

BIMETALLIC NANOPARTICLES IN HETEROGENEOUS CATALYSIS: AN INSIGHT TO SUZUKI HOMOCOUPLING REACTION

*A project report submitted in partial fulfillment of the requirements for
the award of the degree of*

Master of Science

In Chemistry

By

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1. The project work reported in the thesis is original & has been done by myself under the general supervision of my supervisor.
2. The work has not been submitted to any other institute for any degree or diploma.
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Anubhav Nath



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CERTIFICATE

This is to certify that the report of the project work entitled “**Bimetallic nanoparticles in heterogeneous catalysis: an insight to Suzuki homocoupling reaction**” which is being submitted by **Anubhav Nath**, in partial fulfillment for the award of degree of Master of Science in Chemistry is a record of bona-fide investigation carried out by him in the School of Basic Sciences, Indian Institute of Technology, Bhubaneswar under my supervision & guidance. This report has not been submitted for the award of any degree or diploma before.

In my opinion, this project has fulfilled the requirements according to the regulations & has reached the standard for submission.

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ABSTRACT

Bimetallic nanoparticles have advanced into a promising zone in the field of homogeneous as well as heterogeneous catalysis. We have focused our entire study on the comparative catalytic activities of different nanoparticles (monometallic or bimetallic) in the field of Suzuki homocoupling reaction, one of the major carbon-carbon bond forming reactions which has emerged as a hot field in the past decade. Though many catalysts have been developed in this context, only one bimetallic Au-Pd bimetallic nanocatalyst was reported. Hence, we have tried to achieve the coupling between two C_{sp^2} centres using three systems namely Sn nanoparticles, Pd nanoparticles & Pd-Sn nanoparticles of which Pd-Sn nanoparticles have been found to be the most effective one at low temperature.

A number of optimization experiments have been performed by varying (a) solvent, (b) atmospheric conditions, (c) temperature, (d) catalyst & (e) substrate. The homocoupling of 4-methoxy phenyl boronic acid in anisole has been found to be the most successful one giving a yield of 75-80%. Variations in solvent have been done leading to biaryls in the range of trace to 65% yield.

Abbreviations

CDCl ₃	Deuterated chloroform
°C	Degree Celsius
d	Doublet
s	Singlet
DCM	Dichloromethane
NP	Nanoparticle
mg	Miligram
mL	Mililitre
hrs	Hours
K	Kelvin
MeCN	Acetontrile
IR	Infrared
NMR	Nuclear magnetic Resonance
ppm	Parts per million
SEM	Scanning electron microscope
EDX	Energy dispersive x-ray

1. Introduction

Nanoparticles, which have become greatly important nowadays, are the solid particles having size between 1 & 100 nm and they are surrounded by an interfacial layer.¹ The properties of the nanoparticles are fundamentally affected by the layer which is nothing but an inherent segment of the nanometer-sized particles. The layer may be an inorganic or organic molecule or an ion. When organic molecules coat inorganic nanoparticles they are termed as stabilizers or capping ligands or passivizing agents.

Nanoparticles play a significant role in nanotechnology since they function as a correlating unit between bulk material & atomic or molecular structures. They show attractive, sometimes astonishing, properties owing to their large surface area available e.g. nanoparticles of titanium dioxide are used as one of the primary constituents in sunscreen products which scatter harmful UV rays while allowing only visible light to go beneath human skin.

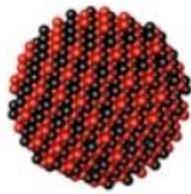
Bimetallic nanoparticles, as the name suggests, are composed of two different metal atoms. They have emerged as a field of much greater interest than monometallic ones not only in the scientific world but also in the technological world in recent times. This yet untouched field of synthesis as well as distinct catalytic, electronic & optical properties of bimetallic nanoparticles has become a hot topic in the last decade. This is due to the fact that they are supposed to exhibit the combining properties of the two different metals involved as well as new properties arising due to the synergy between two metals. The mode of distribution of the two metals in the bimetallic nanoparticle determine the structure of it. Preparative methods & employed conditions – these two factors are solely responsible for defining the shape & size of a particular monometallic or bimetallic nanoparticle.²

Only 40 years back, it was found that heterogeneous, composite particles work much more efficiently than their corresponding single particles.³ Normally, bimetallic nanoparticles can be classified in several groups.

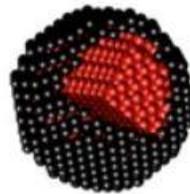
1.1 Alloy structure

1.2 Core-shell structure

Besides that, other structural forms such as alloy with an intermetallic compound type, clusters, sub-clusters etc. are also known. As mentioned earlier, which form the final nanoparticle would adopt (e.g. alloy, core-shell, random alloy etc.) is dependent on the synthetic approach.³



Ru-Pt Alloy



Ru-Pt core shell

Fig 1A

Fig 1B

Alloy nanoparticles

- An alloy is a combination of metals which is defined by a metallic bond character. Alloying of metals allow us to develop new materials which show much enhanced technological activities than the individual ones. Increase in solid solubility of the components of the alloy with diminishing particle size is one of the most notable effects that an alloy nanoparticle can offer unlike its bulk version.
- Alloy nanoparticles are the bedrocks of nanoscience as well as nanotechnology. Their unusual & promising applications are attributed to two main factors –
 - I. Nanoparticles possess a much greater surface area to volume ratio (which can be proved mathematically) affecting their activity & leading to greater chemical spontaneity.**
 - II. At the level of nano scale, quantum effects also become much more prominent since they are tiny enough to hold their electrons.⁴**

- Engineered alloy nanoparticles which are designed for and already being employed in commercial fields are showing their effectiveness. They are used in different fields like sporting goods, stain resistant clothing, sunscreens, cosmetics, tires, electronics, paints, varnishes as well as in medicinal field for diagnosis, imaging & drug delivery and many more still counting.

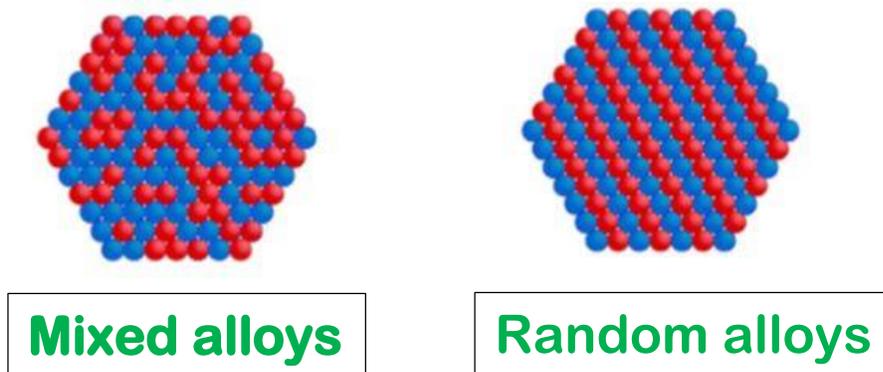


Fig 2A

Fig 2B

Core-shell nanoparticles

- As a very recent development, in search of upgrading the property of heterogeneous, composite or sandwich colloidal semiconductor particles, concentric multilayer semiconductor materials were developed by researchers. Eventually the terminology “core-shell” was validated.
- The properties of core-shell nanoparticles are size as well as actual shape. Both physical & chemical properties e.g. melting point, optical & electrical properties, catalytic activity, selectivity etc. are highly dependent on shape. Besides, sensitivity towards surface-enhanced Raman scattering (SERS) & the plasmon resonance characteristics of nanoparticles rely a lot on the particle morphology. Temperature is a very important factor to mention to control the kinetics of core-shell nanoparticle formation reaction.
- Core-shell nanoparticles have secured their superior position especially in the field of biomedical & electronics. Examples include:

- I. **Biomedical applications**
- II. **Colorimetry & biosensing**
- III. **Chemical libraries**
- IV. **Therapeutic applications & drug delivery**
- V. **Enhancing photoluminescence**
- VI. **Creating photonic crystals etc.**

1.3 Bimetallic nanoparticles as efficient heterogeneous catalysts

Bimetallic nanoparticles have emerged as a matter of remarkable scientific interest due to their function as a superior catalyst with greatly advanced activity & selectivity in comparison to their monometallic analogues. In recent times, majority of the industrial methods rely heavily upon the catalyst, **backbone of the chemical industry**. Majority of the chemical processes in day to day life such as food, fertilizers, petrochemical & pharmaceutical industries are catalyst dependent. Hence the sketch and evolution of catalysts for the conversion of materials to value-added chemicals have become a significant zone of research in industry & academia. Comparatively, heterogeneous catalysts have noteworthy applications owing to their ease of separation, regeneration & recyclability whereas homogeneous catalysts are famous for their high selectivity & conversion. Regarding catalysis, it is essential to diminish the size of the particle of bulk materials from several micrometers to nanometers to cause an increase in the surface area. However, nanoparticles with such a tiny size are prone to aggregate to minimize their surface area leading to a prominent deterioration in their catalytic activity.¹ That's why the stabilizers or capping agents come into picture which hold the high surface area & catalytic activity of the nanoparticles.

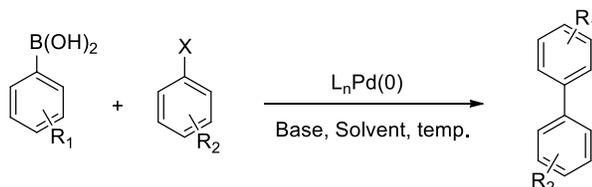
The topic of synthesis of bimetallic Pd-Sn nanoparticle & their introduction as an efficient catalyst in the organic chemistry world has remained as a quite untouched topic. Salts of Pd and Sn both being relatively cheaper, an attempt to develop a well-designed nanoparticle of Pd-Sn has been approached from easily available starting materials under ambient conditions.

1.4 Suzuki Coupling Reaction

The well-known & versatile Suzuki-Miyaura cross coupling reaction (commonly referred to as

Suzuki coupling reaction) was reported in 1979 by Akira Suzuki & N. Miyaura

- 1) It is a famous palladium catalyzed cross coupling reaction between aryl & aromatic boron compounds & organic halides or pseudohalides establishing C-C bonds.
- 2) The general reaction is shown below –



Scheme 1: Suzuki-Miyaura Cross-coupling reaction

Common conditions

- Solvent* : Toluene, THF, Dioxane, BuOH, DMF, Water
- Base*: Na/K₃PO₄, Na/K₂CO₃, Na/KOH, Na/KOt-Bu (1.5-3 equiv.)
- Boronate*: Boronic acid, Potassium trifluoroborate, MIDA boronate (1.2-2 equiv.)
- Pd source*: Palladium pre-catalyst or [L + Pd(OAc)₂] (0.1-10 mol %)
- Temperature*: rt-110⁰ C.

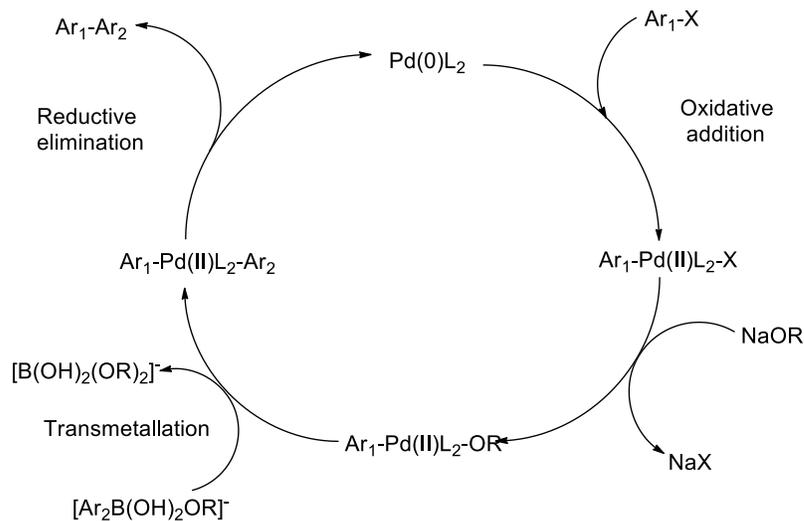


Fig 3: Catalytic cycle for Suzuki coupling

This is one of the most powerful reactions in organic chemistry for carbon-carbon bond formation since it has the following advantages which make it superior to other cross coupling reactions:

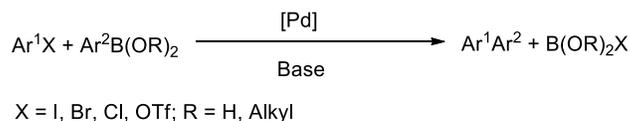
- a) It can tolerate presence of functional groups in the coupling partners while the older conventional methods for coupling of aryl groups typically require reagents & catalysts that are incompatible with molecules bearing polar functional groups.
- b) The Suzuki reaction demands milder conditions than the Heck reaction.
- c) The boronic acids are air & water stable as well as nontoxic. The pharmaceutical industry therefore prefers this reaction since the boron species formed as a side product during this reaction is relatively nontoxic unlike the Stille coupling which leads to tin based toxic byproducts.

One basic difference between the Suzuki reaction & the Stille coupling is that unless boronic acid is activated with a base the reaction doesn't proceed. This activation smoothens the transmetallation step since the organic ligand gets polarized enough.⁵

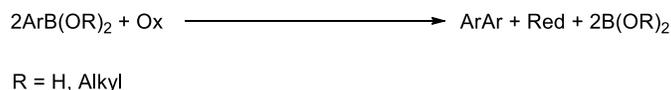
There has been a vast improvement & increase in the scope & utility of this reaction in the recent past. This includes

- Use of aryl chloride as substrate
- Very low catalyst loading
- To carry out the reaction at room temperature
- To couple highly hindered substrates
- To carry out asymmetric synthesis

1.5 From heterocoupling (cross coupling) to homocoupling



Scheme 1: Heterocoupling



Scheme 2: Homocoupling

This oxidative homocoupling was first observed under stoichiometric conditions & then as a side-reaction in Pd-catalyzed Suzuki-Miyaura cross coupling reactions. Indeed, the symmetrical biaryl ArAr generated from the aryl boronic acid ArB(OH)₂ is often observed in Suzuki-Miyaura cross couplings..

- *The homocoupling of aryl boronic acids was first reported by Moreno-Manas et al. in 1996, using catalysts as Pd(0) or Pd(II) complexes associated with monodentate phosphines.*
- *The oxidative homocoupling reaction could be driven faster by an oxidant e.g. Cu(NO₃)₂.*⁶

1.6 Literature Reviews

1.6.1 Developments in the field of Suzuki homocoupling reaction in recent past

1. Thomas Vogler & Armido Studer in the year of 2008 performed homocoupling reaction of alkenyl & aryl boronic acids with the help of Wilkinson's catalyst. TEMPO was stoichiometrically employed as an oxidating agent.

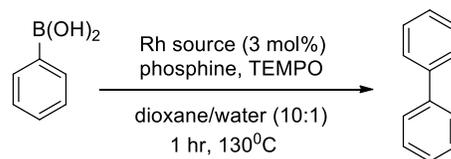


Fig 6

They obtained a maximum yield of 86% using $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst and TEMPO as an oxidant in 3 eq. amount.⁷

2. As a very recent study, Xing Li, Dongjun Li, Yana Bai, Congxia Zhang, Honghong Chang, Wenchao Gao, Wenlong Wei of department of chemistry & chemical engineering of Taiyuan University of Technology in the year of 2016 produced an efficient method of preparing symmetrical biaryls by using palladium nanoparticles supported on newly generated $\text{Al}(\text{OH})_3$ under mild conditions giving >99% yields.⁸

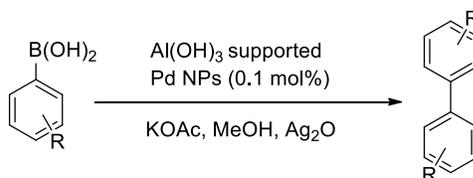


Fig 7

Reaction conditions

- a) Aryl boronic acid (0.2 mmol)
- b) KOAc (0.2 mmol)
- c) CH_3OH (0.8 ml)
- d) Ag_2O (45 mol%)
- e) Temperature: 40°C
- f) Time: 15 hrs.

3. A one step synthesis of symmetrical biaryls has been reported by Claudia Araceli Contreras-Celedon, Jose Arturo Rincon-Medina, Dario Mendoza-Rayo, Luis Chacon-Garcia in the year of 2015 under very mild conditions by the homocoupling reaction of substituted aryl boronic acids using an air & moisture stable 4-aminoantipyrine-Pd(II) complex as catalyst.⁹

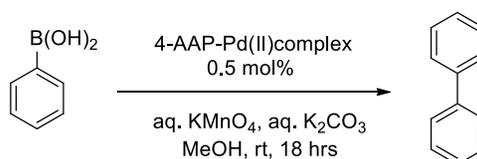


Fig 8

Reaction conditions

- Aryl boronic acid: 0.4 mmol*
 - 2 eq. 2 M K_2CO_3*
 - 0.5 eq. 0.25 M KMnO_4*
 - MeOH (1 ml)*
 - Room temperature*
 - Time: 18 hrs.*
4. Aerobic oxidative homocoupling of arylboronic acid under acidic aqueous conditions (pH 4.0) using bimetallic Au/Pd alloy nanoclusters stabilized by chitosan has been investigated in the year of 2012 by Onsulang Sophiphun, Jatuporn Wittayakun, Raghu Nath Dhital, Setsiri Haesuwannakij, Arumugam Murugadoss and Hidehiro Sakurai.¹⁰

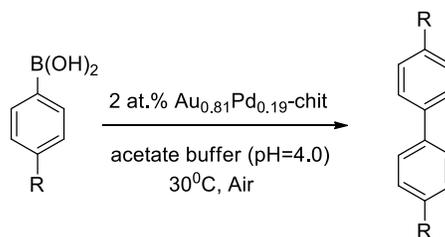


Fig 9

Reaction conditions

- a) Aryl boronic acid: 0.25 mmol
 - b) Acetate buffer (pH=4.0)
 - c) Water
 - d) Room temperature
 - e) Time: 3 hrs.
5. In 2016, Shaodan Xu, Huadong Sheng, Shangfu Liao, Dan Hu, Deqing Yu & Tao Ye reported an effective method to improve the biphenyl selectivity by incorporating a biphasic solvent of water-toluene mixture over hydrophilic Pd catalyst. By using such a catalyst the conversion of phenyl boronic acid & selectivity of biphenyl could reach as high as 99.0% & 83.0% respectively, much higher than those in monophasic solvent under similar conditions. The heterogeneous Pd catalyst exhibited excellent recyclability.¹¹

Reaction conditions

- a) Phenyl boronic acid: 1 mmol
- b) 0.2 mmol Na₂CO₃
- c) Toluene: 5 ml
- d) Pd/MCM-41 catalyst: 30 mg
- e) 1.5 MPa of O₂
- f) Temperature: 80°C
- g) Time: 6 hrs.

6. In 2013, Md Palashuddin Sk, Chandan K. Jana & Arun Chattopadhyay synthesized carbon nanoparticles supported gold nanoparticles starting with an Au nanoparticle-chitosan composite which coherently produced biphenyl through producing a yield of almost 90%.¹²

Reaction conditions

- a) *Phenylboronic acid (0.3 mmol)*
- b) *Gold-carbon nanoparticle composite (0.66 mol%)*
- c) *Toluene/water (2:1) 1.5 ml*
- d) *Temperature: 70⁰C*
- e) *Atmospheric oxygen*
- f) *Time: 7 hrs.*

7. An electrooxidative method for producing biaryls from arylboronic acids or esters has been described by Koichi Mitsudo, Takuya Shiraga, Daisuke Kagen, Deqing Shi, James Y. Becker & Hideo Tanaka in 2009 by using TEMPO & Pd(OAc)₂ giving moderate to good yields.¹³

Reaction conditions

- a) *Aryl boronic acid: 0.2 mmol*
- b) *Pd(OAc)₂ (10 mol%)*
- c) *TEMPO (30 mol%)*
- d) *K₂CO₃ (2 eq.)*
- e) *Et₄NClO₄ (0.05 M)*
- f) *MeCN/Water (7:1) 10 ml*
- g) *5 mA, 3 F/mol*

8. An anaerobic electrooxidative homocoupling of arylboronic acids was developed by Christian Amatore, Chama Cammoun and Anny Jutand in the year of 2008 using catalytic amounts of p-benzoquinone & Pd(OAc)₂.¹⁴

Reaction conditions

- a) Arylboronic acid (1 mmol)
- b) Pd(OAc)₂ (10 mol%)
- c) *p*-benzoquinone (10 mol%)
- d) DMF (10 ml)
- e) 0.3 M *n*Bu₄NBF₄
- f) Temperature: 80^oC
- g) Time: 2.2 hrs

9. In 2010, Alessandro Prastaroa, Pierpaolo Cecic, Emilia Chiancone, Alberto Boffib, Giancarlo Fabrizia & Sandro Cacchia developed an efficient palladium nanoparticle catalyst which is stabilized by highly thermally stable Dps protein. It catalysed homocoupling of boronic acids in aqueous medium producing a yield of almost 90% in absence of any phosphine.¹⁵

Reaction conditions

- a) Arylboronic acid (0.25 mmol)
- b) *Te*-Dps stabilized Pd NPs (0.05 mol%)
- c) Water
- d) 2 ml 1 M Tris-HCl buffer (pH=8.9)
- e) Temperature: 100^oC

1.6.2 Developments in the field of synthesis of bimetallic Pd-Sn nanoparticles in recent past

1. Xiangwen Liu et al in the year of 2011 performed a synthesis of bimetallic Pd-Sn hollow nanosphere by using oleylamine with the help of a swift one-pot strategy.¹⁶
2. Xu Fang & Deren Fang developed synthesis of Pd-Sn nanoparticles in different molar ratios (supported on activated carbon) in the year of 2017 & employed those in hydrodechlorination of chlorophenols.¹⁷

2. Objectives:

- a) To develop a facile way to design different kinds (mono & bimetallic) of nanoparticles.
- b) Employment of the nanoparticles in the Suzuki homocoupling reaction.
- c) Optimization of the reaction conditions & to check the superior activity of the bimetallic nanocatalyst.

3. Experimental section

All the solvents & reagents were distilled before use. Solvents were dried using the standard procedures. All the other reagents were used as received from either Sigma Aldrich or Spectrochem chemical companies. Ultrapure distilled water was used to perform all the experiments. All reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60 F254) with UV light. Silica gel (100-200 mesh) was used for column chromatography. ^1H (400 MHz) NMR was recorded on a Bruker Avance III 400 MHz spectrometer. Chemical shifts are reported in ppm from TMS as the internal standard with the solvent (deuteriochloroform) resonance at 7.261 ppm. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet), coupling constant, no. of protons.

3.1 Chemicals used

1. Palladium chloride (PdCl_2)
2. Acetonitrile
3. 1,5-cyclooctadiene
4. Stannous chloride (SnCl_2)
5. Dry Dichloromethane (DCM)
6. Polyvinyl pyrrolidone
7. Oleyl amine
8. Acetone
9. Ethylene glycol

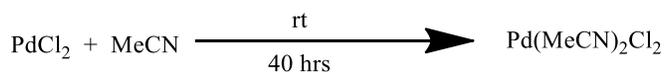
This portion consists of two parts -

1. **Synthesis of the monometallic & bimetallic nanoparticles &**
2. **Their use as a heterogeneous catalyst in suzuki homocoupling reaction.**

3.2A Preparation of Sn, Pd & Pd-Sn nanoparticles

Preparation of palladium & palladium-tin nanoparticles comprises of three steps –

- a) ~500 mg PdCl₂ was taken in a 100 ml round bottom flask & ~20 ml acetonitrile was added to it. The mixture was stirred at room temperature for ~40 hrs.



The solution was filtered & a yellow-brown coloured solid was obtained (~700 mg)

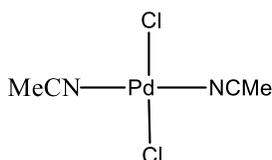


Fig 10

- b) In this step, the monometallic & bimetallic precursors were synthesized.

Reagent	Molecular weight (g/mol)	Amount	m mol
Pd(MeCN) ₂ Cl ₂	259.30	260 mg	1.0
1,5-COD	108.18	132 μL	1.02
SnCl ₂	190.00	190 mg	1.0
Dry DCM	-	~20 mL	-
PET ether	-	~30 mL	-

Reaction scheme

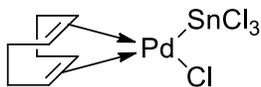
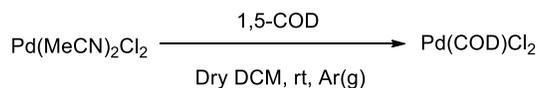
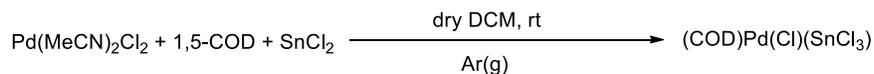


Fig 11a

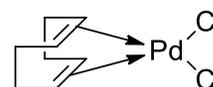


Fig 11b

Procedure

Pd-Sn nanoparticle precursor

A 100 ml double-necked round bottom flask was taken and SnCl₂ was dissolved in 1 ml acetone. Then one Ar(g) filled balloon was attached to it & 1,5-COD was added to the mixture along with dry DCM under stirring conditions at room temperature. A milky white suspension was observed then. Thereafter the Pd(MeCN)₂Cl₂ complex (after washing it with MeCN) was added to the solution. The colour of the solution started changing gradually from yellow to orange-yellow. Ultimately, PET ether was added to the reaction mixture which caused the complex to precipitate out. The solution was filtered through a sintering funnel and dried under vacuum. When the complex came contact with air, its colour changed to greenish brown.

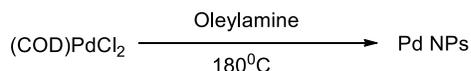
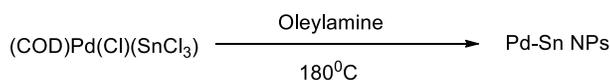
Pd nanoparticle precursor

A 100 mL double-necked round bottom flask was taken & one Ar(g) filled balloon was attached to it. 1,5-COD was added to the mixture along with dry DCM under stirring conditions at room temperature. Thereafter the Pd(MeCN)₂Cl₂ complex (after washing it with MeCN) was added to the solution. The colour of the solution started changing gradually

from yellow to orange-yellow. Ultimately, PET ether was added to the reaction mixture which caused the bright yellow complex to precipitate out. The solution was filtered through a sintering funnel and dried under vacuum.

c) Synthesis of PdSn & Pd nanoalloys from its mono & bimetallic precursor in oleylamine

Reagent	Molecular weight (g/mol)	Amount	m mol
(COD)Pd(Cl)(SnCl ₃)	475	100 mg	0.210
(COD)PdCl ₂	285	100 mg	0.351
Oleyl amine	267.493	5 ml	15.20



Procedure

First, 2 ml oleylamine was taken in a schlenk tube to which a balloon filled with Ar(g) is attached & heated at 100⁰C under vigorous stirring. Then 100 mg mono or bimetallic complex dissolved in 3 ml oleyl amine was added to the schlenk tube & heated at that temperature for 10 minutes first & then at 180⁰C for another 5 hours.

Then it was cooled & when temperature reached ~65⁰C, 5 ml acetone was added. It was kept standing at room temperature for sometimes & the mother liquor was taken out. Again 5 ml acetone was added to the solution and kept standing. This was repeated for a couple of times (until the color of the mother liquor turns colorless from light yellow) & the solution was filtered to obtain the black PdSn or Pd NPs. It was kept in a voil (~55 mg, ~36 mg), inside a desiccator.

Preparation of Sn nanoparticles was performed via standard procedure as follows –

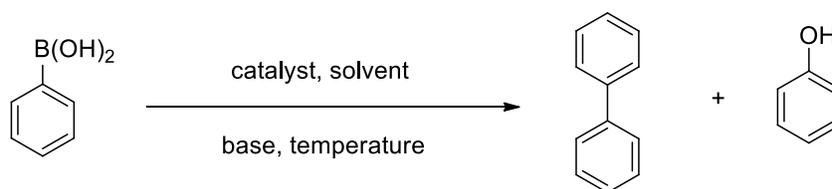
A 100 mL double-necked round bottom flask was taken & a balloon filled with Ar(g) was attached to it. Then 0.015 g PVP (mol. Wt. 40000) along with 0.5 g NaBH₄ were dissolved completely in 3 mL ethylene glycol and added to the RB flask. 0.4741 g SnCl₂ was dissolved in 9 mL ethylene glycol and injected carefully to the previous solution. The color of the solution at once changed to dark grey indicating formation of Sn nanoparticles. Another 20 mL ethylene glycol was added to the mixture & stirred vigorously at room temperature for 3 hours.¹⁸

After that, the solution was taken out into two different falcon tubes & 35-40 mL acetone was added to those each. They were shaken well & allowed to stand for sometimes. The mother liquor was decanted & again acetone was added. This was repeated for a couple of times. Then a mixture of 2 mL water & 25 mL acetone was added and same was repeated twice. These took away all the organic & inorganic impurities present. The residue was then dried under vacuum & grey colored Sn nanoparticles were stored inside a desiccator.

3.2B Homocoupling of phenylboronic acid by different nanoparticles

Reagent	Molecular weight (g/mol)	Amount (mg)	mmol
Phenyl boronic acid	121.93	45.75	0.375
Caesium carbonate	325.82	249.80	0.766 (2 eq.)
PdSn or Pd or Sn NPs		2	

General scheme:



Phenyl boronic acid along with NPs were taken in the said amount in a vol & caesium carbonate was added to it. Then 1 ml solvent was added & heated at particular temperature with stirring for ~40 hrs. Ethyl acetate (~4 ml) was added to the light yellow coloured reaction mixture & filtered. The filtrate was concentrated under vacuum & product was obtained by column chromatography.

4. Results & discussion

4.1 Role of oleylamine in the synthesis of mono & bimetallic nanoalloys:

Oleylamine is a high boiling colourless liquid which is commercially used as a surfactant or precursor to them. Here, its function is multidirectional i.e. it acts as both solvent for the thermal reduction step of the bimetallic precursor & also as a stabilizing or capping agent to stabilize the nanoalloy surface.

- It can affect the form of the metal ion.
- It can coordinate to the metal ion.
- It can also change the kinetics of formation of the nanoalloys at the time of synthesis.

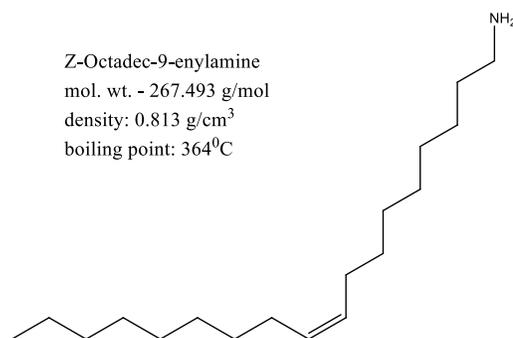


Fig 13

4.2 IR Spectrum of oleylamine, Pd NPs & Pd-Sn NPs:

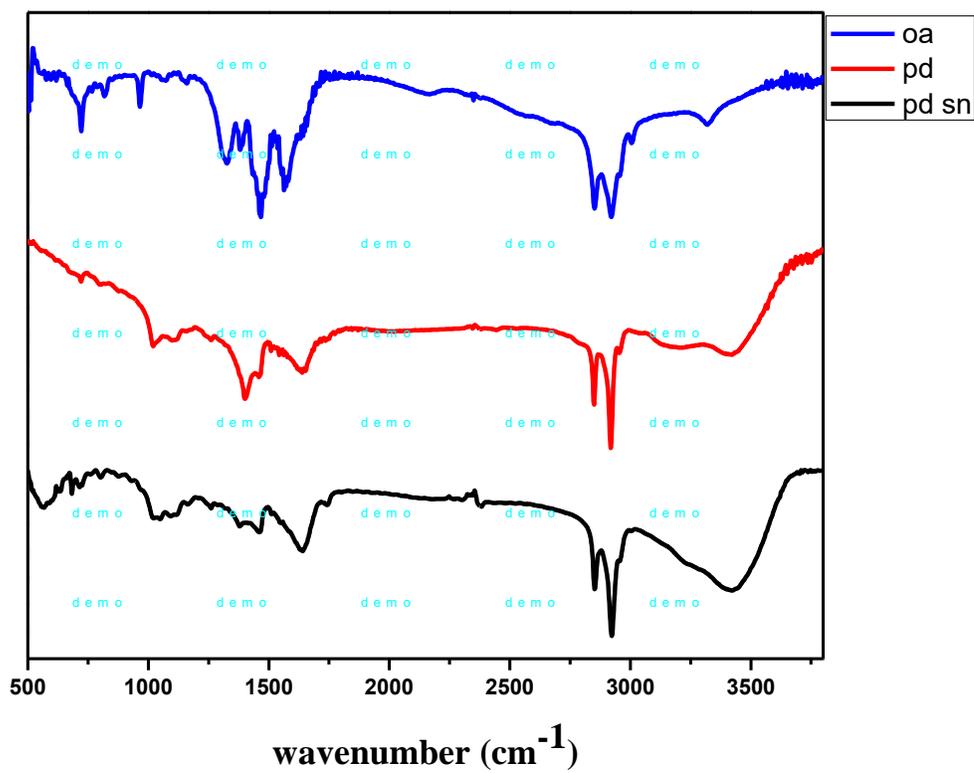
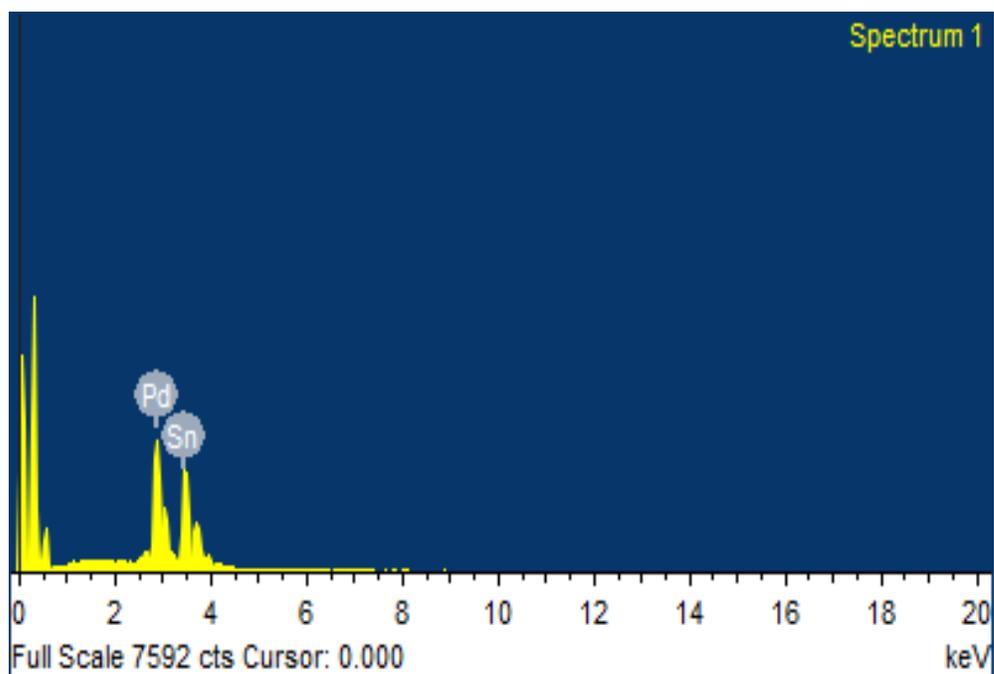


Fig 14

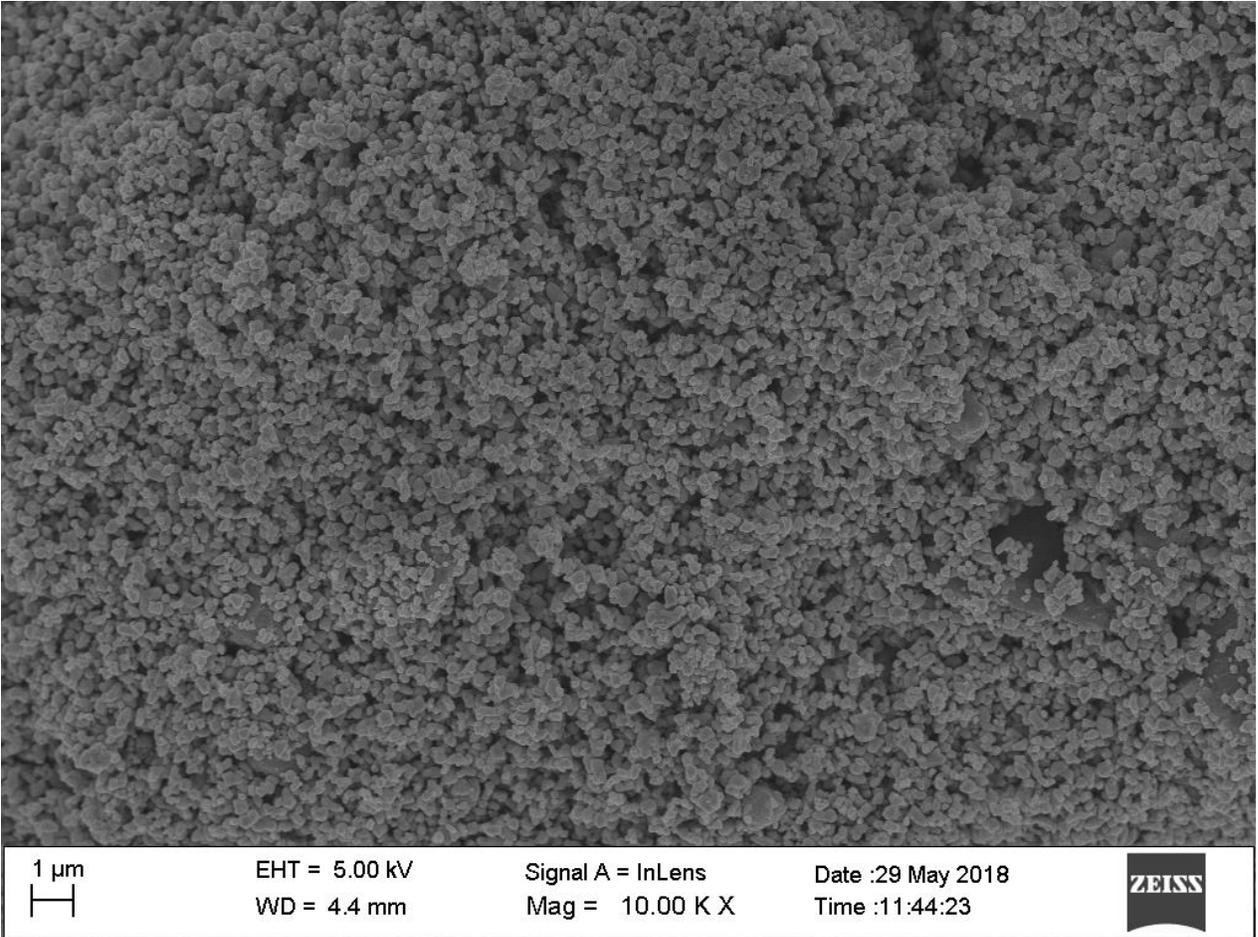
Oa = Oleyl amine ; pd = Pd NPs & pd sn = Pd-Sn NPs

4.3 Energy dispersive X-Ray spectra of Pd-Sn NPs:



Element	Weight%	Atomic%
Pd L	45.41	48.13
Sn L	54.59	51.87
Totals	100.00	

4.4 SEM image of Pd-Sn NPs:



4.5 We employed various reaction conditions i.e. we varied catalyst, base, solvent, temperature etc. to optimize the reaction conditions.

- It was found that reaction doesn't proceed in hexane (entry 4,5) i.e. neither by Pd NPs nor by Pd-Sn NPs.
- DCE, o-xylene & anisole have shown promising results (entry 1,6,7).
- Anisole comes out to be the most effective solvent for homocoupling (entry 7).

Table 1: Optimization of the reaction conditions of homocoupling of phenyl boronic acids

Entry no.	Catalyst	Base	Solvent	Temperature (°C)	Time (hrs)	Yield ^a (%)
1	PdSn NPs	Cs ₂ CO ₃	DCE	70-75	40	60 %
2	Pd NPs	Cs ₂ CO ₃	DCE	70-75	40	45 %
3	PdSn NPs	Cs ₂ CO ₃	DCE	70-75	40	50 %
4	PdSn NPs	Cs ₂ CO ₃	Hexane	55-60	24	NIL
5	Pd NPs	Cs ₂ CO ₃	Hexane	55-60	24	NIL
6	PdSn NPs	Cs ₂ CO ₃	o-xylene	120-125	40	63 %
7	PdSn NPs	Cs ₂ CO ₃	Anisole	130	40	65 %
8	PdSn NPs	Cs ₂ CO ₃	p-Dioxane	90-95	40	52 %

a : isolated yield

Reaction conditions : 0.375 mmol phenyl boronic acid, 0.77 mmol caesium carbonate, 1 mol % catalyst

Table 2: Optimization of the homocoupling step under O₂(g) atmosphere

Entry no.	Catalyst	Base	Solvent	Temperature (°C)	Time (hrs.)	Yield (%)
1	Pd NPs	Cs ₂ CO ₃	o-Xylene	120-125	24	35
2	Pd-Sn NPs	Cs ₂ CO ₃	o-Xylene	120-125	24	50
3	Pd NPs	Cs ₂ CO ₃	Anisole	130	24	38
4	Pd-Sn NPs	Cs ₂ CO ₃	Anisole	130	24	53

Hence, incorporation of oxygen (g) enhanced the conversion rate. But enhancement of yield hasn't yet been observed.

To check for substrate scope, we tried the same reaction by using Pd-Sn nanoparticles as catalyst and employing p-chloro phenyl boronic acid as the substrate, caesium carbonate as base, time 24 hours.

Table 3: Optimization of the homocoupling step taking 4-chloro phenyl boronic acid as substrate

Entry no.	Solvent	Temperature (°C)	Yield (%)
1	Anisole	115-120	70
2	Toluene	85-90	65
3	DCE	70-75	54
4	p-Dioxane	85-90	27

To account for the superior activity of the bimetallic nanoparticle over the other two monometallic ones, we carried out the reaction using chloro phenyl boronic acid as substrate, Cs₂CO₃ as base & anisole as solvent at 115°C.

Table 4: Comparative catalytic activity of various nanoparticles in the homocoupling reaction

Entry no.	Catalyst	Yield (%)
1	Pd NPs	67
2	Sn NPs	Trace
3	Pd-Sn NPs	70

Unfortunately, no significant superior action was found between the Pd & Pd-Sn nanoparticles as catalysts. Hence, an alternative pathway was thought to investigate the senior activity of the nanocatalyst for homocoupling reaction & it was to carry out the reaction at low temperature, here at 60°C.

Table 5: Comparative catalytic activity between Pd & Pd-Sn nanoparticles

Entry no.	Catalyst	Yield (%)
1	Pd NPs	49
2	Pd-Sn NPs	65

On an attempt to check for the substrate variation, we decided to take two different kinds of phenyl boronic acids viz. one with electron withdrawing group (-Cl) & another with electron donating group (-OMe).

Table 6: Variation of substrates for the homocoupling reaction

Entry no.	Substrate	Yield (%)
1	p-Chloro phenyl boronic acid	70
2	p-Methoxy phenyl boronic acid	78

5. Summary & conclusion

As a matter of fact, our entire work has been divided into three segments -

- I. Synthesis of monometallic Pd & Sn nanoparticle and bimetallic Pd-Sn nanoparticle by easily available starting materials.
- II. Characterization of the synthesized nanoparticles by different modes i.e. IR Spectroscopy, EDX spectroscopy, SEM techniques etc.
- III. Initial success in employing the nanoparticles in homocoupling reaction of aryl boronic acids to prepare symmetrical biaryls.

As described in the results & discussion section, high temperature reaction conditions doesn't reveal about the comparative activity of Pd & Pd-Sn nanoparticles as catalyst but at low temperature Pd-Sn NPs show their superior action over Pd NPs may be due to the synergistic action prevailing in a bimetallic nanoalloy.

6. Future plan:

In the upcoming stages we are thinking of the following:

- I. Attempt to enhance the yield of the reaction.
- II. Performing the reaction in more eco-friendly environment e.g. in water.

7. Spectral data of the coupling products

a) 4,4' - dimethoxy biphenyl

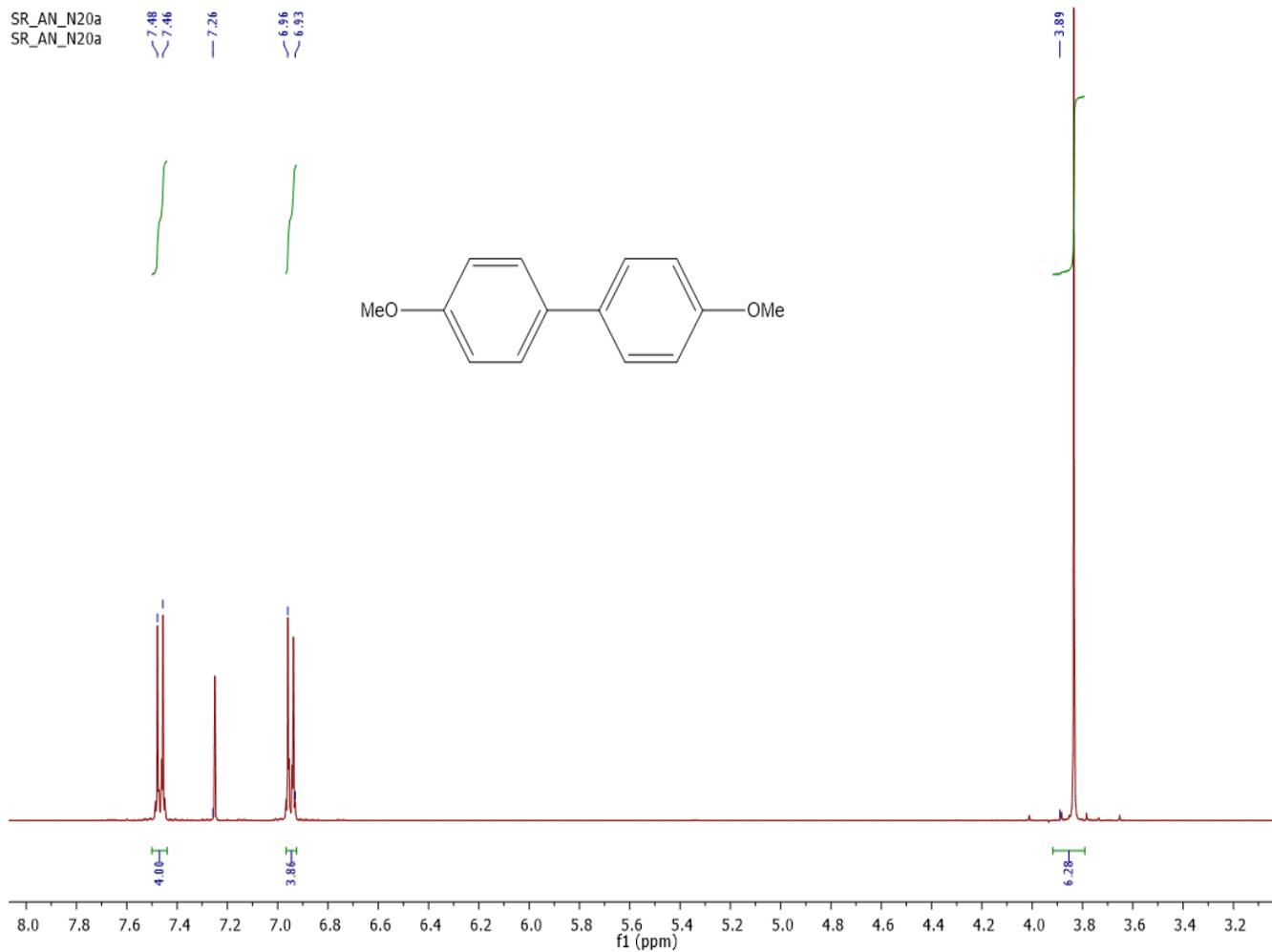
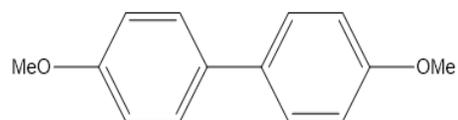
^1H NMR (CDCl_3 , 400 MHz): 6.95 (d, 12 Hz, 4H), 7.47 (d, 9 Hz, 4H), 3.89 (s, 6H).

b) 4,4' - dichloro biphenyl

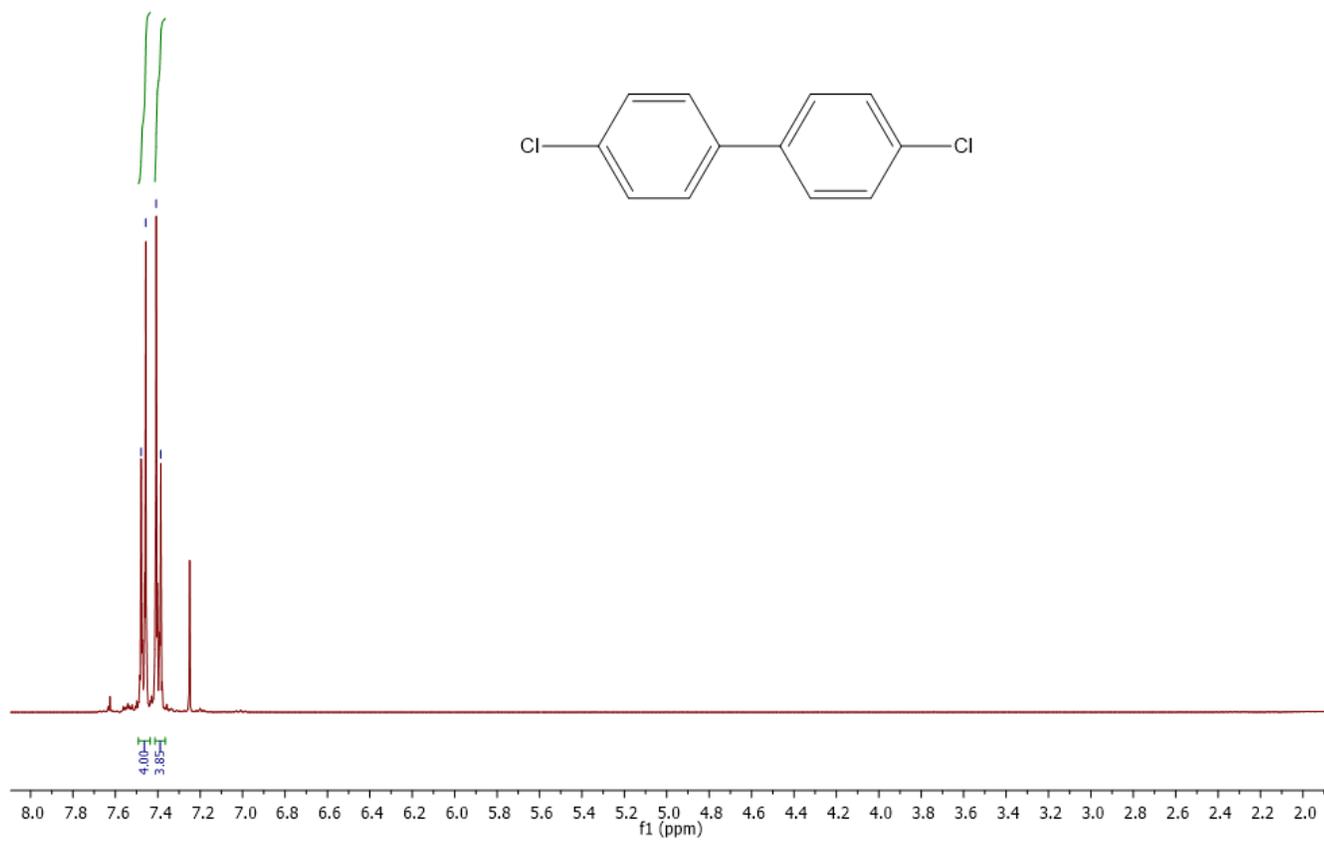
^1H NMR (CDCl_3 , 400 MHz): 7.40 (d, 8 Hz, 4H), 7.47 (d, 8 Hz, 4H)

SR_AN_N20a
SR_AN_N20a

7.48
7.46
7.26
6.86
6.83



SR_AN_N21a
SR_AN_N21a



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