**, *126*, 3058-3059; (b) Tang, Z. Y.; Hu, Q. S., *Adv. Synth. Catal.* **2004**, *346*, 1635-1637.
24. (a) Gao, H.; Li, Y.; Zhou, Y. G.; Han, F. S.; Lin, Y. J., *Adv. Synth. Catal.* **2011**, *353*, 309-314; (b) Zhao, Y. L.; Li, Y.; Li, S. M.; Zhou, Y. G.; Sun, F. Y.; Gao, L. X.; Han, F. S., *Adv. Synth. Catal.* **2011**, *353*, 1543-1550; (c) Chen, G. J.; Han, F. S., An efficient Suzuki–Miyaura coupling of aryl sulfamates and boronic acids catalyzed by NiCl₂ (dppp). *Eur. J. Org. Chem.* **2012**, *2012*, 3575-3579.
25. West, M. J.; Watson, A. J., *Org. Biomol. Chem.* **2019**, *17*, 5055-5059.
26. (a) Ramgren, S. D.; Hie, L.; Ye, Y.; Garg, N. K., *Org. Lett.* **2013**, *15*, 3950-3953; (b) Xu, L.; Li, B.-J.; Wu, Z.-H.; Lu, X.-Y.; Guan, B.-T.; Wang, B.-Q.; Zhao, K.-Q.; Shi, Z.-J., *Org. Lett.* **2010**, *12*, 884-887; (c) Shi, S.; Meng, G.; Szostak, M., *Angew. Chem.* **2016**, *128*, 7073-7077.
27. (a) Zhou, W.-J.; Wang, K.-H.; Wang, J.-X.; Gao, Z.-R., *Tetrahedron* **2010**, *66*, 7633-7641; (b) Arcadi, A.; Cerichelli, G.; Chiarini, M.; Correa, M.; Zorzan, D., *Eur. J. Org. Chem.* **2003**, *2003*, 4080-4086; (c) Liu, C.; Ni, Q.; Bao, F.; Qiu, J., *Green Chem.* **2011**, *13*, 1260-1266.
28. Adamo, C.; Amatore, C.; Ciofini, I.; Jutand, A.; Lakmini, H., *J. Am. Chem. Soc.* **2006**, *128*, 6829-6836.
29. (a) Jhulki, S.; Bajpai, A.; Nagarajaiah, H.; Chow, T. J.; Moorthy, J. N., *New J. Chem.* **2017**, *41*, 4510-4517; (b) Islam, K.; Narjinari, H.; Bisarya, A.; Kumar, A., *Org. Biomol. Chem.* **2021**, *19*, 9692-9704.
30. Huang, J.; Su, J.-H.; Tian, H., *J. Mater. Chem.* **2012**, *22*, 10977-10989.
31. (a) Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R., *Nature* **2006**, *440*, 908-912; (b) Schwartz, G.; Reineke, S.; Rosenow, T. C.; Walzer, K.; Leo, K., *Adv. Funct. Mater.* **2009**, *19*, 1319-1333; (c) Kondakova, M. E.; Deaton, J. C.; Pawlik, T. D.; Giesen, D. J.; Kondakov, D. Y.; Young, R. H.; Royster, T. L.; Comfort, D. L.; Shore, J. D., *J. Appl. Phys.* **2010**, *107*, 014515; (d) Sun, N.; Wang, Q.; Zhao, Y.; Chen, Y.; Yang, D.; Zhao, F.; Chen, J.; Ma, D., *Adv. Mater.* **2014**, *26*, 1617-1621.
32. Johansson, N.; Salbeck, J.; Bauer, J.; Weissö rtel, F.; Brö ms, P.; Andersson, A.; Salaneck, W.R., *Adv. Mater.* **1998**, *10*, 1136.
33. Kim, R.; Lee, S.; Kim, K.-H.; Lee, Y.-J.; Kwon, S.-K.; Kim, J.-J.; Kim, Y.-H., Extremely deep blue and highly efficient non-doped organic light emitting diodes using an asymmetric anthracene derivative with a xylene unit. *Chem. Commun.* **2013**, *49*, 4664-4666.
34. (a) Saito, S.; Oh-Tani, S.; Miyaura, N., *J. Org. Chem.* **1997**, *62*, 8024-8030; (b) Yang, Y.; Cai, J.; Luo, G.; Jiang, Y.; Su, Y.; Su, Y.; Li, C.; Zheng, Y.; Zeng, J.; Liu, Y., *Org. Chem. Front.* **2019**, *6*, 1463-1470; (c) Rosen, B. M.; Huang, C.; Percec, V., *Org. Lett.* **2008**, *10*, 2597-2600.
35. Cho, C. S.; Tran, N. T., *Catal. Commun.* **2009**, *11*, 191-195.

36. Liu, L. L.; Zhang, S.; Chen, H.; Lv, Y.; Zhu, J.; Zhao, Y., *Chem. Asian J.* **2013**, *8*, 2592-2595.
37. (a) Williams, D. B. G.; Lawton, M., *J. Org. Chem.* **2010**, *75*, 8351-8354; (b) Burfield, D. R.; Lee, K.-H.; Smithers, R. H., *J. Org. Chem.* **1977**, *42*, 3060-3065.
38. Sheldrick, G. M., *Acta Crystallogr. Sec C Struct. Chem.* **2015**, *71*, 3-8.
39. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M., *Appl. crystallogr.* **2020**, *53*, 226-235.
40. Dhital, R. N.; Sen, A.; Sato, T.; Hu, H.; Ishii, R.; Hashizume, D.; Takaya, H.; Uozumi, Y.; Yamada, Y. M. A., *Org. Lett.* **2020**, *22*, 4797-4801.
41. West, M. J.; Watson, A. J. B., *Org. Biomol. Chem.* **2019**, *17*, 5055-5059.
42. Kran, E.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Studer, A., Synthesis of Stannylated Aryl Imines and Amines via Aryne Insertion Reactions into Sn–N Bonds. *Chem. Eur. J.* **2021**, *27*, 9281-9285.
43. Karimi, B.; Mansouri, F.; Vali, H., *Green Chem.* **2014**, *16*, 2587-2596.
44. Shan, X.-H.; Zheng, H.-X.; Yang, B.; Tie, L.; Fu, J.-L.; Qu, J.-P.; Kang, Y.-B., *Nature Commun.* **2019**, *10*, 908.
45. Yan, M.-Q.; Yuan, J.; Lan, F.; Zeng, S.-H.; Gao, M.-Y.; Liu, S.-H.; Chen, J.; Yu, G.-A., *Org. Biomol. Chem.* **2017**, *15*, 3924-3929.
46. Wang, Z.-Y.; Ma, Q.-N.; Li, R.-H.; Shao, L.-X., *Org. Biomol. Chem.* **2013**, *11*, 7899-7906.
47. Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K., *Nature Commun.* **2015**, *6*, 7508.
48. Abe, T.; Mino, T.; Watanabe, K.; Sakamoto, M., *Eur. J. Org. Chem.* **2014**, *2014*, 6983-6991.
49. Kamio, S.; Kageyuki, I.; Osaka, I.; Yoshida, H., *Chem. Commun.* **2019**, *55*, 2624-2627.
50. Yang, L.; Zhang, C.-P., *ACS Omega* **2021**, *6*, 21595-21603.
51. Han, B.; Ma, P.; Cong, X.; Chen, H.; Zeng, X., *J. Am. Chem. Soc.* **2019**, *141*, 9018-9026.
52. Cao, B.; Deng, Q.; Zuo, B.; Li, W.; Huang, M., *ChemistrySelect* **2021**, *6*, 2894-2900.
53. Melvin, P. R.; Hazari, N.; Beromi, M. M.; Shah, H. P.; Williams, M. J., *Org. Lett.* **2016**, *18*, 5784-5787.
54. Suryawanshi, S. B.; Mahajan, P. G.; Kolekar, G. B.; Bodake, A. J.; Patil, S. R., *J. Phys. Org. Chem.* **2019**, *32*, e3923.
55. Sun, H.; Zhang, X.; Miao, L.; Zhao, L.; Luo, Q.; Xu, J.; Liu, J., *ACS Nano* **2016**, *10*, 421-428.
56. Kotha, S.; Ghosh, A. K.; Deodhar, K. D., *Synth.* **2004**, *2004*, 549-557.
57. Mo, Y. Q.; Deng, X. Y.; Jiang, X.; Cui, Q. H., *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 3286-3295.
58. Nikitin, K.; Müller-Bunz, H.; Ortin, Y.; Muldoon, J.; McGlinchey, M. J., *Org. Lett.* **2011**, *13*, 256-259.
59. Kauffman, J. M., *Synth.* **2001**, *2001* (02), 0197-0199.
60. Seo, T.; Ishiyama, T.; Kubota, K.; Ito, H., *Chem. Sci.* **2019**, *10*, 8202-8210.
61. Reimann, S.; Ehlers, P.; Sharif, M.; Spannenberg, A.; Langer, P., *Tetrahedron* **2016**, *72*, 1083-1094.
62. Kumar, S.; Huang, D.-C.; Venkateswarlu, S.; Tao, Y.-T., *J. Org. Chem.* **2018**, *83*, 11614-11622.
63. Harada, K.; Hart, H.; Frank Du, C. J., *J. Org. Chem.* **1985**, *50*, 5524-5528.

Summary & Outlook



This thesis describes the synthetic protocol of multi-fold cross-coupling reaction to access polyarylated/alkynylated polycyclic aromatic hydrocarbons in the presence of Ni- and Pd-based catalysts. Versatile application of PAHs with promising photophysical properties towards sensing and application in cytotoxic studies have been investigated.



Chapter I describes a brief introduction of polycyclic aromatic hydrocarbons (PAHs), their synthetic methodology and versatile applications. The multi-fold C-C cross coupling (Sonogashira and Suzuki) reaction have proven to be a powerful synthetic tools to obtain polyarylated/arylnylated π -conjugated polycyclic aromatic hydrocarbons. The application of a library of π -conjugated (PAHs) in biological activity, sensing and optoelectronic devices have been discussed. The chapter winds up with a section that discusses on the scope of the current thesis.

Chapter II includes the designing of highly π -conjugated polyarylnylatedanthracenes compounds containing various electron-donating and withdrawing substituents. A new efficient single step multi-fold Sonogashira coupling reaction has been formulated to access new nine polyarylnylatedanthracenes. Five compounds have been crystallographically characterized, two of them displays numerous interactions that greatly reduce the inter-planar distances in the solid-state structure. They exhibited rich photophysical properties and two of them demonstrate halochromism and solvatochromism, with one of them showing a low bandgap of 1.79 eV. The remaining molecules displays low band gaps in the range of 1.79-2.04 eV.

Highly sensitive, selective, low-cost and room temperature hydrogen gas sensors were fabricated based on D- π -A- π -D motif small organic semiconductor. These sensors were found to detect H₂ at concentrations as low as 150 part per million (ppm) at room temperature. Various additive microfabrication techniques were used to fabricate the devices. A precisely controlled fabrication is enabled by employing a μ -gridded printing system. The gas sensor shows excellent sensitivity, fast response, and high recovery to H₂ at room temperature. Moreover after the interaction with H₂, the surface electron of the *N,N*-dimethyl amine containing tetraarylnylatedanthracene gets enhanced and shows a decrement in the resistance of the fabricated device. Sensor exhibits a limit of detection of 49 ppb with the highest sensitivity of 19.95% for the detection of 900 ppm of H₂, with a response time of 10 to 20 seconds.

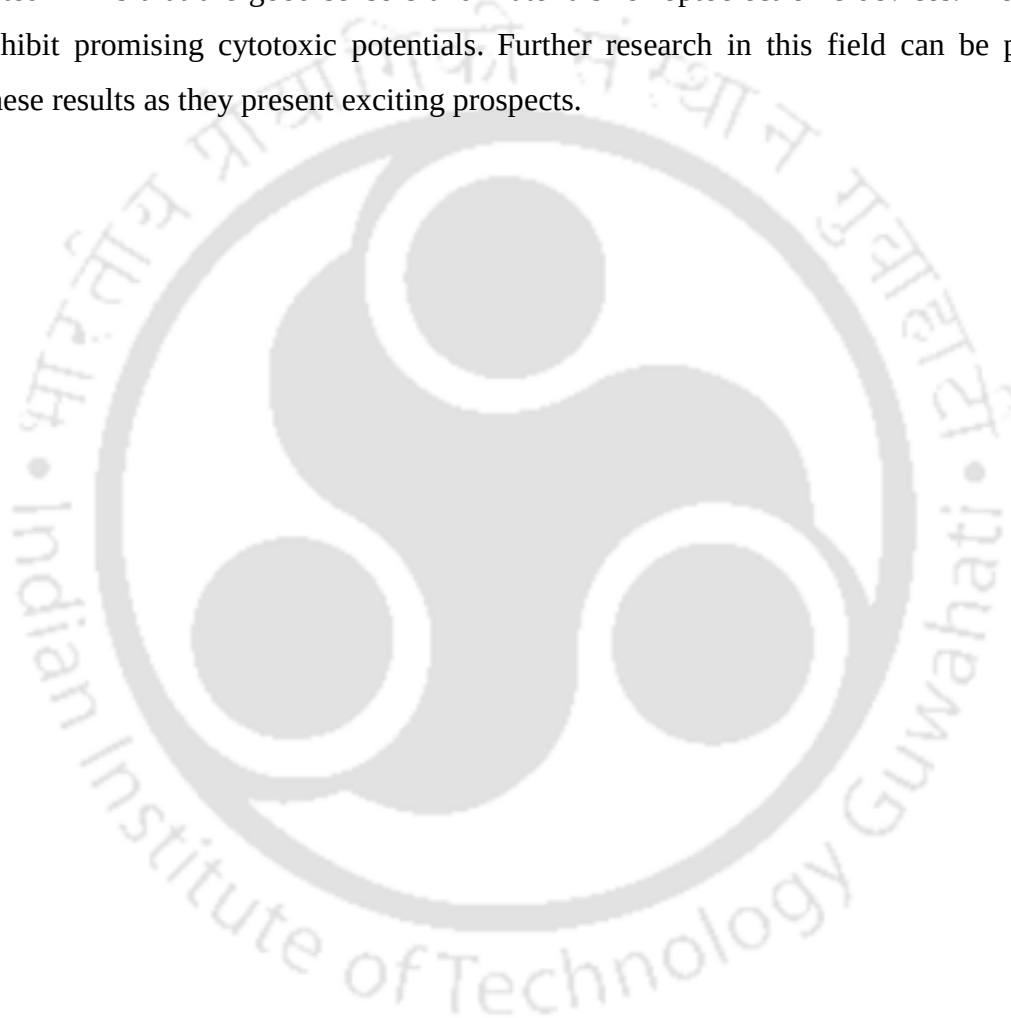
Chapter III formulated an efficient copper-free and amine-free multi-fold Sonogashira coupling reaction of a variety of aryl halides with aryl acetylene in the presence of Pd(CH₃CN)₂Cl₂ (0.5 mol%) and CataCXium® A (1 mol%) with an equivalent amount of Cs₂CO₃ at room temperature in a readily available green solvent (2Me-THF). The products of the reaction were obtained in moderate to excellent yields with vast substrate scope. The

strength of the C-X (X = Cl, Br, and I) bond determined the reactivity of different aryl halide substrates, which followed the sequence Ar-I > Ar-Br > Ar-Cl. This suggests that the RDS of the entire catalytic cycle involves the oxidative addition of Ar-X.

An attempt was made to examine the cytotoxic potential of tetraalkynylatedanthracenes. Amongst them, two of the evaluated anthracene derivatives could be potential candidates for anti cancer therapy. It is interesting to note that even at concentrations as low as 3.12 μ M, the most effective anthracene derivatives exhibit cytotoxicity. According to DAPI and PI staining, the anthracene derivatives caused apoptosis by nuclear fragmentation and membrane rupture. Comparing MDA-MB-231 cells to HDF cells, a more pronounced nuclear fragmentation and membrane disruption has been observed in the former. This illustrates that the MDA-MB-231 cell lines will be specifically targeted by the anthracene derivatives. Thankfully, the anthracene derivatives that weren't as cytotoxic are still useful due to their fascinating fluorescence characteristics, making them potentially effective fluorescent dyes for bio-imaging applications.

Chapter IV investigates the utility of commercially available, inexpensive 3d-metal salt NiBr₂ to accomplish the catalytic Suzuki coupling reaction of a variety of aryl halides with numerous aryl boronic acids in moderate to good yields with vast functional group tolerance. The reactivity follows the order Ar-I > Ar-Br > Ar-Cl, which suggests that the oxidative addition may be the slowest step in the catalytic cycle according to the C-X (X= I, Br and Cl) bond strength. Radical species are not present in the catalytic cycle, as evidenced by the reaction mixture's EPR silent nature and the fact that the inclusion of the radical scavenger TEMPO had no effect on the reaction. The NiBr₂ catalysed Suzuki reaction is most likely to proceed through a pure organometallic pathway that involves well-defined molecular Ni(0)/Ni(II) species in the catalytic cycle. The π -acceptor ligand such as 1,5-cyclooctadiene significantly reduced the yields of the products. The aryl halide's easy oxidative addition to Ni(0) species, which is probably the step that determines rate, is favoured by the π -donating solvent dioxane (RDS). For the first time, the multi-fold Suzuki coupling of tetra-/dibromoanthracene and tetraiodobenzene with various aryl boronic acids leading to important novel PAHs has been effectively accomplished using this NiBr₂ based catalytic system.

The current thesis has shown how to access π -conjugated polycyclic aromatic hydrocarbons such as polyarylated and polyarynylatedanthracenes through a single step multi-fold coupling procedure. The photophysical characteristics of polyarynylatedanthracenes have been investigated, and their potential for sensing and cytotoxicity has thus been established. It is reassuring to see that a sizable portion of current global research has focused on the diverse applications of π -conjugated polycyclic aromatic hydrocarbons. Not surprisingly, the current thesis also offers exciting leads, such as the capacity to synthesize a significant number of π -conjugated PAHs that are good sensors and materials for optoelectronic devices. Moreover, they exhibit promising cytotoxic potentials. Further research in this field can be pursued using these results as they present exciting prospects.







Khadilum Islam

Ph.D Student

Department of Chemistry

Indian Institute of Technology Guwahati

Guwahati-781039, Assam, India

Email-islam176122018@iitg.ac.in
abuhanachem23@gmail.com

Academic Qualification

2011-2014	B.Sc Chemistry (Honours), Physics and Mathematics (Subsidiary) Department of Chemistry City College, Affiliated to University of Calcutta, Kolkata, India
2014-2016	M. Sc in Chemistry Department of Chemistry Indian Institute of Technology Guwahati Guwahati, Assam-781039, India
2017-Present	Ph.D in Organic Chemistry Department of Chemistry Indian Institute of Technology Guwahati Guwahati, Assam-781039, India

Area of Research

- Synthetic organic chemistry
- Synthesis of π -conjugated polycyclic aromatic hydrocarbons and characterization.
- Tuning the optical properties of π -conjugated polycyclic aromatic hydrocarbons.
- Sensing of environmental pollutants.
- Application on optoelectronic devices.
- Catalysis

List of Publications

1. Das, K.; Nandi, P. G.; **Islam, K.**; Srivastava, H. K.; Kumar, A., SolventFree and Efficient Pincer-Ruthenium Catalytic Systems for N-Alkylation of Amines Promoted by a Base Generated In-Situ from Alcohols. *Eur. J. Org. Chem.* **2019**, 2019, 6855-6866.
2. **Islam, K.**; Narjinari, H.; Kumar, A., Polycyclic Aromatic Hydrocarbons Bearing Polyethynyl Bridges; Synthesis, Photophysical Properties and their Applications. *Asian J. Org. Chem.* **2021**, 10, 1544-1566.
3. **Islam, K.**; Narjinari, H.; Bisarya, A.; Kumar, A., Multi-fold Sonogashira coupling: a new and convenient approach to obtain tetraalkynyl anthracenes with tunable photophysical properties. *Org. Biomol. Chem.* **2021**, 19, 9692-9704.
4. **Islam, K.**; Arora, V.; Vikas; Nag, B.; Kumar, A., Nickel Bromide Catalyzed Ligand-Free and Activator-less Suzuki Coupling Reactions. *ChemCatChem* **2022**, 14, e202200440
Highlighted in the Noteworthy section of ChemViews Magazine.
<https://www.chemistryviews.org/nickel-bromide-catalyzed-suzuki-coupling-reactions/>
5. **Islam, K.**; Bhunia, K.B.; Mandal, G.; Nag, B.; Jaiswal, C.; Manda, B.B; Kumar, A., Copper-Free and Amine-Free Sonogashira Reaction at Room Temperature in a Green Solvent. Synthesis of Tetraalkynylated Anthracenes and *In-Vitro* Assessment of their Cytotoxic Potentials. *Manuscript Submitted*, 2022
6. **Islam, K.**; Daniel, T. T.; Paily P. R.; Kumar, A., Polycyclic Aromatic Hydrocarbon Based Electrical Sensor: Dimethylamine Substituted Alkynylated Anthracene for H₂ Detection. *Manuscript Under Preparation*

PATENT

1. A Kumar, RP Paily, **K Islam**, T Daniel, SYMMETRIC ETRAALKYNYLATED ANTHRACENES AND THE PROCESS FOR PREPARING THE SAME FOR SENSING AND OPTOELECTRONIC APPLICATIONS, IN Patent App. 202131035020, Date: August 03, 2021
2. A Kumar, RP Paily, **K Islam**, T Daniel, SYMMETRIC ETRAALKYNYLATED ANTHRACENES AND THE PROCESS FOR PREPARING THE SAME FOR SENSING AND OPTOELECTRONIC APPLICATIONS, PCT/IB2022/057185, Date: August 03, 2022

CONFERENCES ATTENDED

- 1 **Islam, K.;** Narjinari, H.; Bisarya, A. Kumar, A. Oral presentation during National Organic Symposium Trust XVII-JNOST- 2022, School of Chemistry, University of Hyderabad, Hyderabad, India, January 06-10, **2021**.

“Multi-Fold Sonogashira Coupling: A New Convenient Approach to Obtain Tetraalkynylatedanthracene with Tunable Photophysical Properties.”

- 2 **Islam, K.;** Narjinari, H.; Bisarya, A. Kumar, A. Poster presentation during 2021, 28th Chemical Research Society of India National Symposium in Chemistry, IIT Guwahati, Guwahati, March 25-27, **2022**.

“A New Convenient Approach to Obtain Tetraalkynylatedanthracene by Multi-fold Sonogashira Coupling and their Tunable Photophysical Properties”

- 3 **Islam, K.;** Narjinari, H.; Bisarya, A.; Kumar, A. Oral Presentation during 2022, ACS National Meeting & Exposition, ACS Fall 2022, August 21-25, **2022**.

“Tunable Photophysical Properties of Tetraethynylated Anthracenes Synthesized via Multi-Fold Sonogashira Coupling”

- 4 **Islam, K.;** Arora, V.; V.; Nag, B.; Poster presentation during 2022, Frontiers in Chemical Sciences (FICS-2022), IIT Guwahati, Guwahati, December 02-04, **2022**.

“Ligand and Activator-Free Nickel Bromide Catalyzed Suzuki-Miyaura Coupling Reaction.”