DESIGN, SYNTHESIS AND CHARACTERIZATION OF 1,2,3-TRIAZOLE BASED COMPOUNDS

M.Sc. Thesis

By

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DISCIPLINE OF CHEMISTRY

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DESIGN, SYNTHESIS AND CHARACTERIZATION OF 1,2,3-TRIAZOLE BASED COMPOUNDS

A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

of

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by

DONDINATH DEORI

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DESIGN, SYNTHESIS AND CHARACTERIZATION OF 1,2,3-TRIAZOLE BASED COMPOUNDS** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my own work carried out during the time period from July 2016 to June 2018. Thesis submission under the supervision of Dr. Shaikh M. Mobin, Associate professor, IIT 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.

Signature of the student with date

(DONDINATH DEORI)

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

Signature of the Supervisor with date

Dr. Shaikh M. Mobin

DONDINATH DEORI has successfully given his/her M.Sc. Oral Examination held on ……...

Signature of the thesis Supervisor
Date:

Convener, DPGC
Date:

Signature of PSPC Member
Date:

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Date:

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This thesis is the end of my trip to the master's degree. This thesis has been revised on how to complement the support and encouragement of many people including my friends, friends, colleagues and various institutions. At the end of my thesis, it is a pleasant task to express my thanks to all those who have contributed in many ways to the success of this study and I made it an unforgettable experience for me. First and foremost I wish to thank my advisor, Dr. Shaikh M. Mobin. He has been supportive since the days I began working on the lab. Who has reviewed a draft of my text provides important suggestions and asks difficult questions. His knowledge, his valuable advice, his constant motivation, affectionate attitude, understanding, patience and good criticism have greatly improved my experience. Without continuous inspiration, this study could not be completed.

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Dondinath Deori

DEDICATED TO MY BELOVED FAMILY

Abstract

The work described in this thesis concerns the synthesis of series of novel 1,2,3-triazole based compounds. The triazole based compounds 4-(4-ethynylphenyl)-1-methyl-1H-1,2,3-triazole (L1), 4,4'-(5'-(4-(1-propyl-1H-1,2,3-triazol-4-yl)phenyl)-[1,1':3',1"-terphenyl]-4,4"-diyl)bis(1-propyl-1H-1,2,3-triazole) (L2) and 1,3,5-tris(1-(pyridin-3-ylmethyl)-1H-1,2,3-triazol-4-yl)benzene (L3) were synthesized by Cu(I)-catalyzed azide alkyne cycloadditon reaction (Known as click reaction) of 1,4-diethynyl benzene with methyliodide, 4,4"-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1"-terphenyl with 1-bromopropane and 1,3,5-triethynylbenzene with 2-(bromomethyl)pyridine in presence of sodium azide respectively. This compounds have been characterized by NMR spectroscopy and Mass spectrometry.

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NOMENCLATURE

D	Debye
π	Pi
δ	delta
gm	Gram
v	Volume
%	percentage
mmol	Milimol

ACRONYMS

N	Nitrogen
P	Phosphorus
S	Sulphur
O	Oxygen
C	Carbon
H	Hydrogen
Ph	Phenyl
Cu	Copper
Pd	Palladium
DMSO	Dimethyl Sulphoxide
Br	Bromine
I	Iodide
MeOH	Methanol
ESI-MS	Electron Spray Ionization - Mass Spectrometry
NMR	Nuclear Magnetic Resonance

Chapter 1

Introduction

1.1 General Introduction and Literature Background

Chemistry, traditionally being the science of synthesis and structural manipulations of molecules, has gradually undertaken the more challenging task of biology-oriented synthesis. The 1,2,3-triazole offers several N-coordination modes including coordination via anionic and cationic nitrogen donors of triazolate and triazolium ions, respectively. After CH-deprotection of the triazole and the triazolium, powerful carbanionic and mesoionic carbine donors, respectively become a subject of interest in organometallic chemistry [1]. Due to this structural and functional diversity of 1,2,3-triazole scaffold, over the past decades the chemistry of 1,2,3-triazole based compounds has been a subject of interest. Many papers and reviews were published concerning the use of triazole derivatives in medicinal and organometallic chemistry.

1,2,3-triazole based compounds are stable to hydrolysis in acidic and basic conditions as well as to oxidation and reduction, which indicates their high aromatic stabilization. 1,2,3-triazoles are able to participate actively in hydrogen bond formation as well as dipole-dipole, van der Waals force, hydrogen bonds, ion-dipole, cation-π, π- π stacking interactions [2] and also they have a high dipole moment (about 5 D) [3], which endows them in binding easily with the biological targets and metal ions and also form supramolecular aggregate.

1.2 General preparation

The 1,2,3-triazole preparation was discovered in the dawn of 20th century, but it didn't gain much attention until the 1960s when Huisgen et al explored the reaction and unveil the reaction mechanism [4-5]. Despite the high versatility of this reaction, it has several disadvantages, such as the

requirement of heating and a long reaction time for completion, lack of product selectivity. It gives the 1,4- and 1,5-linked regioisomers which are difficult to separate by classical chromatographic techinques. The reaction scheme is as shown in the Figure 1.1.

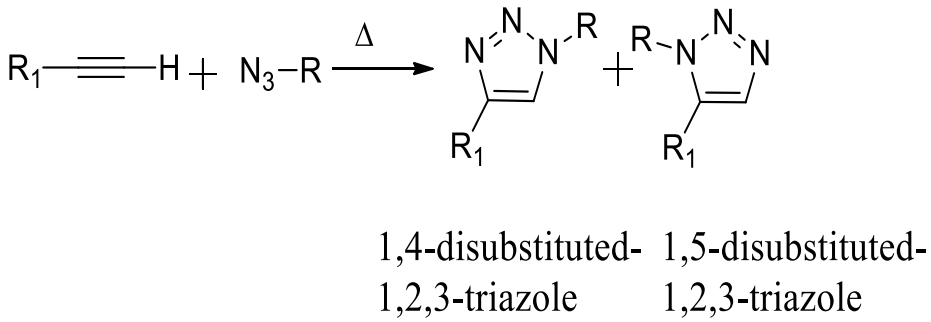

Figure 1.1 *Huisgen's 1,3-cycloaddition reaction.*

In 2002, the Meldal et al and Sharpless et al brought the ability of Cu(I) salt in accelerating this reaction at moderate temperature with higher regioselectivity of 1,4-disubstituted-1,2,3-triazole over 1,5-disubstituted-1,2,3-triazole. And this Cu(I)-catalyzed azide alkyne cycloaddition reaction (CuAAC) between azides and terminal alkynes as shown in the Figure 1.4 referred to as a "click chemistry" [6] reaction. This reaction has an extremely high application potential due to the comparatively very facile functionalization of organic moiety with azides and alkynes which remain unaffected throughout subsequent transformations in the presence of immensely functionalized biomolecules, molecular oxygen, water, and other common synthesis conditions.

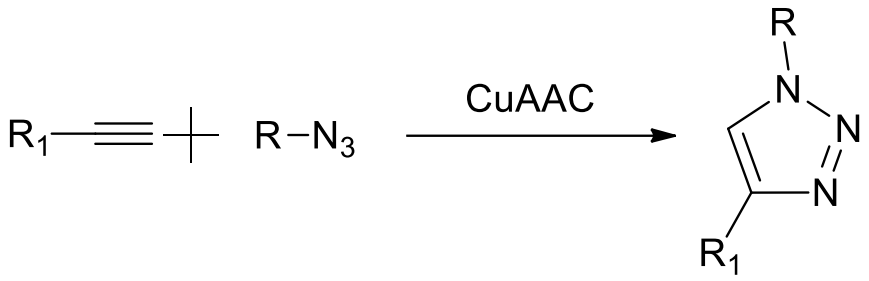

Figure 1.2 *Cu(I)-catalyzed azide alkyne cycloaddition reaction.*

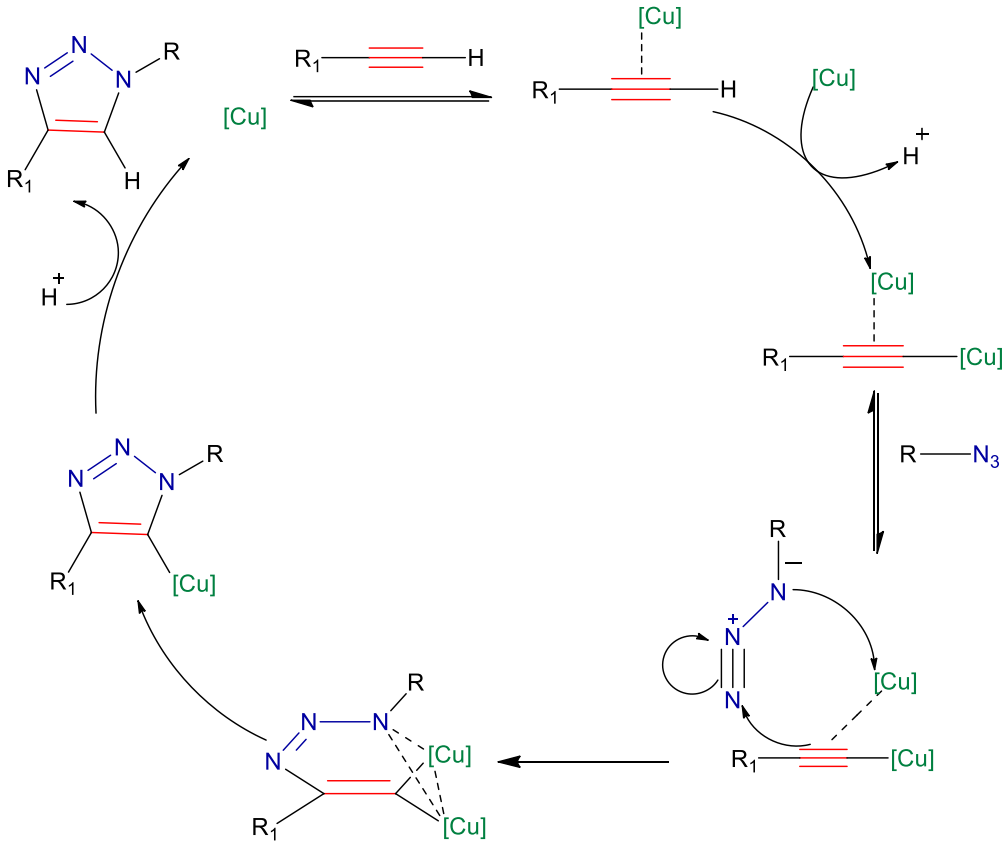

Figure 1.3 *schematic mechanism of 1,2,3-triazole formation by CuAAC.*

1.3 Applications of 1,2,3-triazoles

The 1,2,3-triazole moiety is ubiquitous in various fields ranging from organic synthesis, medicinal chemistry, catalysis and supramolecular chemistry.

1.3.1 Application in medicinal chemistry

1,2,3-Triazoles are one of the main class of heterocycles in medicinal chemistry because of their extensive range of biological properties such as anticancer [7-8], antituberculer [9], anti-HIV [10], antiallergic [11], antiviral [12-13], antidiabatic [14], antibacterial [15-16], anti-inflammatory [17-18] behavior. 1,2,3-Triazole finds use in research as a building block for more complex chemical compounds, including pharmaceutical drugs such as tazobactam. Therefore many researchers have synthesized these compounds as target structures and evaluated their biological activities.

These observations help the researchers for the development of new triazole compounds with enhanced biological activities.

1.3.2 Application in supramolecular chemistry

Since 1,2,3-triazole have a polarized CH bond which could be used as a potential H-bond donor and also it has three nitrogen atom, two which can coordinate with metal ions. This properties of 1,2,3-triazole moiety endows to form supramolecular aggregate.

Poly-1,2,3-triazole-based functional materials have shown more widespread applications, including self-assembly, DNA labelling [19], surface modification, supramolecular chemistry [20], dendrimer chemistry and combination chemistry, and as well as functional macromolecules.

1.3.3 Application in sensing

Since anions and cations are playing a vital role in many biochemical and physiological operation in living systems, sensing of neutral molecules [21] anions [22-23] and cations [24], become a subject of interest owing to their applications in chemistry and biology. The 1,2,3-triazole ring has high chemical stability, hydrogen bond donating and hydrogen bond accepting ability, which enable 1,2,3-triazole ring to interact with various anions, cations and neutral molecules.

They are also used as fluorescence chemosensors [25], optical brighteninig agents [26-27] and corrosion retarding agents.

1.3.4 Application in organometallic and catalytic chemistry

1,2,3-triazole receiving high interest for their application in new ligand systems for transition metal complexes. Generally 1,2,3-triazole form complexes with transition metal through nitrogen atom. In addition to this 1,2,3-triazoles allow access to a rich diversity of organometallic ligands including triazolylidene, cyclometalates and triazolide based ligands [28]. Complexes of this ligand are shows application in light emitting devices, solar energy conversion and in catalysis.

1.3.5 Application in gas storage

On the road to a sustainable, low-carbon future, the design and construction of chemical or physical adsorbents for CO_2 capture and clean energy storage are key technologies. The incorporation of accessible nitrogen donor sites into the pore walls of porous adsorbents can significantly influence CO_2 absorption capacity and selectivity due to dipole-quadrupole interactions between the polarizable CO_2 molecule and the accessible nitrogen site. So, now a days it become subject of interest on metal organic framework (MOF) containing 1,2,3-triazole for gas adsorption (like CO_2, H_2) [29-32].

1.4 Organization of the thesis

The aim of the this project was to synthesize different structural motifs of 1,2,3-triazole based compounds. This was to be achieved by click reaction between alkyne and azide.

Chapter 2: In this chapter, we have discussed about the past works on the 1,2,3-triazole containing compounds.

Chapter 3: This chapter includes materials, techniques and experimental procedure which were used to synthesize 1,2,3-triazole compounds.

Chapter 4: In this chapter, we have discussed about the results that was obtained during synthesis of these compounds.

Chapter 5: In this chapter, we have concluded all the results of our work and their future aspects.

Chapter 2

Review of past work

As 1,2,3-triazole ring has three nitrogen atom, so it can strongly bind with metal ion and biological targets as well as form supramolecular aggregate through non-covalent interaction. Thus the many researchers studying this interaction of 1,2,3-triazole ring in different ways.

2.1. Medicinal application

Amino acid frames come together to give different proteins, where amide bond represents a binding key strategy. 1,2,3-triazole ring is one the best isosteres to amide linkage [33]. Which make them very important in drugs or medicinal chemistry. In 2011 Boechat et al reported a novel 1,2,3-triazole derivatives for use against Mycobacterium tuberculosis H37Rv strain [34]. Recently Pokhodylo et al reported a 1,2,3-triazole derived compound as an anticancer agent [35].

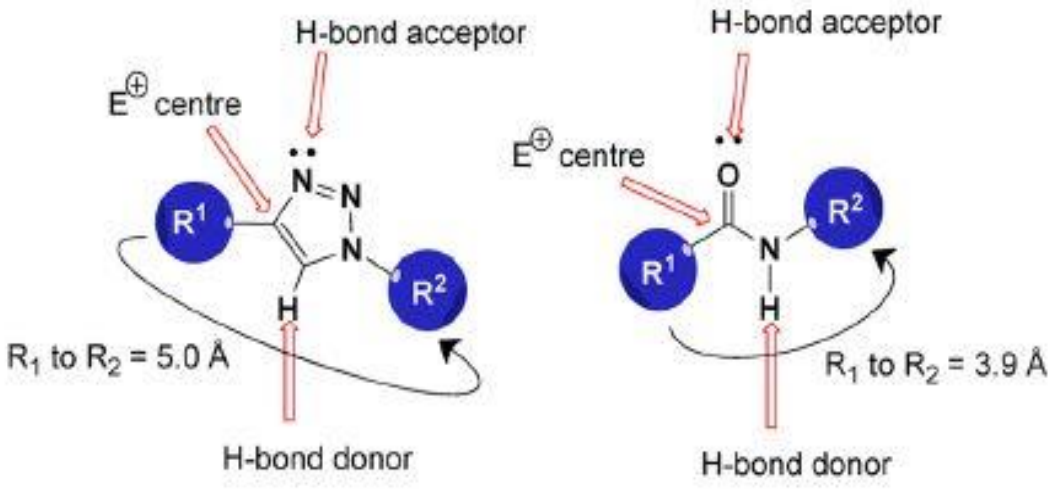

Figure 2.1 *Isosteric similarities between 1,2,3-triazole and amide.*

2.2 Supramolecular application

The potential of 1,2,3-triazole to form supramolecular arrays become a subject of interest due to their wide structural diversity and theirs possible applications in nonlinear optics, electrical conductivity, catalysis, ion exchange, biochemistry and others. Damijana et al has reported four complexes of 2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine ligand with Rh, Pd, Au and Hg metals, which are forming supramolecular associations [36]. In 2008 Li and Flood et al synthesized a shape-persistent triazole based macrocycle for halide ion sensor [37].

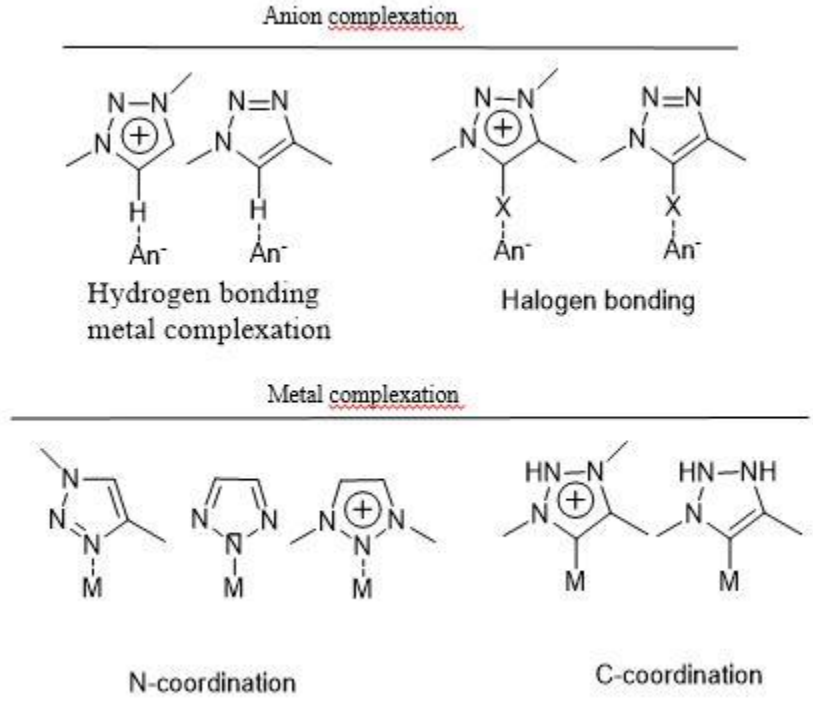

Figure 2.2 *supramolecular interaction of 1,2,3-triazole and their derivatives*

2.3 Application in sensing

In 2015, Osman et al synthesized a 1,2,3-triazole connected ferrocene complex to sense phosphate ion [38]. Serkan et al reported a simple 1,2,3-triazole based "turn on" fluorescent sensor for Al^{3+} ion in MeCN-H_2O and F^- ion in MeCN [39].

2.4 Application in organometallic and catalytic chemistry

1,2,3-triazole NHC ligand are mimicking the properties of PPh_3 ligand. But 1,2,3-triazole has much more advantage over PPh_3 ligand because tryazolylidene has more sigma donating power than the PPh_3 as well as other NHC ligand.

The first 1,2,3-triazole abnormal NHC ligand was reported by the group of Albrecht [40]. Imidazolylidene carbene [41] ligands become ubiquitous as supporting ligands in enormous organic coupling reactions as catalyst. Recently in 2011 Hohloch et al reported a Cu(I)-1,2,3-triazole NHC complex which is an active catalyst for CuAAC reaction [42-43]. In recent years many papers were published on PEPPSI type catalyst for cross coupling reactions [44-45].

2.5 Application in gas storage

Metal organic framework (MOF) of 1,2,3-triazole compounds are good gas adsorber as reported in the literature. In 2012 Gao et al synthesized a MOF by using, 4,4′-(2H-1,2,3-triazole-2,4-diyl)dipyridine as a ligand and Zn(II) ion as metal ion source, which shows remarkable enhancement of CO_2 uptake [46].

Recently in 2016 Li and Wang et al reported a MOF of Cu(II) ion as a metal precursor with ligand 5,5′,5″,5‴-((methanetetrayltetrakis-(benzene-4,1-diyl)) tetrakis (1H-1,2,3-triazole-4,1-diyl)) tetraiso-phthalic acid , which effectively act as catalyst for CO_2 conversion.

Chapter 3

Experimental section

3.1 Reagent chemical

All chemicals and reagent were purchased from commercial available sources. Reagent are of analytical grade and were used without purification. Cu(II) sulphate pentaydrate, Cu(I) iodide, bis(triphenyphosphine)palladium(II) dichloride, sodium ascorbate, trimethylsilyl acetylene, methyl iodide, 1-bromopropane, 2-(bromomethyl)pyridine hydrobromide, 1,4-dibromobenzne, 4,4"-dibromo-5'-(4-bromophenyl)-1,1':3',1"-terphenyl, 1,3,5-tribromobenzene and Sodium azide were purchased from Merck India company limited.

3.2 Methods and instrumentation

Reactions were monitored by TLC on Merck silica gel plates and spot were viewed under UV lamp. Column chromatography were performed using silica gel or neutral alumina. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using $CDCl_3$ or DMSO-d_6 on a Bruker Avance 400 spectrometer at 298 K. Chemical shifts are reported in ppm relative to tetramethylsilane, singlet at 7.26 ppm for $CDCl_3$ and 2.49 ppm for DMSO-d_6. ^{13}C NMR are reported in ppm with relative to tetramethylsilane, sep at 39.50 ppm in ^{13}C NMR for DMSO-d_6. The splitting patterns of ^{1}H NMR peaks are denoted as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplate. ESI-mass spectra were recorded on Bruker-daltonics, microTOF-Q II mass spectrometer. GC-TCD analysis was performed on a Shimadzu GCMS-QP2010 Ultra and GC-2010 plus system in electron impact mode using RT-Msieve 5A column.

3.3 Synthesis of 1,2,3-triazole Ligands

3.3.1 Synthesis of 1,4-diethynyl benzene

1,4-dibromobenzene (0.233 g, 1 mmol), trimethylsilylacetylene (0.345 ml, 2.5 mmol), bis(triphenyphosphine)palladium(II) dichloride (0.140 g, 0.2 mmol) and copper iodide (0.38 g, 0.2 mmol) as a catalyst were mixed in 20 ml dry THF and 10 ml triethyl amine with inert condition. The reaction mixture was refluxed for 10 hr according to previous report [47]. Then solvent was evaporated and crude pale yellow solid product was extract through column chromatography with 95 % yield, desired 1,4-diethynyl is then obtained by desilylation of this pale yellow product with aqueous KOH (0.140 g, 2.5 mmol) in methanol and reflux for 4 hr. After 4 hr solvent was evaporated, brown colored precipitate was obtained with 100% yield. The precipitate was filtered off, wash with water and dried in vacuum oven.

GC-MS $(EI)^+$ calcd for $C_{10}H_6$ is 126; ^1H NMR δ_H (400 MHz, $CDCl_3$) 7.43 (s, 4H), 3.16 (s, 2H); ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 132 (Ar-C), 122.55 (Ar-C), 83.02 (Acetylene-C), 79.06 (Acetylene-C).

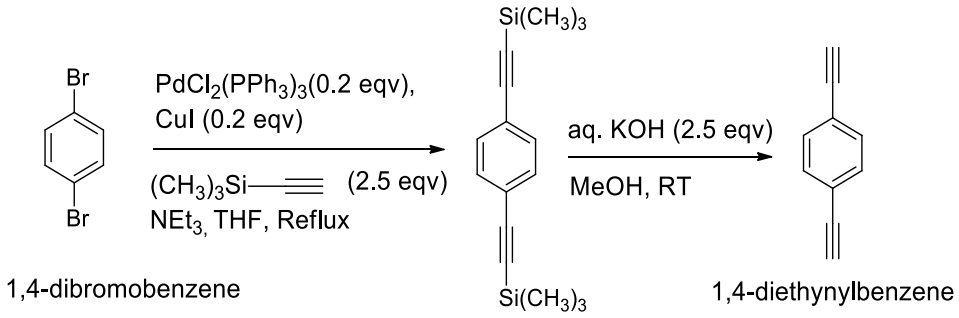

Figure 3.1 *Reaction scheme for the synthesis of 1,4-diethynylbenzene.*

3.3.2 Synthesis of 4-(4-ethynylphenyl)-1-methyl-1H-1,2,3-triazole (L1)

1,4-diethynyl benzene (0.126 g, 1 mmol), MeI (0.093 ml, 1.5 mmol) and sodium azide (0.065 g, 1 mmol) were dissolved in 1:3 (v/v) water and THF. Then solution of sodium ascorbate (0.059 g, 0.3 mmol) in 5 ml water was added and then on add solution $CuSO_4.5H_2O$ (0.049, 0.2 mmol) in 5 ml water. The reaction mixture was stirred for 12 hr in reflux condition. Solvent was evaporated and white colored precipitate was obtained with 60 % yield, which was filtered off and washed with water for several times and finally dried in vacuum.

GC-MS $(EI)^+$ calcd for $C_{11}N_3H_9$ is 183; ^1H NMR δ_H (400 MHz, $CDCl_3$) 7.78 (d, 2H), 7.74 (s, 1H), 4.13 (s, 3H), 3.11 (s, 1H); ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 147.27 (Triazole-C), 132.62 (Ar-C), 130.94 (Ar-C), 125.48 (Ar-C), 121.72 (Triazole-C), 120.88 (Ar-C) 83.42 (Acetylene-C), 77.90 (Acetylene-C), 36.77 (Methyl-C).

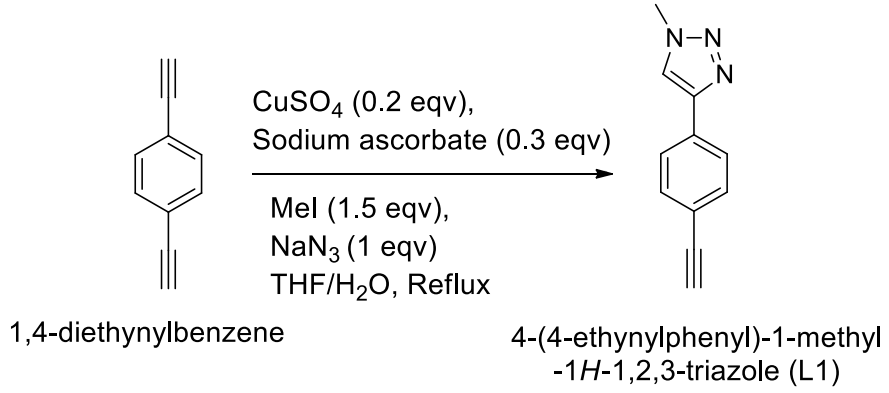

Figure 3.2 *Reaction scheme for the synthesis of ligand L1.*

3.3.3 Synthesis of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl

4,4"-diethynyl-5'-(4-bromophenyl)-1,1':3',1"-terphenyl (0.539 g, 1 mmol), trimethylsilylacetylene (0.484 ml, 3.5 mmol), bis(triphenyphosphine)palladium(II) dichloride (0.210 g, 0.3 mmol) and copper iodide (0.571 g, 0.3 mmol) as a catalyst were mixed in 25 ml dry

THF and 10 ml triethyl amine with inert condition. Then reaction mixture was stirred for 10 hr in reflux condition. Then solvent was evaporated and crude pale yellow solid product was extracted through column chromatography with 90% yield. 4,4"-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1"-terphenyl was obtained by desilylation of this pale yellow product with aqueous KOH (0.196 g, 3.5 mmol)) in methanol and reflux for 4 hr with 100% yield. After 4 hr solvent was evaporated, white colored precipitate was obtained. The precipitate was filtered off, wash with water and dried in vacuum oven.

^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.75 (s, 3H), 7.63 (d, 6H), 7.61 (d, 6H), 3.15 (s, 3H); ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 141.67 (Ar-C), 141.08 (Ar-C), 132.67 (Ar-C), 127.18 (Ar-C), 125.26 (Ar-C), 121.51 (Ar-C), 83.38 (Acetylene-C), 78.09 (Acetylene-C)

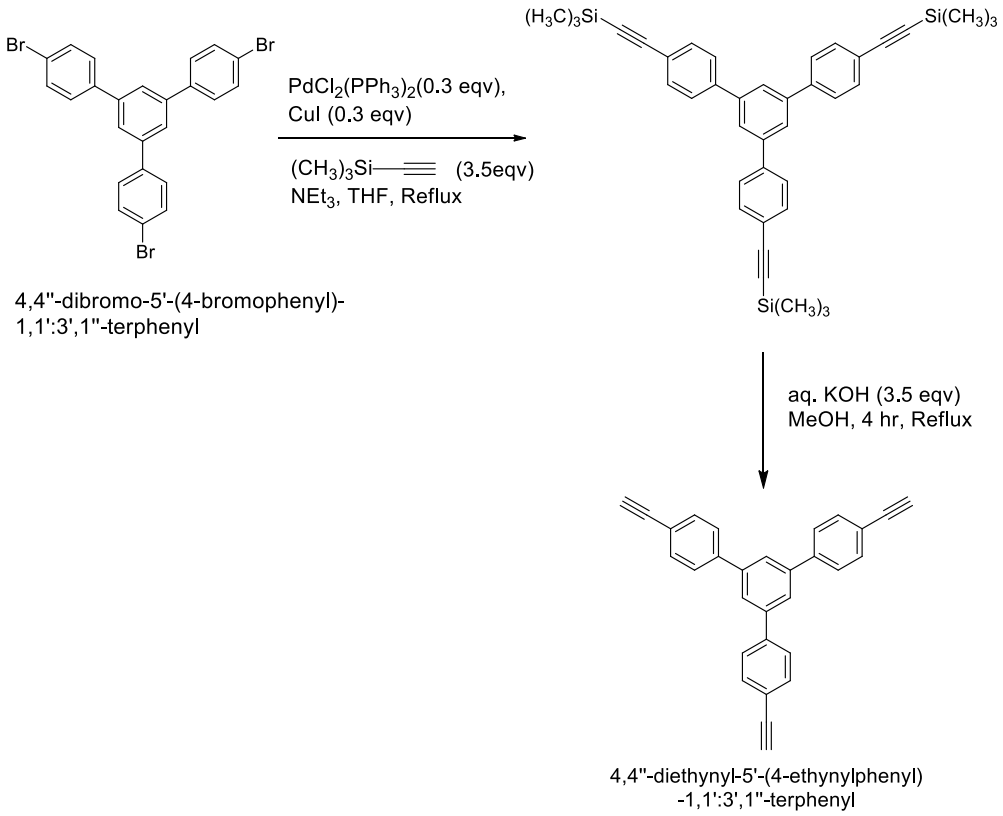

Figure 3.3 *Reaction scheme for synthesis of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl.*

3.3.4 Synthesis of ligand 4,4'-(5'-(4-(1-propyl-1H-1,2,3-triazol-4-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(1-propyl-1H-1,2,3-triazole) (L2)

4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl (0.189 g, 0.5 mmol), 1-bromopropane (0.159 ml, 1.75 mmol) and sodium azide (0.113 g, 1.75 mmol) were dissolved in 1:3 (v/v) water and THF. Then solution of sodium ascorbate (0.039 g, 0.2 mmol) in 5 ml water was added and then on add solution $CuSO_4.5H_2O$ (0.037 g, 0.15 mmol) in 5 ml water. The reaction mixture was stirred for 15 hr in reflux condition. Solvent was evaporated and white colored precipitate was obtained with 58% yield, which was filtered off and washed with water for several times and finally dried in vacuum.

ESI-MS calcd for $[M+Na]^+$ $C_{39}H_{39}N_9$ 633.33, found 656.33; ^1H NMR δ_H (400 MHz, DMSO-d_6) 8.67 (s, 3H), 7.99 (s, 15H), 4.37 (t, 6H), 1.91 (m, 6H), 0.89 (t, 9H); ^{13}C NMR δ_C (100 MHz, DMSO-d_6) 146.13 (Triazole-C), 141.32 (Ar-C), 139.44 (Ar-C), 130.49 (Triazole-C), 127.85 (Ar-C), 125.78 (Ar-C), 124.23 (Ar-C), 121.63 (Ar-C), 51.33 (Methylene-C), 23.28 (Methylene-C), 11.03 (Methyl-C).

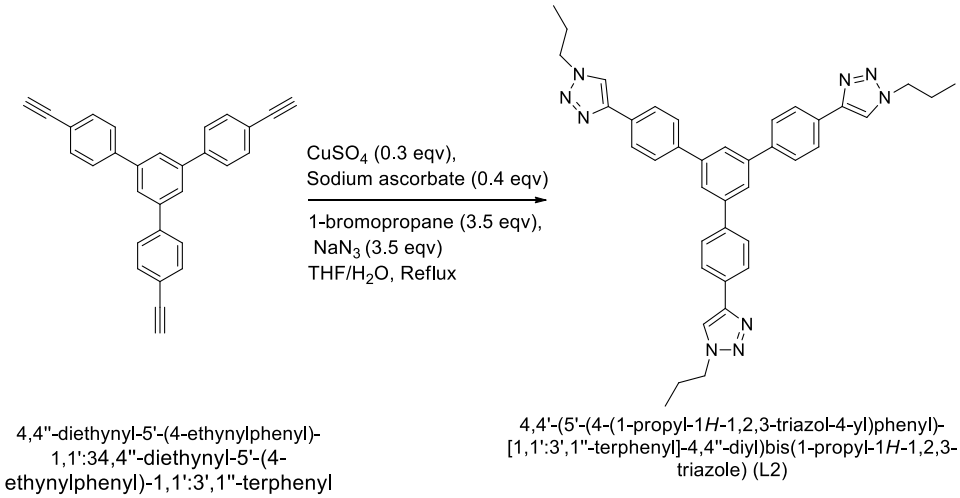

Figure 3.4 *Reaction scheme for synthesis of ligand L2.*

3.3.5 Synthesis of 1,3,5-triethynylbenzene

1,3,5-tribromobenzene (0.311 g, 1 mmol), trimethylsilylacetylene (0.484 ml, 3.5 mmol), bis(triphenyphosphine)palladium(II) dichloride (0.210 g, 0.3 mmol) and copper iodide (0.571 g, 0.3 mmol) as a catalyst were mixed in 25 ml dry THF and 10 ml triethyl amine with inert condition. Then reaction mixture was stirred for 10 hr in reflux condition. Then solvent was evaporated and crude pale yellow solid product is extract through column chromatography with 90% yield. Finally 1,3,5-triethynylbenzene was obtained by desilylation of this pale yellow product with aqueous KOH (0.196 g, 3.5 mmol)) in methanol and reflux for 4 hr. After 4 hr solvent was evaporated, white colored precipitate was obtained with 100% yield. The precipitate was filtered off, wash with water and dried in vacuum oven.

GC-MS $(EI)^+$ calcd for $C_{12}H_6$ is 150; ^1H NMR δ_H (400 MHz, $CDCl_3$) 7.56 (s, 3H), 3.09 (s, 3H), ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 131.98 (Ar-C), 122.52 (Ar-C), 83.01 (Acetylene-C), 77.32 (Acetylene-C)

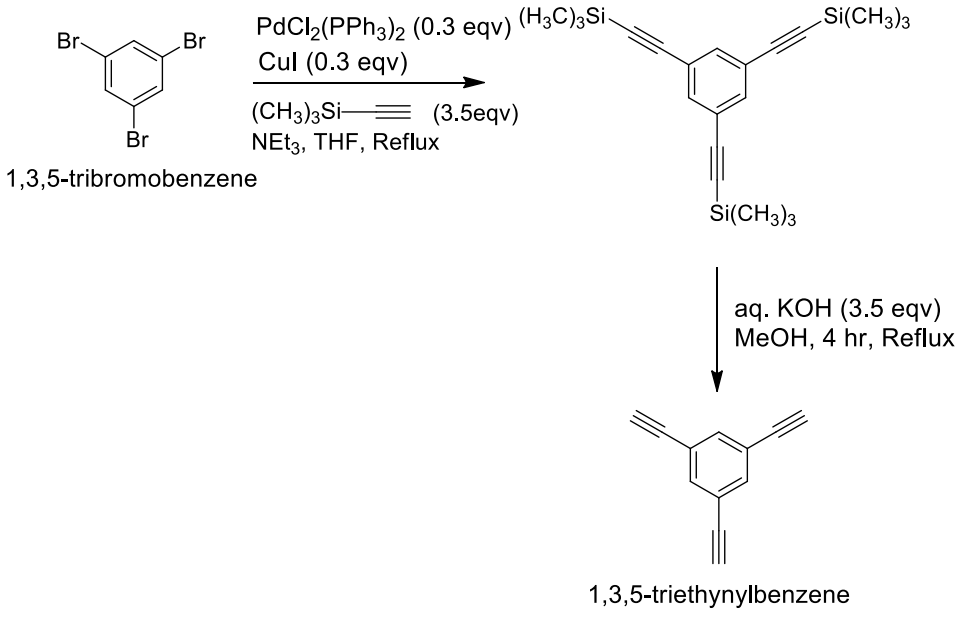

Figure 3.5 *Reaction scheme for synthesis of 1,3,5-triethynylbenzene.*

3.3.6 Synthesis of ligand 1,3,5-tris(1-(pyridin-3-ylmethyl)-1H-1,2,3-triazol-4-yl)benzene (L3)

1,3,5-triethynylbenzene (0.156 g, 0.5 mmol), 3-(bromomethyl)pyridine hydrobromide (0.442 g, 1.75 mmol) and sodium azide (0.113 g, 1.75 mmol) were dissolved in 1:3 (v/v) water and THF. Then solution of sodium ascorbate (0.039 g, 0.2 mmol) in 5 ml water was added and then on add solution $CuSO_4.5H_2O$ (0.037 g, 0.15 mmol) in 5 ml water. The reaction mixture was stirred for 20 hr in reflux condition. Solvent was evaporated and white colored precipitate was obtained with 55% yield, which was filtered off and washed with water for several times and finally dried in vacuum.

ESI-MS calcd for $[M+Na]^+$ $C_{34}H_{24}N_{12}$, found 575.22, ^1H NMR δ_H (400 MHz, DMSO-d_6) 8.81 (s, 3H), 8.68 (3H,), 8.55 (d, 3H), 8.29 (s, 3H), 7.80 (d, 3H), 7.43 (q, 3H), 5.74 (s, 6H); ^{13}C NMR δ_C (100 MHz, DMSO-d_6) 149.32 (Py-C), 149.11 (Triazole-C), 146.08 (Py-C), 135.76 (Py-C), 131.64 (Py-C), 131.36 (Ar-c), 123.71 (Triazole-C), 121.97 (Ar-C), 121.13 (Py-C), 50.46 (Methylene-C).

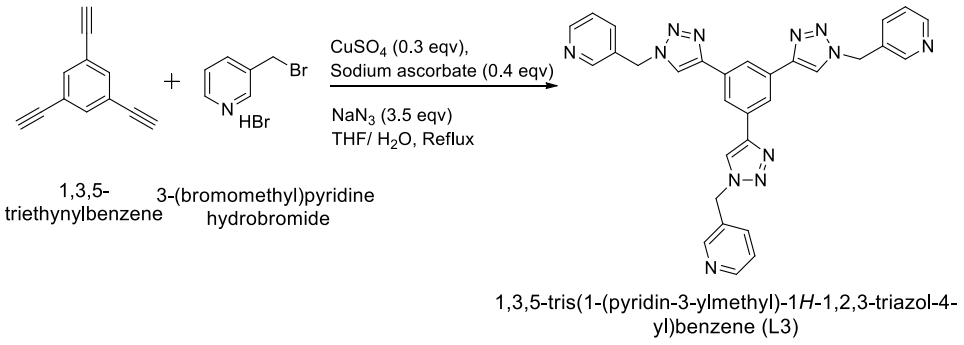

Figure 3.6 *Reaction scheme for synthesis of ligand L3.*

Chapter 4

Result and discussion

4.1 Characterization of 1,4-diethynylbenzene

4.1.1 Mass Spectrometry

EI-MS data supports the formation of 1,4-diethynylbenzene with molecular ion peak at m/z 126 which corresponds to $[M]^+$.

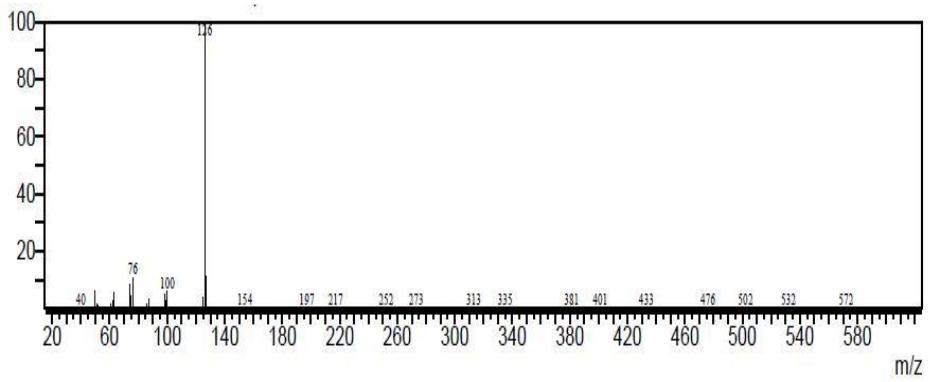

Figure 4.1 *EI-MS spectrum of 1,4-diethynylbenzen.*

4.1.2 NMR Spectroscopy

NMR spectrum of 1,4-diethynylbenzene were recorded in $CDCl_3$ using TMS as an internal standard. In ^1H NMR aromatic proton peaks were observed at about 7.43 ppm and peak at 3.16 ppm corresponds to acetylene proton. In ^{13}C NMR spectrum of 1,4-diethynylbenzene aromatic carbon peaks were shown at 132-120 ppm and acetylene carbon peaks shown at 84-78 ppm.

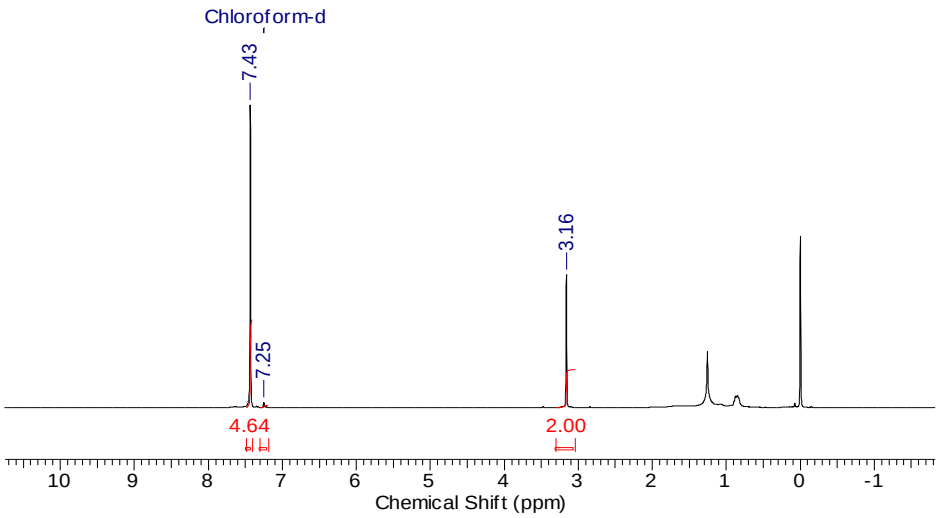

Figure 4.2 *^{1}H NMR spectrum of 1,4-diethynylbenzene.*

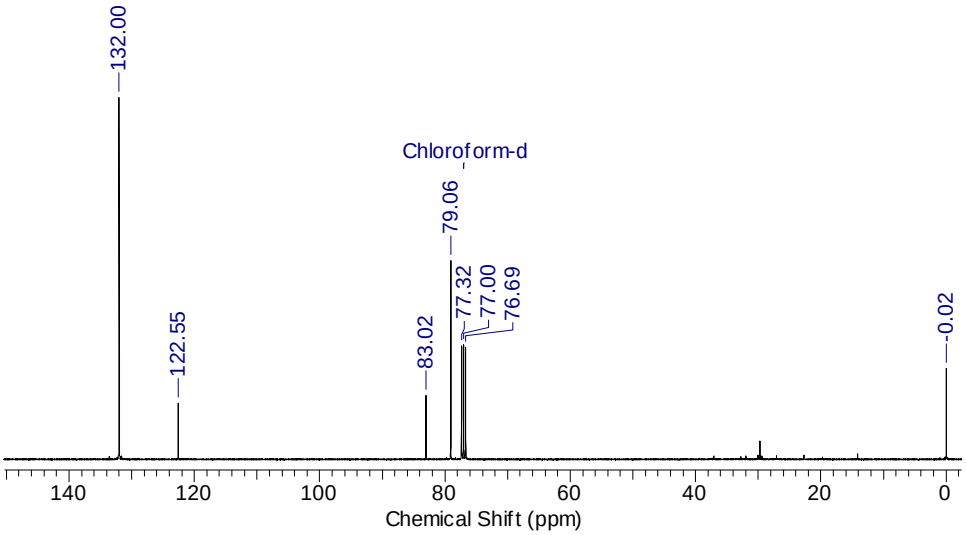

Figure 4.3 *^{13}C NMR spectrum of 1,4-diethynylbenzene.*

4.2 Characterization of L1

4.2.1 Mass spectrometry

EI-MS data supports the formation of L1 with molecular ion peak at m/z 183 which corresponds to $[M]^+$.

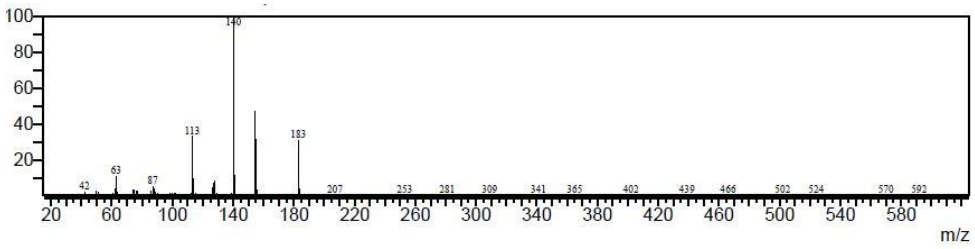

Figure 4.4 *EI-MS spectrum of L1.*

4.2.2 NMR Spectroscopy.

NMR spectrum of L1 were recorded in $CDCl_3$ using TMS as an internal standard. In ^1H NMR benzene ring proton peaks were observed at about 7.78 and 7.54 ppm and peak at 7.14 ppm corresponds to triazole proton. Peaks at 4.13 and 3.11 ppm are correspond to methyl and acetylene proton respectively. ^{13}C NMR spectrum of L1 shows 9 different types of carbon. Peak at 147.27 and 121.72 ppm corresponds to triazole and peak at 83.42 and 77.90 ppm corresponds to acetylene carbon and 36.77 ppm corresponds to methyl carbon.

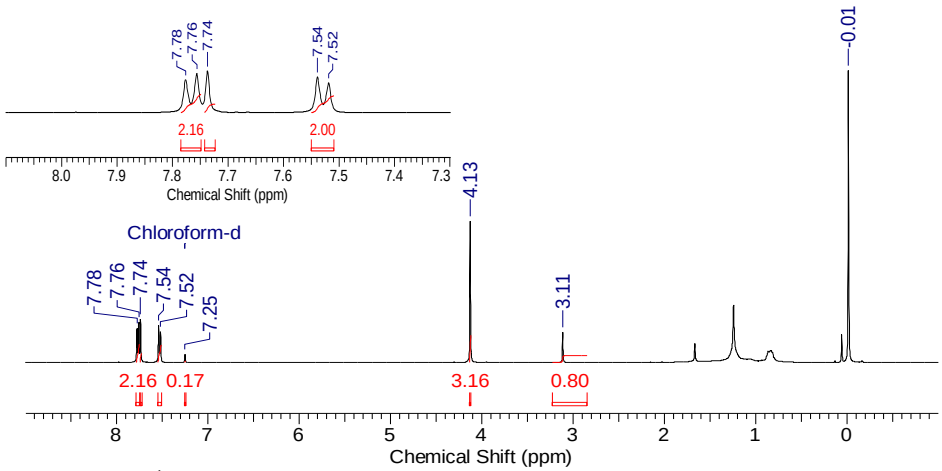

Figure 4.5 *^1H spectrum of L1.*

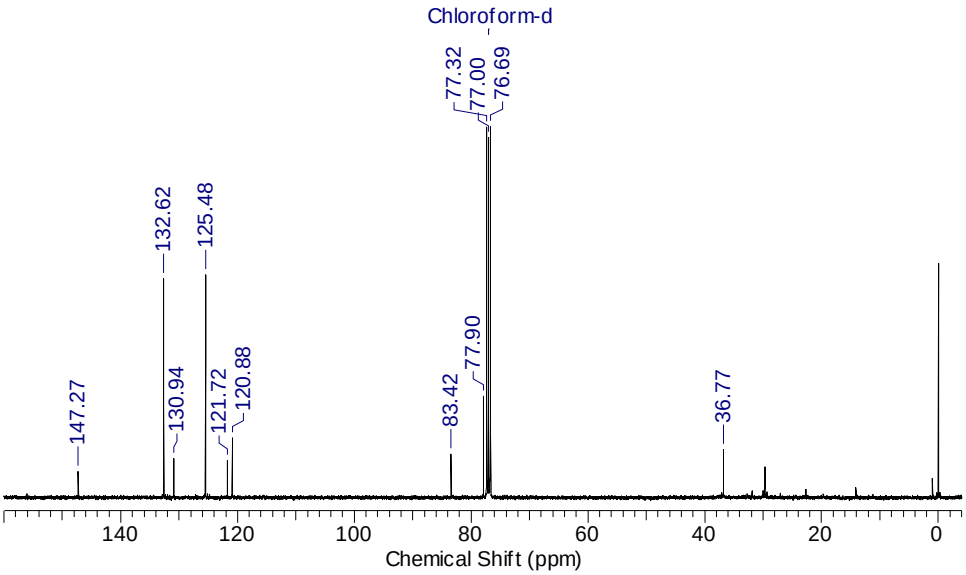

Figure 4.6 *^{13}C spectrum of L1.*

4.3 Characterization of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl

4.3.1 NMR Spectroscopy

NMR spectrum of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl were recorded in $CDCl_3$ using TMS as an internal standard. In ^1H NMR, aromatic ring proton peaks were observed at about 7.75-7.59 ppm and peak at 3.15 corresponds to acetylene protons. In ^{13}C spectrum peaks at 142-120 ppm corresponds to aromatic carbons and peaks at 83.38 and 78.09 ppm corresponds to acetylene carbon.

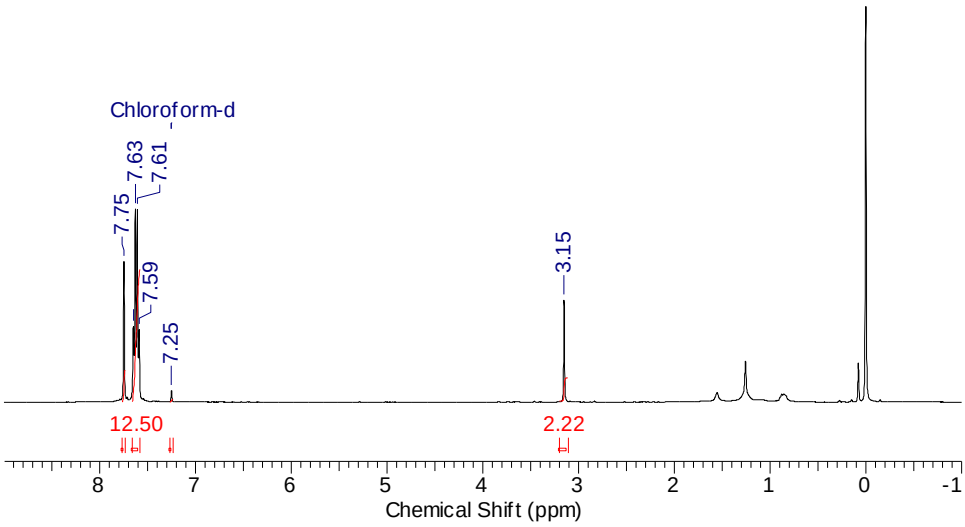

Figure 4.7 *^{1}H spectrum of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl.*

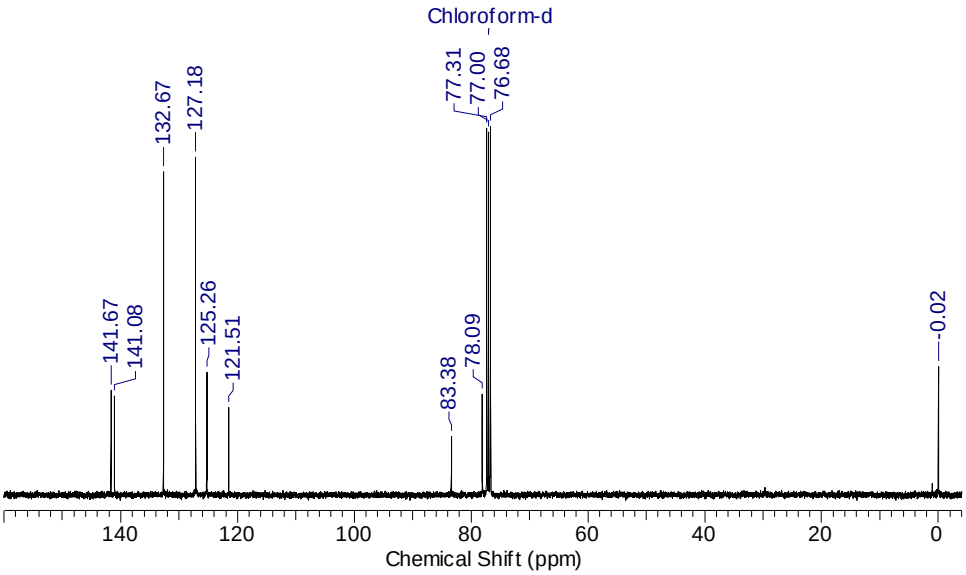

Figure 4.8 *^{13}C spectrum of 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl.*

4.4 Characterization of L2

4.4.1 Mass Spectrometry

ESI-MS data supports the formation of L2 with molecular ion peak at m/z 656.33 which corresponds to the $[M+Na]^+$.

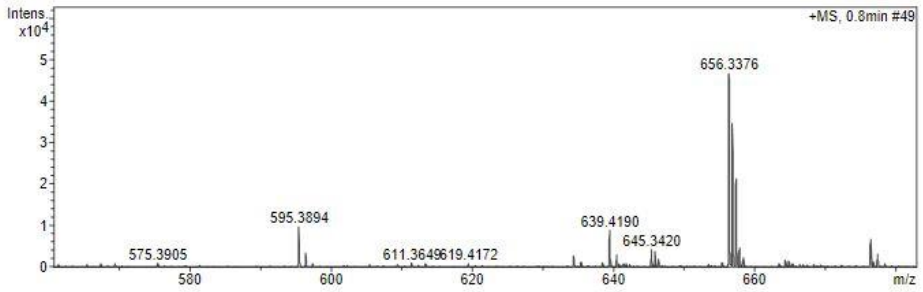

Figure 4.9 *ESI-MS spectrum of L2.*

4.4.2 NMR Spectroscopy

NMR spectrum of L2 were recorded in DMSO-d_6 using TMS as an internal standard. In ^{1}H NMR, benzene ring proton peaks were observed at about 7.99 ppm and peak at 8.67 ppm corresponds to triazole proton. Peaks at 4.37, 1.91 and 0.89 ppm corresponds to propyl group. In ^{13}C spectrum peaks at 146-120 ppm corresponds to aromatic carbons and peaks at 51.12, 23.06 and 10.82 corresponds to propyl carbons.

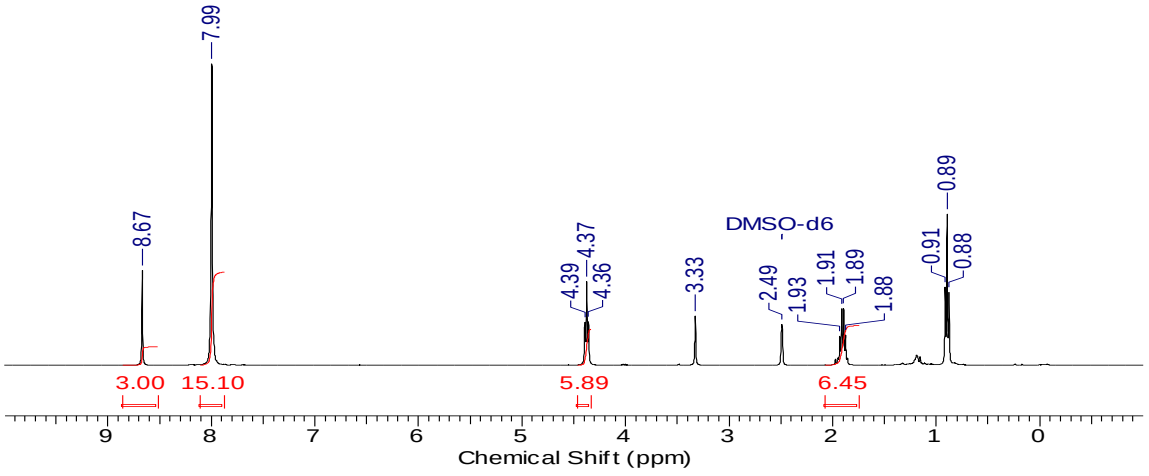

Figure 4.10 *^{1}H spectrum of L2*

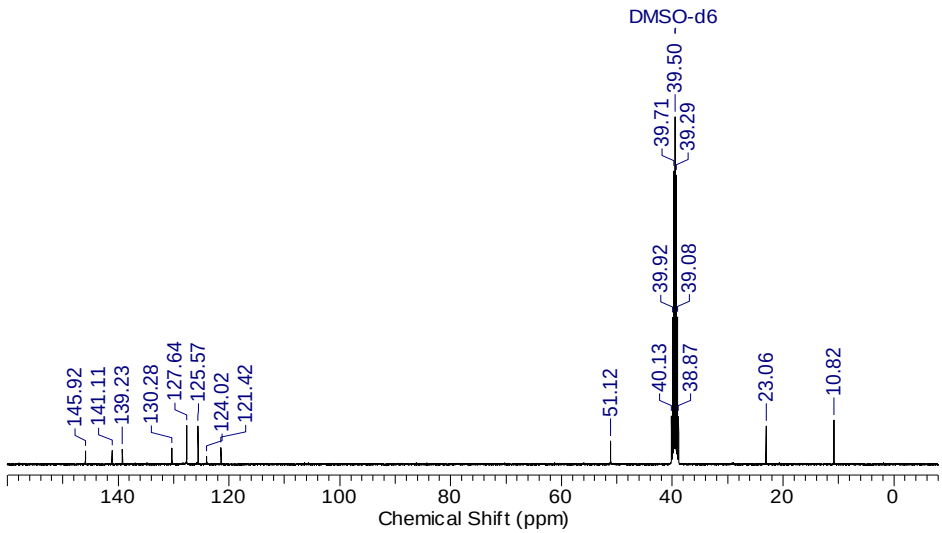

Figure 4.11 *^{13}C spectrum of L2*

4.5 Characterization of 1,3,5-triethynyl benzene

4.5.1 Mass Spectrometry

EI-MS data supports the formation of 1,3,5-triethynylbenzene with molecular ion peak at m/z 150 which corresponds to $[M]^+$.

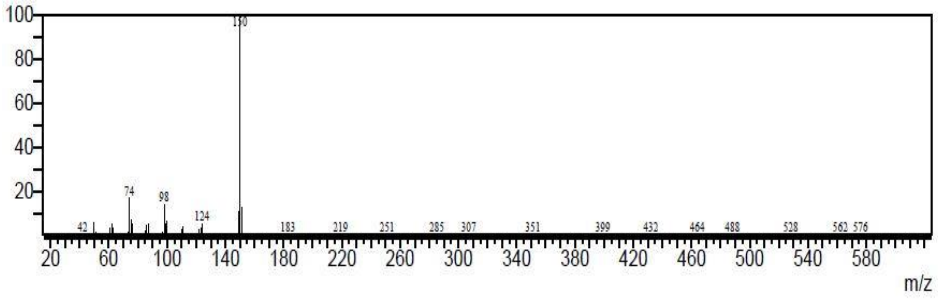

Figure 4.12 *EI-MS spectrum of 1,3,5-triethynylbenzene.*

4.5.2 NMR Spectroscopy

NMR spectrum of 1,3,5-triethynylbenzene were recorded in $CDCl_3$ using TMS as an internal standard. In ^1H NMR, aromatic ring proton peaks were observed at about 7.56 ppm and peak at 3.09 ppm corresponds to acetylene protons. In ^{13}C spectrum peaks at 131.98 and 122.52 ppm corresponds to

aromatic carbons and peaks at 83.01 and 79.07 ppm corresponds to acetylene carbon.

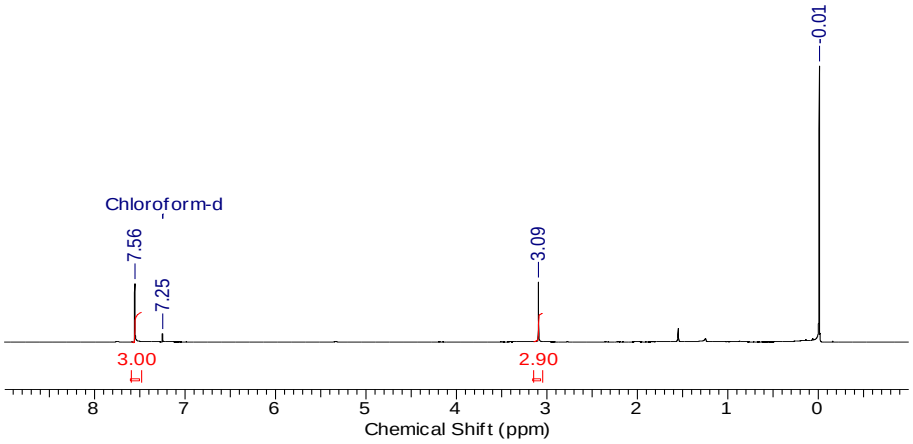

Figure 4.13 *^{1}H NMR spectrum of 1,3,5-triethynylbenzene.*

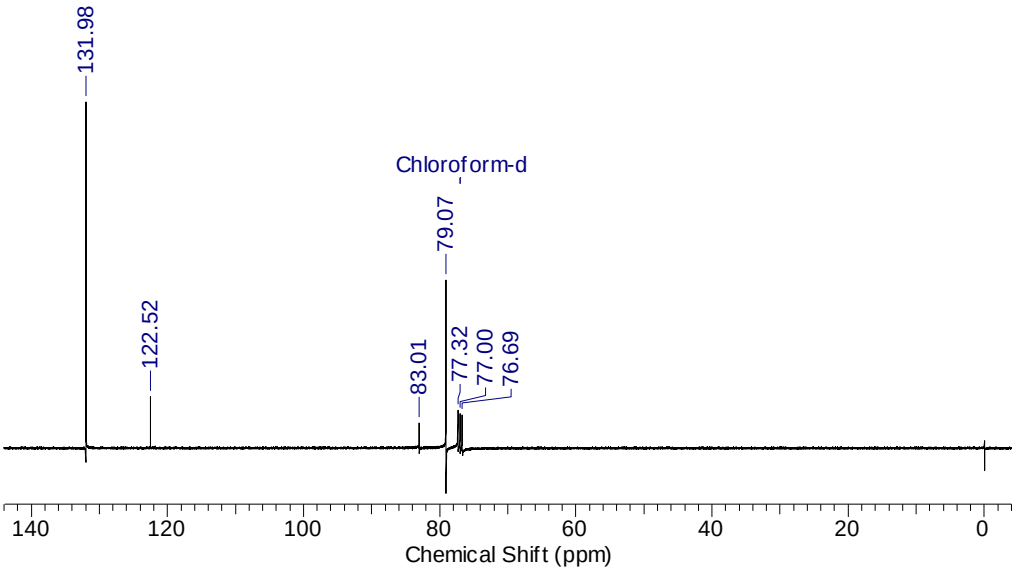

Figure 4.14 *^{13}C spectrum of 1,3,5-triethynylbenzene.*

4.6 Characterization of L3

4.6.1 Mass Spectrometry

ESI-MS data supports the formation of L3 with molecular ion peak at m/z 575.22, which corresponds to the $[M+Na]^+$.

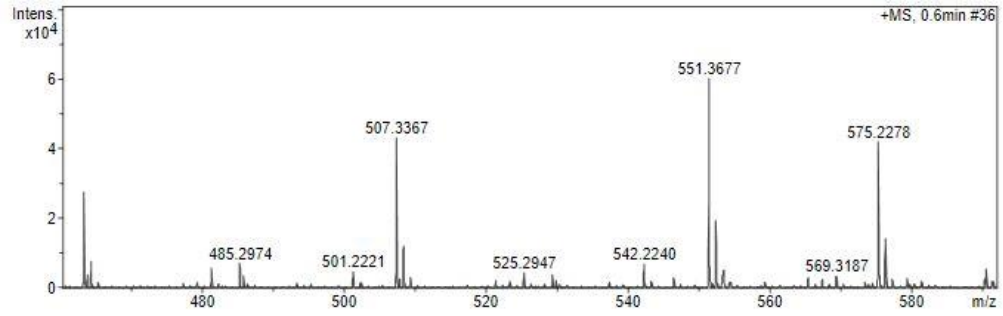

Figure 4.15 *ESI-MS spectrum of L3.*

4.6.2 NMR Spectroscopy

NMR spectrum of L3 were recorded in DMSO-d_6 using TMS as an internal standard. In ^{1}H NMR, aromatic ring proton peaks were observed at about 9-7.4 ppm and peak at 5.74 ppm corresponds to methylene protons. The ^{13}C spectrum shows 10 different types of carbon in L3 molecule. Aromatic carbons shows peak at about 150-120 ppm and peak at 50.46 corresponds to methylene carbon.

Chapter 5

Conclusion and Future Scope

In this thesis, three different 1,2,3-triazle based compounds have been synthesized successfully by CuAAC reaction. In every cases yield was near to 60%. Their molecular structure were confirmed by mass spectrometry and NMR spectroscopy.

1,2,3-triazole compounds shows a broad range of applications in pharmaceutical and organometallic chemistry. 1,2,3-triazole can formed mesoionic carbine, which can form complex with several transition metals which can show catalytic activity in organic reactions and also can show medicinal properties.

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