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AN EFFICIENT SUZUKI REACTION USING A NEW BENZOTHIAZOLE/ PD(II) SPECIES AS CATALYST IN AQUEOUS MEDIA

Mayank J. Mamtora, Javed G. Mahetar, Juvansinh J. Jadeja, Rohit B. Manawar, Manish K. Shah*

Chemical Research Laboratory, Chemistry Department, Saurashtra University, Rajkot

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***Correspondence for Author**
Dr. Manish K. Shah
Department of Chemistry
Saurashtra University
Rajkot-360005

ABSTRACT

N,N,O-donating ligand was prepared from the condensation of 2-amino benzothiazole with various aromatic aldehyde. Metal complex of this ligand is neither air nor moisture sensitive. The effects of varying solvents, bases, and ligand/copper ratio on the performance of the coupling reaction were investigated. This method is a very simple, efficient and mild protocol for the cross-coupling of aryl bromides with arylboronic acids, and the reactions proceeded effortlessly in excellent yields within short reaction times. All reactions are carried out in anhydrous condition.

KEYWORDS: N, O, O-donating ligand, Copper complex, Chan-Lam cross coupling.

INTRODUCTION

Suzuki cross-coupling reaction of aryl halides with organoboron reagents is one of the most significant and consistent methods for the transformation of biaryls, which are present in pharmaceuticals, natural products, and functional polymer, agrochemicals materials.[1–8]

In present studies the Suzuki reaction is carried out in aqueous phases including water and water/organic mixtures as solvents for the Suzuki reaction has also received significant attention, as water is, environmental friendly, economical, and allows simple separation and catalyst recycling.[9-10]

Recently the application of nitrogen-based ligands species, such as schiff bases, , aryloximes, arylimines, guanidine, has also consider as a highly active catalysts for Suzuki reaction in aqueous media.[11-16]

Nature of ligand is very important in the Suzuki coupling. Bulky, electron-rich ligands are outstanding in Suzuki cross-coupling reaction, resulting from their higher donor ability and stabilization effects.[17–20]

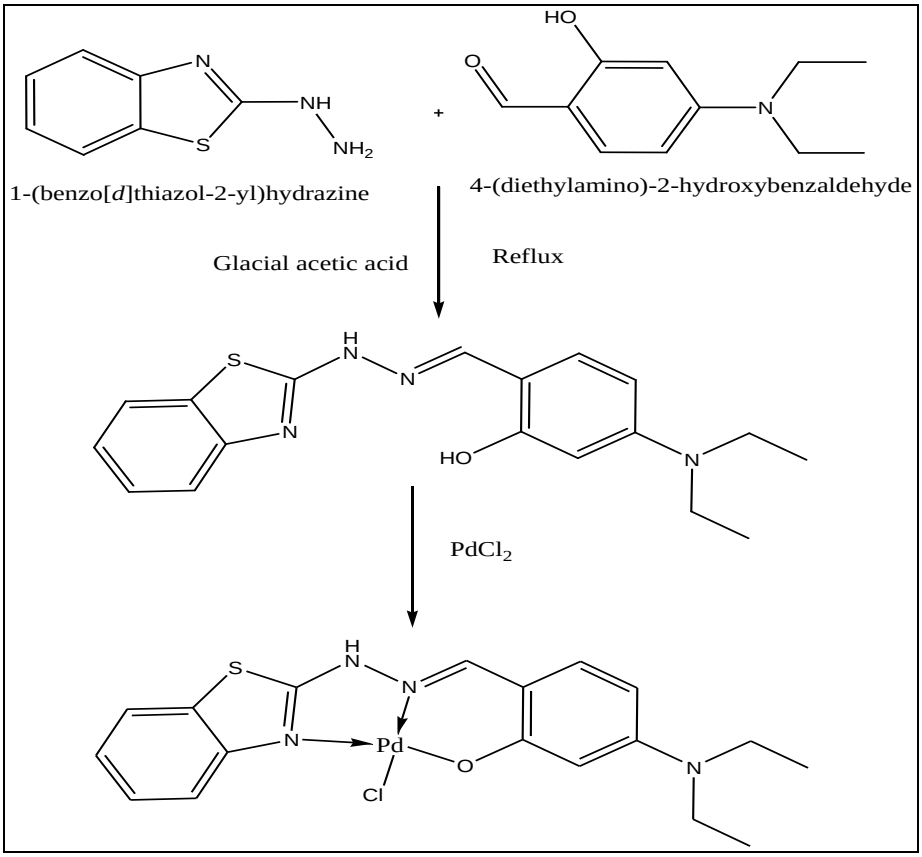

Figure 1. Reaction Scheme of ligand and metal complex

General procedure for the synthesis of benzothiazole ligand

A solution of 1-(benzo[d]thiazol-2-yl)hydrazine (0.01 mole) and 4-(diethylamino)-2-hydroxybenzaldehyde condensed in presence of glacial acetic acid (10 ml) as a catalytic amount. The reaction mixture heated to 60-65 ˚C for appropriate time. The reaction is being monitored by TLC using hexane : ethyl acetate (3:7). After completion of the reaction, the mixture was poured into crushed ice. Light green precipitate fall out and Filtered out the separated solid product and dried under reduced pressure. M.P. 180°C, MS (m/z): 340.44 (M^+); ^{1}H-NMR (DMSO-d_6): δ ppm,; 1.21 (t, 6-H,); 3.61, (m, 4H, CH_2,); 3.89, (s, 1H, -OH); 6.40 (s, H,); 6.45 (d, 1H,); 7.08 (d, 1H, Ar-H,); 7.28(s, H, CH=N);7.41(m, 2H, Ar-H), 7.91(d, 1H, Ar-H), 8.02(d, 1H, Ar-H), 8.29 (s, 1H, -NH). ^{13}C-NMR (DMSO-d_6): δppm 13.01 (-CH_3); 46.34, 97.12, 103.50, 108.33, 118.71, 121.34, 122.86, 125.53, 132.48, 134.41, 147.87 (CH=N), 151.38, 155.91, 160.73, 165.56

Preparation of Metal Complexes

Pd(II) complexes were prepared by mixing calculated quantity of ligand in methanol and an aqueous solution of the corresponding metal chlorides in 1 : 1 molar ratio. The reaction mixture was refluxed on an oil bath for 2-3 hrs.The completion of the reaction was monitored by thin layer chromatography. Once the reaction was completed, then the residue was cooled to room temperature. The solid complexes formed were filtered, washed with hot water (2 times) and ethyl alcohol, and finally dried in vacuum desiccators over anhydrous Calcium Chloride.

Suzuki Coupling of 4-Bromo Benzaldehyde with Phenylboronic Acid under Different Conditions

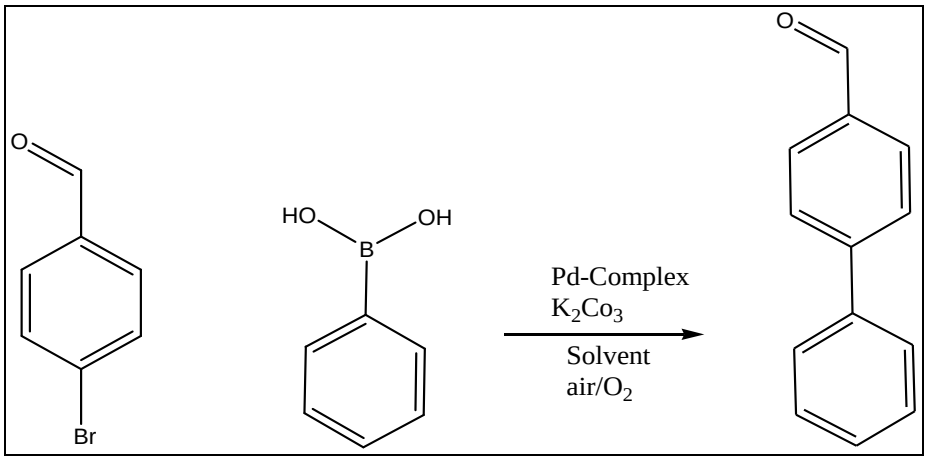

Figure 2.

Table 1.

No.	Solvent	Bases	Yield %
1.	Et-OH/ H_2O (1:1)	K_2CO_3	72
2.	Et-OH/ H_2O (1:2)	K_2CO_3	65
3.	Et-OH/ H_2O (1:3)	K_2CO_3	32
4.	Et-OH/ H_2O (3:1)	K_2CO_3	40
5.	Me-OH/ H_2O (1:1)	K_2CO_3	45
6.	Et-OH/ H_2O(1:1)	NaOH	78
7.	Et-OH/ H_2O(1:1)	NaOMe	55
8.	Et-OH/ H_2O(1:1)	Et_3N	35
9.	Et-OH/ H_2O(1:1)	Na_2CO_3	63

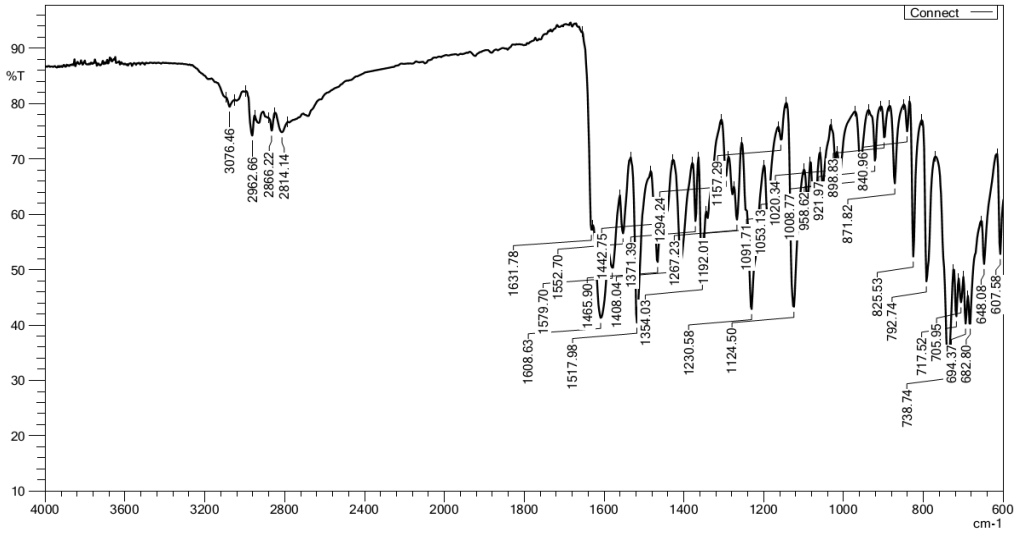

Figure 3. IR SPECTRUM OF LIGAND

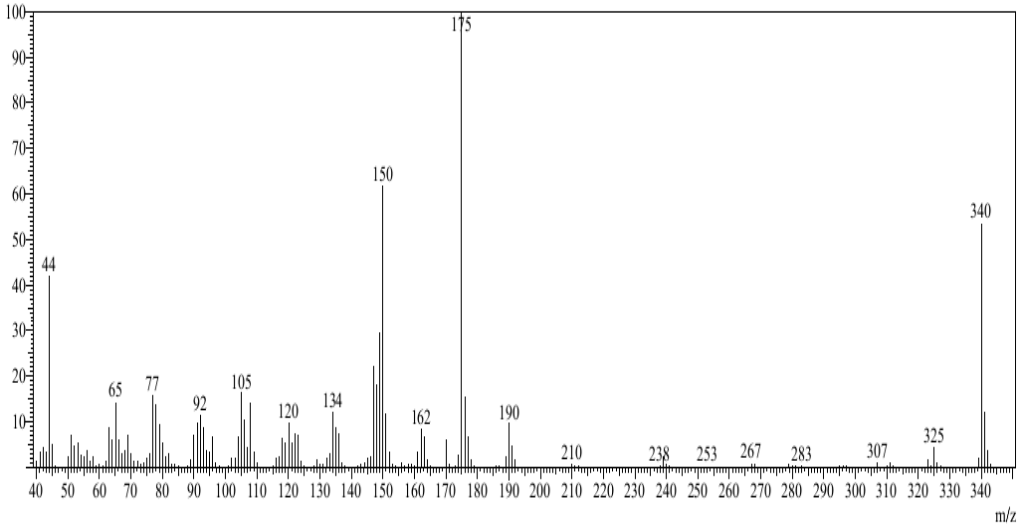

FIGURE 4. MASS SPECTRUM OF LIGAND

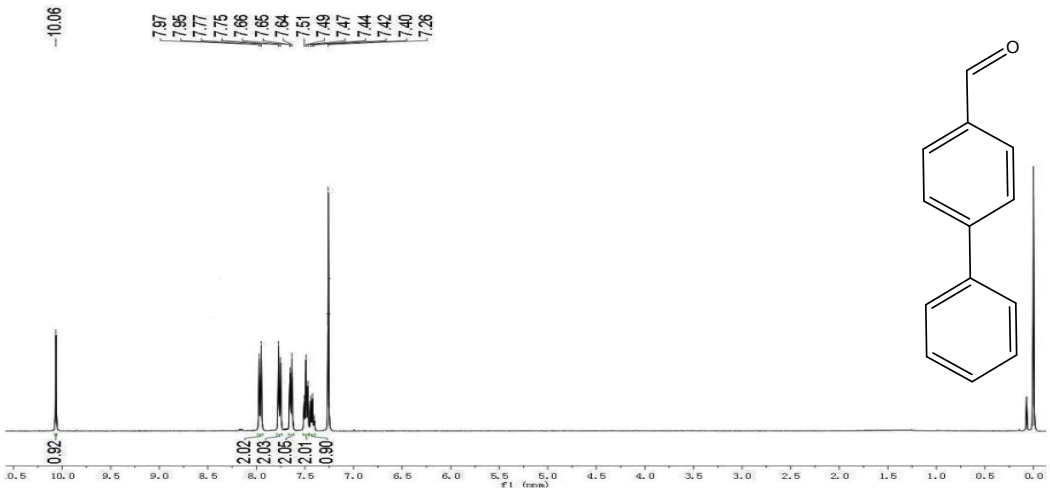

FIGURE 5. NMR SPECTRUM OF 4-PHENYL BENZALDEHYDE

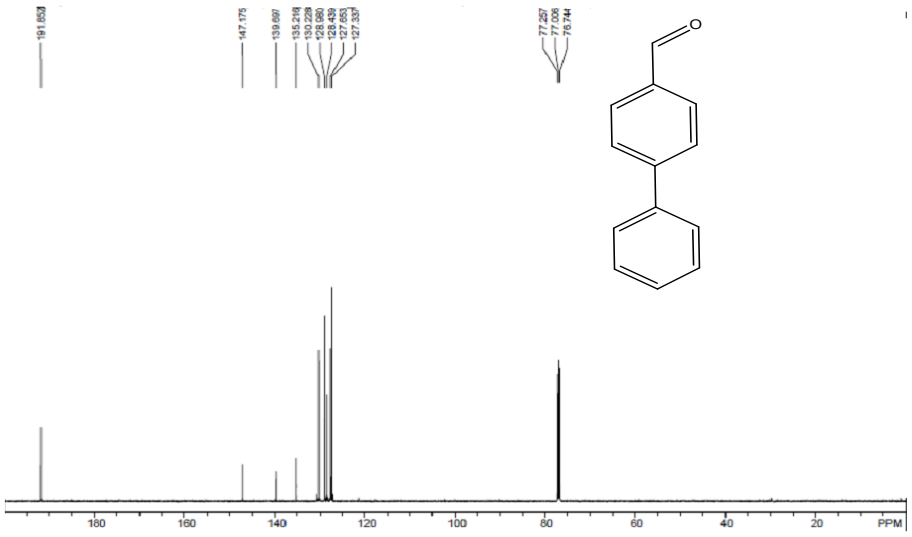

FIGURE 6. ^{13}C NMR SPECTRUM OF 4-PHENYL BENZALDEHYDE

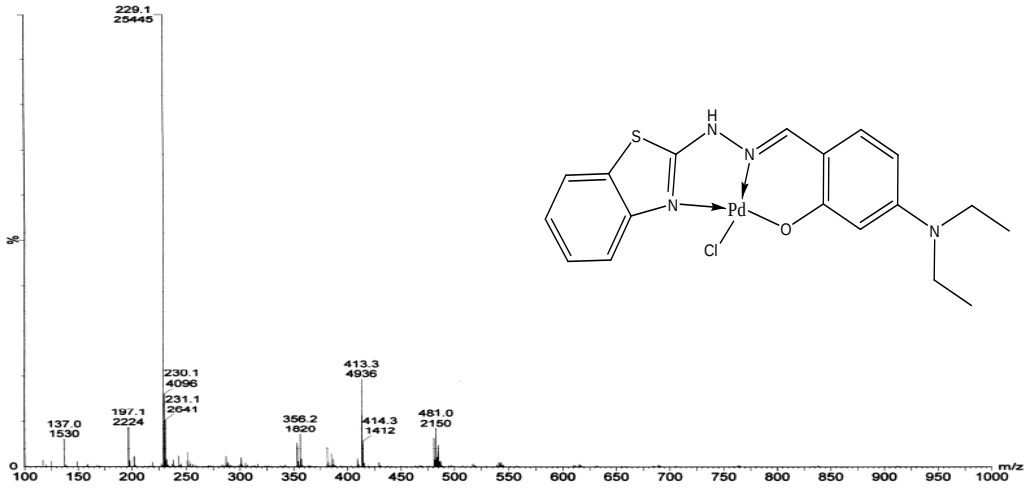

FIGURE 7. ESI MASS SPECTRUM OF 4-PHENYL BENZALDEHYDE

CONCLUSION

In this paper, benzothiazole metal complex has been synthesized and successfully used as a catalyst in Suzuki cross coupling reaction. The benefit of catalyst is easy to handle, recoverable and also cheap. These reactions were carried out in several bases in aqueous media. Hence, we observed that, in Suzuki reaction K_2CO_3 as base has given excellent yield as compared to other bases.

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