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Research Article

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Efficient and convenient Suzuki cross-coupling reaction catalyzed by a new synthesized palladium co-ordination metal complex of cyano-acetohydrazide Schiff base

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ABSTRACT

N,O-donating bidentate ligand was prepared from the condensation of cyano-acetohydrazide and4-cyano benzaldehyde. Palladium Metal complex of this ligand is stable at room temperature. The effect of different solvents, bases, and palladium complex on the yield of the coupling reaction were studied.

Keywords: Schiff Bases, Cyanoacetohydrazide, IR Spectra, NMR spectra, Mass spectra; Suzuki cross-coupling, Palladium Complex.

INTRODUCTION

Suzuki cross-coupling reaction of aryl halides with aryl boronic acid is one of the most important method for thesynthesis of biaryls, in recently the application of N,O-based ligands moiety, such as Schiff bases, guanidine, aryloximes, acetohydrazide, arylimines, has also consider as a highly active catalysts for Suzuki cross coupling reaction in aqueous media.[1-6]Nature of ligand is important in the Suzuki cross coupling reaction. Bulky and more electron-rich ligands are important in Suzuki cross-coupling reaction. Due to their higher donor ability and stability effects[7–10].Its present in pharmaceuticals, agrochemicals materials natural products, polymer, [11–18] .In recent Suzuki cross coupling reaction is carried out in aqueous phases including water and water/organic mixtures assolvents. comparatively to other solvent water is environmental friendly, easily available and easily for separation of organic products and catalyst recycling[19-20] .

EXPERIMENTAL SECTION

All the compounds and solvents were purchased from spectrochem and lobachemie, and checked TLC.IR spectra were taken with Shimadzu IR Affinity-1S FTIR spectrometer. Mass spectra were done on GCMS QP2010 mass spectrometer, ^{1}H NMR spectra were taken on Bruker NMR spectrometer (400 MHz), using TMS [as internal standard]. Elemental data was recorded by Carlo Erba EA 1108 elemental analyzer.

General procedure for the synthesis of 2-cyanoacetohydrazide

Cyan acetichydrazide was prepared according to (Bondock et al., 2006) procedure. Added hydrazine hydrate (0.1 mol) and ethyl cyanoacetate (0.1 mol) and 20 ml ethanol as solvent was taken in flatted-bottom flask at 0–10 °C temperature under stirring. . A white precipitate formed after about 10 min. The precipitate was .Filtered and washed with 20 ml ethanol and dried in a hot air oven at 60°Cfor 1 hour. Yield: 95%, m.p =109°C.

General procedure for the synthesis of Schiff base of 2-cyanoacetohydrazide

The Schiff bases, N'-(4-cyanobenzylidene)-2-cyanoacetohydrazide was prepared by adding equimolar amounts of 2-cyanoacetohydrazide and 4-cyano benzaldehyde in 50 mL absolute ethanol with 2-3 drops of glacial acetic acid respectively. The mixture was stirred at room temperature for 30 min. The reaction was monitored by TLC using hexane: ethyl acetate(2:3). The precipitated products were filtered off, crystallized from ethanol and dried under vacuum for 1 hour. schiff base N'-(4-cyanobenzylidene)-2-cyanoacetohydrazide [BJ-08] is white powder in 85% yield and melting point- 210°C

General Procedure for the Synthesis of Palladium Metal Complex:

Pd(II) metal complexes were prepared by adding 1:1 equimolar ratio of ligand in methanol and an aqueous solution of the palladium chloride. The reaction mixture was refluxed for 2-3 hrs. The completion of the reaction was monitored by TLC. After the reaction was completed, then the residue was cooled to room temperature. The solid Pd[II]-complexes formed were filtered and washed with hot water and ethyl alcohol, then followed by petroleum ether to remove any traces of unreacted metal salts, and finally dried in vacuum desiccators over anhydrous Calcium(II)Chloride**.**

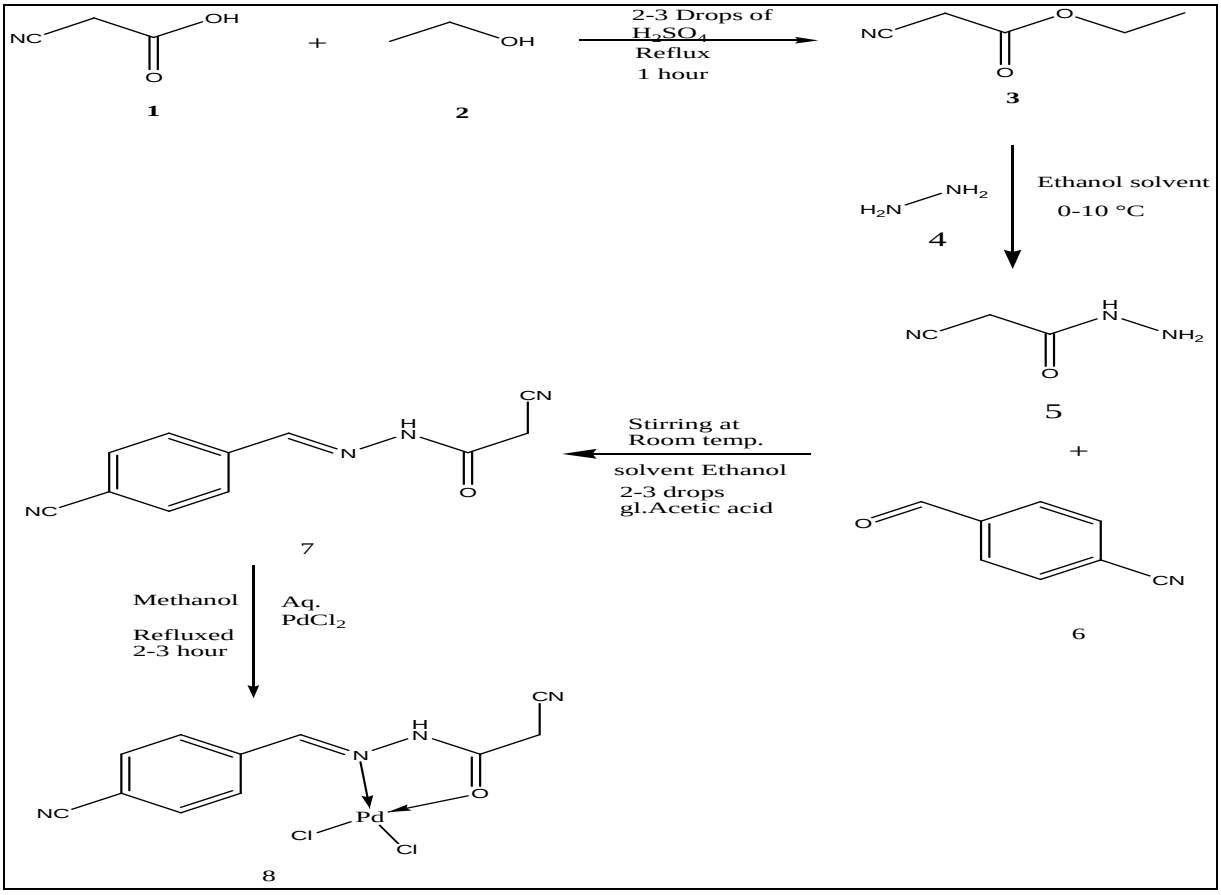

Figure 1. Scheme for synthesis of metal complex

Suzuki cross Coupling reaction of 4-Chloro Benzaldehyde with Phenylboronic Acid under Different Conditions

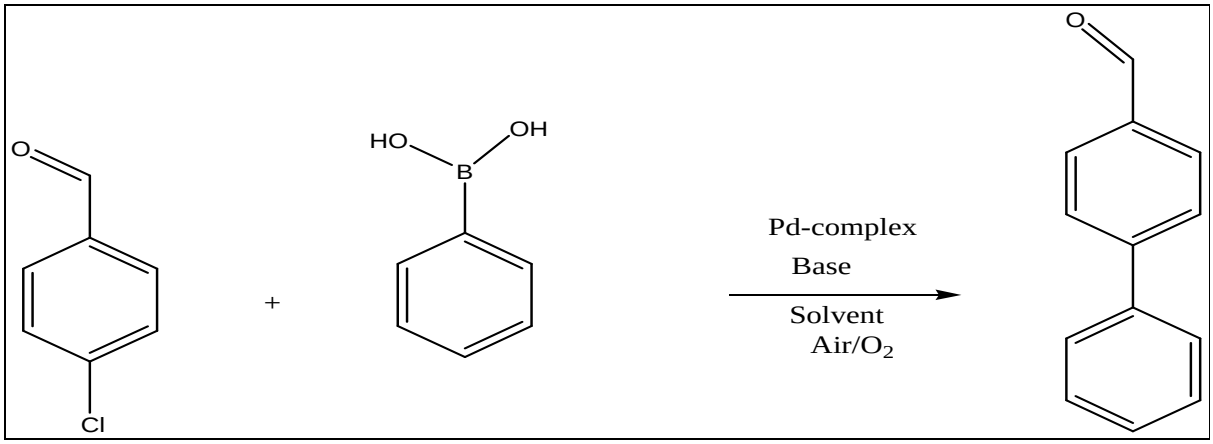

Figure 2. Suzuki cross coupling reaction

Table-1

No.	Solvent	Bases	Yield %
1.	Me-OH/H_2O (1:1)	Na_2CO_3	60%
2.	Me-OH /H_2O (1:2)	Na_2CO_3	55%
3.	Me-OH /H_2O (1:3)	Na_2CO_3	26%
4.	Me-OH /H_2O (3:1)	Na_2CO_3	59%
5.	Me-OH /H_2O (1:1)	K_2CO_3	70%
6.	Me-OH /H_2O (1:1)	KOH	45%
7.	Me-OH /H_2O (1:1)	NaOH	65%
8.	Me-OH /H_2O (1:1)	NaOMe	28%
9.	Me-OH /H_2O (1:1)	Et_3-N	82%
10.	Et-OH /H_2O (1:1)	K_2CO_3	53%

N'-(4-cyanobenzylidene)-2-cyanoacetohydrazide [BJ-08]

Elemental Analytical Calculation for $C_{11}H_8N_4O$(212.07g/mol): C, 62.26%; H, 3.80%; N, 26.40%; O, 7.54%. Found: C, 62.20%; H, 3.75%; N, 26.33%; O, 7.52%; MS (m/z): 212; IR, (cm−1): ν(OH) 3196; ν(NH) 3089; ν(C=N) 1680; ν(N-N) 1143; ν(Ar–C-H) 2964; ν(Ar–C=C) 1500; ν(C=N)2223, 2270; ^{1}H-NMR (DMSO-d_6): δ ppm 4.27 (s, 2H, CH_2); 7.88, (d, 1H, J = 8.92 Hz, Ar-H); 7.90 (d, 1H, J =8.92 Hz, Ar-H); 7.92, (d, 1H, J = 8.90 Hz, Ar-H); 8.04, (d, 1H, J = 8.92Hz, Ar-H); 8.21 (s, 1H, HC=N); 12.04 (s, 1H, NH). ^{13}C-NMR (DMSO-d_6): δ ppm 29.66 (CH_2); 121.23, 123.85(CN), 117.37, 132.76, 137.86(C=C), 143.38(C=C) (Ph); 147.62 (HC=N); 170.49 (C=O).

Palladium (II) complex of N'-(4-cyanobenzylidene)-2-cyanoacetohydrazide

Color: Dull Brown, Elemental Analytical Calculation for $C_{11}H_8C_{l2}N_4OPd$ (389.91g/mol): C, 33.92%; H, 2.07%; N, 14.38%; Cl, 18.20%; O, 4.11%; Pd, 27.32%. Found: C, 33.90%; H, 2.02%; N, 14.30%; Cl, 18.15%; O, 4.10%; Pd, 27.30%; ESI-MS (m/z): 389.4 $(PdL1)^+$; IR(cm^{-1}): ν(NH) 3290; ν(C=N) 1666; ν(N-N)1107; ν(Ar–C-H) 2953; ν(Ar–C=C) 1456; ν(C=N) 2276, 2370.

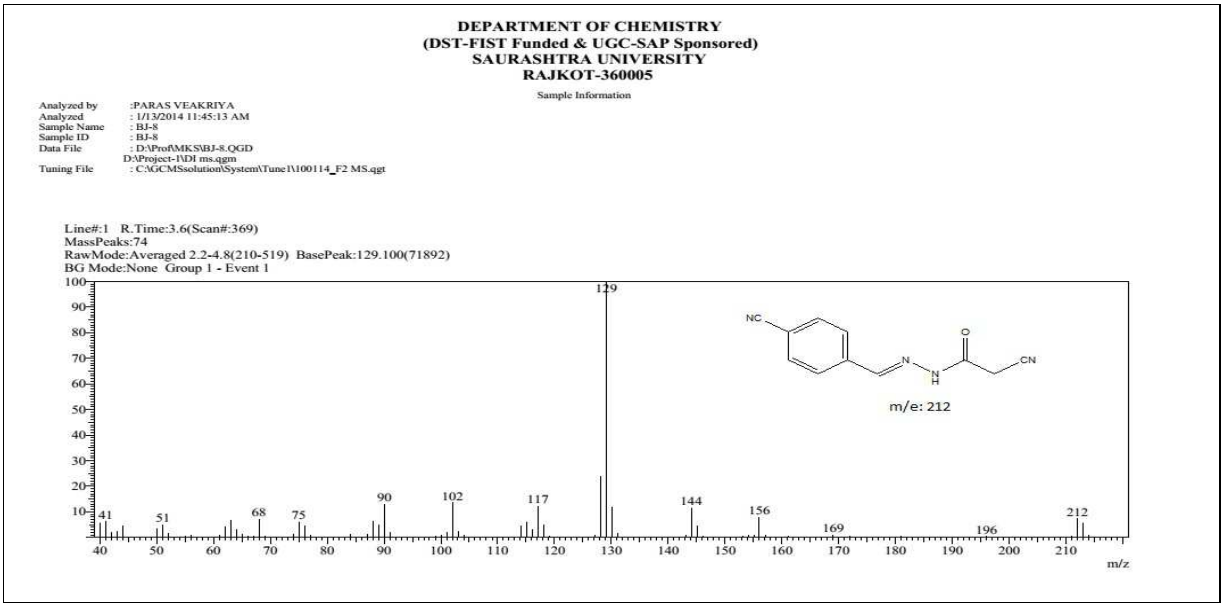

Figure3. Mass spectra of ligand

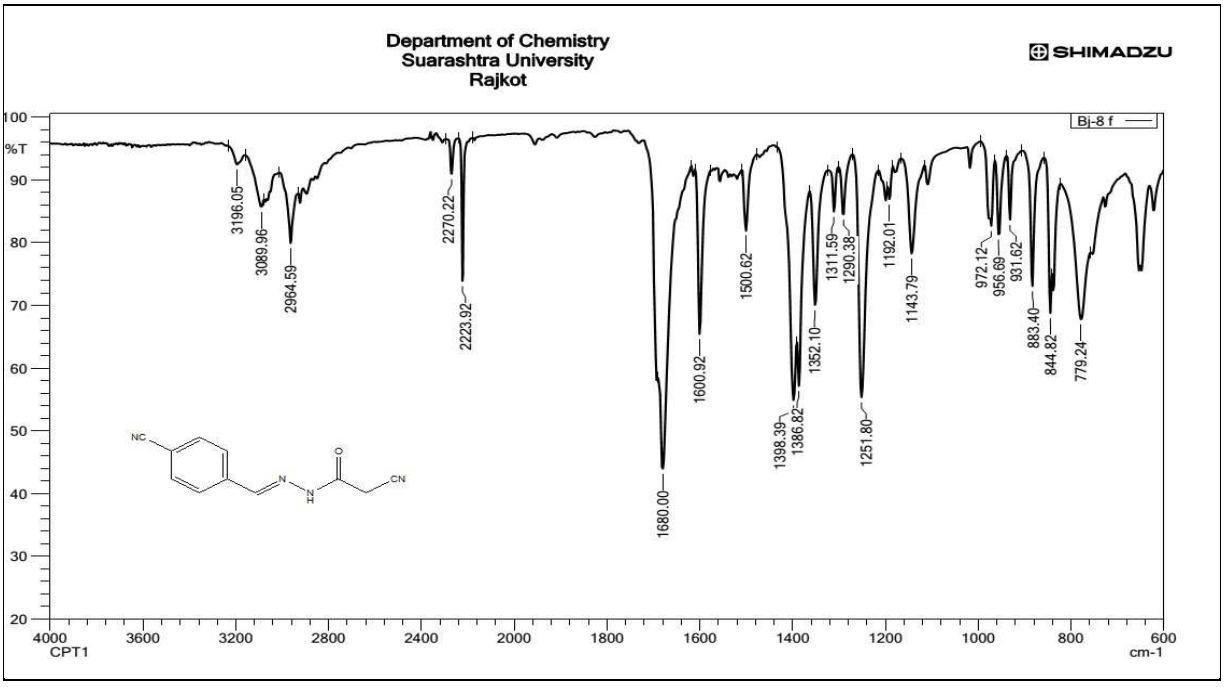

Figure4. IR spectra of ligand

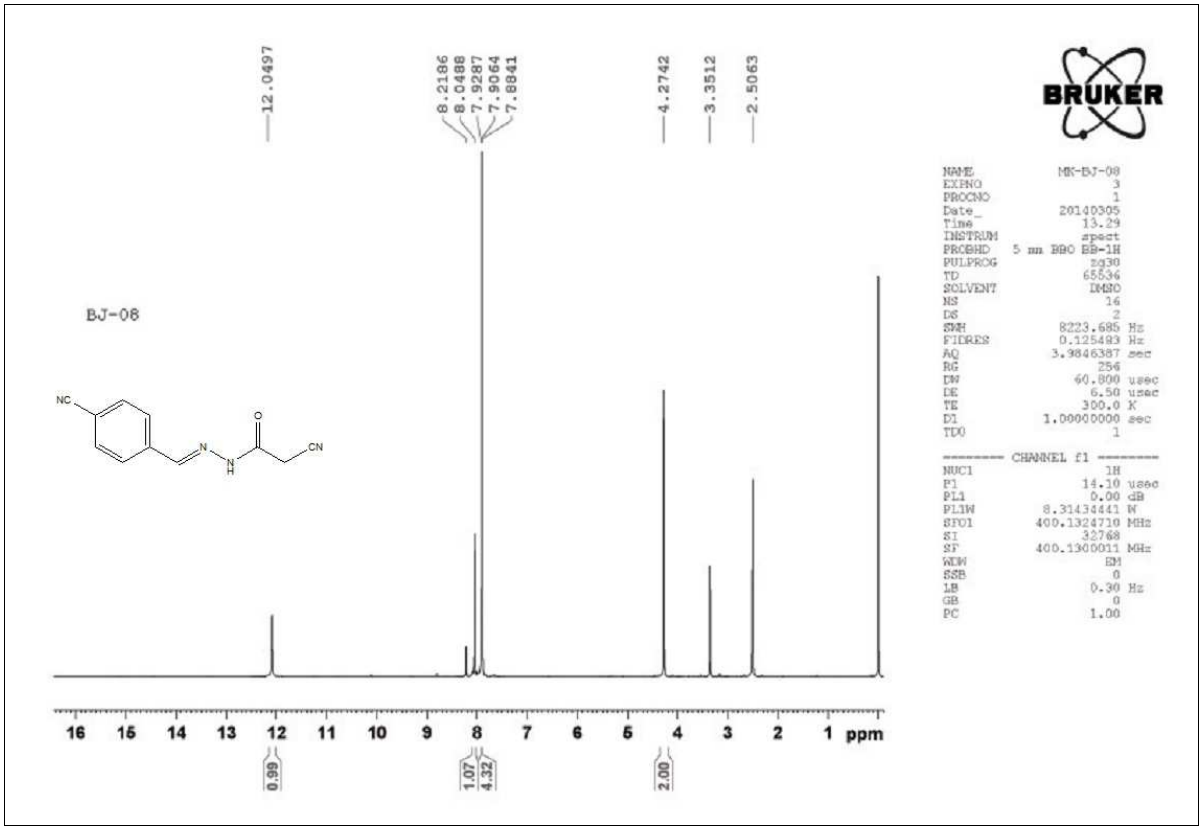

Figure5.[1]H NMR spectra of ligand

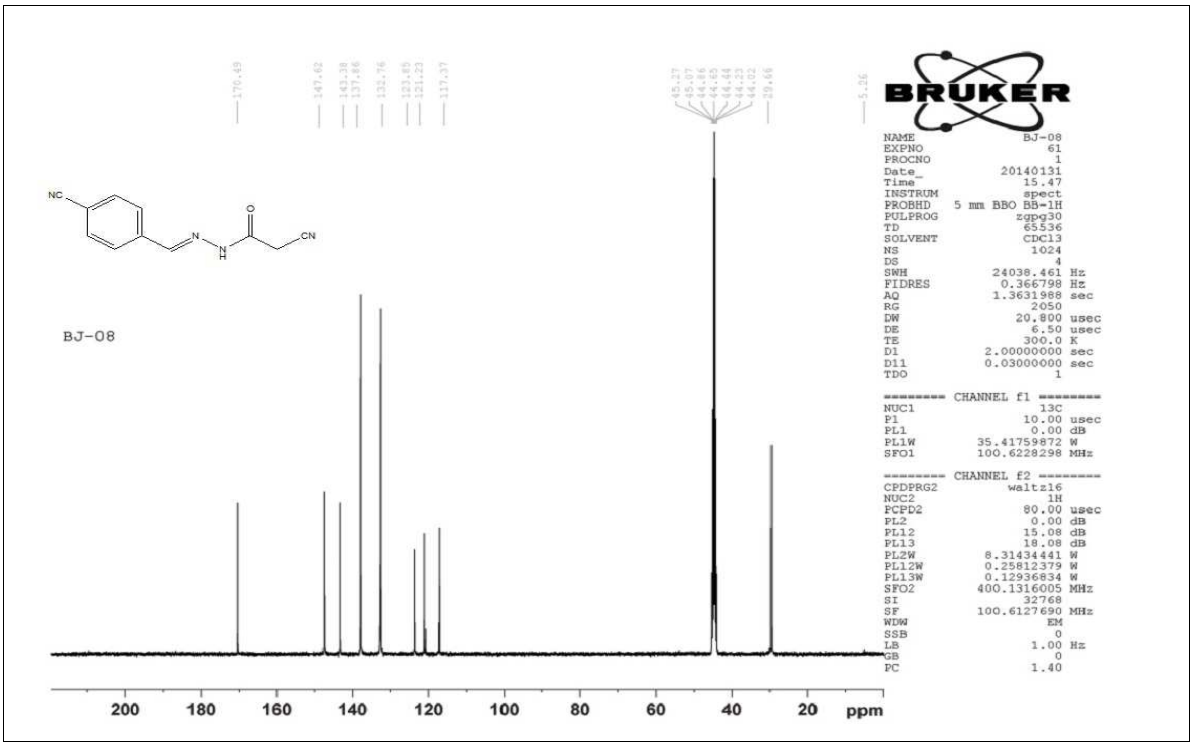

Figure6.[13]C NMR spectra of ligand

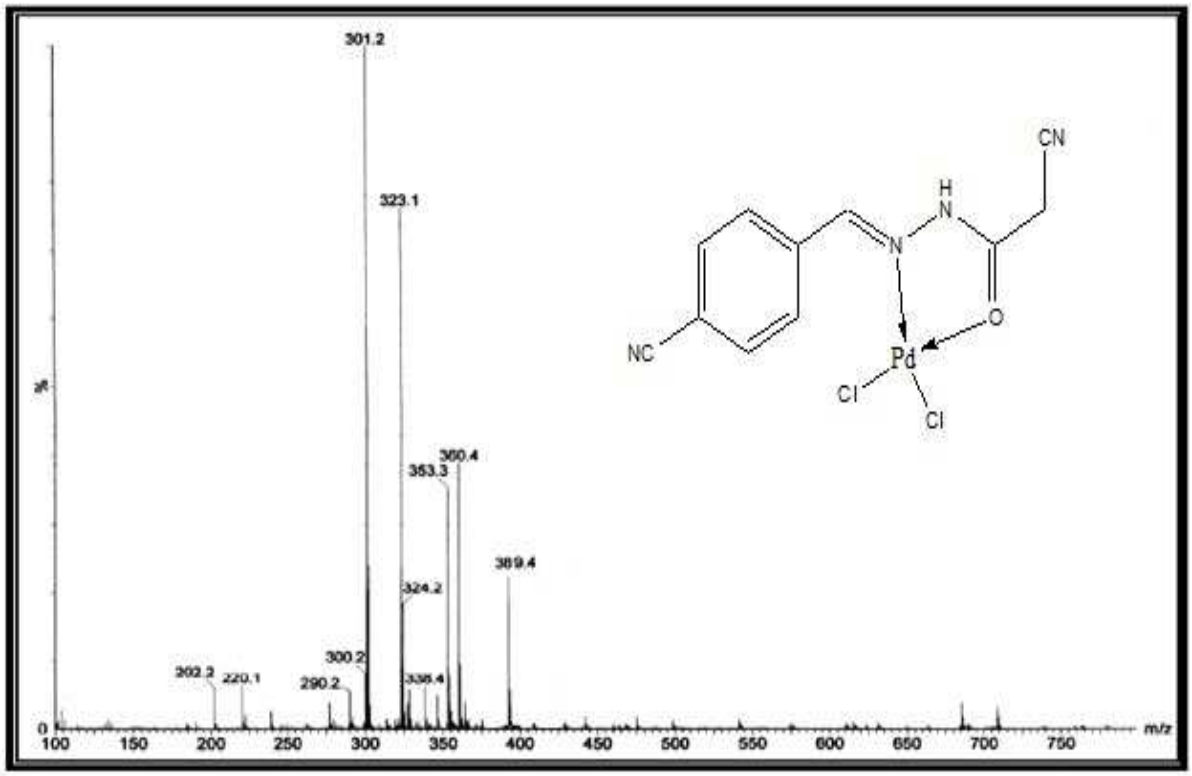

Figure7:ESI-MASS spectra of Metal Complex

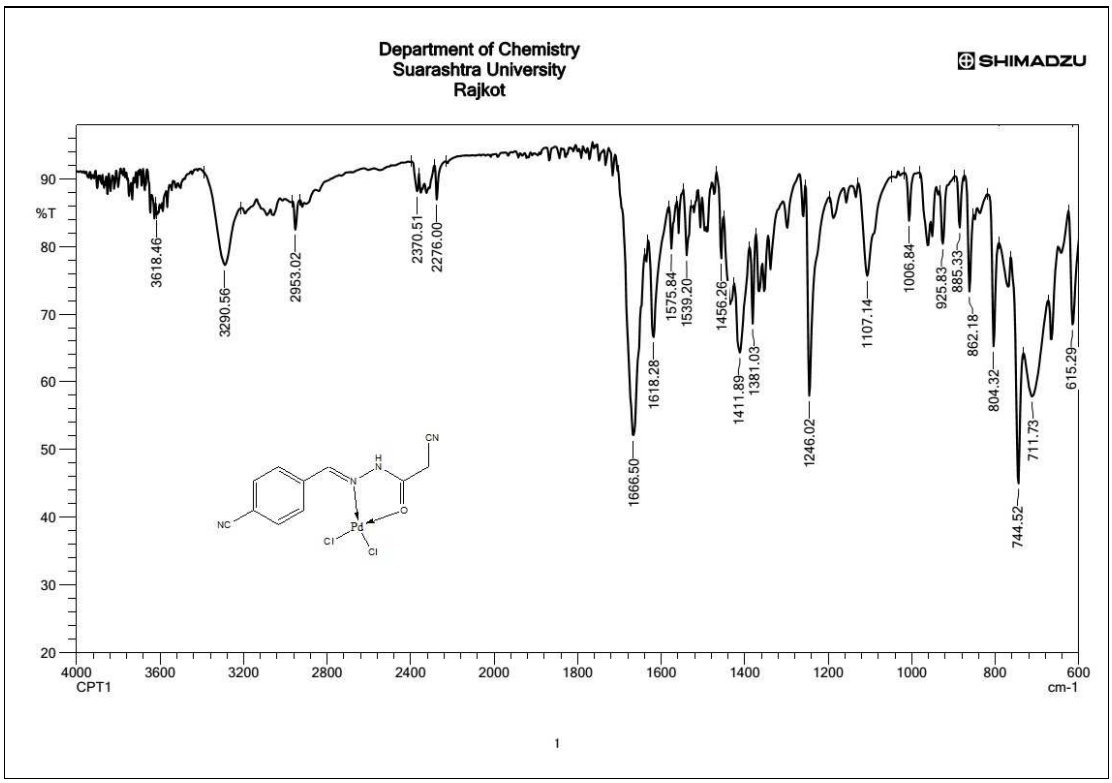

Figure8.IR spectra of Metal Complex

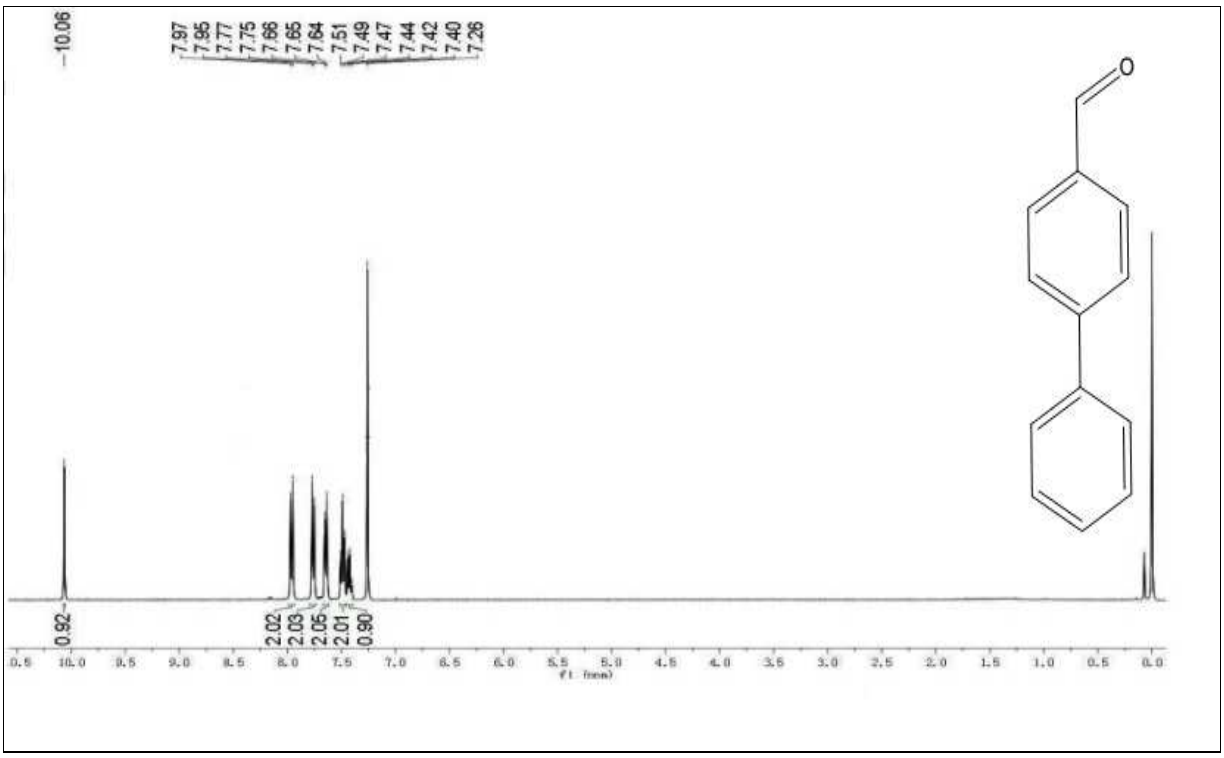

Figure9. [1]H NMR spectra of 4-Phenyl Benzaldehyde

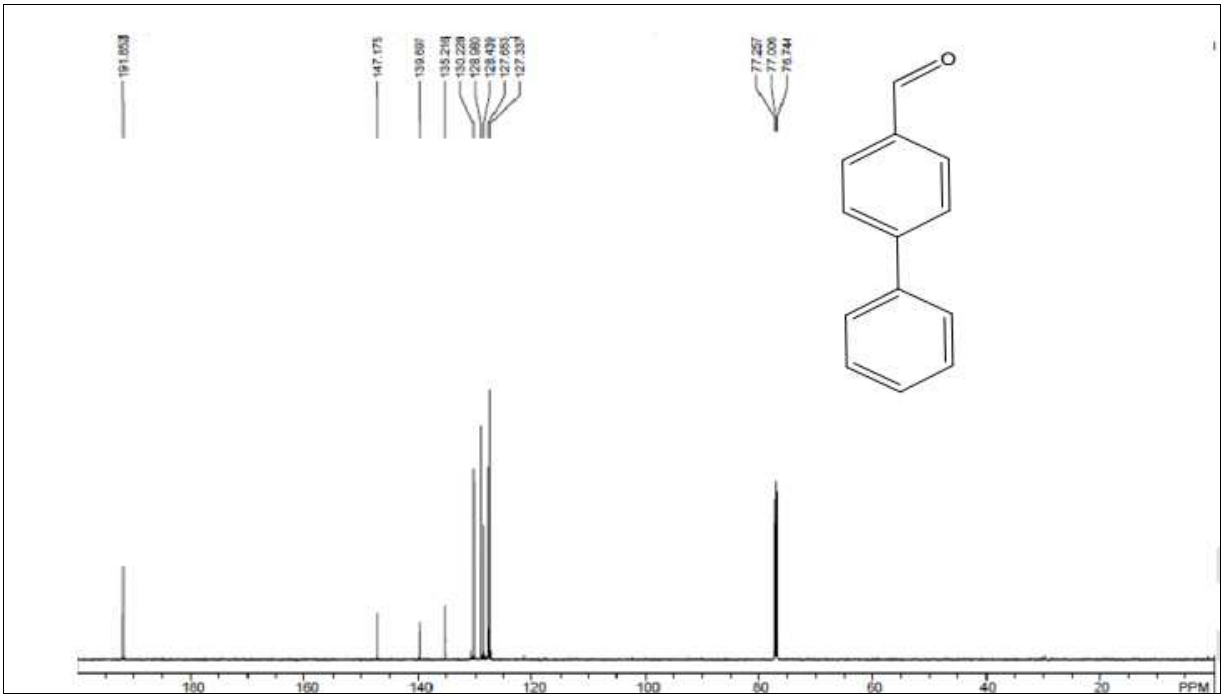

Figure10. [13]C NMR spectra of 4-Phenyl Benzaldehyde

RESULTS AND DISCUSSION

Generally suzuki cross-coupling is carried out in presence of Palladium salts and N_2 atmosphere, here we are used a metal complex of palladium with cyanoacetohydrazide Schiff base ligand in Suzuki cross coupling reaction in presence of different bases and obtain good yield. Here we used many bases; in which triethylamine we got a good yield, as compared to other bases.

CONCLUSION

In this research paper, cyanoacetohydrazide schiff base ligand with palladium metal co-ordination metal complex has been synthesized and successfully used as a catalyst in Suzuki cross-coupling reaction. The advantage of catalyst is easy to synthesize and recoverable. These cross coupling reactions were carried out in several bases. Hence, we observed that, in Suzuki cross coupling reaction triethylamine as base has given excellent yield as compared to other bases.

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REFERENCES

[1]MM Haag R.*Chem Sus Chem*,**2008**, 1, 637–642.
[2]IDKostas;AGCoutsolelos;GCharalambidis;ASkondra.*TetrahedronLett*,**2007,** 48, 6688–6691.
[3] AMOertel; VRitleng; MJChetcuti.www.wjpr.net, **2015**, Vol 4, Issue 2.
[4] DBZhao; ZFFei; TJGeldbach; RScopelliti;PJDyson.*J. Am. Chem. Soc*.,**2004**, 126, 15876-15882.
[5] P Liu; MYan; RHe.*Appl*. *Organometallic. Chem.*,**2010**, 24, 131–134.
[6] ICobo; MIMatheu; SCastillón;OBoutureira;BGDavis.*Org. Lett*.,**2012**, 14, 1728-1731.
[7]ZWeng;ATeos; S Hort. *Acc. Chem. Res*.,**2007,** 40, 676.
[8]RMartin; SLBuchwald.*Acc. Chem. Res*.,**2008**, 41, 1461.
[9] GCFu.*Chem. Res.*,**2008**, 41, 1555.
[10] GAMolander; BCanturk *Angew. Chem. Int. Ed*.,**2009,** 48, 9240.
[11] NMiyaura; ASuzuki. *Chem. Rev.*,**1995,**95, 2457.
[12] A Suzuki. *Organomet.Chem.*,**1999,** 576, 147.
[13] ASuzuki. *Chem. Commun.*,**2005**, 4759.
[14] AFLittke; GCFu.*Angew.Chem. Int. Ed*.,**2002**, 41, 4176.
[15] NTSPhan; MVan Der Sluys; CWJones.*Adv. Synth. Catal*,**2006**,348, 609.
[16] FAlonso; IPBeletskaya; MYus. *Tetrahedron*, **2008**, 64,3047.
[17] VFSlagt; AHMDe Vries; JGDe Vries; RMKellogg.*Org. Process Res. Dev*., **2010**, 14, 30.
[18]VPolshettiwar;ADecottignies; CLen;AFihri. *Chem. Sus. Chem*, **2010,** 3, 502.
[19]MMondal;UBora.*Green Chem.*,**2012,** 14,1873–1876.
[20]BInés; RSanMartin; MJMoure; EDomínguez.*Adv. Synth. Catal*,**2009,** 351, 2124–2132.