

PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION

CHANCHAL PREMI



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JUNE 2016

PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION

by

CHANCHAL PREMI

Department of Chemistry

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JUNE 2016

CERTIFICATE

This is to certify that the thesis entitled, “**PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION**” being submitted by **Miss CHANCHAL PREMI** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. **Miss Chanchal Premi** has worked under my guidance and supervision. She has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in this thesis have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

Date:

Dr. NIDHI JAIN
Associate Professor
Department of Chemistry
Indian Institute of Technology Delhi
New Delhi-110016

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my supervisor Dr. Nidhi Jain, who has been a marvellous mentor for me. Your guidance, motivation, knowledge and continuous support have been priceless through my Ph.D life. Your supervision helped me in facing difficult times during research, and encouraged me to work even harder. I could not have imagined having a better advisor for my Ph.D study. I am extremely lucky to have a supervisor who cared so much about my work, and responded to my queries promptly. Her understanding, encouragement, inspiration, advice, appreciation and guidance have made the thesis.

Besides my supervisor, I would like to thank my DRC committee: Prof. Ravi Shanker, Prof. N. G. Ramesh, and Prof. Jayashree Bijwe for their insightful comments and brilliant suggestions which encouraged me to broaden my research from different perspectives.

My sincere thanks are to the Head, Department of Chemistry for providing necessary research facilities. I acknowledge the help extended by all faculty members and all the technical staff members for their help rendered during this work.

I could not be thankful enough to God who made me capable to achieve my goal, and showered millions of blessings at every step of my life.

Words cannot define how grateful I am to my parents Mr. Narayan Singh Premi and Mrs. Savitri Premi for all of the sacrifices that they have made for me and letting me follow my dreams. I always felt your blessings for me. Your love and support sustained me this far. Today this thesis is the fruit of the moral support, encouragement and discipline that you have bestowed upon me throughout my life. I would also like to thank my sister Vandana and my brother Ashish for their love and support; they were always there when I needed those most.

I thank my friend Priyanka who was my family away from home, and supported me to achieve my goal.

I would also like to thank all my labmates: Ananya, Awadh, Poonam, Sandeep, and Shyam for providing healthy environment to carry out my research work.

Final support from IIT Delhi, Council of Scientific and Industrial Research, India for fellowship is greatly acknowledge.

Chanchal Premi

ABSTRACT

Chapter 1: An overview of the use of palladium as catalyst in cross-coupling and C-H functionalization reactions has been provided, role of ligands, pre-formed Pd catalyst, and directing group assisted strategy has been emphasized. Heterogeneous catalyst on graphene has been discussed.

Chapter 2: Pd(OAc)₂-catalyzed decarboxylative alkylation of unactivated arenes with aliphatic carboxylic acids as inexpensive alkyl source is demonstrated. The alkylation is controlled by the directing group, and is regioselective in nature. It shows high functional group tolerance, and provides mild access to alkylated indolines, 2-phenylpyridines, and azobenzenes under solvent-free conditions in moderate to good yields.

Chapter 3: A palladium catalyzed regioselective *ortho*-acylation of *N*-aryl-1,2,3-triazoles has been discussed under aqueous conditions without the assistance of any surfactant or additive. The reaction takes place with benzylic, heterocyclic, as well as aliphatic alcohols as the acylating reagents, and TBHP as the oxidant. The method provides a mild and easy route for synthesis of triazole substituted aryl, heteroaryl, and aliphatic ketones in excellent yield.

Chapter 4: Palladium nanoparticles (PdNPs) 2–5 nm in size, and preformed by thermal reduction in nitrile-functionalized 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate {[CN-bmim]PF₆} act as an *in situ* catalyst for carbon–carbon bond-forming reaction of aromatic and heterocyclic halides with aryl- and vinyltrimethoxysilanes. A variety of biphenyl derivatives, substituted styrenes, and aromatic heterocycles have been synthesized by employing this catalyst. Use of 1-butyl-3-methylimidazolium fluoride as an activator of the organosilanes is shown. The NPs could be reused and recycled up to four times with only a slight loss in catalytic activity.

Chapter 5: A nanocomposite comprising of PdNPs supported on chemically modified graphene (CMG) has been fabricated. The efficacy of CMG-PdNP system as a catalyst towards Heck cross coupling reaction with a variety of functionalized substrates has been demonstrated. Functionalization of reduced graphene oxide with heteroatoms like sulfur and nitrogen enhanced its dispersibility in organic solvents, and also help in stabilizing the active palladium species by acting as a ligand. The CMG-Pd composite exhibits an excellent catalytic activity with a substantially low catalytic loading (0.02 mol %), with the activity sustainable up to three reaction cycles.

TABLE OF CONTENTS

	Page No.
<i>Certificate</i>	<i>i</i>
<i>Acknowledgements</i>	<i>ii</i>
<i>Abstract</i>	<i>iv</i>
<i>List of Figures</i>	<i>x</i>
<i>List of Tables</i>	<i>xii</i>
<i>List of Schemes</i>	<i>xiii</i>
<i>List of Spectra</i>	<i>xvii</i>
<i>Glossary of Symbols and Abbreviations</i>	<i>xviii</i>
<i>Material and Methods</i>	<i>xxii</i>

Chapter 1: Introduction

1.1 Palladium in Cross-Coupling Reactions.....	1
1.1.1 Palladium as a versatile catalyst	1
1.1.2 Preformed Pd catalysts	2
1.1.3 Pseudohalides as cross-coupling partners	4
1.2 Palladium in C-H Bond Functionalization	5
1.2.1 Carbonylation	8
1.2.2 Acetoxylation	9
1.2.3 Halogenation.....	9
1.2.4 Arylation.....	10
1.2.5 Alkylation	10
1.2.6 <i>Ortho</i> -Alkenylation	11
1.3 Heterogenous Catalysis.....	11
1.3.1 Catalysis with palladium nanoparticles.....	11
1.3.2 Catalysis in ionic liquids	12
1.3.3 Catalysis on graphene support	15
1.4 References.....	17

Chapter 2: Palladium-Catalyzed Regioselective Decarboxylative Alkylation of Arenes and Heteroarenes with Aliphatic Carboxylic Acids

2.1	Introduction.....	25
2.2	Results and Discussion	30
2.2.1	Decarboxylative alkylation on indoline	34
2.2.2	Decarboxylative alkylation on 2-phenylpyridine	35
2.2.3	Azo-Directed decarboxylative alkylation	36
2.2.4	Proposed mechanism	37
2.2.5	Mechanistic study	39
2.3	Conclusion	39
2.4	Experimental Section	40
2.4.1	Procedure for synthesis of 1-(pyrimidin-2-yl)indoline	40
2.4.2	Procedure for synthesis of 2-methyl-1-(pyrimidines-2-yl)indoline	40
2.4.3	Procedure for synthesis of 2-arylpyridines	41
2.4.4	Procedure for synthesis of (<i>E</i>)-1, 2-diphenyldiazene.....	41
2.4.5	Procedure for synthesis of 7-(<i>tert</i> -butyl)-1-(pyrimidin-2-yl)indoline.....	42
2.4.6	Procedure for synthesis of 2-(2-(<i>tert</i> -butyl)phenyl)pyridine	42
2.4.7	Procedure for synthesis of (<i>E</i>)-1-(2-(<i>tert</i> -butyl)phenyl)- 2-phenyldiazene	42
2.5	Spectral Data.....	43
2.6	References.....	94

Chapter 3: Regioselective *Ortho*-acylation of *N*-aryl-1,2,3-triazoles with Alcohols in Water

3.1	Introduction.....	99
3.2	Results and Discussion	103
3.2.1	<i>Ortho</i> -acylation of <i>N</i> -aryl 1,2,3-triazoles with benzylic alcohol	105
3.2.2	<i>Ortho</i> -acylation of <i>N</i> -aryl 1,2,3-triazoles with heterocyclic alcohol	107
3.2.3	Synthesis of fluorenone.....	108
3.2.4	Proposed mechanism	110
3.3	Conclusions.....	111
3.4	Experimental Section.....	111
3.4.1	General procedure for preparation of Glyoxalbis(<i>N</i> -phenyl)osazone.....	111

3.4.2 General procedure for preparation of <i>N</i> -aryl 1,2,3-triazoles.....	111
3.4.3 Typical procedure for <i>ortho</i> -acylation of <i>N</i> -aryl 1,2,3-triazoles.....	112
3.4.4 Typical procedure for <i>ortho</i> -acylation of <i>N</i> -aryl-1,2,3-triazoles	112
3.4.5 Synthesis of 4-methyl-1-(2H-1,2,3-triazol-2-yl)-9H-fluoren-9-one	113
3.5 Spectral Data.....	113
3.6 Single Crystal X-ray Data.....	123
3.7 References.....	160

Chapter 4: Phosphane-Free Hiyama Cross-Coupling of Aryl and Heteroaryl Halides Catalyzed by Palladium Nanoparticles in Ionic Liquids

4.1 Introduction.....	165
4.2 Results and Discussion	171
4.2.1 Preparation of ionic liquids	171
4.2.2 Generation of palladium nanoparticles (PdNPs).....	172
4.2.3 Characterization of Pd NPs	174
4.2.4 Hiyama coupling of aryl and heterocyclic halides with trimethoxyphenyl silane	178
4.2.5 Hiyama coupling of aryl iodides with trimethoxyvinylsilane.....	181
4.2.6 Mechanism	182
4.3 Conclusions.....	182
4.4 Experimental Section.....	183
4.4.1 Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium bromide [bmim]Br.....	183
4.4.2 Synthesis of 1-(3-cyano-propyl)-3-methyl-3H-imidazol-1-ium bromide [CN-bmim]Br.....	183
4.4.3 Synthesis of 3-(3-cyanopropyl)-1-methyl-1H-imidazol-3-ium fluoride [CN-bmim]F	184
4.4.4 Synthesis of 1-(3-cyano-propyl)-3-methyl-3H-imidazol-1-ium hexafluoro phosphate [CN-bmim]PF ₆	184
4.4.5 Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium fluoride [bmim]F	185
4.4.6 Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium acetate [bmim]OAc	186
4.4.7 Synthesis of palladium nanoparticles.....	186
4.4.8 General procedure for the C-C cross coupling of aryl halides with aryl silane	186

4.4.9 Recycling experiment	187
4.5 Spectral Data	187
4.6 References.....	211

Chapter 5: Nitrogen and Sulphur Functionalized Graphene oxide- Palladium Nanoparticle Hybrid Catalyst for an Efficient Heck Coupling

5.1 Introduction.....	215
5.2 Results and Discussion	220
5.2.1 Synthesis of GL-Pd nanocomposite	220
5.2.2 Characterization of GO, GSH, GS-Py, GL-Pd.....	221
5.2.3 Palladium catalyzed Heck reaction between aryl/heteroaryl halides and acrylates.....	228
5.2.4 Recycling experiment	229
5.2.5 Mechanism	230
5.3 Conclusions.....	230
5.4 Experimental Section	231
5.4.1 Synthesis of graphene oxide	231
5.4.2 Thiolation of graphene oxide	231
5.4.3 Pyridine insertion in GSH.....	232
5.4.4 Synthesis of GO-PdNPs.....	232
5.4.5 General Procedure for Heck cross coupling	232
5.5 Spectral Data.....	233
5.6 References	237

Curriculum Vitae	243
-------------------------------	------------

LIST OF FIGURES

Figure No.	Description	Page No.
Figure 1.1	List of phosphorus based common ligands	1
Figure 1.2	Name reactions catalyzed by palladium	2
Figure 1.3	Preformed Pd complex	4
Figure 1.4	List of cross-coupling partners	5
Figure 1.5	Representation of C-H bond functionalization.....	6
Figure 1.6	Comparison between conventional and C-H bond activation approach	7
Figure 1.7	Nitrogen containing directing groups	8
Figure 1.8	ILs containing imidazolium nucleus	13
Figure 3.1	List of directing groups containing nitrogen.....	99
Figure 3.2	List of acylating agents.....	100
Figure 3.3	Medicinally important triazoles.....	101
Figure 3.4	Overview of reactions on <i>N</i> -aryl 1,2,3-triazole	101
Figure 3.5	Comparison of acylation on <i>N</i> -aryl 1,2,3-triazoles	102
Figure 3.6	Single Crystal X-ray structure of 20f	108
Figure 3.7	Different methods for synthesis of fluorenone	109
Figure 4.1	Overview of Hiyama coupling under different conditions	164
Figure 4.2	List of Phos ligands	166
Figure 4.3	Representation of stabilization of PdNPs by imidazolium IL	169
Figure 4.4	List of synthesized imizadoium ILs	171
Figure 4.5	PXRD, EDX and UV-Vis spectra	173
Figure 4.6	SEM, TEM, DLS spectra and histogram.....	175
Figure 5.1	PXRD of graphite, GO, GSH, GS-Py and GL-Pd.....	220
Figure 5.2	FTIR of graphite, GO, GSH, GS-Py and GL-Pd.....	221
Figure 5.3	Raman of GO, GSH, GS-Py and GL-Pd	222

Figure No.	Description	Page No.
Figure 5.4	XPS of GL-Pd NPs (a) Full spectrum (b) Pd high resolution spectrum.....	223
Figure 5.5	EDX of GL-Pd NPs	223
Figure 5.6	SEM images of GO, GSH and GS-Py	224
Figure 5.7	TEM images of GL-Pd NPs	224
Figure 5.8	Histogram, size distribution of GL-PdNP dispersion.....	225
Figure 5.9	TEM image of GL-Pd after 3 rd recycle.....	228

LIST OF TABLES

Table No.	Description	Page No.
Table 2.1.	Optimization of reaction conditions for decarboxylative alkylation	32
Table 2.2.	Scope of alkylation with indolines.....	34
Table 2.3.	Scope of alkylation with 2-phenylpyridines	35
Table 2.4.	Scope of alkylation with azo-benzenes.....	37
Table 2.5.	Inhibition by ascorbic acid.....	39
Table 3.1.	Optimization of reaction conditions for acylation of <i>N</i> -aryl 1,2,3-triazole.....	104
Table 3.2.	Substrate scope with benzyl alcohols and triazoles	106
Table 3.3.	Substrate scope with heteroaryl alcohols.....	107
Table 3.4.	Crystal data and structure refinement for 2furancm1	124
Table 3.5.	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)	125
Table 4.1.	Optimization of Pd NPs in different ionic liquids	173
Table 4.2.	Hiyama coupling of aryl halides: optimization of the catalytic conditions	177
Table 4.3	Substrate scope of substituted biphenyls	179
Table 4.4	Substrate scope for styrene derivatives.....	181
Table 5.1	Optimization of the reaction conditions for Heck coupling	227
Table 5.2	Substrate scope for Heck coupling	228

LIST OF SCHEMES

Scheme No.	Description	Page No.
Scheme 1.1	Buchwald–Hartwig amination.....	3
Scheme 1.2	Suzuki–Miyaura coupling	3
Scheme 1.3	Buchwald–Hartwig aminations of tertiary amine	3
Scheme 1.4	One-pot conversion of isoindolines to 1-arylisindoles.....	3
Scheme 1.5	α -arylation reactions of 4-chlorotoluene	4
Scheme 1.6	Olefination of benzene	6
Scheme 1.7	Carbonylation of benzylamine with CO.....	8
Scheme 1.8	Carbonylation with aldehyde	8
Scheme 1.9	Acetoxylation of 2-phenylpyridine	9
Scheme 1.10	Halogenation with NBS	9
Scheme 1.11	Arylation with [Ph ₂ I]BF ₄	10
Scheme 1.12	Alkylation with alkylboronic acid.....	10
Scheme 1.13	Alkylation with alkylhalide	10
Scheme 1.14	<i>Ortho</i> -Alkenylation of <i>N,N</i> -dimethyl-1-phenylmethanamine.....	11
Scheme 1.15	Thermal decomposition of palladium salts	14
Scheme 1.16	Reduction with hydrogen gas or hydrides.....	14
Scheme 1.17	Bombardment of bulk metal precursors	14
Scheme 1.18	Reductive elimination of a palladacycle	14
Scheme 2.1	Suzuki coupling with methylboroxine	25
Scheme 2.2	Coupling of 8-alkyl-1-naphthylamide with <i>n</i> -butyl iodide	25
Scheme 2.3	Coupling of 2-(2-fluorophenyl)pyridine with Grignard reagents	26
Scheme 2.4	Coupling of 8-aminoquinolyl carboxamide with alkyl tosylates	26
Scheme 2.5	Coupling of 8-aminoquinoline auxiliary with alkyl bromides	27
Scheme 2.6	Coupling of benzoxazole/benzthiazole with aliphatic carboxylic acids	27

Scheme No.	Description	Page No.
Scheme 2.7	Alkylation/arylation on Boc protected indoline	28
Scheme 2.8	Arylation on 1-(indolin-1-yl)ethanone	29
Scheme 2.9	Arylation on <i>N,N</i> -dimethylindoline-1-carboxamide	29
Scheme 2.10	Dehydrogenative arylation on annulated indoline	29
Scheme 2.11	Alkenylation on <i>N,N</i> -dimethylindoline-1-carboxamide with butyl acrylate.....	29
Scheme 2.12	Acylation on 1-(indolin-1-yl)-2,2-dimethylpropan-1-one with aldehyde	29
Scheme 2.13	Methylation on 1-(indolin-1-yl)ethanone with alkylborates	30
Scheme 2.14	Coupling of <i>N</i> -pyrimidylindoline with pivalic acid	31
Scheme 2.15	Coupling of indoline with pivalic acid.....	31
Scheme 2.16	Coupling of 1-phenylindoline with pivalic acid.....	31
Scheme 2.17	Alkylation on <i>N</i> -pyrimidylindoline with pivalic acid	34
Scheme 2.18	Alkylation on 2-methyl-1-(pyrimidin-2-yl)indoline and acetic acid.....	35
Scheme 2.19	Alkylation on 2-phenylpyridines with pivalic acid	35
Scheme 2.20	Alkylation on azobenzenes with pivalic acid.....	36
Scheme 2.21	Plausible mechanism of decarboxylative alkylation	38
Scheme 2.22	Mechanistic study between 30a and 31a in presence of ascorbic acid	39
Scheme 2.23	Procedure for synthesis of <i>N</i> -pyrimidylindoline	40
Scheme 2.24	Procedure for synthesis of 2-methyl-1-(pyrimidines-2-yl)indoline	41
Scheme 2.25	Procedure for synthesis of 2-phenylpyridines.....	41
Scheme 2.26	Procedure for synthesis of (<i>E</i>)-1, 2-diphenyldiazene with aniline	42
Scheme 3.1	Coupling of <i>N</i> -phenyl-1,2,3-triazole with benzyl alcohol.....	102
Scheme 3.2	<i>Ortho</i> -acylation of <i>N</i> -aryl-1,2,3-triazoles with benzyl alcohols	104
Scheme 3.3	<i>Ortho</i> -acylation of <i>N</i> -aryl 1,2,3-triazoles with heterocyclic alcohols.....	106
Scheme 3.4	Synthesis of 1,2,3-triazole substituted fluorenone	108
Scheme 3.5	Proposed mechanism of acylation on <i>N</i> -phenyl-1,2,3-triazole	109

Scheme No.	Description	Page No.
Scheme 3.6	Synthesis of <i>N</i> -aryl-1,2,3-triazoles.....	110
Scheme 4.1	Coupling of vinyltrimethoxysilanes with aryl halides	165
Scheme 4.2	Coupling of phenyltrimethoxysilanes with aryl halides.....	165
Scheme 4.3	Fluoride free coupling of phenyltrimethoxysilanes with aryl halides.....	166
Scheme 4.4	Coupling of aryl tosylate with phenyltrimethoxysilanes.....	166
Scheme 4.5	Coupling of aryl mesylate with phenyltrimethoxysilanes.....	167
Scheme 4.6	Coupling of phenyltrimethoxysilanes with aryl halides.....	167
Scheme 4.7	Synthesis of (<i>E</i>)-1,4-pentadienes with allyl acetates.....	168
Scheme 4.8	Coupling of phenyltriethoxysilanes with cyclohexenyl carbonate	169
Scheme 4.9	Coupling of aryl halide with vinyltrimethoxysilanes	170
Scheme 4.10	Generation of PdNPs in IL-17.....	172
Scheme 4.11	Hiyama coupling of aryl and heterocyclic halides with trimethoxyphenylsilane.....	177
Scheme 4.12	Hiyama coupling of aryl iodide with trimethoxyvinylsilane	180
Scheme 4.13	Proposed mechanism of Hiyama coupling.....	181
Scheme 4.14	Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium bromide	182
Scheme 4.15	Synthesis of 1-(3-cyano-propyl)-3-methyl-3H-imidazol-1-ium bromide	183
Scheme 4.16	Synthesis of 3-(3-cyanopropyl)-1-methyl-1H-imidazol-3-ium fluoride	183
Scheme 4.17	Synthesis of 1-(3-cyano-propyl)-3-methyl-3H-imidazol-1-ium hexafluoro-phosphate	184
Scheme 4.18	Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium fluoride.....	184
Scheme 4.19	Synthesis of 1-butyl-3-methyl-3H-imidazol-1-ium acetate	185
Scheme 5.1	Synthesis of GO-SBu from GO.....	217
Scheme 5.2	Synthesis of organo diamine functionalized grapheme	218
Scheme 5.3	Oxidation of benzyl alcohol into aldehyde	218
Scheme 5.4	Suzuki coupling.....	218

Scheme No.	Description	Page No.
Scheme 5.5	Synthesis of PdNPs on Fe ₃ O ₄ @amine functionalized grapheme.....	219
Scheme 5.6	Synthesis of <i>N</i> -heterocyclic carbene ligand with a pyrene tag.....	219
Scheme 5.7	Reduction of nitrobenzene and alkene	219
Scheme 5.8	Synthesis of GL-Pd nanocomposite	220
Scheme 5.9	Heck reaction between aryl/heteroaryl halides and acrylates	228
Scheme 5.10	Proposed mechanism for Heck reaction.....	230

LIST OF SPECTRA

Spectra No.	Page No.
-------------	----------

Chapter 2

32a-32j	54-63
39a-39f	64-69
40a-40f	70-75
42a-42h	76-83
43a-43h	84-91

Chapter 3

18a-18z.....	125-150
20a-20g	151-157
Compound 27.....	158

Chapter 4

Compound 19.....	191-192
Compound 19 (^{19}F -NMR).....	192
4a-4o	193-204
6a-6d	205-209

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

Å	:	Angstrom
a.u	:	Arbitratry unit
AAPTMS	:	[3-(2-Aminoethylamino)propyl]trimethoxysilane
Ac	:	Acetic
Alk	:	Alkyl
Approx.	:	Approximately
Ar	:	Aryl
BINAP	:	2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene
BMI.PF ₆	:	1- <i>n</i> -butyl-3-methylimidazolium hexafluorophosphate
Boc	:	<i>tert</i> -butyloxycarbonyl
BQ	:	Benzoquinone
¹³ C	:	¹³ Carbon
Cat	:	Catalyst
CMG	:	Chemically modified graphene
CNSs	:	Carbon nanosheets
CNT	:	Carbon nanotubes
cps	:	Counts per second
Cy	:	Cyclohexyl
DCE	:	Dichloromethane
DLS	:	Dynamic light scattering
DMA	:	Dimethylacetamide
DMF	:	Dimethylformamide
DMSO	:	Dimethyl sulfoxide
Dppe	:	Ethylenebis(diphenylphosphine)
EDX	:	Energy-dispersive X-ray spectroscopy

Equiv	:	Equivalent
Et	:	Ethyl
eV	:	Electron volt
¹⁹ F	:	19 Fluorine
Fcc	:	Face centered cubic
FTIR	:	Fourier transform infrared spectroscopy
G	:	Gram
GL-Pd	:	Graphene ligand-palladium complex
GO	:	Graphene oxide
GSH	:	Thiol-functionalized GO
GS-Py	:	GSH-pyridine ligand
¹ H	:	Proton
h	:	Hour
Hz	:	Hertz
ICP-MS	:	Inductively coupled plasma mass spectrometry
IL	:	Ionic liquid
<i>i</i> -Pr	:	<i>iso</i> -propyl
IPr	:	<i>N,N'</i> -bis(2,6- diisopropylphenyl)imidazol-2-ylidene
JCPDS	:	Joint Committee on Powder Diffraction Standards
kV	:	Kilovolt
L	:	Litre
M	:	Molar
mg	:	Milligram
MIDA	:	<i>N</i> -methylinodiacetic acid
min	:	Minute
mL	:	Millilitre

mmol	:	Millimol
NBS	:	<i>N</i> -bromosuccinimide
<i>n</i> -Bu	:	Butyl
NHC	:	<i>N</i> -heterocyclic carbene
nm	:	Nanometer
NMR	:	Nuclear magnetic resonance
%	:	Percent
PdNPs	:	Palladium nanoparticles
Piv	:	Pivalic
Ppm	:	Parts per million
PTC	:	Phase transfer catalyst
PTSA	:	<i>para</i> -toluenesulfonic acid
PXRD	:	Powder X-ray diffraction
Pym	:	Pyrimidine
rGO	:	Reduced graphene oxide
Rpm	:	Rotation per minute
Rt	:	Room temperature
S.No	:	Serial number
SDS	:	Sodiumdodecasulfate
<i>sec</i>	:	Secondary
SEM	:	Scanning electron microscope
SIPr	:	<i>N,N'</i> -bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene
TBAB	:	Tetrabutylammonium bromide
TBAF	:	Tetrabutylammoniumfluoride
TBAI	:	Tertabutylammoniumiodide
TBHP	:	<i>tert</i> -butyl hydroperoxide

<i>t</i> -Bu	:	Tertiary butyl
TEAB	:	Tetraethylammonium borohydride
TEM	:	Transmission electron microscope
Temp	:	Temperature
TEMPO	:	2,2,6,6-Tetramethyl-1-piperidinyloxy
<i>Tert</i>	:	Tertiary
TFA	:	Trifluoroacetic acid
TFE	:	Trifluoroethanol
THF	:	Tetrahydrofuran
TLC	:	Thin layer chromatography
TMEDA	:	<i>N,N,N',N'</i> -Tetramethylethylenediamine
UV	:	Ultra-Violet
Vis	:	Visible
XPS	:	X-ray Photoelectron Spectroscopy
α	:	Alpha
β	:	Beta
μ L	:	Microlitre
π	:	Pie
γ	:	Gamma

MATERIALS AND METHODS

Physical measurement:

The size of nanoparticles was determined by Malvern DLS nano ZS90. EDX spectra were recorded on ZEISS EVO 50 model QuanTax 200 which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K alpha. Elemental analysis was carried out on Perkin-Elmer 2400 Series II CHNS/O analyzer. HRMS were recorded on microTOF-Q II 228888.10262 using electrospray ionization (ESI) as the ionization method. Inductively Coupled Plasma Mass Spectrometry or ICP-MS on Agilent ICP-MS 7900. NMR spectra (^1H and ^{13}C) were measured on a Bruker DPX-300 MHz spectrometer (^1H 300 & 400 MHz, ^{13}C 75MHz).

Powder X-ray diffraction (PXRD) data was collected on X-ray diffractometer (Bruker). Raman spectroscopy was performed using the 2.54 eV (488 nm) line of an Ar ion laser on a HORIBA JOBIN YVON Lab RAM HR 800 instrument by placing a pellet on a cleaned glass slide. Scanning electron microscopy (SEM) image was captured with a Zeiss Evo series SEM model EVO 50. The sample was then coated in a sputter coater (EMITECH K 550 x) with a gold layer in vacuum.

Single-crystal X-ray data of compounds was collected on Bruker SMART CCD-Diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data integration and reduction were processed with Crys Alis Pro software. The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of software using the WinGX (version 1.80.05) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have been drawn using ORTEP software. Copies of the data can be found free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk).

TEM analyses were performed on DeLong instrument, Q imaging Retiga 4000 R by dropping 10 μL of dispersed solution in HPLC grade hexane on copper grid. High resolution transmission electron microscope (HRTEM) experiments were conducted in a JEM-2010 FEI TEM with an accelerating voltage of 200 KV. UV-vis spectroscopy was recorded on Lambda

Bio 20, Perkin Elmer. X-ray photoelectron spectroscopy (XPS) was carried out on SPECS, MCD-9, serial number-172-05.01.

Analytical Information:

All the isolated compounds were characterized by ^1H NMR, ^{13}C NMR spectroscopy and HRMS using CDCl_3 and DMSO as the solvents with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ (ppm) relative to TMS, the coupling constants (J) are given in Hz.

Chemicals and reagents:

All reactions were carried out under air in septum covered oven dried round bottom flask/10 mL vial. All the solvents were bought from Aldrich, Spectrochem and Alfa-aesar were used as received. Palladium (II) acetate was purchased from Alfa-Aesar (98% purity). For column chromatography, silica gel (230–400 mesh) from SRL Co. was used. A gradient elution using ethyl acetate-hexane was performed on Merck aluminium TLC sheets (silica gel 60F254).