Transition Metals Catalyzed C-C And C-Het. Atom Bond Formation in Important Heterocycles

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DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in partial fulfillment
of the requirement for the award
of the degree of
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by
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **TRANSITION METALS CATALYZED C-C AND C-HET. ATOM BOND FORMATION IN IMPORTANT HETEROCYCLES** is the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the period from July 2020 to June 2021 under the supervision of Dr. Umesh A. Kshirsagar, Assistant Professor, Department of Chemistry, Indian Institute of Technology, Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

L.Suresh.

Signature of the student
Date: 10/06/2021

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

09/06/2021

Signature of Thesis Supervisor with date

(Dr. UMESH A. KSHIRSAGAR)

LAVUDI SURESH has successfully given his/her M.Sc. Oral Examination held on. 09/06/2021.

09/06/2021

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Date: 09/06/2021

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Signature of PSPC Member #2
Date:09/06/2021

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Dedicated to my parents, teachers, and friends

Abstract

Study of imidazole derivatives using photocatalyst on various carbonyl and ester radical's generation found to be eco-friendly and novel method. The reaction mainly carried in incidence of Blue LED which is ideal towards green chemistry. The derivatives of imidazole formation led to investigate in formation of new C-C bond. The C-H activation functional group through radical pathway which is the novel strategy for the synthetic organic chemistry.

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Table 1. Reaction conditions.

Table 2. Reaction conditions.

ACRONYM

UV	Ultraviolet spectroscopy
DMSO	Dimethyl sulfoxide
DCM	Dichloromethane
$CDCl_3$	Chloroform-D
CH_3CN	Acetonitrile
CH_3OH	Methanol
EtOAc	Ethyl acetate
HRMS	High-Resolution Mass Spectrometry
NMR	Nuclear magnetic resonance spectroscopy
^1H NMR	Proton NMR spectroscopy
^{13}C NMR	Carbon-13 NMR spectroscopy
IR	Infrared spectroscopy

NOMENCLATURE

λ	Wavelength
δ	Chemical shift
cm	Centimeter
nm	Nanometer
^{O}C	Degree Celsius
mmol	Millimole
mL	Milliliter
rt	Room temperature
M	Molar

Chapter 1

INTRODUCTION

1.1 Introduction

The discoveries for preparation of C-C and C-X bonds in new approaches plays a vital role in past few years[1]. In recent studies of nitrogen containing heterocycles in organic synthesis is majorly focused because of their biologically active, natural products and in medicinal uses. The derivatives of imidazole attracted for synthetic chemistry, in particular bioactive compounds such as zolpidem[2], miroprofen[3], zolimidine[4], alpidem[5], necopidem[6], saripidem[7] etc., [as shown in figure 1] many of these compounds have affective medicinal values in antiviral, antibacterial, antifungal, anti-inflammatory etc., as we mainly investigated on 2-phenylimidazo[1,2-a] pyridine derivatives[8]. There are many direct methods for acetylation and esterification using various transition metal catalyst in thermal conditions, to simplify the process, we used photocatalyst. Most of the photocatalyst are environment friendly and easily available. In this thesis investigation we used eosin-y, acridine red and $Ru(bPy)_2Cl_2$ photocatalyst to construct the C-C bond. The advancement of transition-metal-catalyzed processes for growth of heterocycles continues to be a significant field of research[9].

Recently many thermal reactions on 2-phenylimidazo[1,2-a] pyridine have recently been reported for synthesis of nitrogen-containing heterocycle (NHC) via direct formation of C-N bond. The construction of C-C/C-N bonds for photocatalyst use was extensively researched in this thesis. Glorius[10], Ackermann[11], Matsuga/kanai[12], daugulis[13], Yoshikai[14] and many other report[15] alkyne annulation using a cobalt catalyst, gave an idea to synthesize acetylation of 2-phenylimidazo[1,2-a] pyridine.

Du, Li. And Loh, Tian and Yuet[16] *et al.* independently reported the all oxycarbonylation of terminal alkenes or N-venyl acetamides by cyclization 2-phenylimidazo[1,2-a] pyridine reaction with carbazates via radical mechanism[17] to synthesize phenanthridine-6-carboxylates using $FeCl_3.4H_2O$ as catalyst. Taking inspiration from all the recent works that have been carried out we investigated to construct the C-C bond

generation using direct C-H/C-N activation for photocatalyst application. The acetylation and esterification of 2-phenylimidazo [1,2-a] pyridine with methyl carbazates, benzylformic acid, and tery-butyl carbazates are tried to synthesize using various reaction conditions in this thesis.

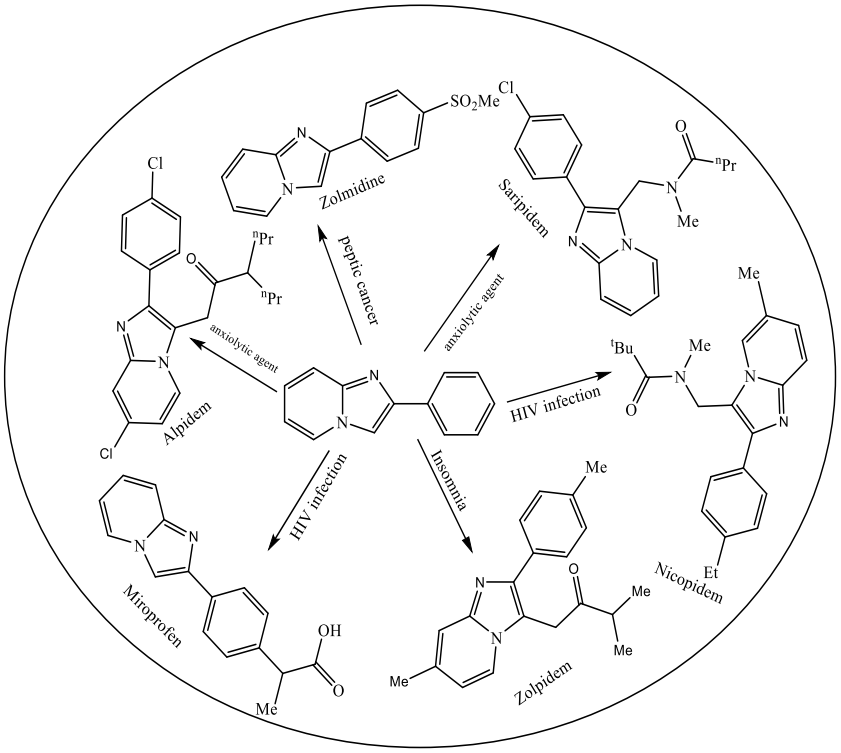
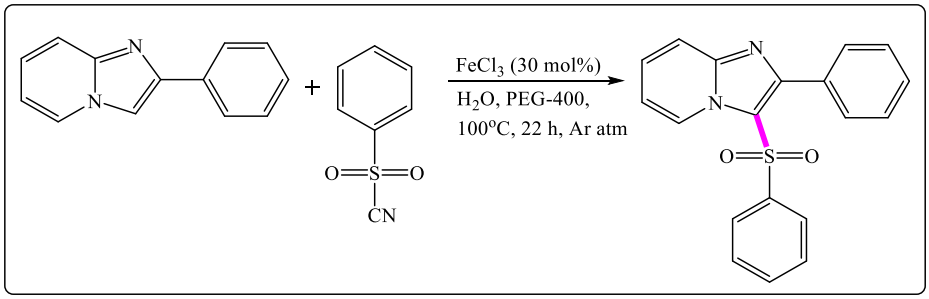


Figure 1. Medicinal uses of derivatives of 2-Phenylimidazo[1,2-a] pyridine.

1.2 Literature review

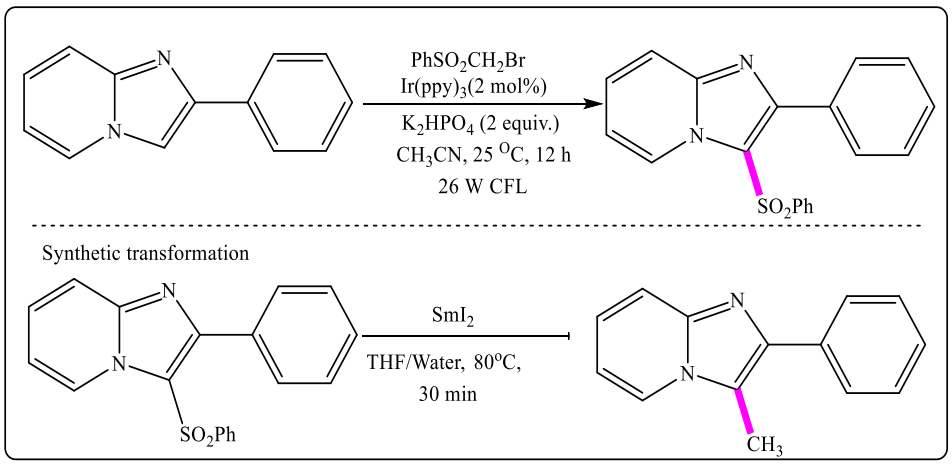
In recent discoveries various new methods are reported by coupling of active C-H to form new C-C bond. Some of scheme which provoke new idea for synthesize compound via transition metal as catalyst.

Lu[18] *et al.* reported simple and environmentally in which imidazo [1,2-a] pyridine reacts with benzenesulfonyl cyanide which is catalyzed by iron (III) chloride at 100 ^{0}C along with PEG-400 (7:3) in an argon atmosphere. The reaction is performed in various optimization condition as they used TEMPO, benzoquinone the yield continued to decrease in followed reaction. In scheme 1[18] scale, up good amount of yield of 94%.



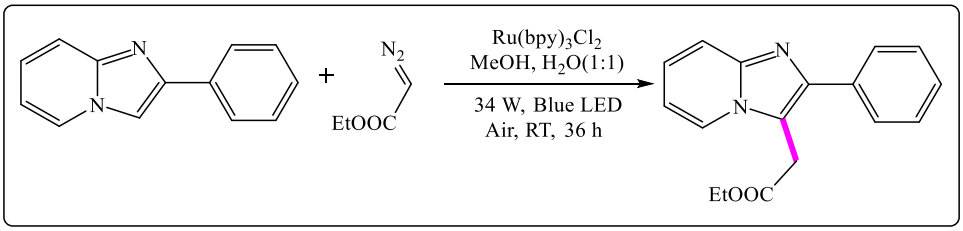
Scheme 1. Tosylmethylation of 2-phenylimidazo[1,2-a]pyridine

Cui and colleagues[19] achieved 2-phenyl-3-(phenylsulfonyl) imidazo [1,2-a] pyridine in visible light by using iridium catalyst. In this synthesis phenyl imidazole reacted with phenyl sulfonyl bromide in acetonitrile at room temperature utilizing K_2HPO_4 as a base and iridium catalyst (Scheme 2). With a high functional group acceptance at C3 position lead large scope by using this technique produced moderate-high amount of yields (47–99%). Indoles, pyrroles and other NHC could be used for this process to activate the compounds C-H bonds. The converting of 3-methylimidazo[1,2-a] pyridines as synthetic transformation via SmI_2-mediated desulfonylation, synthetic usefulness has been proven by this scheme.



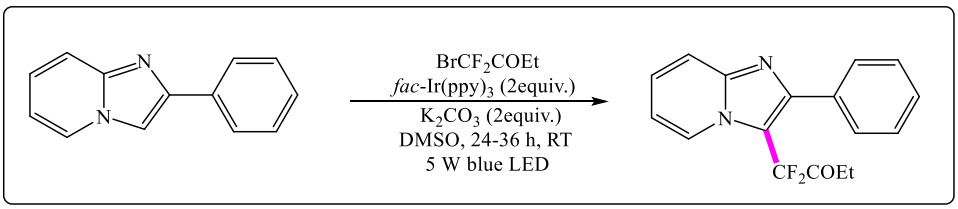
Scheme 2. Sulfonylmethylation of 2-phenylimidazo[1,2-a]pyridine

Hajra and colleagues worked on ruthenium photo sensitive catalyst regioselective at 3rd position of imidazo [1,2-a] pyridines through ethyl 2-diazoacetate in methanol at room temperature, employing $Ru(bpy)_3Cl_2$ as photo catalyst and at 34 W blue LED lamp (Scheme 3)[20]. Imidazo [1,2-a] pyridines including electron with drawing group reacted by ethyl 2-diazoacetate to generate the target products at high yields, whereas imidazo pyridines reacted with election with drawing groups reacted with 10 mol% N, N-dimethyl-toluidine as active additive and synthesized target product with 65-97% yield.



Scheme 3. Ethoxycarbonyl-methylation of 2-phenylimidazo[1,2-a] pyridine

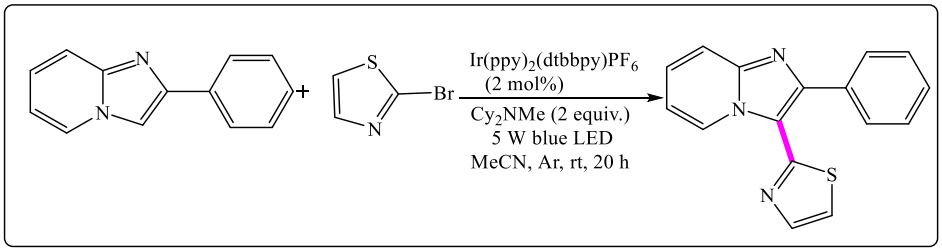
Fu and coworkers synthesized difluoro-acetylatized imidazo [1,2-a] pyridine with difluroacetyl bromide as radical source by taking same reaction conditions of Xu and coworkers in which *fac* iridium is catalyzed, K_2CO_3 as oxidant and DMSO as solvent (Scheme 4)[21]. Various functionalities of benzo[d] imidazo [2,1-b] thiazoles and imidazo pyridines yielded anticipated products from medium to excellent yields (60–95%). The synthetic utility has proved by synthesizing the target compound in 83% yield using a gram-scale process.



Scheme 4. Diflouroacetylation of 2-phenylimidazo[1,2-a] pyridine

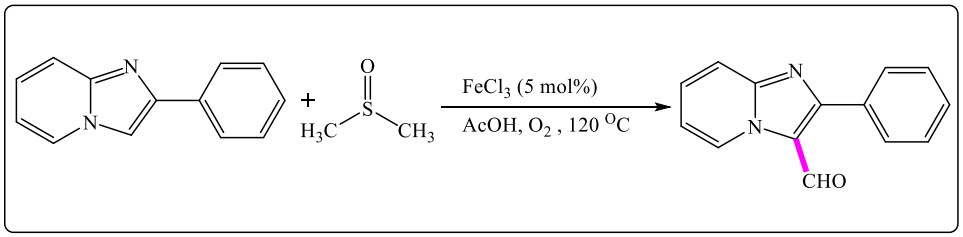
Sun and his colleagues used N, N-dicyclohexylmethylamine in CH_3CN as solvent and $Ir(ppy)_2(dtbbpy)PF_6$ as catalyst for imidazo pyridine with 2-bromo thiaole (Scheme 5)[22]

This reaction worked well in case of other heterocyles such as 5-methyl-2-bromothiazoles, 2-bromothiazoles, 2-bromobenzo[d]thiazoles, 5-bromo-2-furfuraldehyde, 2-bromothiophene, and 2,4-dibromothiazoles interacted smoothly with C-H active substituted at 1,3 and 4 positions of imidazoheterocycles to give the heteroarylated compounds which yielded 28–83%.



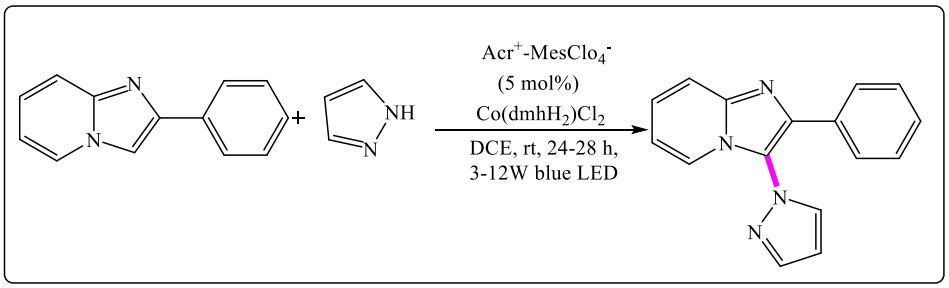
Scheme 5. Heteroarylation of 2-phenylimidazo[1,2-a] pyridine

Liu and Cao[23] independently worked on carbon synthon using acetic acid and DMSO in oxygen atmosphere, iron (iii) chloride catalyzed imidazo[1,2-a] pyridine at 120 ^{O}C. Various derivative of imidazo [1,2-a] pyridine is responded this scheme for C-H activation at C3 formylation (Scheme 6**)** The oxygen and active C-H formyl group CHO were synthesized by DMSO at oxygen atmosphere. These types of reaction resulted 72-83% of yield. According to a comprehensive isotopic labelling investigation utilizing DMSO-d_6 and H_2O.



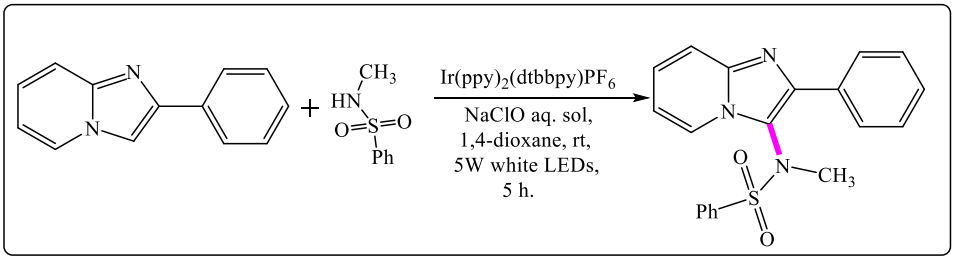
Scheme 6. DMSO as carbon synthon in C3-formylation of 2-phenylimidazo[1,2-a]pyridine

Lie and Adimurthy group separately reported azolyation of Imidazole heterocyles using photocatalyst $AcrMesClO_4$ (9-mesityl-10-methylacridinium perchlorate) in DCE at room temperature using 3-12blue LED. The derivatives of imidazoheterocycle such as imidazole, pyrazoles, 1,2,4-tiazoles, and 1,2,3-triazoles were successfully synthesized by aroylation of phenyl-imidazo-pyridine which yielded the target product at 43-99%. Meanwhile, the proton was caught by Co(I), resulting in Co (III) Hydrogen species. Hydrogen is released when a proton interacts with Co (III). This reactivates the Co (III) catalyst (scheme 7)[24].



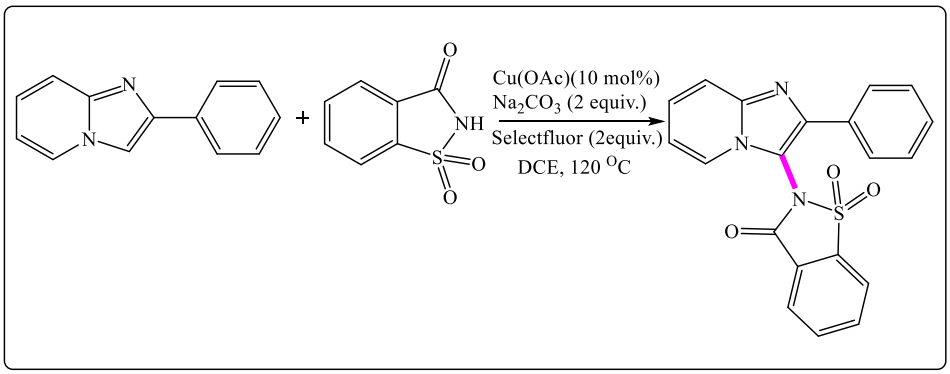
Scheme 7. Azolyation of 2-phenylimidazo[1,2-a]pyridine

Sun group reported photocatalyzed in visible light, sulfonamidation of imidazo-pyridines with N-alkylsulfonamides in presence of $Ir(ppy)_3(dtbbpy)PF_6$ catalyst along with 1,4-dioxane solvent and aqueous NaClO solution as the oxidant (Scheme 7)[25]. Other related imidazoheterocycles yielded the desired compounds in 42–75% yields using this approach.



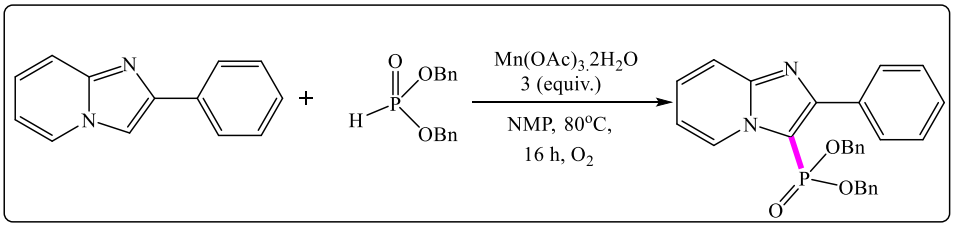
Scheme 8. sulfonamidation of imidazo[1,2-a] pyridines

Sun and colleagues used Na_2CO_3 as a base, and oxidant selectfluor in 1,2-dichloroethane to investigate a copper acetate as catalyst for sulfonylamidation of imidazo [1,2-a] pyridines at C3 position in this scheme sacharrin used as ammine source (Scheme 8)[26]. Various EDGs and EWGs are smoothly participated in functionalization of Imidazo [1,2-a] pyridines this type of reaction are corresponding product 28-90% yield.



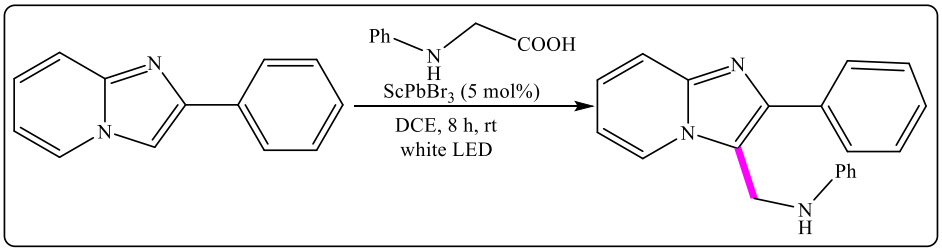
Scheme 9. Sulfonylamidation of 2-phenylimidazo[1,2-a]pyridine

Singh and coworkers worked on Mn (III)-mediated regioselective phosphonation with NMP towards 2-phenylimidazo[1,2-a] pyridines at 80 °C. (Scheme 9)[27]. This reaction takes 16 h under oxygen atmosphere which is suitable for various substituted of 2-phenylimidazo[1,2-a] pyridine with dialkyl phosphite to synthesize 3-phosphonated imidazo [1,2-a] pyridines. This optimized condition is best suitable for to approach N-heterocycles which has wide applications of azaindoles, indoles, and pyrroles, corresponding the desired product 45-82% yields.



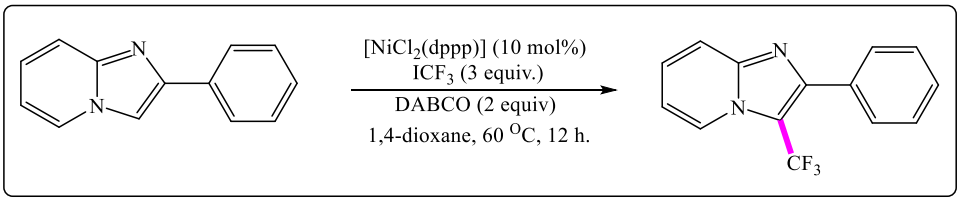
Scheme 10. Phosphonation of 2-phenylimidazo[1,2-a]pyridine

Shi and group recently reported decarboxylative coupling of 2-phenylimidazo [1,2-a] pyridines with N-arylglycines using visible light mediated photocatalyst $ScPbBr_3$ in DCE for 8 h at room temperature (Scheme 10)[28]. Various 2-phenylimidazo [1,2-a] pyridines and benzo [d] imidazo [2,1-b] thiazole is functionalized with several EDGs and EWGs with N-arylglycines with a wide interacted satisfactorily and yielded corresponded products in 45–94% yields.



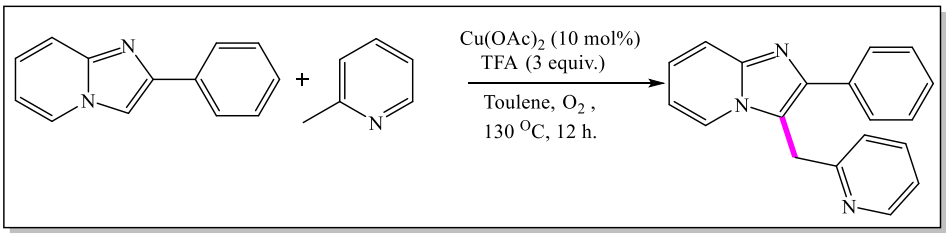
Scheme 11. Decarboxylative aminiometylation of 2-phenylimidazo[1,2-a]pyridine

Wang *et al*. generated trifluoromethyl radical when reacted with 2-phenylimidazo [1,2-a] pyridine with investigation of nickel catalyzed, (DABCO) (1,4-diazabicyclo [2.2.2] octane) as a base in solvent (1,4-dioxane) at 60 °C for 12 h to synthesize C3-trifluoromethylation of 2-phenylimidazo [1,2-a] pyridines (Scheme 10)[29]. Several 2-phenylimidazo[1,2-a] pyridines derivates are synthesized through this reaction by distinct functional groups interacted smoothly and corresponded the desired products in 55–82% of yield. Electron rich heterocycles such as pyrrole, thiophene and indole were successfully synthesized using the described approach, with moderate to good yields.



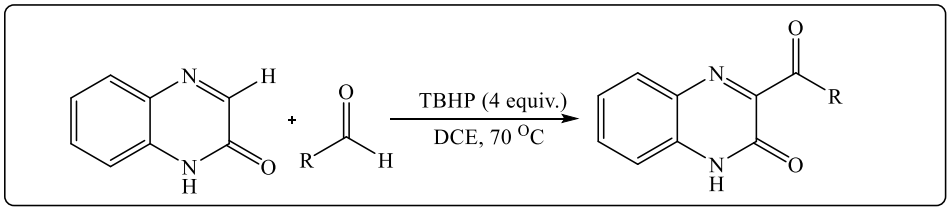
Scheme 12. Trifluoromethylation of 2-phenylimidazo[1,2-a]pyridine

Cao *et al*. used copper acetate catalyst for synthesis of C3 carbonyation of 2-phenylimidazopyridine. 2-phenylimidazo[1,2-a] pyridine reacted with 2-methyl pyridine in presence of $Cu(Oac)_2$, O_2 as oxidant and additive trifluoroacetic acid (TFA) in toluene for 12 h at 130 °C to explore cross dehydrogenative coupling of 2-imidazo[1,2-a]pyridines with methylheteroarenes (Scheme 11)[30]. After studies these optimized condition alkylated imidazo [1,2-a] pyridine is reacted with various types of methyl heteroarene such as 2-methylpyrazene, 2-methylpyridine, 2-chloro-3-methylpyrazine 2,5-dimthylthiazole etc.to give carbonylated corresponding product of 40-80% of yield.



Scheme 13. Carbonylation of 2-phenylimidazo[1,2-a]pyridine

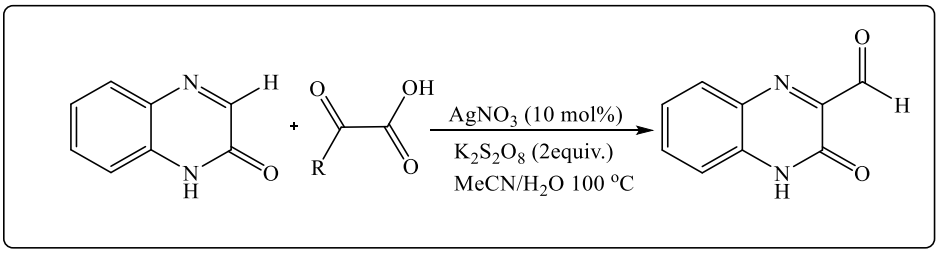
Yuan and coworkers worked on cross dehydrogenative coupling of quinolones with aldehydes in presence of TBHP using dicholoethylene as solvent at 70 ^{O}C. Yuan group succeeded in generation of new C-C bond formation in heterocycles (scheme 14)[31]. This type of CDC reaction in absence of metal free catalyzed reaction is novel method to for carbonylation.



Scheme 14. Metal free catalyzed oxidative coupling of quinoline-2 (1H)-ones with aldehydes.

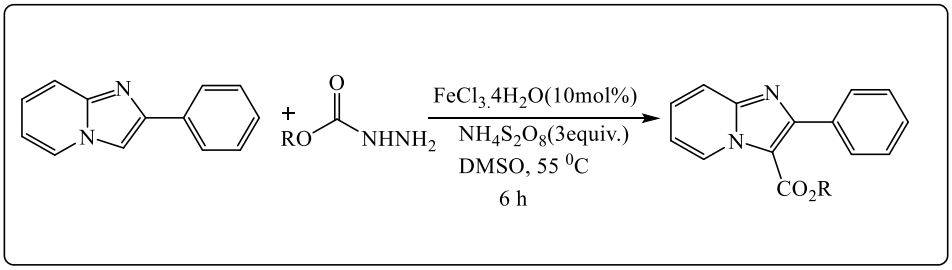
His group reported CDC reaction of quinolones with benzylformic acids (scheme 15)[32] in the presence of silver nitrate catalyst along with potassium per sulfate oxidant and 1:1 equivalent of acetonitrile and water

at 100 ^{O}C reflux temperature through radical mechanism. The group is productive in formation of C-C bond formation in important heterocycles.



Scheme 15. Silver nitrate catalyzed oxidative coupling of quinoalin-2 (1H)-ones with carboxylic acids.

Recently Yong yuan and his coworkers have carried out direct esterification of 2- phenylimidazo [1,2-a] pyridine with carbazates using oxidant and solvent under reflex temperature for 6 h (scheme 16)[33].



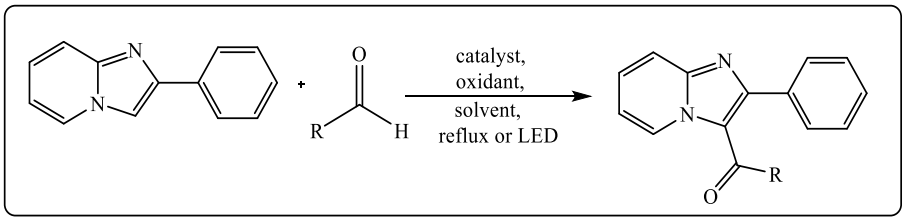
Scheme 16. $FeCl_3$ catalyzed esterification of 2-phenylimidazo[1,2-a]pyridine with carbazates.

1.3. Objectives

We would like to develop the transition metal/photo-redox catalyzed carbonylation reaction of imidazopyridine via carbon-carbon bond formation. Taking the inspiration from above recent literatures, and the main objective of this thesis work, is we tried to optimize the reaction condition with photocatalyst to generate C-H radicals to construct C-C bond. Cross dehydrogenative oxidative coupling is best suitable method for synthesis of organic compounds, heteroarylation, acetylation, aminomethylation, arylation, carboxylation, esterification etc., are the best active in generation of C-H radicals which can easily inserted at C3 position of 2-pheynlimidazo [1,2-a] pyridine. To handle all these reactions

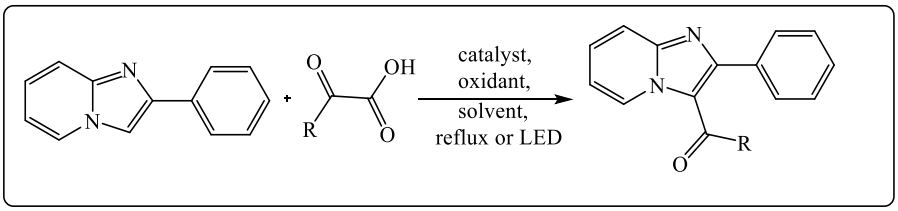
photocatalyzed transition metals is best novel strategy for the formation of C-C bond, thus we explored $Ru(bpy)_2Cl_2$ photocatalyst irradiated with blue LED light.

Acylation of 2-phenylimidazo [1,2-a] pyridine (scheme 17)[34] at active C-H radical generation to form new carbonyl C-C bond using various oxidant and solvent at reflux or blue LED standard conditions for about 6-7 h found smooth reaction at C3 position of imidazole.



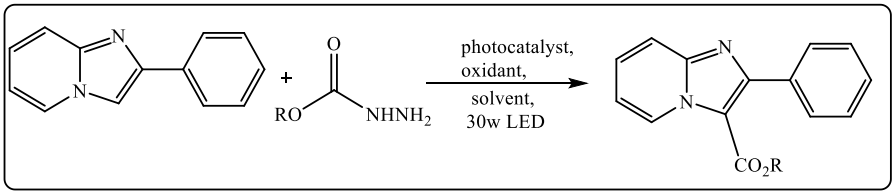
Scheme 17. Synthesis of acylated product of 2-phenylimidazo[1,2-a]pyridine with various metal catalyst and photocatalyst

As mentioned above 2-phenylimidazo [1,2-a] pyridine reacted with phenyl glyoxylic acid using photocatalyst and metal catalyst along with oxidant and solvent under reflux or blue LEDs by radical generation acylation at active C-H bond at imidazole to form new C-C bond in heterocycles (scheme 19)[36].



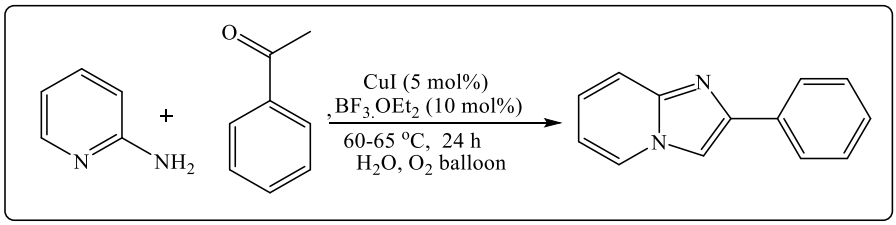
Scheme 18. Synthesis of acylated product of 2-phenylimidazo[1,2-a]pyridine with various metal catalyst and photocatalyst.

Focusing on completely photocatalyst such as eosin-y and $Ru(bpy)_2Cl_2$ and oxidant like ammonium per sulphate, TBHP, DMSO etc., under blue LEDs using these optimized condition reactions with 2-phenylimidazo [1,2-a] pyridine with carbazates direct esterification of NHCs should takes place (Scheme 20)[37].



Scheme 19. Synthesis of esterified product from 2-phenylimidazo[1,2-a]pyridine with carbazetes with various metal and photo catalyst.

Rasheed and group synthesized 2-phenylimidazo[1,2-a] pyridine using 2-aminopyridine and acetophenone in the presence of copper iodide and BF_3Oet_2 at 60-65 °C for 24 hours in an oxygen environment (scheme 18)[35]. We employed this reported strategy to prepare our starting material and ended up with the desired result.

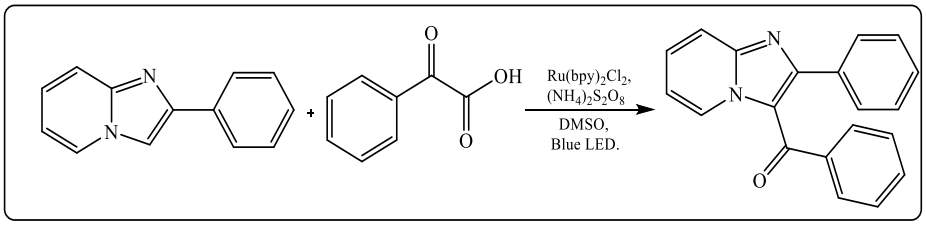


Scheme 20. CuI catalyzed synthesis of 2-phenylimidazo [1,2-a] pyridine in oxygen atmosphere.

Chapter 2

RESULTS AND DISCUSSION

2.1 Results and discussion

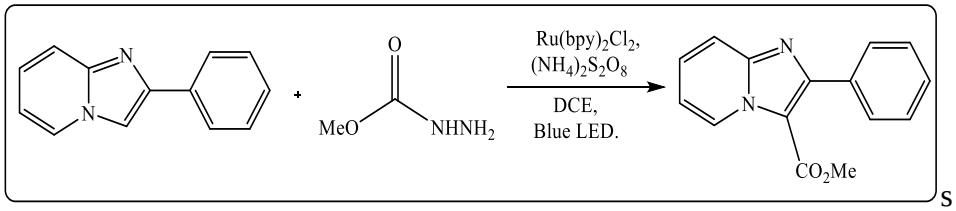


Scheme 21. $Ru(bpy)_2Cl_2$ photocatalyst mediated reaction of 2-phenylimidazo [1,2-a] pyridine with phenyl glyoxylic acid.

Table 2.1 Reaction conditions.

S.No.	Catalyst	Oxidant	Solvent	Time	Temperature	Yield
1	Acridine red	-	DCE	8	rt	-
2	PIDA	-	DCE	8	rt	-
3	-	TBHP	DCE	9	70°C	-
4	$Ru(bpy)_2Cl_2$	$(NH_4)_2S_2O_8$	DMSO	8	rt	-

Initially using photocatalyst for generation of radical in phenylglyoxal through Norrish type 1 is made easy to optimize the reaction condition. Using various catalyst to initiate the photo oxidation of starting material help us to study various reactions. Acridine red and absence of oxidant and using of dichloroethylene found effective. Same way to get desired product we change different reaction condition like in some reaction we use oxidant, absence of catalyst but unable to convert the product. 1,2 and 4 reactions carried under photocatalyst, and 3 reaction is done under reflux temperature at 70 ^{0}C but unsuccessful to convert the product. And finally tried to use ruthenium metal photocatalyst, ammonium per sulphate as oxidant and DMSO as solvent under blue LED at room temperature the reaction found effective but unable to convert the target product. Acridine red and absence of oxidant and DCE as solvent this photo reaction helped us to study further on behalf of photocatalyst. All reaction which we performed formed some new spots in TLC but unable to synthesize the target compound.



Scheme 22. Eosin-Y photocatalyst mediated reaction of 2-phenylmidazo [1,2-a] pyridine with carbazates.

Table 2.2 Reaction conditions.

S. No.	Catalyst	Oxidant	Solvent	Time	Yield
1	Eosin-y	$(NH_4)_2S_2O_8$	DMSO	6	-
2	Eosin-y	TBHP	DMSO	6	-
3	$Ru(bpy)_2Cl_2$	$(NH_4)_2S_2O_8$	DMSO	6	-
4	Eosin-y	$(NH_4)_2S_2O_8$	DCE	6	-

As we are unsuccess in generation of carbonyl keto group then we tried to generate direct esterification of active C-H bond in imidazole ring. All reactions are carried out by photocatalyst. In initial stages of reaction, we found eosin-y is best photo oxidative catalyst in these carbazate reactions. By using eosin-y as investigative catalyst and tried to optimizing reaction at different conditions to couple active C-H bonds in imidazole by using ammonium per sulphate as oxidant and DMSO solvent for 6 h at room temperature the reaction found to be effective, then again, we changed the solvent DMSO with 1,2-dichloroethane which is also found effective. Then we carried out the reaction in ruthenium catalyzed with ammonium per sulphate and DMSO. As mentioned in the above tabular form all the condition are favorable for complete the reaction within 6 h. We tried to explore the ruthenium catalyst also best in generation of C-H radicles formation which is irradiant with blue LEDs.

Chapter 3

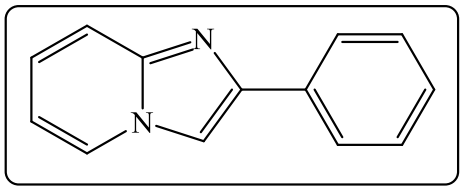
EXPERIMENTAL SECTION

3.1 Experimental section

All chemicals and metal salts were purchased from TCI, AVRA, Sigma-Aldrich, and Spectrochem which were used without any further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in deuterated solvent ($CDCl_3$) using Bruker Advance 400. Chemical shifts were referenced to the internal solvent resonances and were reported relative to tetramethyl silane.

3.1.1 Procedure for the 2-phenyl imidazo [1,2-a] pyridine] synthesis

In a round bottom flask with the capacity of 50 ml, 2 g (21.25 mmol) 2-aminopyridine, 5.106 g (42.5 mmol) acetophenone, CuI 5 mol% (1.06 mmol; 0.2236 g), $BF_3.OEt_2$ (2.25 mmol; 0.3 g), and H_2O (8 mL) were inserted. The mixture is kept for stirring in an oil bath for 24 h at 60-65 ^{O}C in the oxygen environment. After completion of reaction by conforming with new spots in TLC the mixture is permitted to cool to ambient atmosphere. The desired product is extracted by washing with DCM and then dried along with sodium sulphate. The mixture is carefully concentrated and purified using silica gel (ethyl acetate/hexane 35%) using column chromatography to get the desired product of 45.8%.



(Eluent: 35% EtOAc/hexane); yellow white solid; 45.8% yield (0.899 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.80 (s, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.30 – 7.24 (m, 1H), 7.12 (dd, *J* = 9.0, 6.8, 1.3 Hz, 1H), 6.73 (dd, *J* = 6.7, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.54 (d, *J* = 3.1 Hz), 133.44, 128.78, 128.11, 126.11, 125.63, 124.95, 117.49, 112.65, 108.14.

3.1.2 Procedure for the synthesis of phenyl (2-phenylimidazo [1,2-a] pyridine-3yl) methanone

A test tube was filled with 25 mg (0.125 mmol) 2-phenylimidazo[1,2-a] pyridine, 38 mg (0.26 mmol) phenyl glyoxylic acid, 1 mol% acridine red, and 1.28 mL DCE. The solution was stirred at room temperature for 6-8 h while being exposed to blue LEDs. After the completion of reaction, for every 3 hours, monitor it with TLC. The solution is extracted with ethyl acetate before being concentrated using a rotor evaporator. The combination is purified using column chromatography, and a sample is submitted for analysis ^{1}H and ^{13}C NMR, however we were unable to synthesize the desired product.

3.1.3 Procedure for synthesis of methyl 2-phenylimidazo [1,2-a] pyridine-3-carboxylate

In a test tube at room temperature, 25 mg (0.125 mmol) 2-phenylimidazo [1,2-a] pyridine, 26 mg (0.257 mmol) methyl carbazate, 88 mg (0.38 mmol) ammonium per sulphate, 5 mol% eosin-y, and 2 mL DMSO were inserted. The mixture is continuously stirred at ambient atmosphere for 5-6 hours while being carefully monitored with TLC every 3 hours. Ethyl acetate is used to extract the solution, which is subsequently concentrated using a rotor evaporator. The combination is purified using silica gel and column chromatography (45% ethyl acetate/hexane), and the sample is sent for 1H and 13C NMR analysis, however, were unable to synthesize the desired product.

Chapter 4

CONCLUSION

CONCLUSION: In this thesis work, we have investigated various photocatalyst in oxidative coupling of imidazole derivative. This process involves the generation of active C-H radical which is free available at five membered rings of imidazole by using different reactant like phenyl glyoxylic acid, methyl carbazate and tert-butyl carbazate in presence of photocatalyst like acridine red, eosin-y and ruthenium. In this process phenyl glyoxylic acid and carbazate served as the generation of benzaldehyde and ester group radical, respectively. C3 position of 2-phenylimidazo [1,2-a] pyridine is easy site for C-H activation and friendly to attack electron withdrawing and election donating group. As most of the reaction we carried in visible light which is eco-friendly and the 2-phenylimidazo [1,2-a] pyridine derivatives have many medicinal benefits and future scope in synthetic organic chemistry.

APPENDIX

Figure 2. ^{1}H NMR of 2-phenylimidazo[1,2-a] pyridine

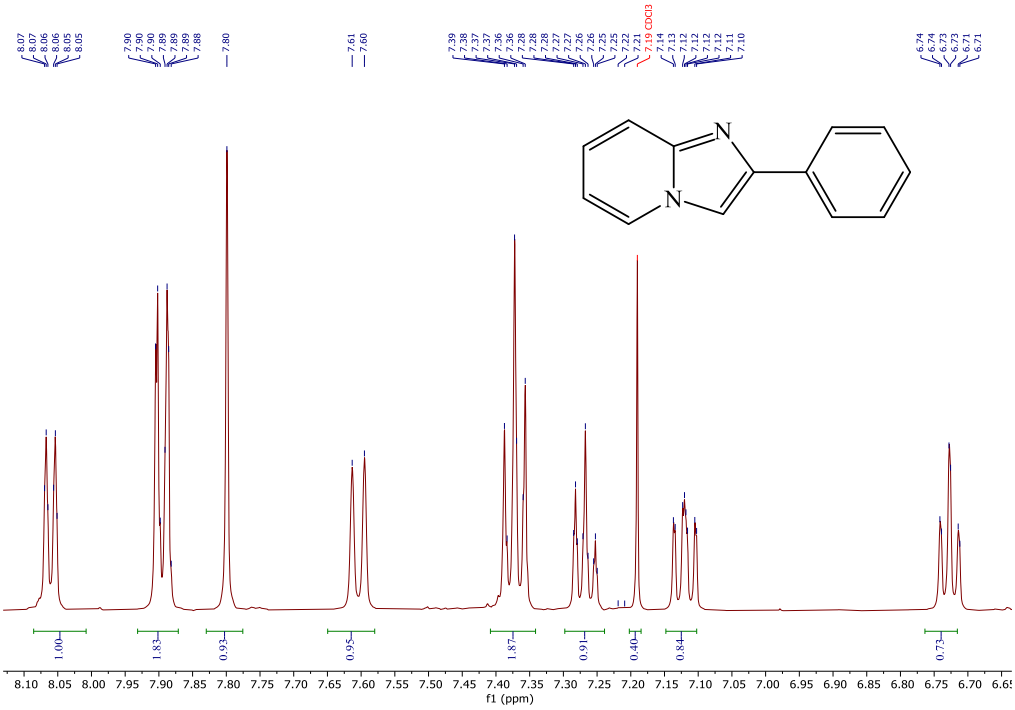
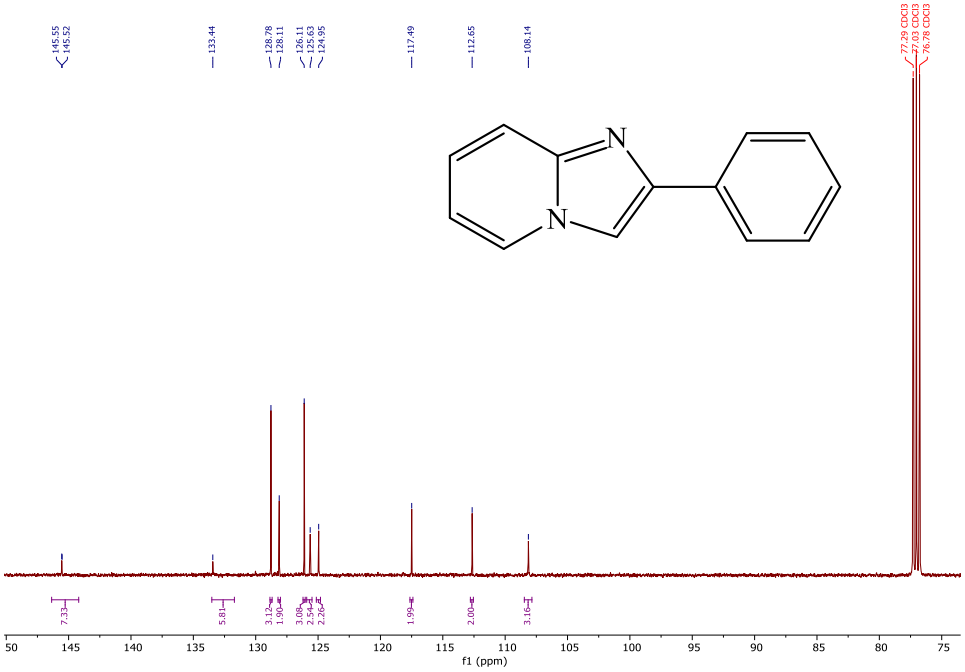


Figure 3. ^{13}C-NMR of 2-phenylimidazo[1,2-a] pyridine



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