

NEW SYNTHESIZED PALLADIUM COMPLEX CONTAINING N,N,O-TRIDENTATE LIGANDS : A CATALYSED CROSS-COUPLING REACTION

Manish K Shah

*Chemical Research Laboratory, Department of Chemistry Saurashtra University,
Rajkot – 360005(Gujarat), (India)*

ABSTRACT

New Tridentate ligands were prepared by the condensation of different hydrazine with substituted salicylaldehydes or different aromatic ketones, and their New synthesized metal complex are thermally stable and neither air- nor moisture-sensitive. Suzuki–Miyaura cross-coupling reaction is carried out in presence of various ligands and palladium salts, Different solvent/water ratio with different Base and studied effects its effect on the performance of the coupling reaction.

Keywords: *Palladium complex, N,N,O -Tridentate ligand, Suzuki-Miyaura cross-coupling reaction.*

I. INTRODUCTION

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.^[1-2] 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.^[3-10] 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.^[11-14] 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.^[15-20]

II. MATERIALS AND METHODS

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

2.1 General procedure for the synthesis of benzothiazole ligand

A solution of 1-(benzothiazol-2-yl)hydrazine (0.01 mole) and 5-Bromo salicylaldehyde refluxed in presence of glacial acetic acid (2 ml) at 60-65°C for 2 hour. The reaction is being monitored by TLC using

hexane:ethyl acetate (1:2). After completion of the reaction, the product mixture was poured into crushed ice. Light yellow ppt. fall out and Filtered out the separated solid product washed by dry ether and dried under reduced pressure.

2.2 Spectral data of ligands

BJ-14 :-

M.P. 184°C, **Elemental Analytical Calculation for $C_{14}H_{10}N_3OSBr$** (346.97 g/mol): C,48.29%; H,2.89%; N, 12.07%; O,4.59% ;Br, 22.59%; S, 9.21 **Found:** C, 48.20%; H, 2.44%; N,12.01%; O, 4.52%; Br, 22.50%; S, 9.18 %. **MS (m/z):** 348 (M^{+2}): **1H -NMR (DMSO- d_6):** δ_{ppm} ; 10.64, (s, 1H, -OH); 7.80-7.41 (d, 2H, Ar-H,); 7.40-6.89 (d, 5H, Ar-H,); 8.39(s, 1H,CH=N); 12.31 (s, 1H, -NH). **^{13}C -NMR (DMSO- d_6):** δ_{ppm} 166.86 (N=C-N); 155.53 (C-OH), 110.15 (C-Br), 132.93 (CH=N), 128.59,126.15,122.26,121.81,121.67,118.42 (10 C-Ar).**IR, (cm⁻¹):** ν (OH) 3176; ν (-NH) 2980; ν (N-N) 966,939; ν (Ar-C-H) 2989; ν (Ar-C=C) 1506; ν (C=N)1614.

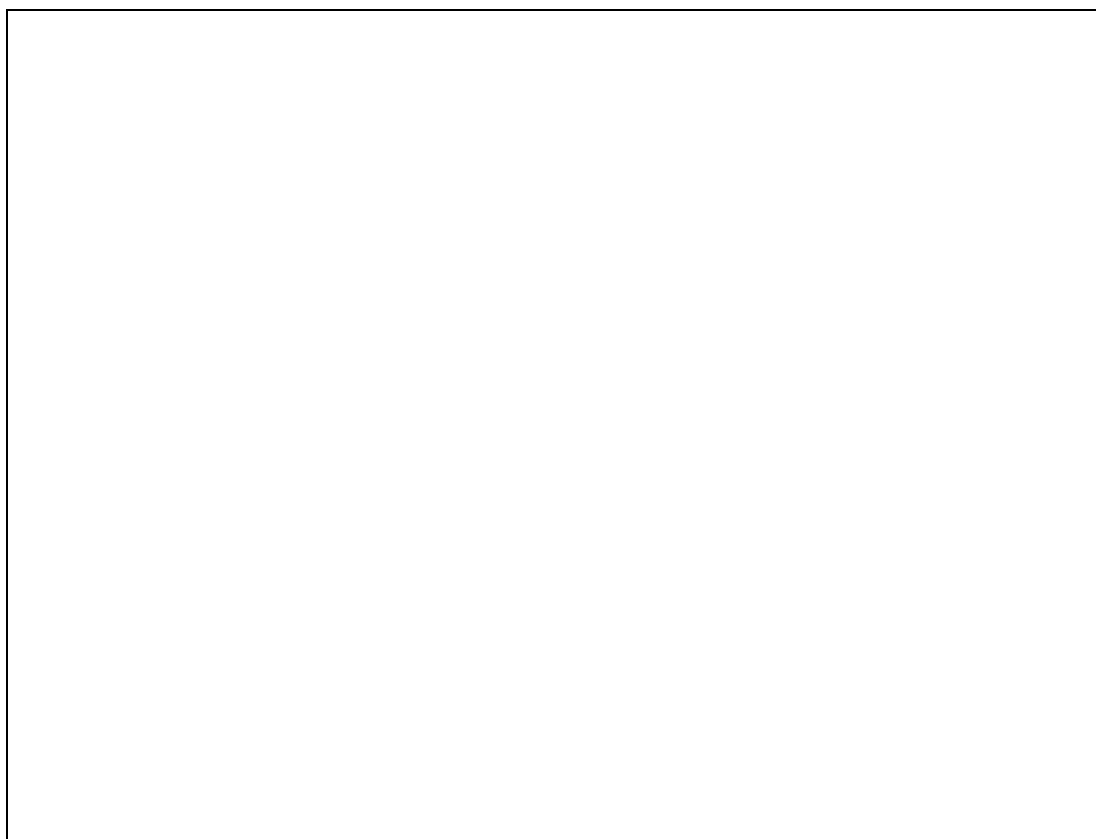


Fig.1 Reaction Scheme

2.3 Preparation of Metal Complexes

Pd(II) Coordination metal complexes were prepared by equamolar mixing of ligand in methanol and an aqueous solution of the corresponding metal chlorides in 1 : 1 molar ratio. The reaction mixture was refluxed for 2-3 hrs. The completion of the reaction was monitored by TLC. After completion of reaction 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.



Fig.2 Suzuki miyura cross coupling Reaction

Table-1. Suzuki-Miyaura cross-coupling reaction in presence of different ratio of Metal salt and ligand

No.	Ligand code	Ligand/ Metal Salts ratio	Pd Complex/ligand (substituted salicylaldehyde) Where R=	TIME	Yield %
1.	BJ-11	1:1	3,5-Dichloro	8 h	15%
2.	BJ-11	1:2	3,5-Dichloro	8 h	30%
3.	BJ-11	1:3	3,5-Dichloro	5 h	50%
4.	BJ-11	1:4	3,5-Dichloro	4 h	70%
5.	BJ-12	1:1	5-Bromo	7 h	20%
6.	BJ-12	1:2	5-Bromo	7 h	34%
7.	BJ-12	1:3	5-Bromo	5 h	52%
8.	BJ-12	1:4	5-Bromo	4 h	75%

Table-2 Suzuki-Miyaura cross-coupling reaction in presence of different solvent Ratio and Bases

No.	Solvent	Bases	Yield %
1.	Me-OH/H ₂ O (1:1)	Na ₂ CO ₃	65%
2.	Me-OH /H ₂ O (1:2)	Na ₂ CO ₃	50%
3.	Me-OH /H ₂ O (1:3)	Na ₂ CO ₃	26%
4.	Me-OH /H ₂ O (3:1)	Na ₂ CO ₃	75%
5.	Me-OH /H ₂ O (1:1)	K ₂ CO ₃	43%
6.	Me-OH /H ₂ O (1:1)	KOH	65%
7.	Me-OH /H ₂ O (1:1)	NaOH	70%
8.	Me-OH /H ₂ O (1:1)	NaOMe	28%
9.	Me-OH /H ₂ O (1:1)	Et ₃ -N	82%
10.	Et-OH /H ₂ O (1:1)	K ₂ CO ₃	53%

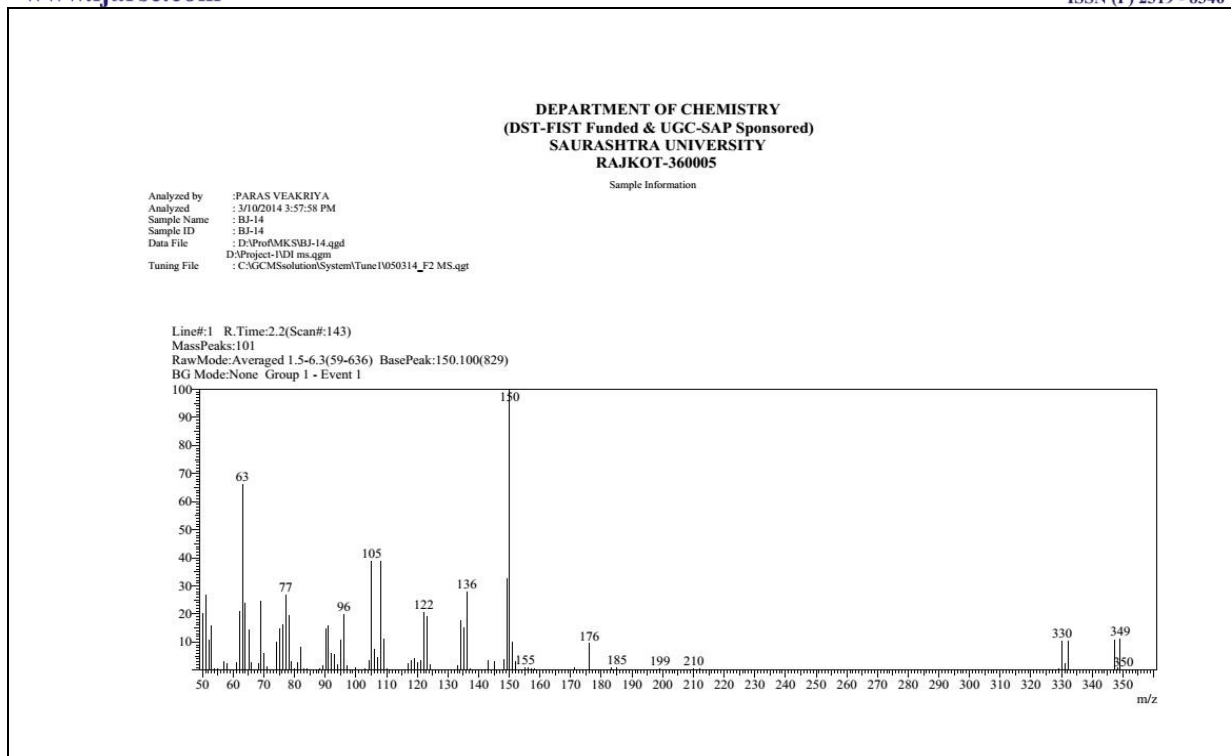


Fig.3 Mass spectrum of ligand BJ-14

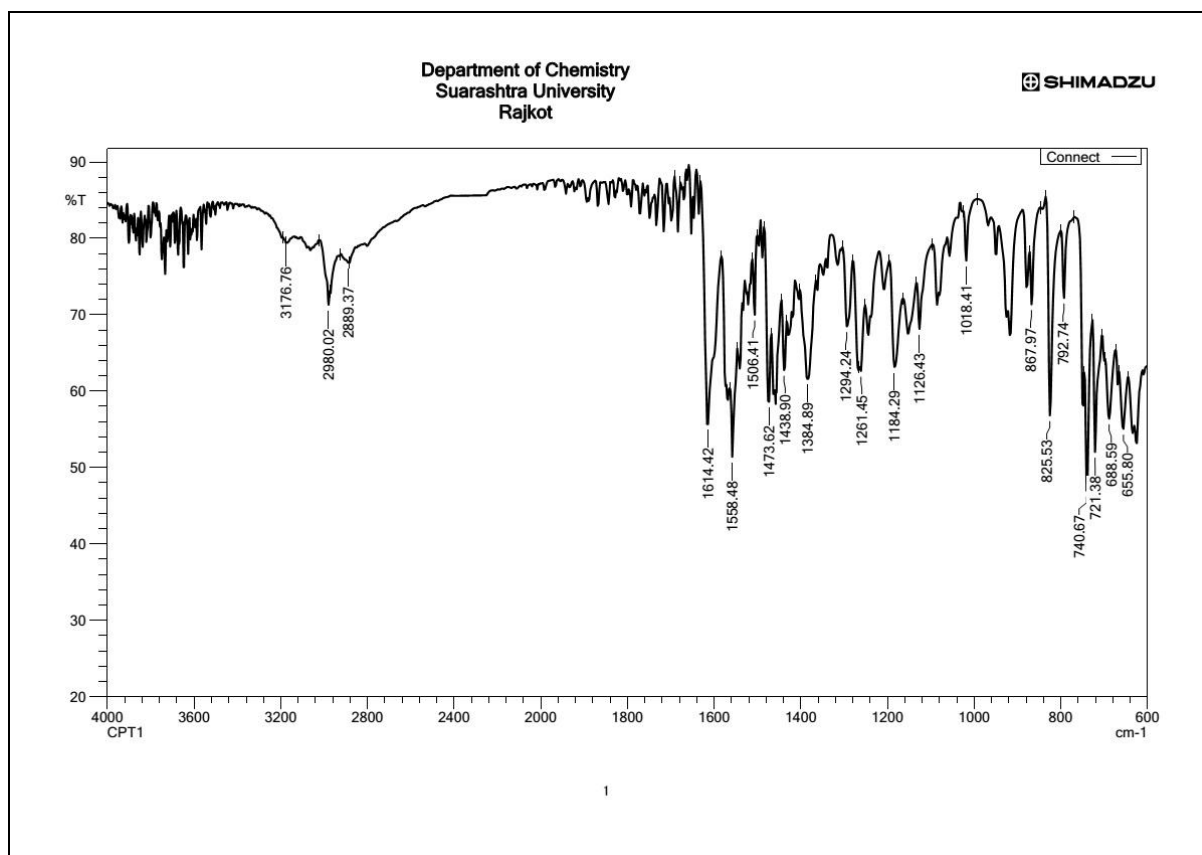
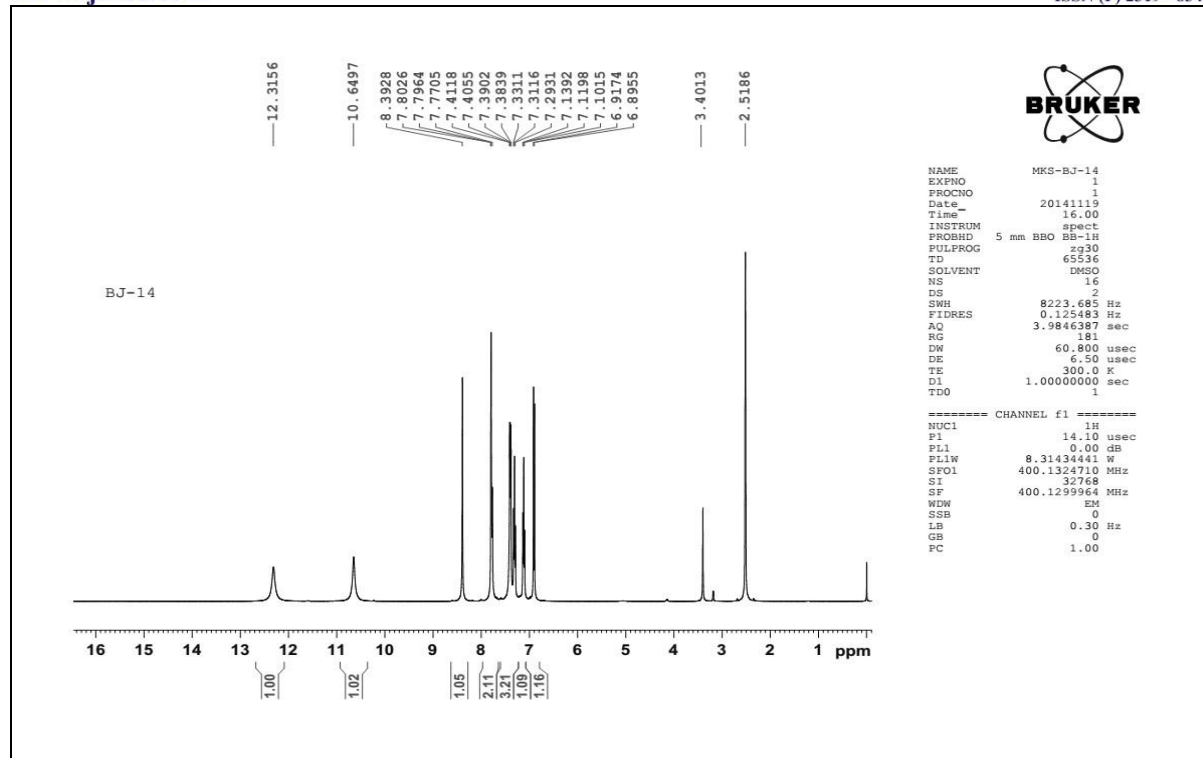
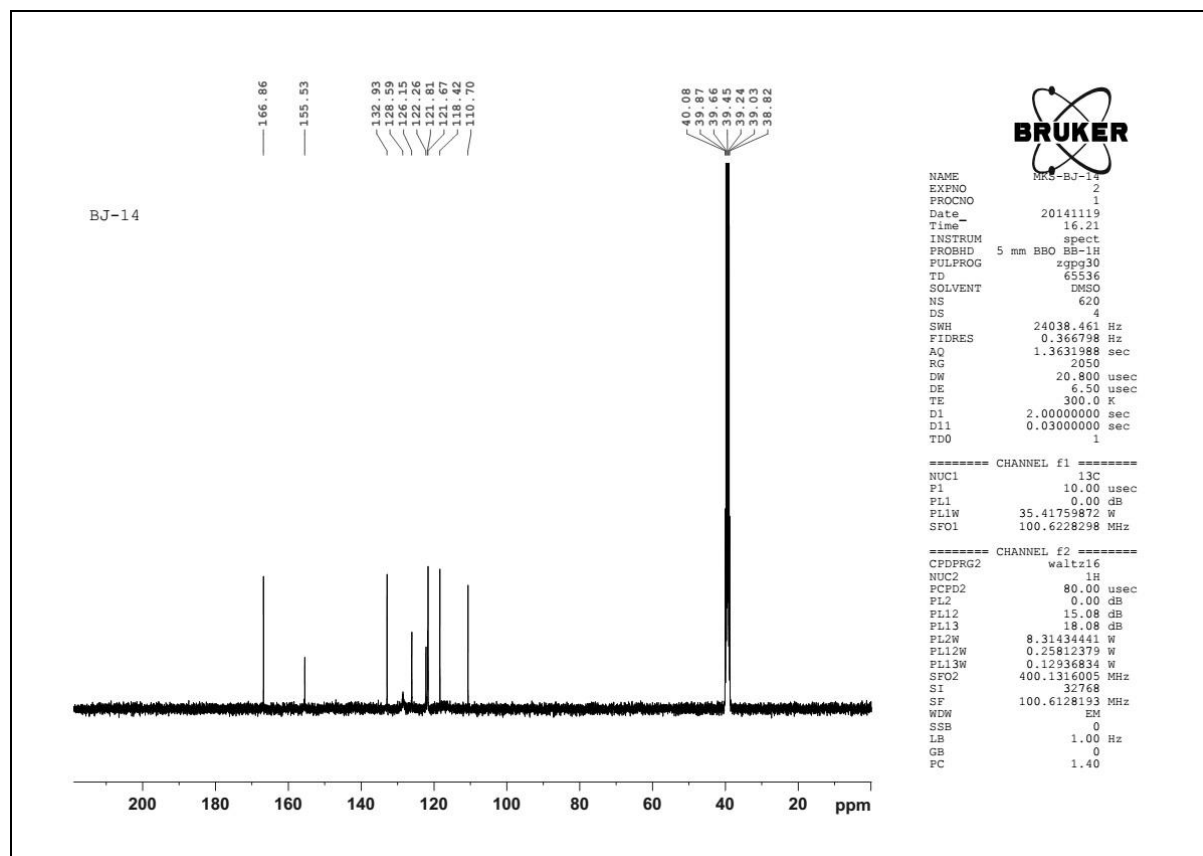


Fig.4 IR Spectra of Ligand


Fig.5 ¹H NMR spectra of Ligand

Fig.6 ¹³C NMR spectra of Ligand

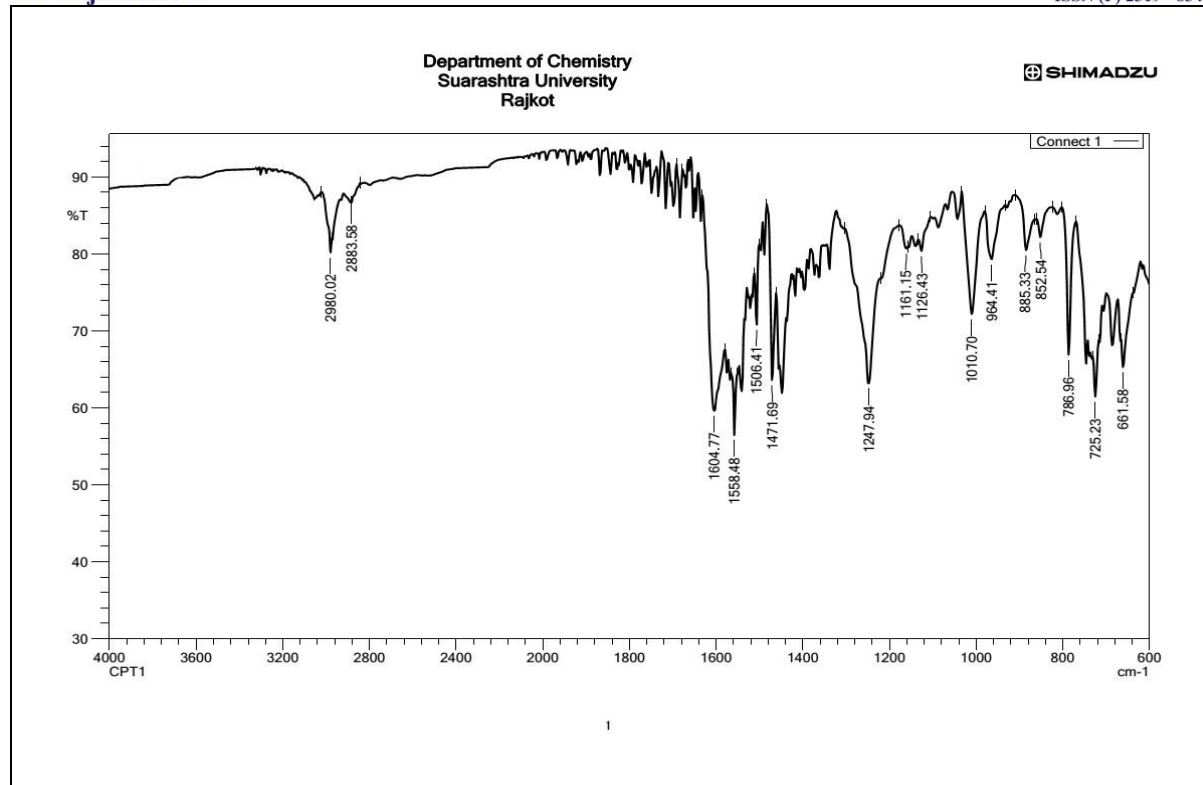


Fig.7 IR spectra of Metal Complex

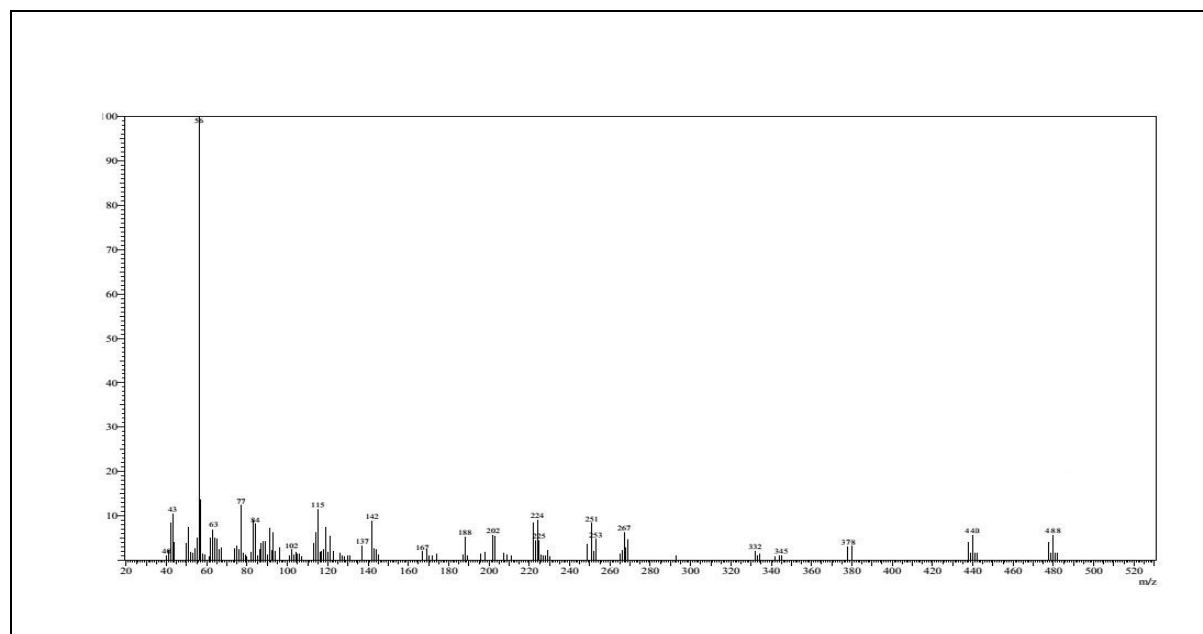


Fig.8 ESI-MASS Spectra of Metal complexes

III. RESULT AND DISCUSSION

Generally Suzuki cross-coupling is carried out in presence of Different Palladium salts and N_2 atmosphere, here we are used metal complex, various ligands and palladium salts, Different solvent/water ratio with different Base base in Suzuki cross coupling reaction and obtain good/moderate yield. Here we used many bases; in which triethylamine we got a good yield, as compared to other bases also same result obtain in metal salts and ligand ratio in which as metal salt ratio increase, yield also increase compare to low ratio metal salts.



IV. CONCLUSION

In this paper, benzothiazole metal complex has been synthesized and successfully used as a catalyst in Suzuki-miyaura 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-miyaura reaction, presence of triethylamine base has given excellent yield as compared to other bases, and also in metal salt/ligand ratio as metal complex ratio increase yield also increase.

V. ACKNOWLEDGMENT

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