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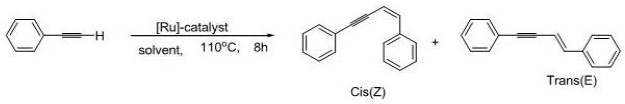
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Synthesis and NMR Characterization of the Cationic Ruthenium Complexes Catalysts for Organic Transformation to Control Over C-C and C-O Bond Formation Reactions

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Abstract:** The cationic ruthenium complexes, [Ru (PPh3)2(CH3CN) 3Cl],) (CH3CN) 2(PPh3)Cl]+, [Ru (dppp) 2(CH3CN) Cl]+ And [Ru(dppp)(CH3CN)2(PPh3)Cl]+ have been synthesized according to standard procedure. The complexes are used as catalysts for several types of organic transformation reactions such as demonization of terminal alkynes via C-C bond formation, addition of phenyl acetylene to 1,3-diketone via C-C bond formation and cinamylacetate-phenol coupling via C-O bond formation reactions. Yield of the products has been improved and stereo selectivity has been achieved by varying the reaction conditions such as solvent, temperature, reaction time and presence of acid and base etc. This is the stereo and regio- selective dimerization reaction of phenyl acetylene. In this reaction two isomer (cis & trans) 1,4 diphenyl-1-en-3-yne compound is formed at different ratio. In the laboratory, the synthesis of cationic ruthenium complexes having phosphate, dppe (1,2-bis biphenylphosphine ethane), dppp & labile acetonitrile legend has been reported. The complexes have been synthesized according to standard procedure. These complexes have been used as a catalysts for C-C, C-N, C-X (X = O, Br, I), C-H bond formation reaction in a single step, by which different organic molecules can be synthesized. In continuation of the previous work the aim of project was set. The aim of the present dissertation is control over C-C and C-O bond formation reactions. In the dissertation results of demonization reactions of phenyl acetylene, anti-Markonikov addition of alkynes with 1,3 dike tone compound and also the addition of phenol with cinamyl acetate, catalyzed by [Ru(dppp)2(CH3CN)(Cl)][BPh4] and [Ru(dppe)(CH3CN)2(PPh3)(Cl)][BPh4] complexes has been described.



***Keywords:** Ru-cationic complexes, regio- and stereo selective enyne, ruthenium-carbene, monoen-yne, column chromatography,*

I. INTRODUCTION

Organ metallic chemistry is the chemistry of compounds containing Metal-Carbon bond. Research in the area of catalysis is fuelled by the fact that organ metallic compounds can be employed as catalysts. The substances that cause the decomposition of H2O2 do not achieve this goal by being incorporated into the new compounds (H_2O and O_2) ; in each case they remain unchanged and hence act by means of an inherent force whose nature is still unknown So long as the nature of the new force remains hidden, it will help our researchers and discussions about it if we have a special name for it. We hence will name it as the catalytic force of the substances, and we will name decomposition by this force catalysis. The catalytic force is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are slumbering in molecules at a given temperature." - Berzelius, 1836. A catalyst is a substance that accelerates the rate of a chemical reaction without being

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consumed in the reaction i.e. it remains unchanged after the end of the reaction. A catalyst opens a new reaction path, which has much lower activation energy than the unanalyzed reaction and thus enhances the rate of the reaction as shown in figure – 1.

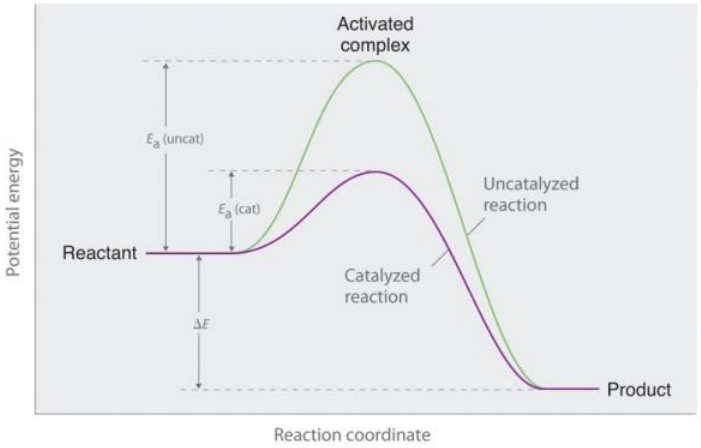


Figure - 1

Catalysis is one of the most important applications of Organo metallic Chemistry and is an emerging field in the research. The application of Catalysis is reflected in the rapid development of the whole area (Research, Industrial etc. field).Catalysis is of two types – i). Homogeneous Catalysis: catalyst and reactant(s) are in same phase. ii). Heterogeneous Catalysis: catalyst and reactant(s) are in different phases. At first, the substrates bind to the metal centre of the catalyst. Then the reaction takes place between them and leads to metal-products complex via metal-intermediate species. Finally, the Product is formed from M-P Complex and active catalyst regenerated. In organ metallic and co-ordination chemistry, common with other platinum metals, ruthenium is an important metal ion for catalysis. Hundreds of ruthenium complexes have been reported synthesized from the common precursor RuCl3.nH2O. These ruthenium complexes contain regular or distorted six-coordinated octahedral or four coordinated tetrahedral (RuO4) geometry. Large numbers of well-defined and stable ruthenium recitalists show catalytic activities which tolerate functional groups for a wide range of chemical transformation reaction. Since, ruthenium has d8 outer electronic configuration, it shows variable oxidation states (from -2 to +8) and several different coordination geometries that enable ruthenium complexes to become effective catalyst for various organic transformation reaction. Ruthenium complexes have number of commercial application and other uses as they show a variety of useful characteristics including high electron transfer ability, high Lewis acidity, low redox potentials and stabilities of reactive species such as π-ally ruthenium, ruthenium-carbine etc. Ruthenium complexes with nitrogen and phosphorus donor atoms are largely formed by the ruthenium in (+2) and (+3) oxidation states, which included ammonia ligands, aromatic amine ligands, pyridine ligands, nitrosyl, triphenyl phosphine ligands, dppp(1,2-bis-3 biphenylphosphine propane) ligands etc. Among this ligand containing ruthenium metal complexes, some of the complex is cultured due to MLCT (t2g to π*). Active ruthenium complexes have promoted several original activation processes and are able to provide various non classical activation modes. Ruthenium complexes are used in several reactions like metathesis,3, C-H activation,4 hydration,5 cycloaddition reaction,6 eons ester synthesis,7 hydrogen transfer8, C-O bond formation reaction9 etc. Among all these reaction C-C bond formation and carbon –heteroatom bond formation reactions are important for various organic compound syntheses in a single step. Apart from the catalytic activities, studies on energy transfer properties10 and site-specific interaction with DNA11 of ruthenium complexes have received much attention. In addition, the medicinal efficacy of ruthenium compounds is now being recognized and ruthenium anticancer agents have recently entered the clinical trial and some of the compounds have been found to have promising activity on resistant tumour. Alkyne cycloaddition, C-C bond formation and polymerisation is a useful method of polymer synthesis & also different organic molecule synthesis using transition metal catalyzed dimerisation or cycloaddition of monoyne compounds as a polymer forming elementary reaction. Therefore we are interested in the formation reaction effected by an easily accessible transition metal catalyst. The activation of carbon-carbon multiple bond through coordination by transition metal catalyst is one of the most interesting and important subjects in organic chemistry. In recent years many organic molecular transformations was done through activation of terminal alkynes by metal catalyst. The most preferred activation process of terminal alkynes into vinylidenes proceeds by η2-coordination of the triple bond then 1,2-H migration, or alkyl metal intermediate via oxidation of alkyne C(sp)-H bond, which rearrange through 1,3-hydrogen migration or by protonation. The control of the region- and stereoselective is the major challenge encountered while performing catalytic dimerization reaction of terminal alkynes. This stero selective

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dimerisation takes place either by Markovnikov's (via π-alkyne coordination) or anti-Markovnikov's addition (via metal vinylidene complex) as depicted below. Various ruthenium complexes have been shown to be active catalyst for the dimerization of terminal alkynes to form disubstituted enzyme compounds. This reaction, which is of potential synthetic utility, involves C-H activation and satisfies the criteria of "atom economy", where one substrate is converted into dissymmetric species. The main concern is still region selectivity either head to head or head to tail substitution, and to competitive formation of two stereo isomers. Significant progress regarding the catalytic efficiency has been made on the use of dentate phosphine, phosphine ligand containing ruthenium complex.as shown in figure– 2

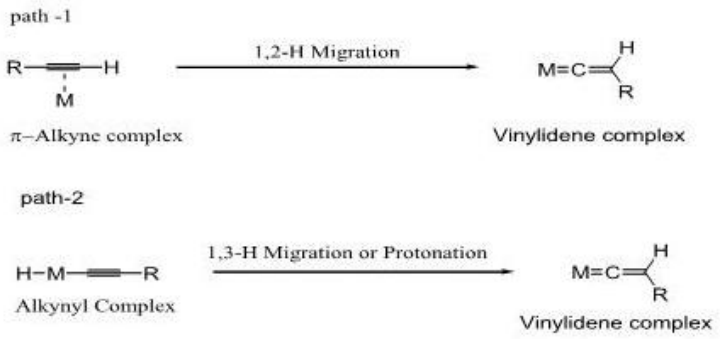


Figure – 2 Activation of terminal alkyne by transition Metal complex

II. EXPERIMENTAL PROCEDURE

The chemicals and solvents used were commercial grade. All the 1H and 13C NMR spectra were recorded in CDCl3 or D2O using TMS as a standard in a Bruker AVANCE (1H frequency = 200 MHz & 400 MHz) NMR spectrometer.

A. Preparation of RuCl2 (PPh3)3

The compound was prepared by literature method describe below Hydrated RuCl3.nH2O (1.0g, 3.8mmol) was dissolved in 25 ml methanol and then the reddish brown solution was refluxed for five minutes under argon. After cooling an excess of triphenylphosphine (7.0g, 26.83mmol) was added. Then the reaction mixture again refluxed for about 3 hrs. The shiny black crystal of Ru(PPh3)3Cl2 were obtained which were filtered and washed with ether and dried under vacuum. [Yield =2.7g, (74%)] Figure – 3

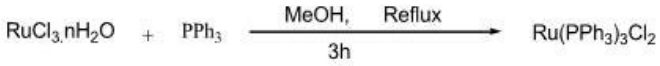


Figure - 3

B. Preparation of Ru(dppe)(PPh3)(CH3CN)2Cl][BPh4](Cat-2)

The complex was prepared by literature method describe below. RuCl2 (PPh3)3 (1.8g, 2.1mmol) and 1,2-bis-iphenylphosphinoethane (0.84g, 2.1mmol) were dissolved in acetonitrile (10ml) and was refluxed for 7hrs. An excess of NaBPh4 (0.85g, 2.5mmol) was added and again refluxed for 1hrs. The solution turned brown to light yellow. The resulting solution was filtered and was concentrated over a water bath. After 2-3 h on cooling to room temperature a yellow crystalline solid separated out. The separated solid was washed with hexane and dried over vacuum. The compound was finally recrystallized from acetonitrile solvent. Yield: 2.01g (80%) as shown in.figure - 4

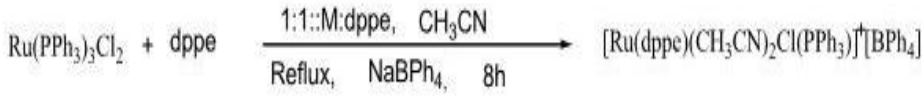


Figure - 4

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C. Preparation Of [Ru (dppp)2(CH3CN)Cl][BPh4](Cat-3)

This catalyst was synthesized according to standard procedure. RuCl2(PPh3)3 (1.8g,2.1mmol) and dppp ligand(1.67g,4.2mmol) were dissolved in acetonitrile solvent(10ml). Then the solution was refluxed for 7hrs. Then an excess of NaBPh4 (0.85g, 2.5mmol) was added and refluxed for 1hrs. The solution turned brown to light yellow with a white precipitate. The resulting solution was then filtered and was concentrated over water bath. After 2-3hr, on cooling to room temperature a yellow crystalline solid separated out. The separated solid was filtered and washed with hexane and dried over vacuum. The compound was finally recrystallized from acetonitrile. Yield: 2.3g(85%).Figure – 5

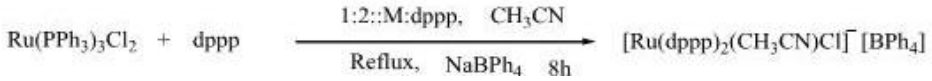


Figure - 5

D. Dimerization Reaction Of Terminal Alkynes

The catalyst (1 mol %) in 3-4 ml solvent (toluene, DMF) was placed in a round-bottom flask and the alkyne (1 moms, 110µL) was added. The mixture was refluxed for 10-12 hour at 110 □C with stirring in an oil bath. After completion (checking by TLC), the reaction mixture was cooled to room temperature. Then the solvent and the other volatile components were removed in vacuum. The resulting products were purified by column chromatography as shown inFigure - 6

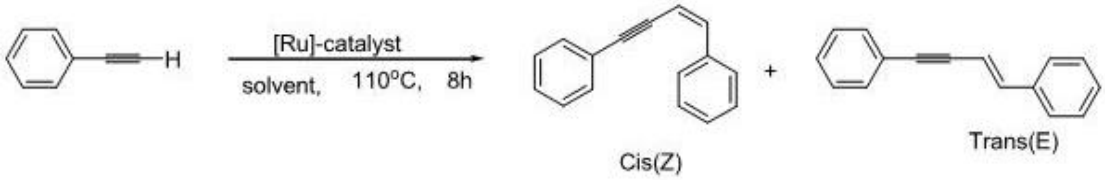


Figure - 6

E. C-O Bond Formation Reaction Procedure

The C-O bond formation reaction was done by reaction of cinnamyl acetate with phenol in presence of catalyst-3. For this reaction, at first catayst-3 (3mol %) and K2CO3 (0.207g, 1.5mmol) was taken in a round bottomed flask and dissolved in 5ml THF. Then cinamyl acetate (0.5mmol, 84µL) and phenol (0.5mmol, 44µL) was added and refluxed for 36 hours continuously in an oil bath at 70^0 temperature. After completion the reaction mixture was cooled in room temperature and the solvent was removed from the reaction mixture by vacuum. The product was separated through column chromatography. Yield: 15%.As shown in fig 7

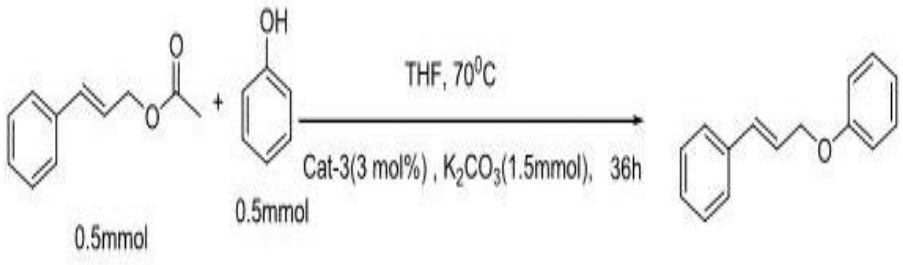


Figure - 7

F. C-C bond formation reaction procedure

At first catalyst-3 (3mol%) was dissolved in 4ml toluene placed in a round bottomed flask and then acetyl acetone (0.5mmol, 52µL) and phenyl acetylene(1mmol, 110 µL) was added. Then the mixture was refluxed for 30 hours at 110^0 c temperature with continuous stirring in an oil-bath. As shown in Fig – 8

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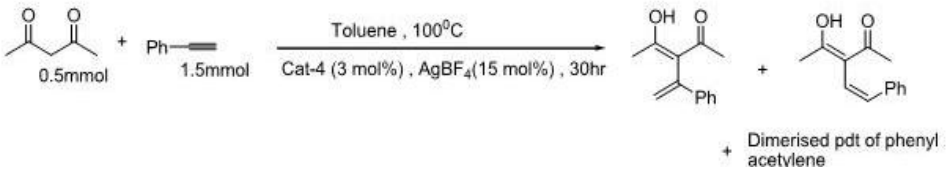


Figure – 8

After completion of the reaction mixture was cooled in room temperature and product was separated through column Chromatography and then 1HNMR was recorded. The reaction mechanism from reactantto productis shown, In This medium of the reaction Dimerised pdt of phenyl acetylene also found as product. From this reaction mechanism we found that c-c is formationis take place.

III. RESULT AND DISCUSSION

Reactant (alkyne)	Catalyst	Solvent	Temp (℃)	Time (h)	Acid/Base	Yield (%)	Cis: Trans
Phenyl acetylene Ph—≡—H	Cat-1	toluene	110	12	Na_2CO_3	65	85:15
Phenyl acetylene	Without cat-1	toluene	110	24	Na_2CO_3	-	-
Phenyl acetylene	Cat-1	toluene	110	12	Na_2CO_3 & PhCOOH	60	95:5
1-octayne	Cat-1	toluene	110	9	Na_2CO_3	-	-
1-hexyne (5mmol)	Cat-1	toluene	110	7	Na_2CO_3	-	-
Phenyl acetylene	Cat-2	toluene	90	12	2,3-dimethyl pyrazole	75	90:1
Phenyl acetylene	Cat-3	toluene	90	12	Na_2CO_3 & PhCOOH	68	33:7
p-Flouro-Phenyl acetylene	Cat-3	toluene	110	12	Na_2CO_3 & PhCOOH	70	13:8
Phenyl acetylene	Cat-3	toluene	110	12	Cinamic acid	65	25:7
Phenyl acetylene	Cat-3	toluene	110	7	TMEDA (0.7mmol)	60	75:2
Phenyl acetylene	Cat-4	THF	65	12	NaOH	64	55:3
Phenyl acetylene	Cat-4	toluene DMF	110	24	-	69	15:8

Table – 1 :Here cat-1= [Ru(PPh3)2(CH3CN)3Cl]+, cat-2 = [Ru(dppe)(CH3CN)2(PPh3)Cl]+, cat-3 =[Ru(dppp)2(CH3CN)Cl]+, cat-4 =[Ru(dppp)(CH3CN)2(PPh3)Cl]+, reactant- phenyl acetylene(1mmol), catalyst(1mol%), solvent-3 to 4ml, acid/base –Na2CO3 or PhCOOH (1mmol) or cinamic acid (8mol%), continuous stirring in an oil bath.

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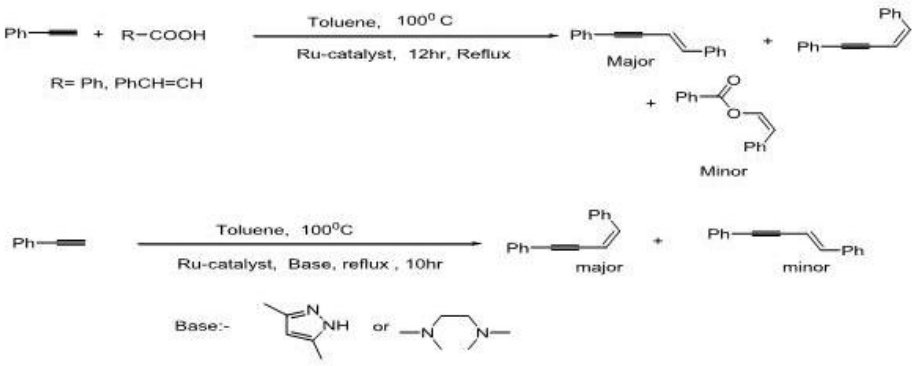


Figure - 9

A. Dimerization Reaction

Dimerization of phenyl acetylene takes place in presence of different ligand containing Ru-cationic complexes. The Ru-metal cationic complex shows regio-selective catalytic property due to the presence of bidentate ligand and PPh3 as well as labile, CH3CN ligand. The results have been given in the above table 1 and complete reaction mechanism is shown in fig 9. It is observed that cis isomer is formed in major amount in presence of Na2CO3 base and cat-1. Similarly Tran's isomer is formed in the presence of acid (as like benzoic acid or cinnamic acid) by bidentate ligand containing metal catalyst. In presence of PhCOOH, Tran's product is the major product and this may be due to the co-ordination of carboxylic group with metal centre. When we used bidentate ligand catalyst (cat-2, cat-3 etc) the stereo selectivity of product and yield also increases. This may be due to π complex formation by the metal. For dimerization reaction when cinnamic acid is used, then cinnamic-ester is formed as a side product. In this dimerization reaction we did not get 100% yield which may be due to the volatile nature of alkyne and also formation of some side product. The aliphatic terminal alkynes do not undergo dimerization reaction by above catalyst. The possible mechanism of dimerization has been shown belowin Figure - 10

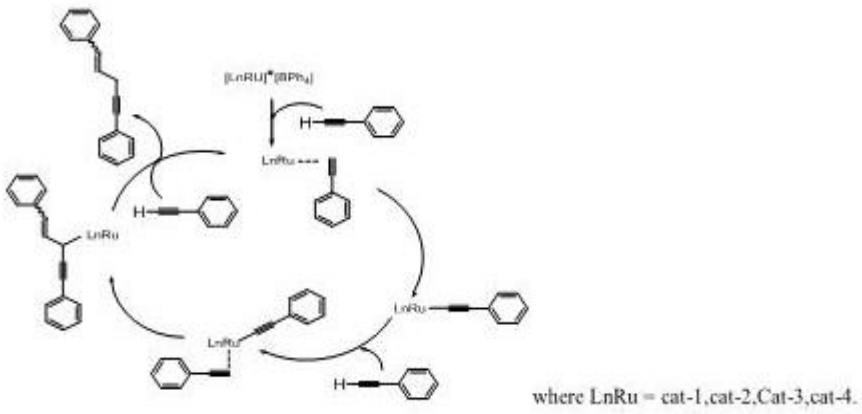


Figure - 10

In the above mentioned C-O bond formation reaction, reaction between Cinnamyl acetate and phenol produce (E)-(cinnamyloxy) benzene. The yield of the reaction is very low due to presence of two 1, 2-bis biphenyl phosphino propane(dppp) ligand. In the above mentioned C-C bond formation reaction between the acetyl acetone and phenyl acetylene produce Markonikov's addition product (major) and anti-Markonikov' addition product form very minor amount. In this reaction dimerization product of phenyl acetylene is formed as a side product.

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B. NMR Data's Of Dimerised Products

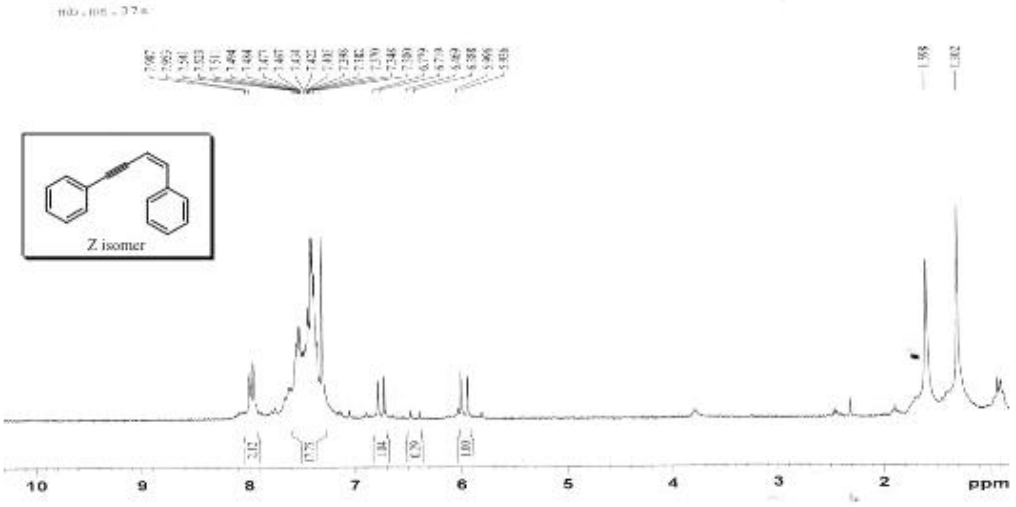


Figure – 11 This is the 1H NMR (CDCl3) in 200MHz of reaction-1.Where the δ values are 5.9(d, 1H, J = 10.0 Hz), 6.7(d, 1H, J = 12 Hz), 7.9(d, 2H, J = 6.8 Hz), 7.3-7.5(m, 8H,)

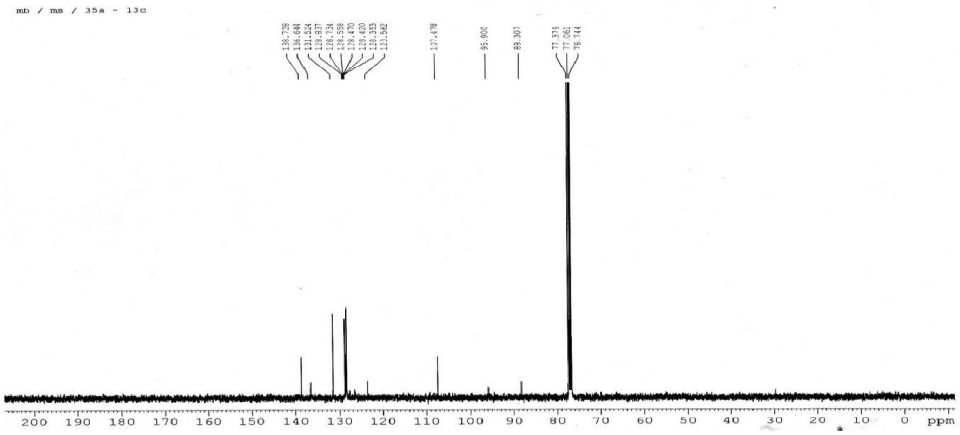
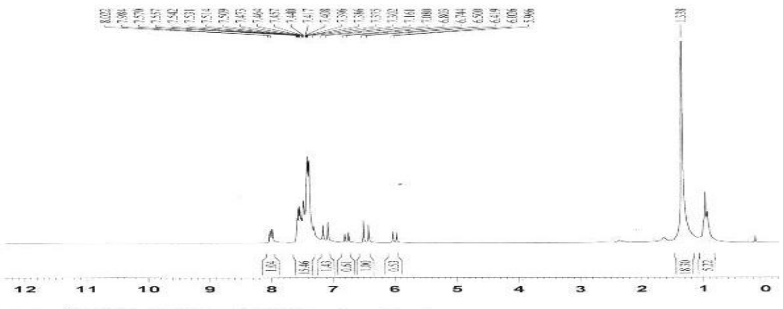


Figure – 12 his is 13C NMR (CDCl3) in 400MHz of reaction-3. Where δ values are 138.7, 136.6, 131.5, 128.8, 128.7, 128.5, 128.47, 128.3, 123.5, 107.4, 95.9, 88.3



This is the ^{1}H NMR ($CDCl_3$) in 200 MHz of reaction-9.

Figure – 13

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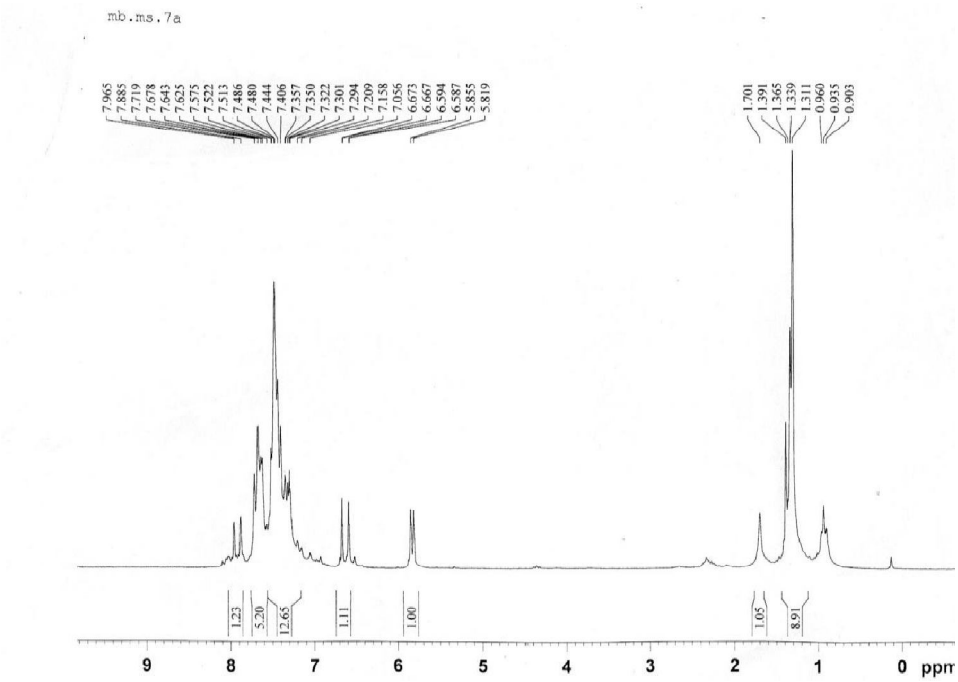


Figure – 14 This is the 1H NMR (CDCl3) in 200MHz of reaction-9.This is the NMR of side product (ester compound of above reaction). Where the δ values are 5.8(d, 1H, J = 7.2 Hz), 6.6(d, 1H, J = 14 Hz), 7.9(d, 1H, J = 16 Hz), 7.0-7.7(m, 11H).

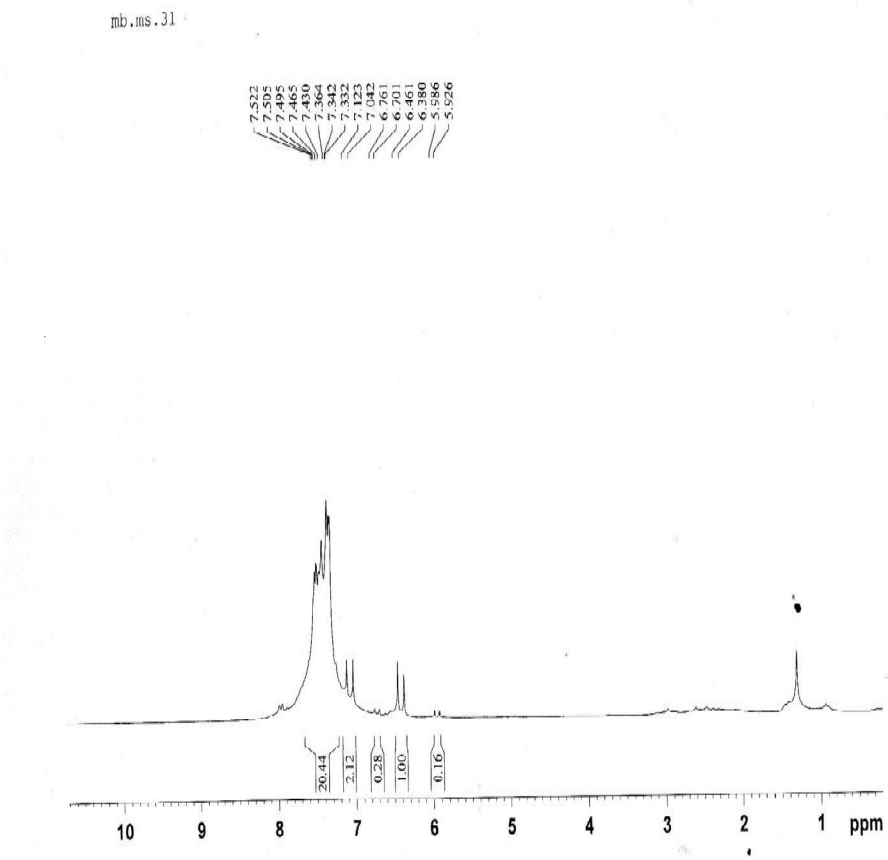


Figure – 15This is the 1H NMR (CDCl3) in 200 MHz of reaction-11. Where the δ values are 6.4 (d, 1H, J = 16 Hz), 7.2 (d, 1H, J = 16 Hz), 7.3-7.5(m, 10H).

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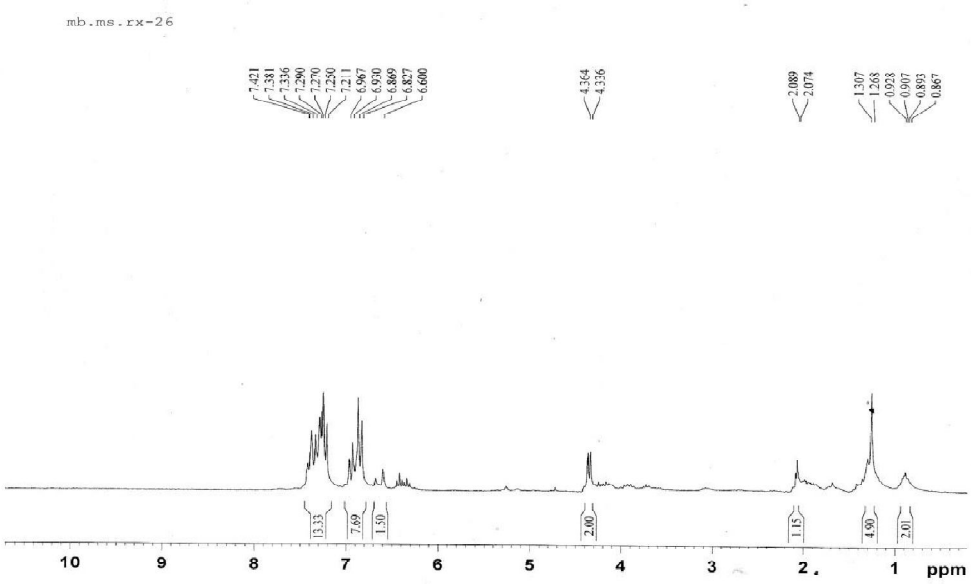


Figure – 16 this is the 1H NMR (CDCl3) in 200MHz of the above C-O bond formation reaction. Where the δ values are 4.7(d, 2H, J = 6.2 Hz), 6.28(m, 1H), 6.6(d, 1H, J = 15.9 Hz), 6.9(d, 2H, J =8.0 Hz), 7.1-7.4(m, 8H)

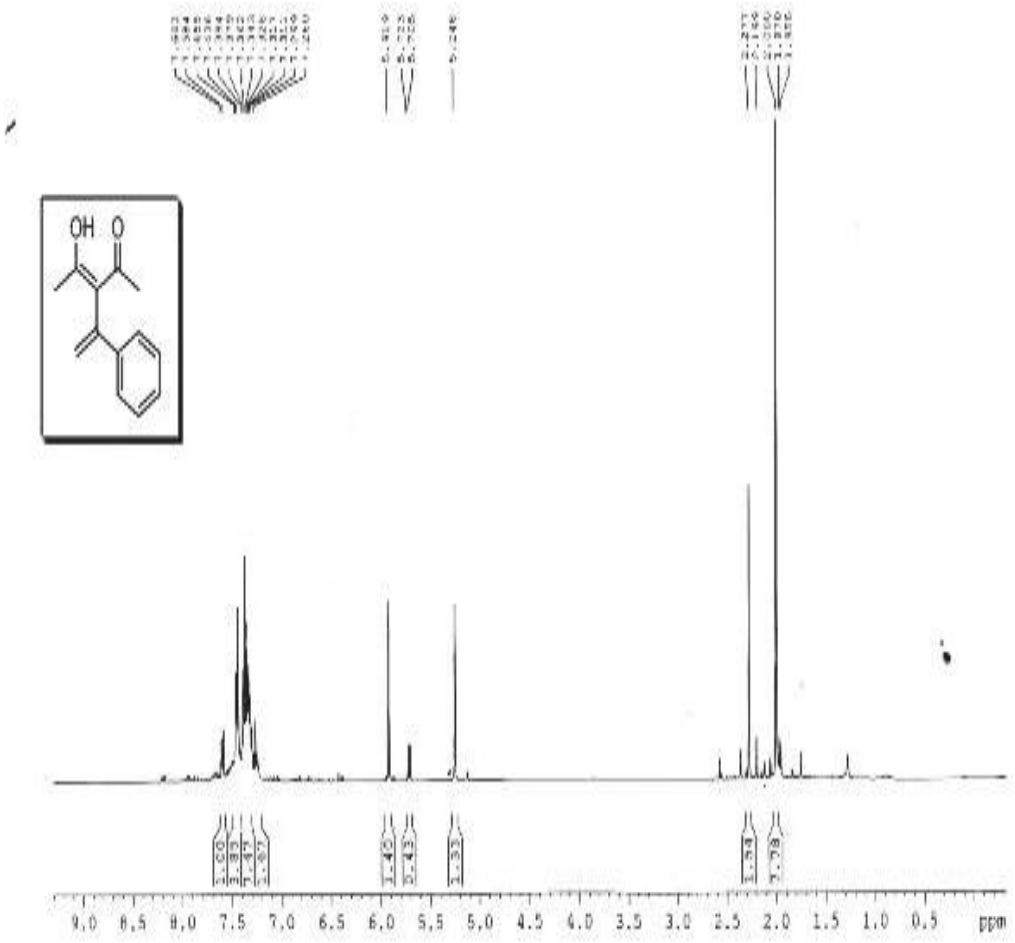


Figure – 17This is the 1H NMR (CDCl3) in 400MHz. Where theδvalues are 1.9(s, 6H), 5.2(d, 1H), 5.9(d, 1H), 7.2-7.6 (m, 5H).

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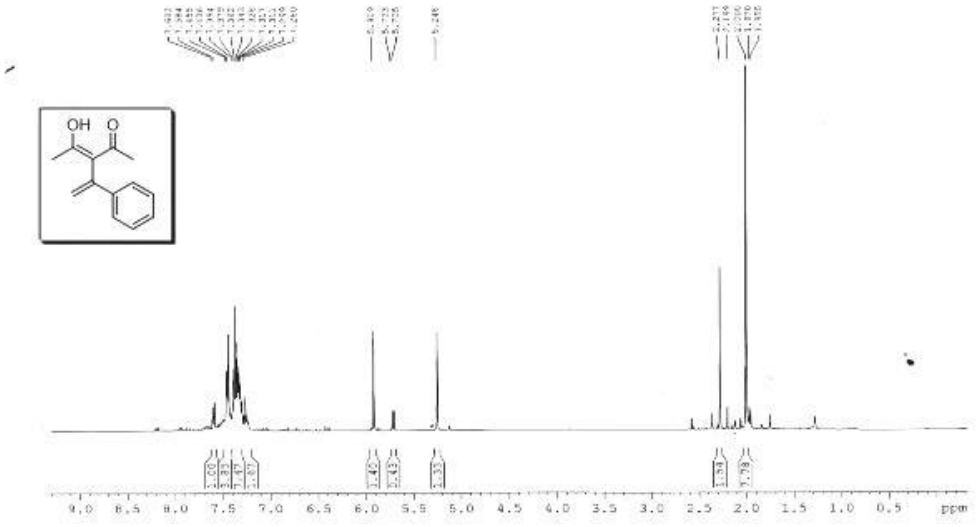


Figure – 18 This is the 13C NMR (CDCl3) of the above compound. Where the δ values are 190.6, 166.8, 142.9, 139.5, 128.6, 127.6, 126.0, 125.6, 117.7, 113.2, 111.2, 22.9, 20.2.

IV. CONSULTATION

We report here the implementation of chemical reaction method in the laboratory atmosphere with extensive studies to achieve repeatability and structure optimization. We have successfully synthesized Ru-cationic complexes and using this complex we have performed the dimerization reaction of terminal alkynes. In this addition reaction catalyst loading is low, though the yield of the reaction is quite good. Use of acid or base along with the catalyst helps in formation of regions- and stereo selective enzymes compounds. In future, we will try to synthesis more Ruthenium catalyst and will perform various type of organic reactions catalyzed by Ru (II)-complexes. Further studies on the optical properties of the Ru-cationic complexes agree well with the standard reported data. We want to extend the addition reaction of phenyl acetylene with diketone. We are also interested in carbon-heteroatom bond along with C-C bond formation reaction using metal catalyst.

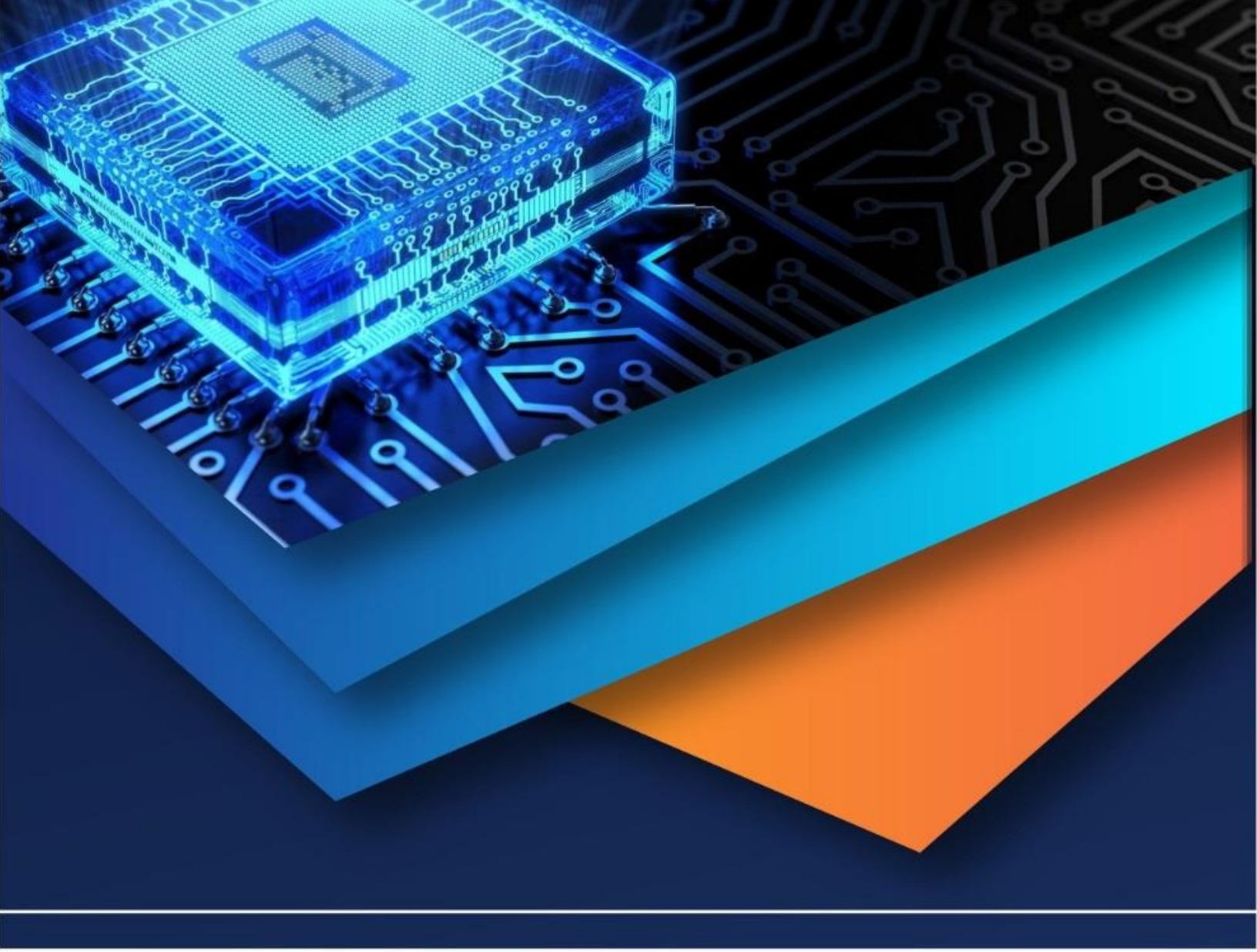
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