SYNTHESIS AND CHARACTERIZATION OF ORGANIC FUNCTIONAL MATERIALS AND STUDIES ON THEIR APPLICATIONS

A Thesis submitted to the
University of North Bengal

For the Award
Doctor of Philosophy
In
Chemistry

By

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January – 2025

Dedicated to all My Dear ones...

DECLARATION

I proclaim that the thesis entitled "**SYNTHESIS AND CHARACTERIZATION OF ORGANIC FUNCTIONAL MATERIALS AND STUDIES ON THEIR APPLICATIONS**" has been made and organized by me under the guidance of Prof. Pranab Ghosh, Department of chemistry, University of North Bengal. No portion of this thesis has manufactured the basis in favor of the award of any degree or fellowship formerly.

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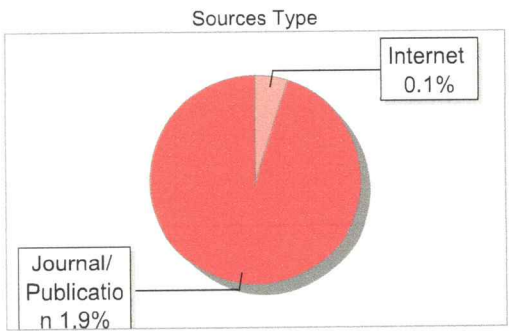
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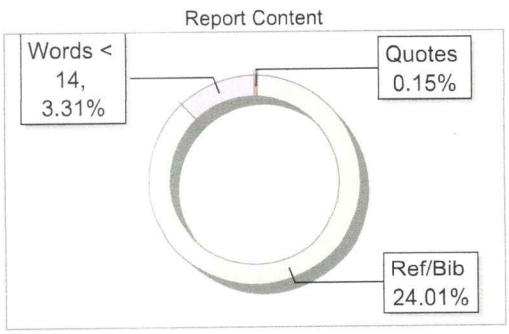
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This is also the chance I must avail to apologize sincerely, for any flaws on my side, as well as for any words or actions that I may have said or done which might have offended anyone around me during my work.

Ultimately, even with my greatest endeavors and earnestness, I may have made a few accidental blunders and errors in my thesis. Appreciated input and critiques from knowledgeable instructors will be thankfully considered.

With Thanks,

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23/ 12/ 2024

ABSTRACT

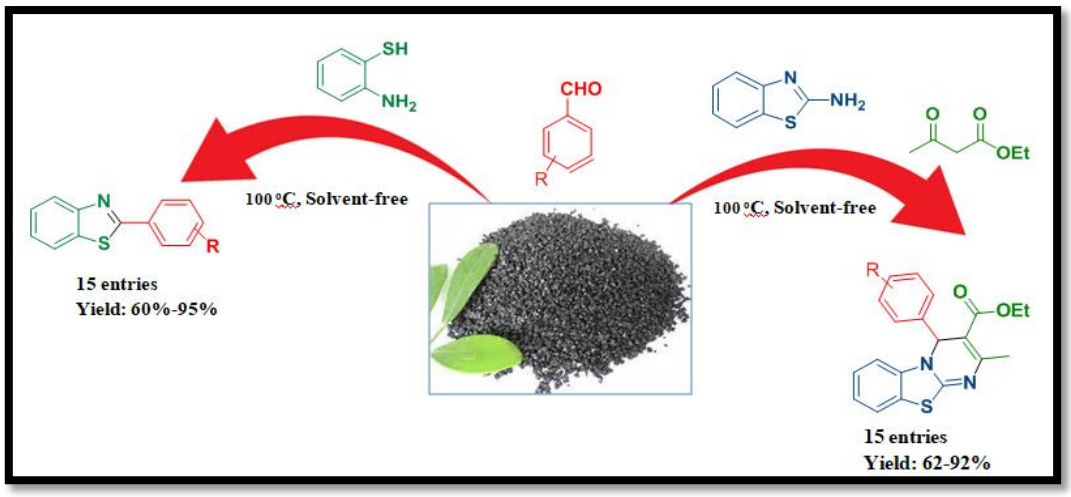
Commencing from the very first days of 2020, this consumed nearly four years long to complete the exploration, investigation and entire study, embraced in this documentation, entitled **"SYNTHESIS AND CHARACTERIZATION OF ORGANIC FUNCTIONAL MATERIALS AND STUDIES ON THEIR APPLICATIONS"**. Actually completion of research work is just a myth. Completion of a productive five years and consequently the creation of such full – length Thesis or an intact documentation of five years, are nothing but an arrival into a new and fresh world of scientific aura. Such work is basically emphasized on uplifment of proficient and ecological pathways for synthesizing biologically convenient heterocyclic substituent. The overall work represented in this documentation has been distributed like the following manner.

A lubricant is a material that is applied to the surfaces that are in proximity with one another in order to minimize friction. This eventually minimizes the amount of heat produced whenever the surfaces circulate. In addition, it might be used for force transmission, the transportation of foreign objects, surface cooling wear resistance, and corrosion prevention.

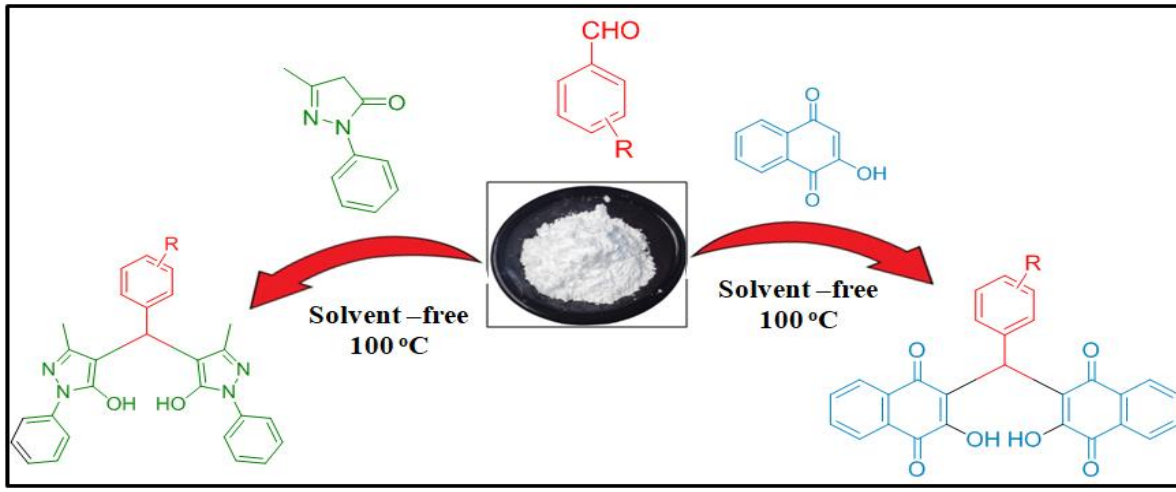
Base oil and additive packages are both present in the lubricant. The purpose of additives is to either add an innovative feature to the base fluid or improve one that already exists. The current work consists of the synthesis, characterization, and efficacy assessment of multifaceted lubricant additives.

Chapter I (A concise explanation about the perspective towards some production of biologically significant compounds with heterocyclic moiety) consists of total two sections.

Section A deals with the fact that Humic acid, a rarely used non virulent, easily accessible, inexpensive, environmentally benign, high molecular weight polymer, because of its extraordinary catalytic activity has been explored for the synthesis of functionalized 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and its derivatives along with functionalized benzo[*d*]thiazole. Environmental friendliness, low catalyst loading, outstanding yield, magnificent functional group forbearance and renewability up to fifth run without any noteworthy loss of its activity at the finishing point of reaction, are the cue significances of these methods.

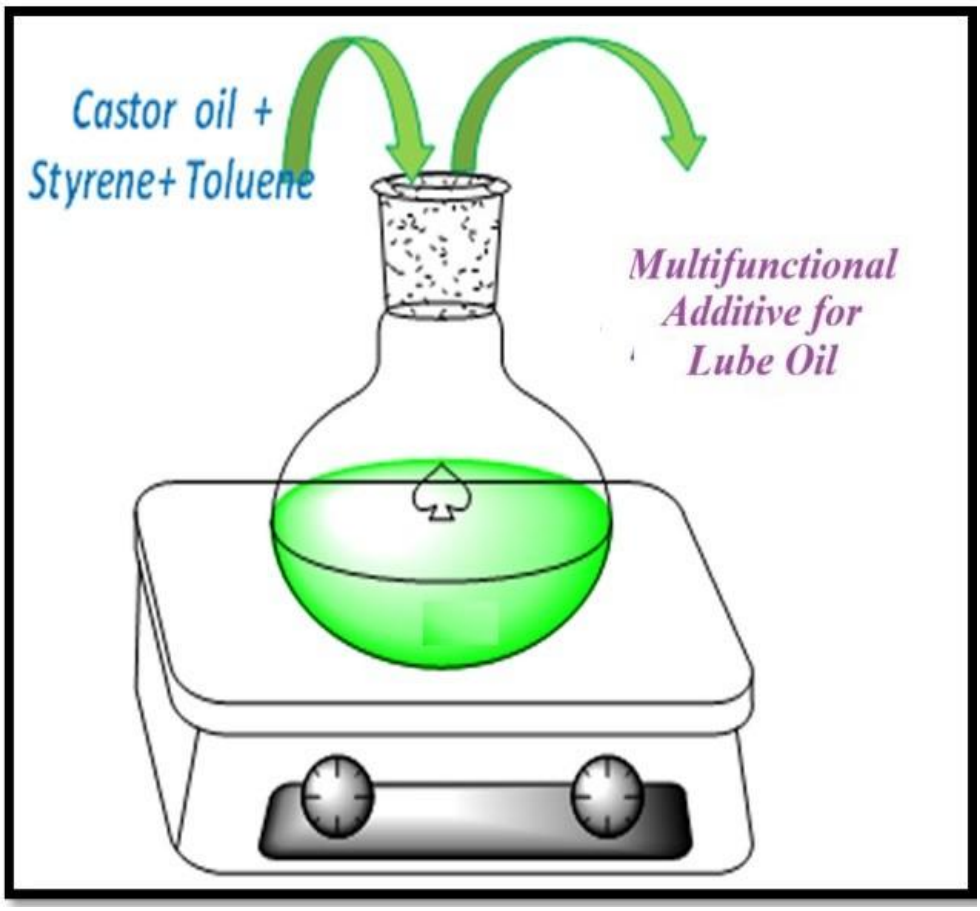


Section B deals with the fact that, a broad spectrum of extensively functionalized biologically convenient heterocyclic constituents such as, 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 2-hydroxy-1,4-naphthoquinone can be synthesized in one pot under the maintenance of metal-free condition and using β-cyclodextrin, a common, water soluble and greener catalyst with supramolecularity. These procedures' primary goal is to investigate the fabrication of this organic supramolecule using a single pot and numerous substances. The main benefits of that study are its superior functional group forbearance, lack of harmful acid or metal catalyst, hard reaction circumstances, low cost, ecological, more sustainable and harmless methodology with respect to the environmental purpose. These procedures don't use any poisonous metal catalysts, dangerous solvents, or severe reaction pathways. The main benefits of these procedures are additionally low catalyst load, exceptional yield quantity, and outstanding functional group compatibility. Such technique is harmless for Mother Nature because it does not employ solvents and makes the utilization of a catalyst.



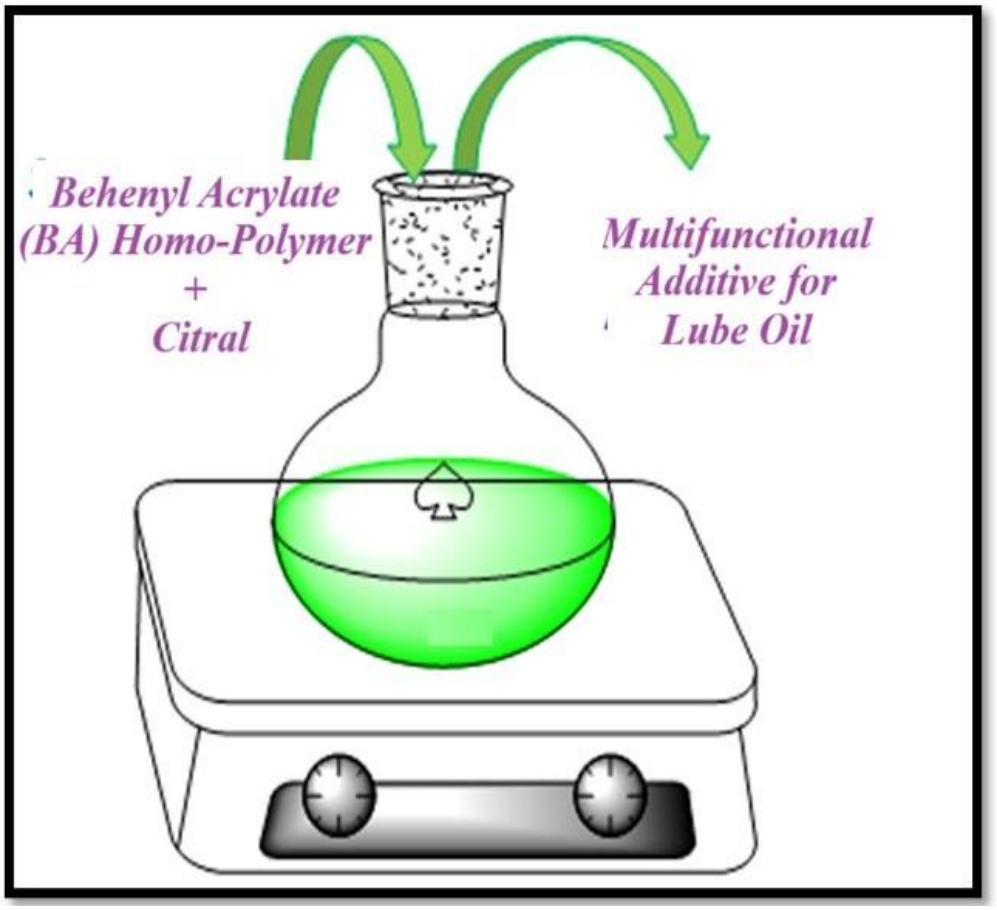
Chapter II (**Wide-ranging analysis of polymeric exploration, synthesis and evaluation),** consists of total three sections.

Section A deals with the fact that, the polymer and chemical industries are actively concentrating on the discovery and application of vegetable oils for polymer composites. In this work, castor oil homopolymers and their copolymers with styrene were made, and their assessment was done by spectroscopic methodology, thermo gravimetric analysis (TGA), and gel permeation chromatographic (GPC) strategy. The ASTM standard approach was employed to determine these polymers' efficiency in base oil. Photo micrographic imaging was utilized to assess the efficacy of additives as pour point depressants by examining their impact on the microstructure. The biodegradability experiment for polymers was conducted too and outcomes are quite promising. Their performance comparisons have also been assessed and reported.

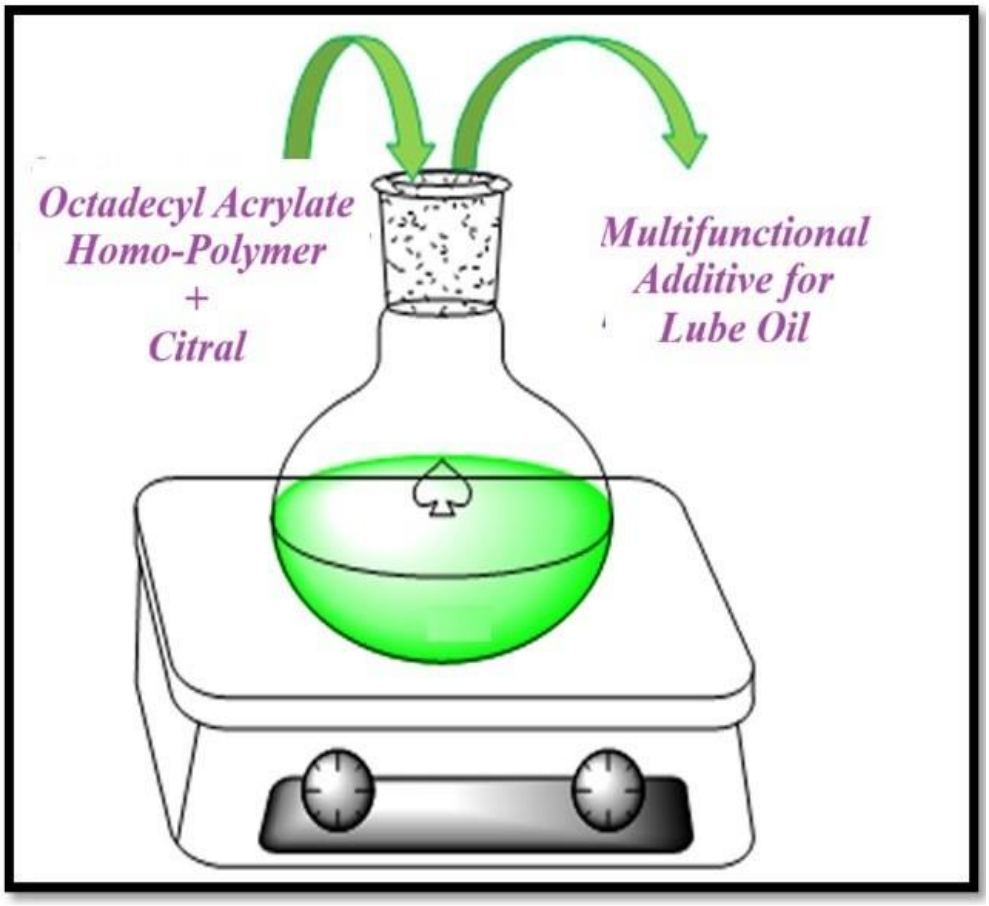


Section B deals with Behenyl Acrylate (BA) homo-polymer and its copolymers with citral were synthesized with varying percentage compositions (w/w) and subjected to thorough characterization through GPC (gel permeation chromatography) analysis and spectroscopic techniques (FT-IR, NMR). The polymers' capability was assessed through viscosity index improvers/viscosity modifiers (VII or VM), antiwear (AW) additives and pour point

depressants (PPD) for base oils (lubricating oil). The action mechanism of the PPD properties was investigated through photomicrographic analysis. Additionally, the polymers' thermal stability was measured using TGA or thermo gravimetric analysis. Biodegradability tests on copolymers were conducted using soil burial test (SBT) and the Disc Diffusion (DD) method. The copolymers exhibited exceptional PPD, VII, and AW performance when incorporated into lubricating oil.



Section C deals with Homopolymer of Octadecyl acrylate, and its different copolymers with varied percentages of Citral have been synthesised via free radical polymerisation. All the prepared polymers were characterised by FT–IR and NMR spectroscopy and their molecular weights were measured by GPC. Their performances as pour point depressant (PPD) and viscosity index improver (VII) in lube oil have been evaluated. Thermo Gravimetric Analysis (TGA) of these polymers accounted for their thermal stability as a polymeric additive. Also eco-friendly nature of the citral based polymers was established via biodegradability test.


Octadecyl Acrylate
Homo-Polymer
+
Citral
Multifunctional
Additive for
Lube Oil

PREFACE

Numerous pharmacologically relevant drugs have been designed using heterocyclic substances. These compounds have a significant impact on the agrochemical sectors as well. In addition, they are thought to be strong building blocks for the synthesis of naturally discovered substances with biological convenience, such as, heterocyclic materials, glycosides, and amino acids.

Reduced friction and wear in between two movable exteriors, heat elimination, pollutant suspension, and other fundamental operations are the main objectives of lubricants. There are further uses for automobiles and industries in addition to these. Essentially, lubricant is a mixture of as much as a 30% additive packaging and lubricating oil. Additives may bring novel features to lubricating oil or improve the ones that already present. They are made up of a vast range of compounds, contingent upon the particular qualities they add. The need for multipurpose additives has grown significantly in recent years. The author of this compilation has synthesized a few multimodal lubricant additives and assessed how well they operate as additions in various base oils. Moreover, the methods for creating a wide variety of biologically relevant heterocyclic compounds are described in this documentation.

In **Chapter I**, after detailed introductory discussion about **Biologically multi - dynamic Organic Molecules as Functional Materials: Their Synthesis and Characterization,** followed by background and entire literature survey, **Section A** has represented, A Rarely Explored, Robust, Green Catalyst, named Humic Acid mediated Solvent-Free, One - pot Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate from benzaldehyde, 2-aminobenzothiazole and ethylacetoacetate; and the synthesis of Benzo[*d*]thiazole from benzaldehyde and 2-aminothiophenol. After that, **Section B** has depicted, A supramolecular, ecological and robust catalyst, named Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent–Free Synthesis of 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) from a number of aldehydes and 2-hydroxy-1,4-naphthoquinone (Lawson Reagent) via simple Nucleophilic Addition Reaction and the synthesis of 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) from a number of aldehydes and 3-methyl-1-phenyl-1H-pyrazol-5-ol via simple nucleophilic addition (Knoevenagel Michael addition) Reaction.

In **Chapter II**, general introductory explanation about **Wide-ranging analysis of polymeric exploration, synthesis and evaluation,** followed by the detailed discussion of the background of the present study, **Section A**, has depicted the analysis of Synthesis and

Performance Evaluation of Castor oil – Styrene Co-polymer in the form of an Outstanding Multipurpose Directional Lubricant Additive along with thorough characterizations. Next in **Section B**, in details study of Evaluation and Synthesis of Environmentally Benign Multifunctional behenyl acrylate and citral based polymer Additives for Lube Oil along with characterization has incorporated. After that, **Section C**, has represented elaborately, Synthesis, efficacy, followed by entire Characterization of Octadecyl acrylate and citral based polymers and this is a comparative study on their performances as Biodegradable Multifunctional Lube Oil Additives.

Overall, the current study has conveyed a little but some honest contribution on to the unbounded spectrum of Sustainable Developmental aspiration.

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APPENDIX A
List of Research Publications

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Poster & Oral Presentations

APPENDIX A

List of Research Publications:

- **Manishita Nandi**, Bijeta Mitra, and Pranab Ghosh, "Humic acid: a rarely explored, robust, green catalyst for solvent-free synthesis of 4H-benzo [4, 5] thiazolo [3, 2-*a*] pyrimidine-3-carboxylate and benzo [*d*] thiazole." ***Research on Chemical Intermediates***, 2024, **50,** 4, 1757-1775.

- **Manishita Nandi** and Pranab Ghosh, "Evaluation and Synthesis of Environmentally Benign Multifunctional Additives for Lube Oil." ***Asian Journal of Chemical Sciences,*** 2024, **14,** 1, 42-49.

- **Manishita Nandi,** Passang Tshering Lepcha and Pranab Ghosh, "Synthesis and Performance Evaluation of Castor Oil – Styrene Co – Polymer: An Outstanding Multipurpose Directional Lubricant Additive", ***Asian Journal of Green Chemistry****,* 2023, **7,** 269-282.

- **Manishita Nandi,** Sultana Yeasmin and Pranab Ghosh, " Synthesis of behenyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives", ***Journal of Emerging Technologies and Innovative Research,*** 2024, **11,** 3, b218-b224

Under the process of Communication:

- A Review Article, on the topic, "Expository Analysis regarding Flow Enhancers for Reliable Crude Oil Transportation in Midstream Pipelines", **Manishita Nandi**, Pranab Ghosh.

- Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent–Free Synthesis of 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol), **Manishita Nandi**, Bijeta Mitra, Pranab Ghosh

APPENDIX B

Poster Presentation

- Poster representation in the INTERNATIONAL SEMINAR **(2020)** OF FRONTIERS IN CHEMISTRY, ON THE TOPIC, **"Olean12(13), 15(16)-diene,Olean-12(13), 15(16)-dien-3β-olandolean-15(16)-en-11*α*-ol: Isolation, characterization and evaluation of their biocidal activity"**.

Oral Presentation

- Oral Presentation in the INTERNATIONAL SEMINAR **(2023)** OF FRONTIERS IN CHEMISTRY AND PROF. C. N. R. RAO ENDOWMENT LECTURE; ON THE TOPIC, **"Solvent-Free Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate, using Humic Acid: A Rarely Explored, Robust, Green Catalyst"**

ABBREVIATIONS

Abbreviation	Full Form
AA	Alternaria alternata
AFM	Atomic Force Microscopy
AIBN	Azobisisobutyronitrile
AO	Antioxidant
ASTM	American Society for Testing and Materials
ASTMD	ASTM Standard D
AW	Anti-Wear
AV	Acid Value
BBO	Broad band Observe
BO	Base Oil
BPL-400B	Butane Propane Lubricant - 400B
BZP	Benzoyl Peroxide
CB	Alkyl Cyanobiphenyl
CBP	Cetyl Pyridinium Bromide
CC	Colletotrichumcamelliae
CD	Cyclodextrin
CE	Curvulariaeragrostidis
CG	Colletotrichum gloeosporioides
CPC	Alkylcyanophenyl Cyclohexane
DD	Disc Diffusion
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DMF	Dimethylformamide
ECB	Alkoxycyanobiphenyl
EVA	Ethylene Vinyl Acetate
FA	Fatty Acid
FBWT	Four Ball Wear Test
FE	Field Emission
FI	Flow Improvers
GC	Gas Chromatography

GPC	Gel Permeation Chromatography
HPLC	High-Performance Liquid Chromatography
IOCL	Indian Oil Corporation Limited
ISO	International Organization for Standardization
LOA	Loss on Aging
MCM-41	Mesoporous Silica Material
MLC	Multilayer Coating
MMT	Montmorillonite
MUFA	Monounsaturated Fatty Acid
MW	Microwave
MWD	Molecular Weight Distribution
NPC	Nano Particles
OEM	Original Equipment Manufacturer
OCP	Olefin Copolymer
PBR	Polybutadiene Rubber
PDI	Polydispersity Index
PE	Polyester
PEB	Poly(ethylene-butene)
PIB	Polyisobutylene
PMAA	Poly(methyl acrylic acid)
PMA	Poly(methyl acrylate)
ppm	Parts Per Million
PPt	Pour point
PUFA	Polyunsaturated Fatty Acid
PVC	Polyvinyl Chloride
PWL	percentage weight loss
RT	Room Temperature
SBD	Sequential Biodegradation
SAE	Society of Automotive Engineers
SBC	Styrene-Butadiene Copolymer
SBA	Santa Barbara Amorphous
SBA-15@ELA	Santa Barbara Amorphous-15 Functionalized with Elaidic Acid
SBT	Soil Burial Test

SIP	Hydrogenated Styrene Isoprene Copolymer
SST5R	Small Molecular Somatostatic Receptor Subtype 5 Antagonist
TBAHS	Tetrabutylammonium Hydrogen Sulfate
TEBFs	Tetrahydro Epoxyetheno Benzo-Furan Propellanes
TFA	Trifluoroacetic Acid
TGA	Thermo Gravimetric Analysis
THF	Tetrahydrofuran
TMSCl	trimethylchlorosilane
TLC	Thin Layer Chromatography
VM	Viscosity Modifier
WIL-471	Lubricant Grade 471
WSD	Wear Scar Diameter

Chapter I

A concise explanation about the perspective towards some production of biologically significant compounds with heterocyclic moiety

I.1. Introduction:

When cyclic compounds, composed of only 'C' (carbon) atoms, within the ring, they are nominated as Carbocyclic Compounds; whereas, the compounds, accommodating minimum one hetero atom, (other than carbon atoms), inside the ring, are elected as, Heterocyclic Compounds. The most well known heteroatoms are sulphur, oxygen and nitrogen. On the other hand, heterocyclic ring holding different heteroatoms including phosphorus, tellurium and selenium, are infrequently familior. About a half of whole organic chemistry research field conducted globally is focused on chemistry of heterocycles, which is also acknowledged as the foundation of traditional organic synthetic phenomenone. Moreover, they are essential to many different procedures and industrial firms. It is commonly recognized that heterocyclic frameworks, which serve as a crucial bridge across biology and chemistry, make up over 90% in newly developed pharmaceuticals. Heterocyclic substances are largely responsible for this inventiveness and advancement of fresh scientific paradigms. **Figure I.1.** lists certain heterocyclic units with one or more heteroatoms and ring skeletons of five or six members that have been documented in the scientific literature.

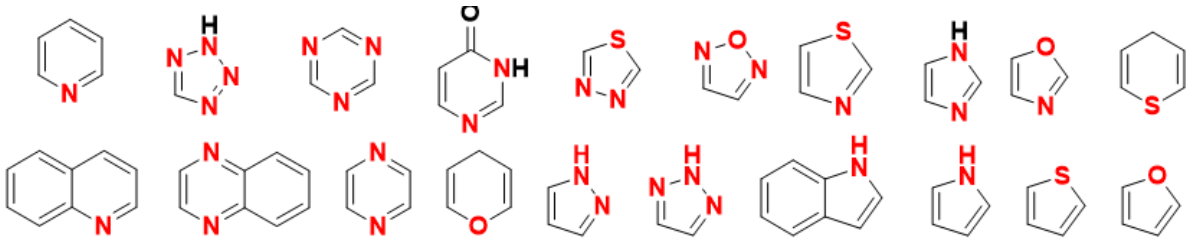


Figure I.1.: Some known five and six membered heterocyclic skeleton

Likewise, heterocyclic subunits have become extremely important for the functioning of any civilized human community in addition to being important in biology and industry. The Heterocycles make up the majority of pharmaceutical drugs that have biological consequences and resemble natural compounds. As a result, scientists are always exploring new ideas and by employing ecological models as a guide, scientists can create more effective medications, rodenticides, insecticides, and weed-killing agents. Heterocyclic substances are essential to biological functions and are necessary components of live cells. Such substances also have important and practical uses as adjusters and preservatives in a wide range of industries, such as

solvents, plastics, vulcanizing acceleration devices, reprography, makeup, and database storage. In addition, they are thought to be strong building blocks for the synthesis of naturally obtainable chemicals with biological activity such as amino acids, glycosides, organically abundant heterocyclic materials, etc. Additionally, they can be widely employed as ligands in the production of several catalysts, (composed of transition metals), which are then utilized in the manufacture of numerous organic molecules, especially compounds with heterocyclic structure.

In the pharmaceutical industry, heterocyclic analogues are widely employed as a crucial instrument in the skeletal manufacturing of many medications. An effective process for the synthesis of novel heterocyclic moieties is always important. As to an overview of the literature, over 85–95% of newly developed medications incorporate heterocyclic compounds that offer valuable scientific insights into the functioning of the biological framework. The most varied physical, chemical, and biological features can be created by combining an enormous quantity of heteroatoms, hydrogen, and carbon atoms to create substances. Over two thirds of the twenty million different chemical substances discovered by the close of the second millennium are either entirely or partly aromatic, with roughly fifty percent being heteroaromatic. Therefore, it is simple to see why the area of organic synthetic chemistry is still driven by the advancement of new techniques as well as the tactical application of established techniques for the production of more complex heterocyclic molecules. To create these heterocyclic molecules, organic chemists have worked hard to create novel, effective synthetic mechanisms.

In this **Figure I.2.**, some biologically active molecules with five and six membered heterocyclic moieties have been represented.

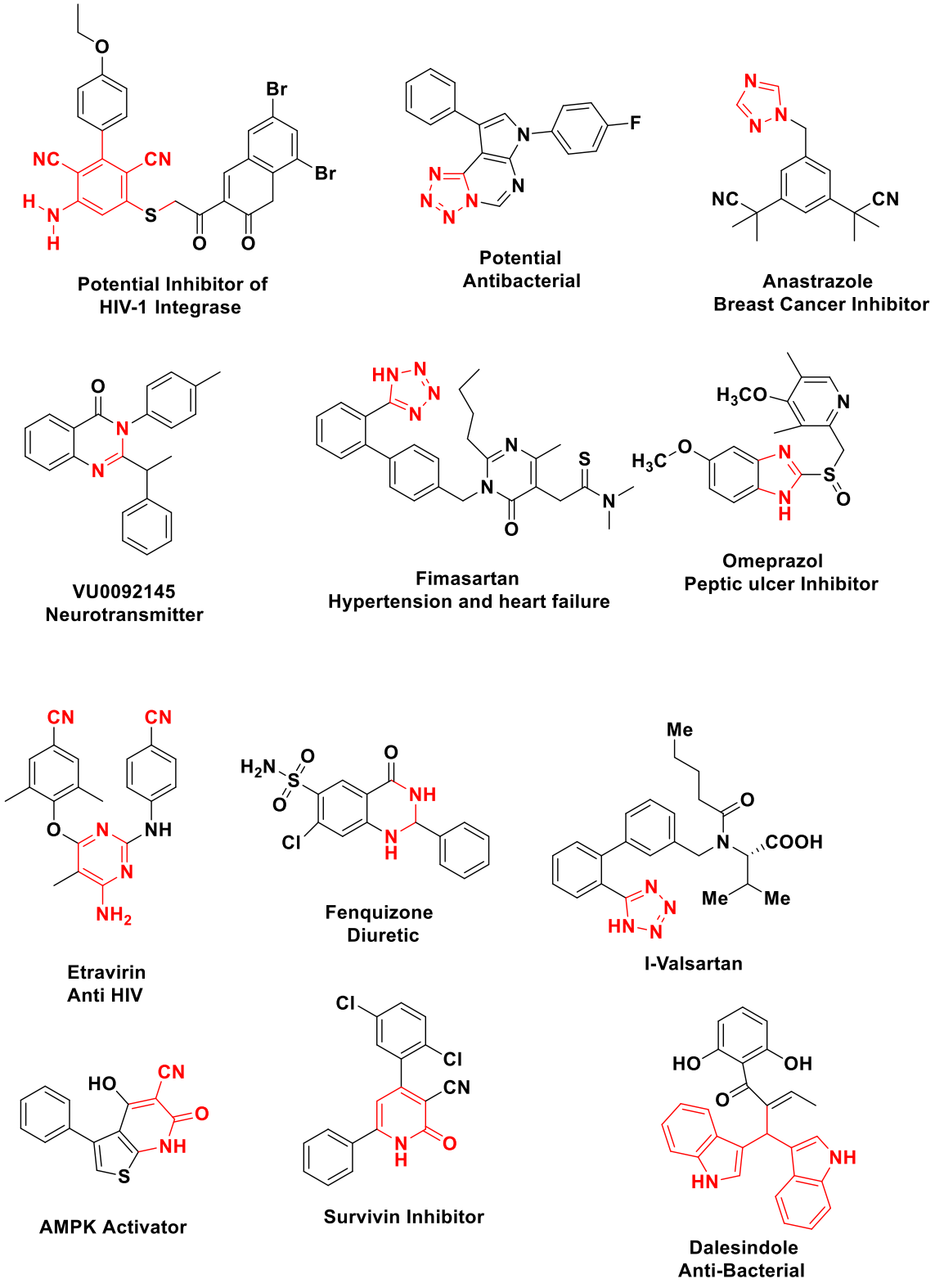
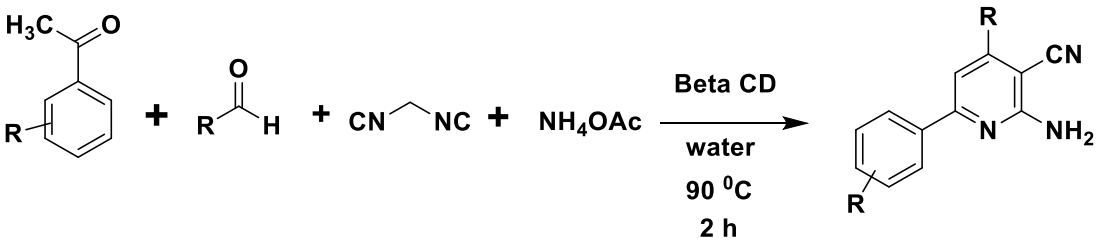


Figure I.2.: Some Biologically active molecules with five and six membered heterocyclic moieties

I.2. Methodology for the production of heterocyclic materials:

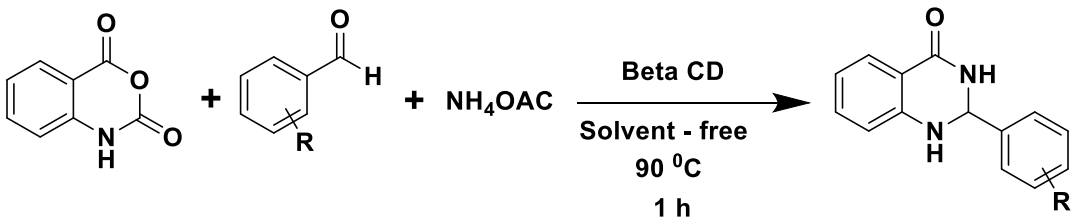
Numerous techniques for synthesizing heterocyclic substances including nitrogen, oxygen, sulfur, and selenium have been documented in the scientific community. In this part, an in-depth investigation has been conducted.

I.2.1. One - pot four - component reaction of aromatic aldehydes, acetophenone, malononitrile and ammonium acetate was carried out in a round-bottom flask to synthesize functionalized 2-amino-4, 6-diphenylnicotinonitrile by B. Mitra et al. in 2021 **(Scheme I.1.).** This reaction proceeds in presence of supramolecular recyclable β-Cyclodextrin catalyst and water solvent under 90 ^{0}C, for 2 hours. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[1]



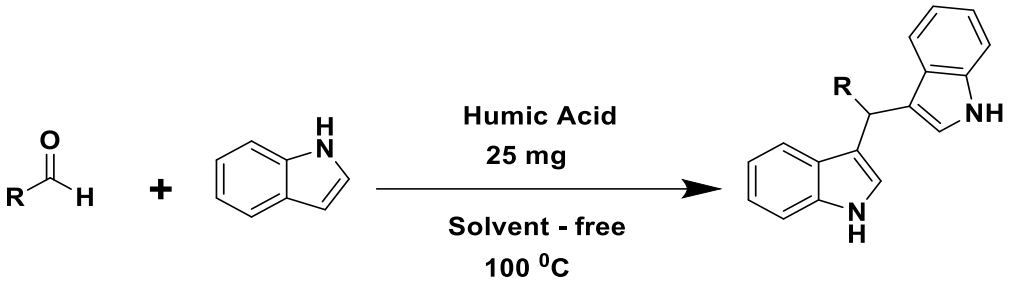
Scheme I.1. : One-pot four-component synthesis of functionalized 2-amino-4, 6-diphenylnicotinonitrile.[1]

I.2.2. One - pot three - component reaction of aromatic aldehydes, isatoic anhydride, and ammonium acetate was carried out to synthesize functionalized 2, 3-dihydroquinazolin-4(1H)-one by B. Mitra et al. in 2021 **(Scheme I.2.).** This reaction proceeds in presence of supra molecular recyclable β-Cyclodextrin catalyst under solvent – free condition at 90 ^{0}C, for 1 hour. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[1]



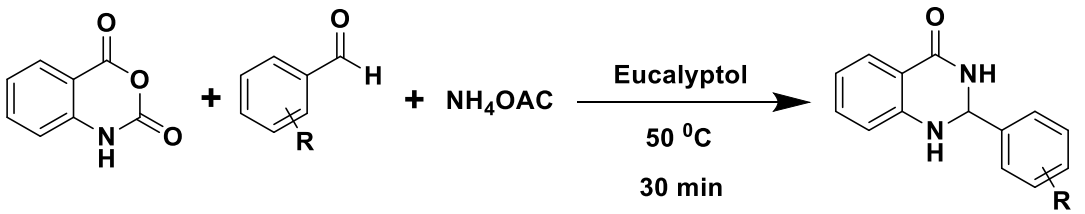
Scheme I.2. : One-pot three-component synthesis of functionalized 2, 3-dihydroquinazolin-4(1H)-one[1]

I.2.3. Two - component reaction of aromatic aldehydes and indole was carried out to synthesize some diversified bis(indolyl)methane by B. Mitra et al. in 2021 **(Scheme I.3.).** This reaction proceeds in presence of 25 gm macro sized recyclable Humic Acid catalyst under solvent – free condition at 100 ^{0}C, for 3 hours. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[2]



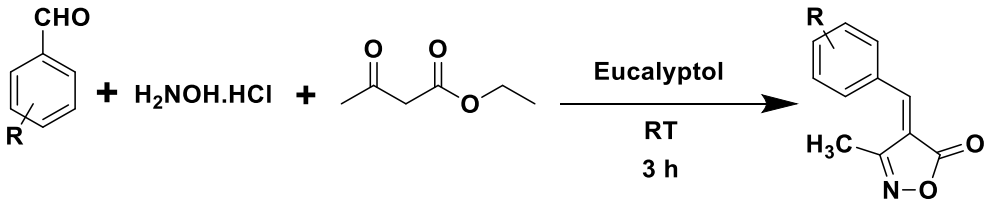
Scheme I.3. : Two - component synthesis of some diversified bis(indolyl)methane[2]

I.2.4. One - pot three - component reaction of aromatic aldehydes, isatoic anhydride, and ammonium acetate was carried out to synthesize functionalized 2, 3-dihydroquinazolin-4(1H)-one by T. Kundu et al. in 2023 **(Scheme I.4.).** This reaction was mediated through greener eucalyptol solvent under metal – free condition at 50 ^{0}C, for 30 min. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[3]



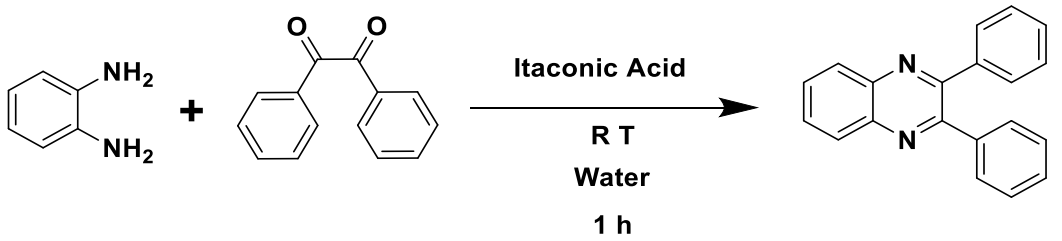
Scheme I.4. : One-pot three-component synthesis of functionalized 2, 3-dihydroquinazolin-4(1H)-one[3]

I.2.5. One - pot three - component reaction of aromatic aldehydes, ethyl acetoacetate, and hydroxylamine hydrochloride was carried out to synthesize isoxazolone derivatives by T. Kundu et al. in 2023 **(Scheme I.5.).** This reaction was mediated through greener eucalyptol solvent under metal – free condition at room temperature, for 3 hours. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[3]



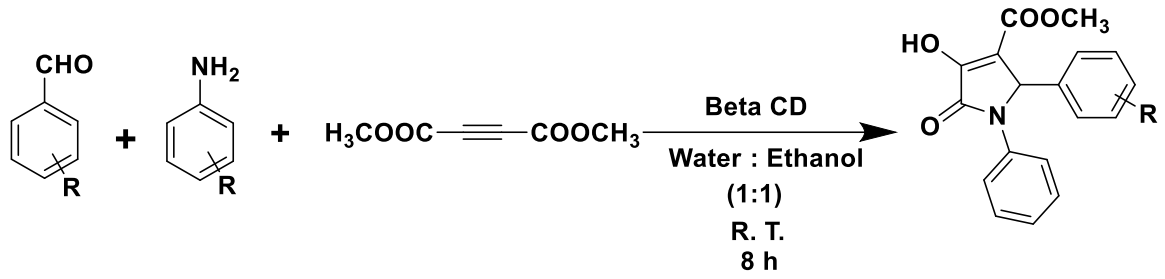
Scheme I.5. : One-pot three-component synthesis of isoxazolone derivatives[3]

I.2.6. Two - component reaction of o-phenylenediamine and benzil was carried out to synthesize some substituted quinoxaline derivatives by K. J. Tamuli et al. in 2021 **(Scheme I.6.).** This reaction proceeds in presence of cheap and biodegradable itaconic acid as a mild acid promotor under the presence of water solvent at room temperature, for 1 hour through cyclo condensation process. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[4]



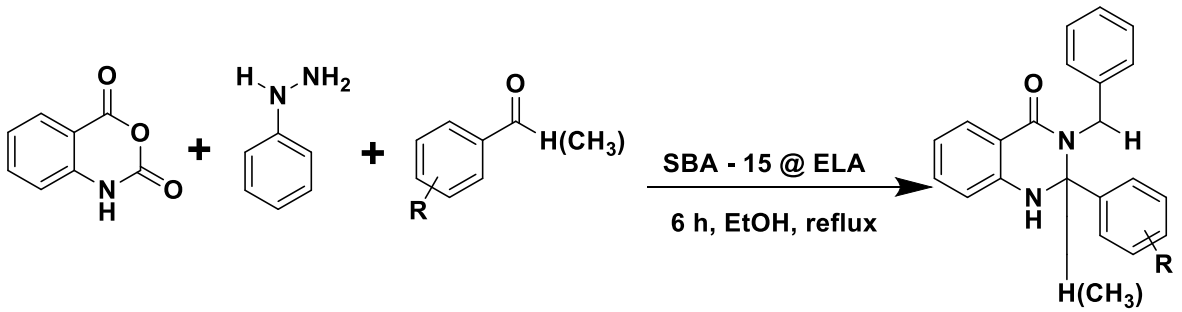
Scheme I.6. : Two - component synthesis of substituted quinoxaline derivatives[4]

I.2.7. One - pot three - component reaction of aromatic aldehydes, aniline, and dimethylacetylenedicarboxylate was carried out to synthesize methyl 2-aryl-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate derivatives by S. Paul et al. in 2023 **(Scheme I.7.).** This reaction was mediated through greener supra molecular β-Cyclodextrin catalyst under metal – free condition, in presence of 1:1 water – ethanol solvent at room temperature, for 8 hours. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[5]



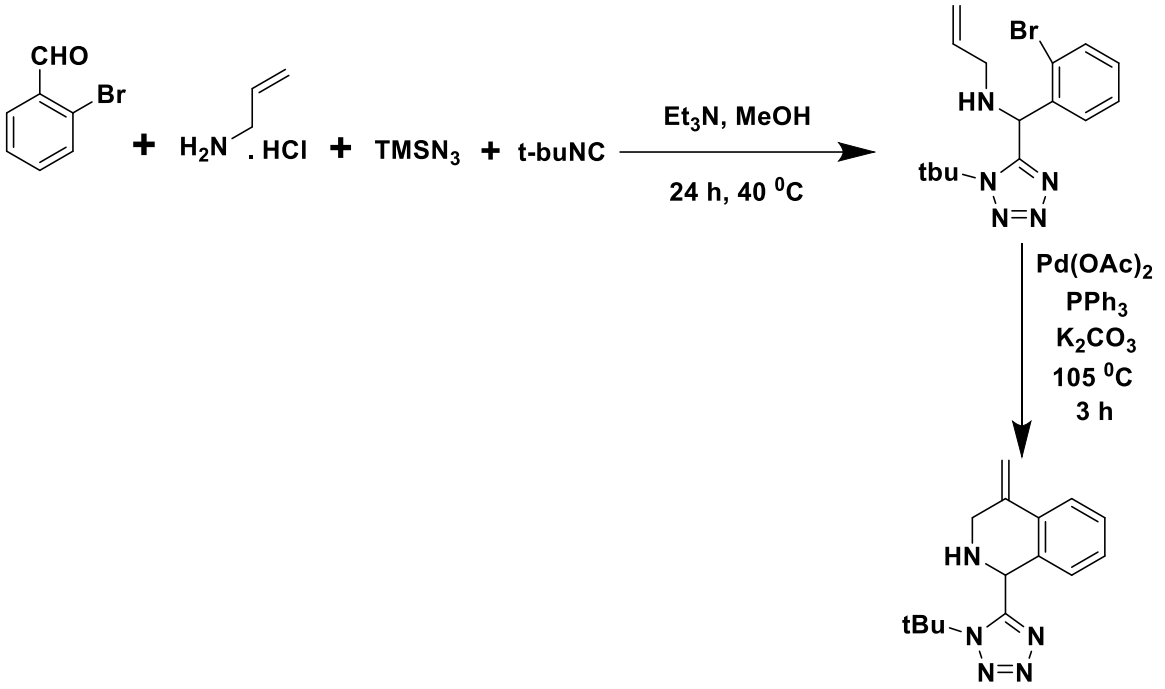
Scheme I.7. : One-pot three-component synthesis of 2-aryl-4-hydroxy-5-oxo-1-phenyl-2, 5-dihydro-1H-pyrrole-3-carboxylate derivatives[5]

I.2.8. One - pot three - component reaction of isatoic anhydride, phenyl hydrazine, and aromatic aldehydes or acetophenone derivatives was carried out to synthesize 4-oxo-dihydroquinazolinone derivatives by N. M. Yazdi et al. in 2024 **(Scheme I.8.).** This reaction was mediated through SBA-15@ELA nano catalyst under reflux condition, in presence of ethanol solvent for 6 hours. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[6]



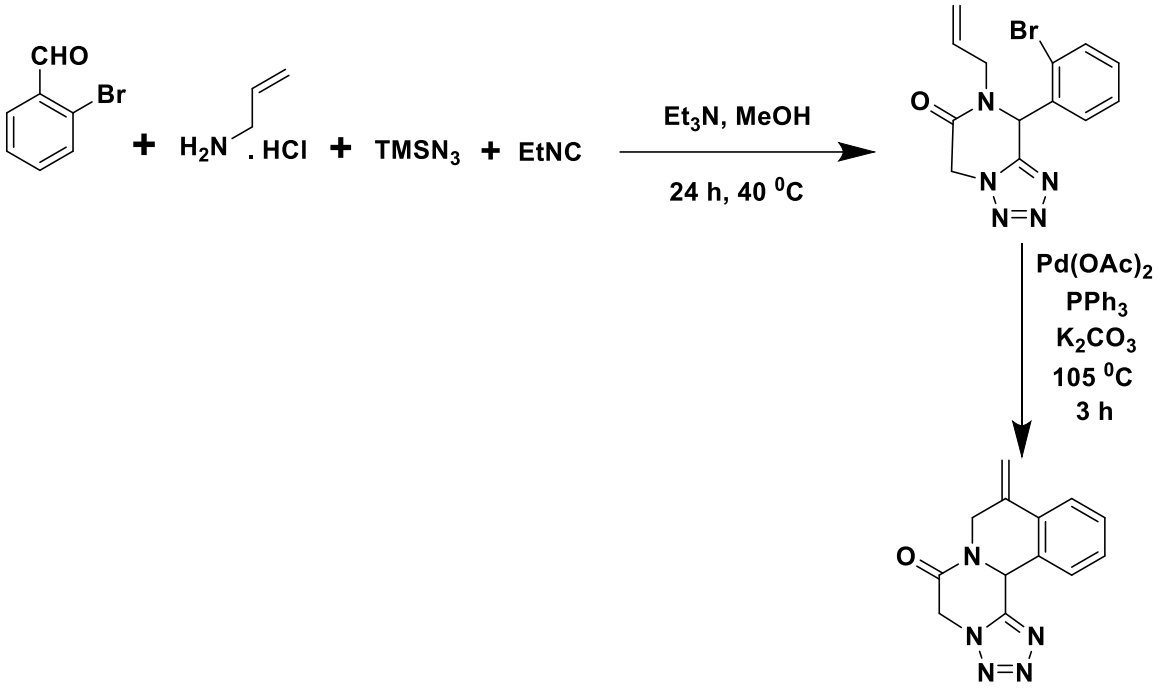
Scheme I.8. : One-pot three-component synthesis of 4-oxo-dihydroquinazolinone derivatives[6]

I.2.9. One - pot four – component Ugi reaction followed by intra molecular Heck reaction of 2-bromobenzaldehyde, allylamine hydrochloride, trimethylsilyl azide and *tert*-butyl isocyanide derivatives was carried out to synthesize functionalized tetrazolyl-1,2,3,4-tetrahydroisoquinolines by J. Niu et al. in 2024 **(Scheme I.9.).** This Ugi reaction was mediated through Et_3N in 5 mL MeOH, at 40 ^{0}C, for 24 hours and Heck reaction was carried out by dissolving in MeCN solvent, $Pd(OAc)_2$ catalyst, PPh_3 and K_2CO_3 reagent for 3 hours at 105 °C under N_2 atmosphere. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[7]



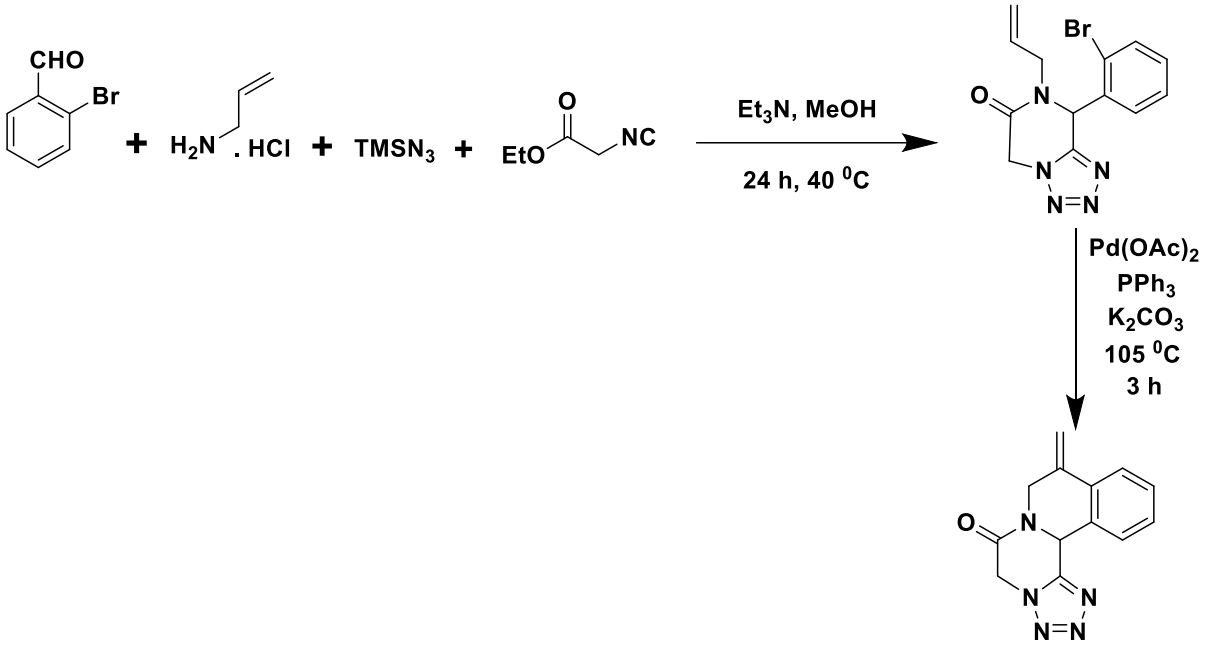
Scheme I.9. : One-pot four-component synthesis of functionalized tetrazolyl-1, 2, 3, 4-tetrahydroisoquinolines[7]

I.2.10. One - pot four – component Ugi reaction of 2-bromobenzaldehyde, allylamine hydrochloride, trimethylsilyl azide and Ethyl isocyanide derivatives was carried out to synthesize tetrazolo[1,5-*a*]pyrazin-6(5*H*)-one derivatives, followed by intra molecular Heck reaction to synthesis functionalized tetracyclic tetrazolo-pyrazino[2,1-*a*]isoquinolin-6(5*H*)-ones by J. Niu et al. in 2024 **(Scheme I.10.).** This Ugi reaction was mediated through Et_3N in 5 mL MeOH, at 40 ^0C, for 24 hours and Heck reaction was carried out by dissolving in MeCN solvent, $Pd(OAc)_2$ catalyst, PPh_3 and K_2CO_3 reagents for 3 hours at 105 °C under N_2 atmosphere. The structures of the prepared products were characterized through their FT - IR, ^1H NMR, ^{13}C NMR spectra and elemental analysis.[7]



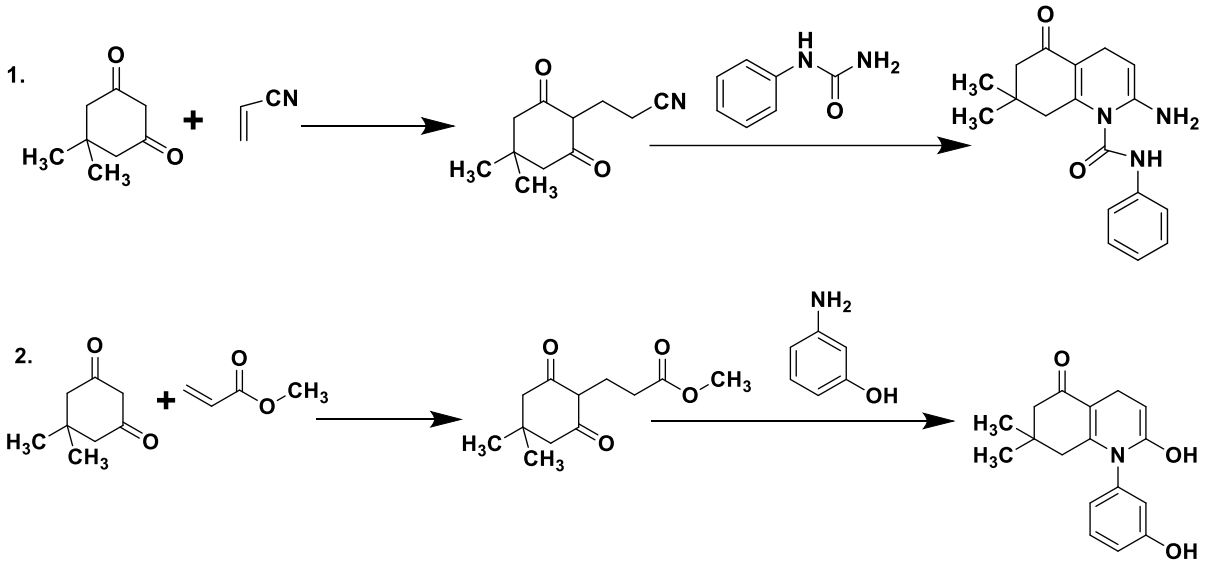
Scheme I.10. : One-pot four-component synthesis of functionalized tetracyclic tetrazolo-pyrazino[2,1-*a*]isoquinolin-6(5*H*)-ones[7]

I.2.11. One - pot four – component Ugi reaction followed by intra molecular Heck reaction of 2-bromobenzaldehyde, allylamine hydrochloride, trimethylsilyl azide and Ethyl 2 - isocyanate derivatives was carried out to synthesize functionalized tetrazolo[1,5-*a*]pyrazin-6(5*H*)-one derivatives, by J. Niu et al. in 2024 **(Scheme I.11.).** This Ugi reaction was mediated through Et_3N in 5 mL MeOH, at 40 ^{0}C, for 24 hours and Heck reaction was carried out by dissolving in MeCN solvent, $Pd(OAc)_2$ catalyst, PPh_3 and K_2CO_3 reagents for 3 hours at 105 °C under N_2 atmosphere. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[7]

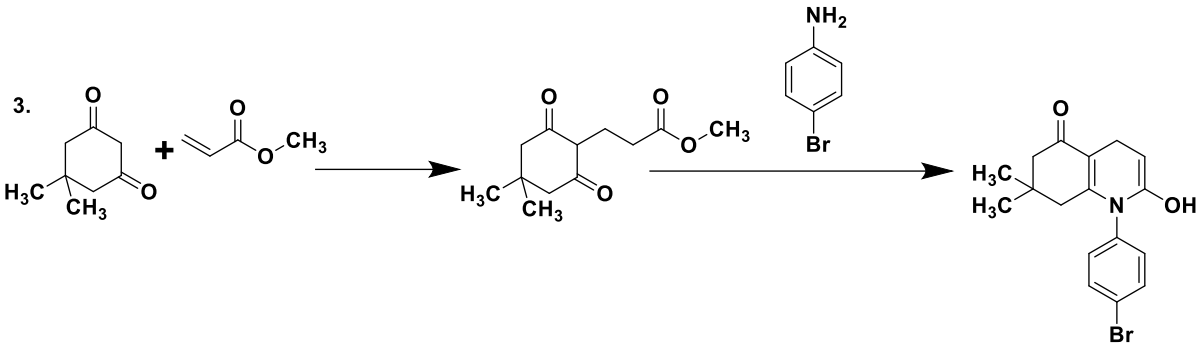


Scheme I.11. : One-pot four-component synthesis of functionalized tetracyclic tetrazolo-pyrazino[2,1-*a*]isoquinolin-6(5*H*)-ones[7]

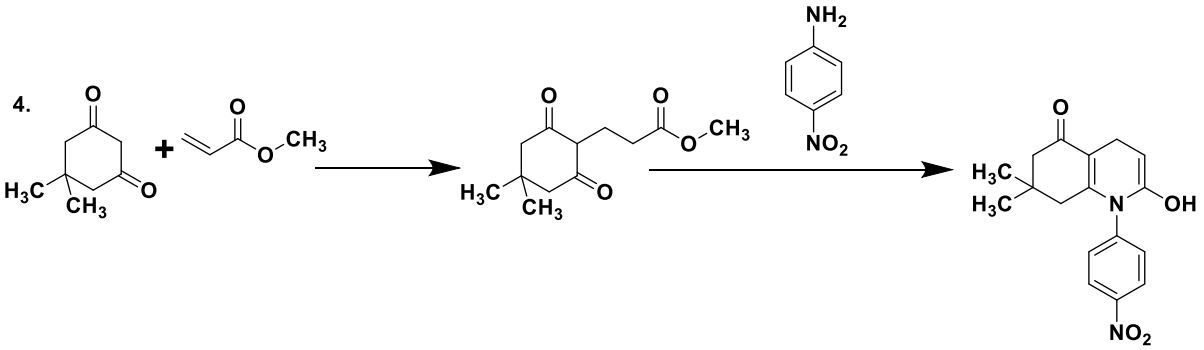
I.2.12. A number of one - pot synthesis of heterocyclic dihydroquinoline analogues, incorporating quinoline and pyrimidine fused rings in condensation reaction using nanocrystalline-TiO_2 on dodecyl-sulfated silica support (NCTDSS) catalyst, under reflux condition was done by S. M. Hughighi et al. in 2022 **(Scheme I.12.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[8]



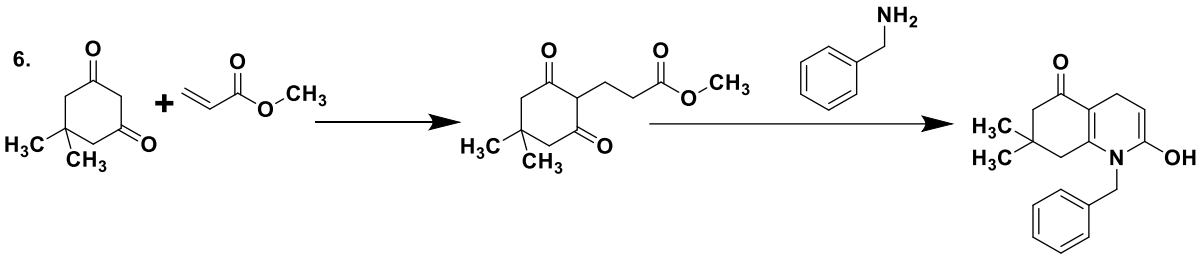
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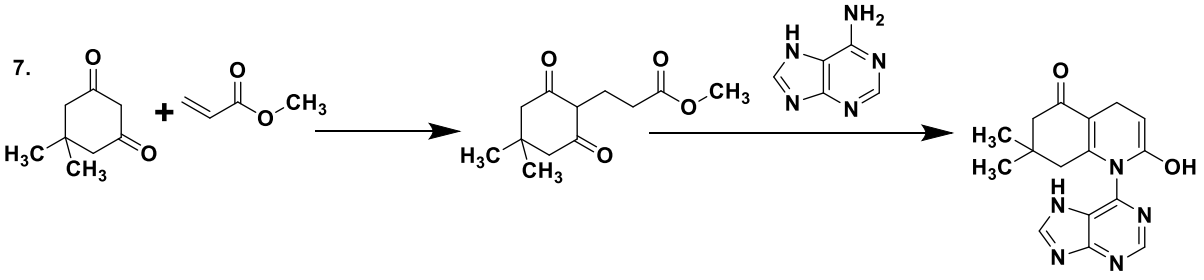
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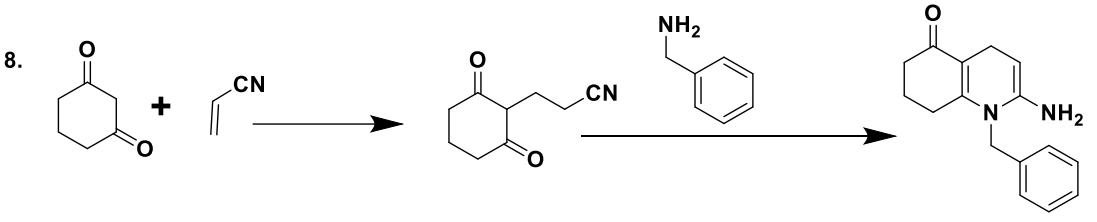
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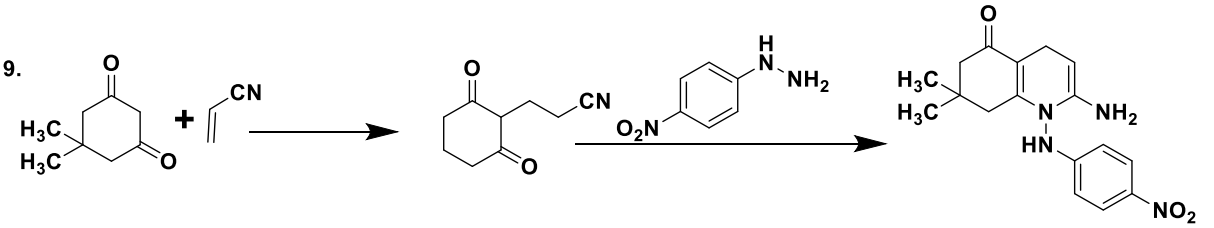
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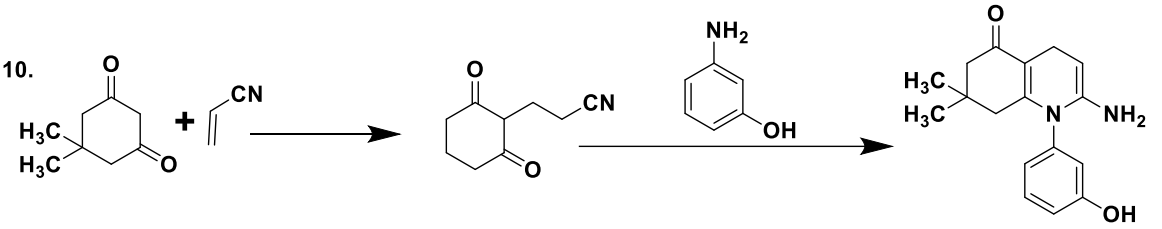
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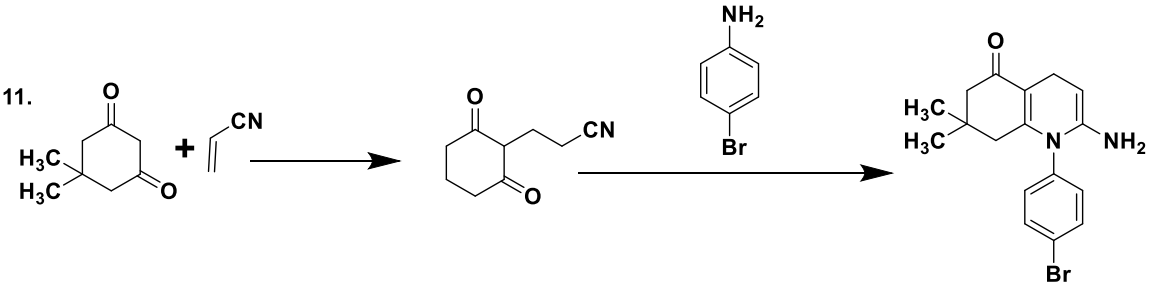
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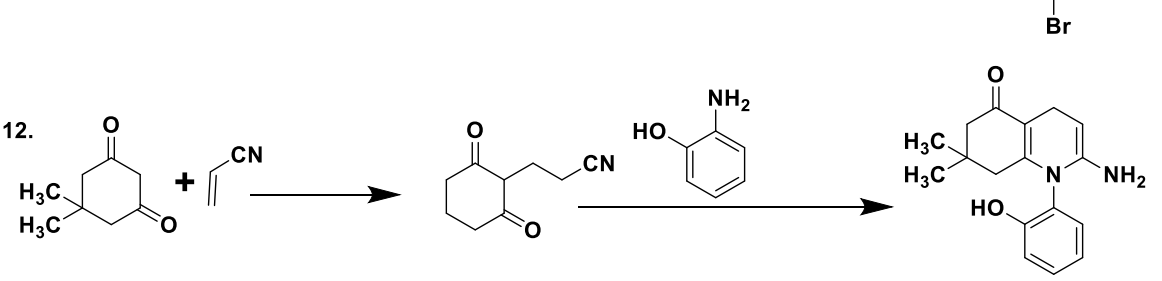
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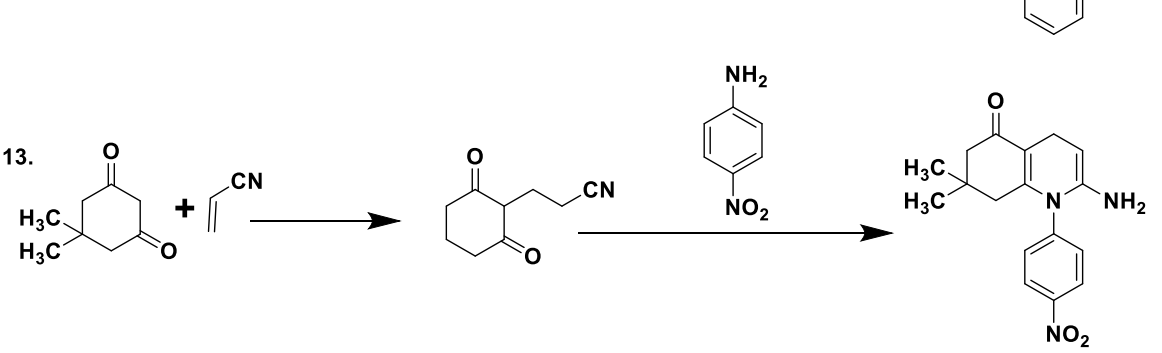
11.



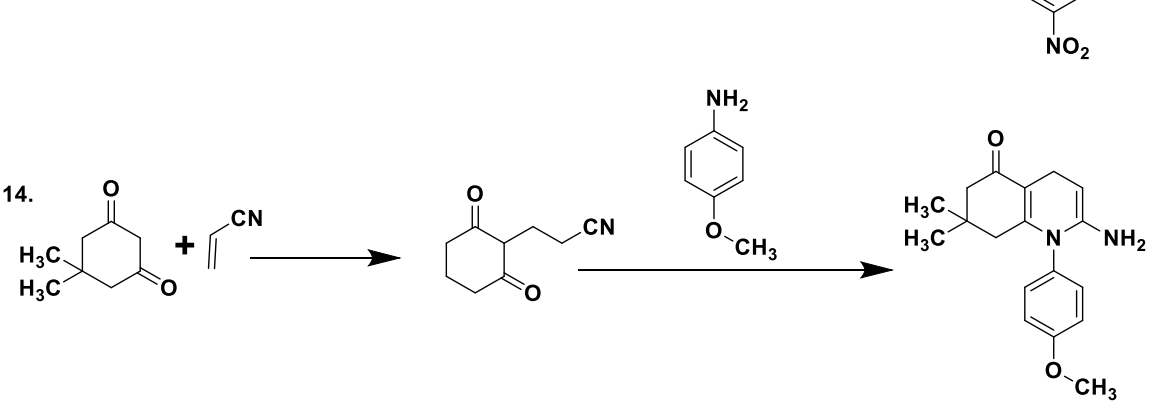
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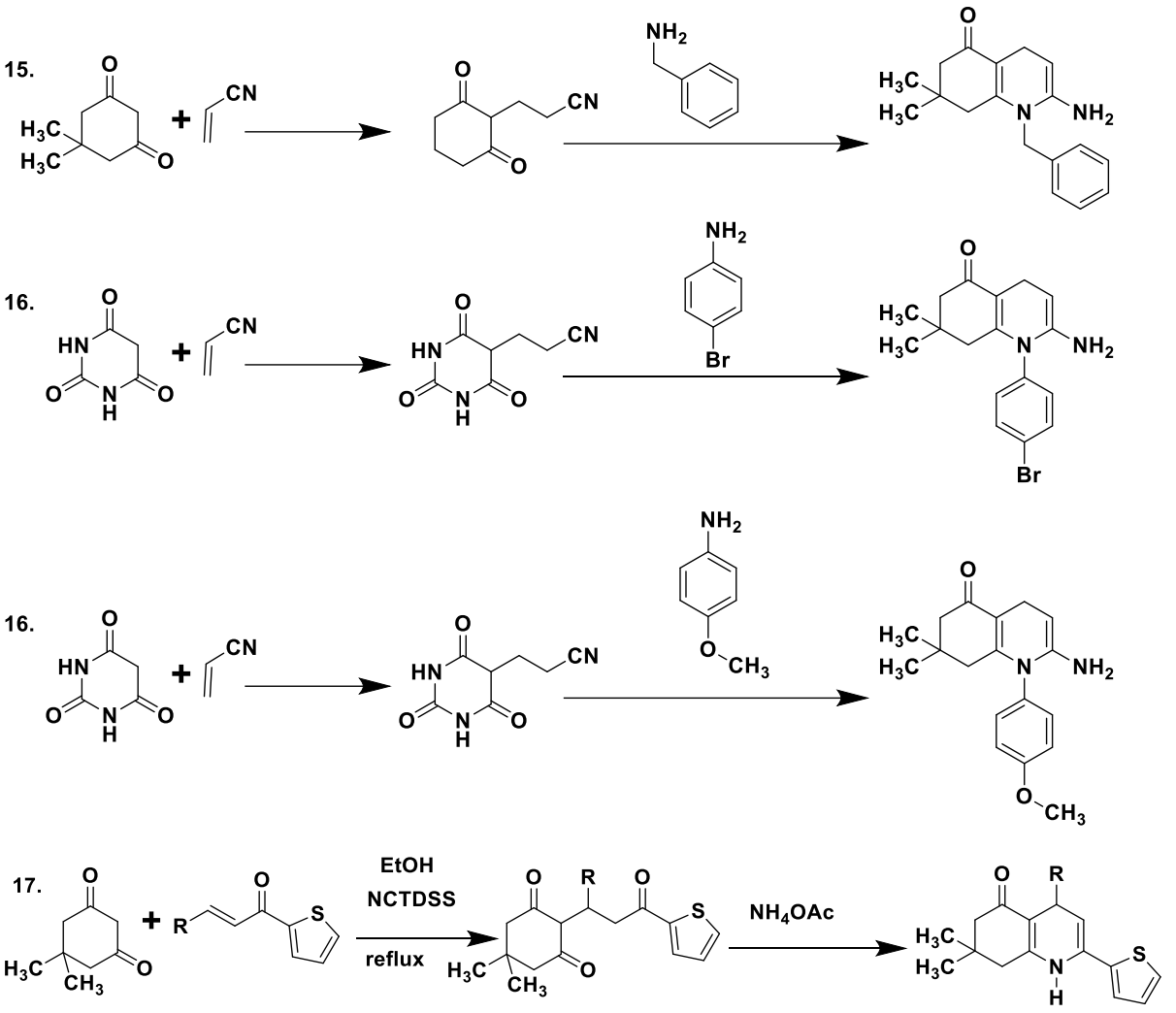


13.



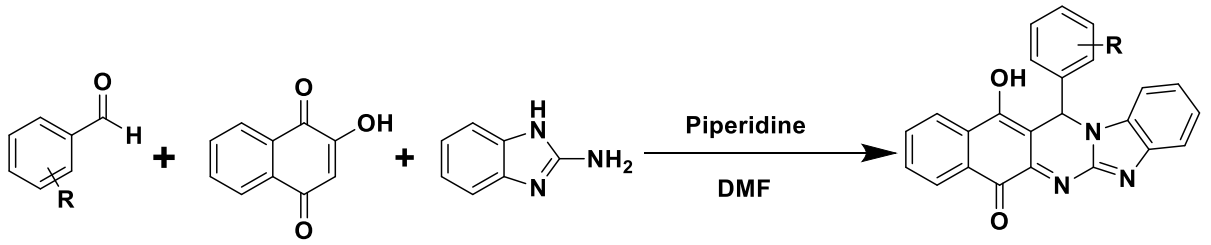
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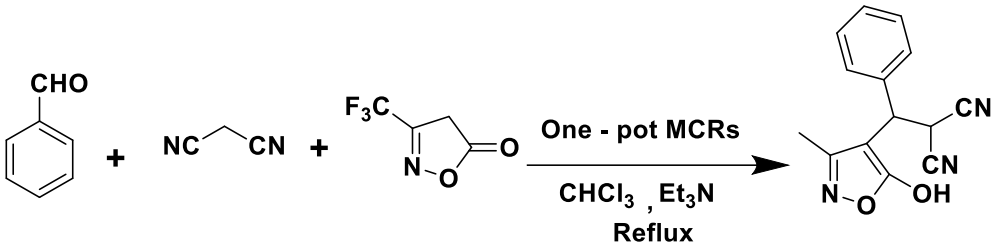
Scheme I.12. : A number of one - pot synthesis of heterocyclic dihydroquinoline analogues[8]

I.2.13.. Domino, cost effective, one - pot three – component reaction of 2-hydroxy-1,4-naphthoquinone, aromatic aldehydes, and 2-aminobenzimidazole was carried out to synthesize functionalized novel benzo[g]benzo[4,5]imidazo[2,1-b]quinazoline derivatives, by M. A. Sarhadi et al. in 2024 **(Scheme I.13.).** This reaction was mediated through piperidine in DMF solvent. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[9]



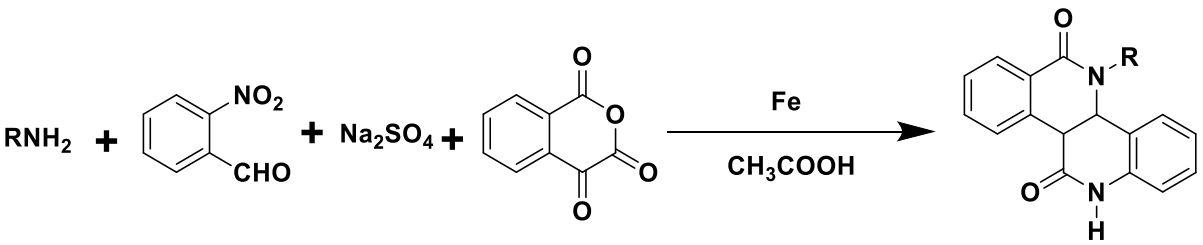
Scheme I.13. : One-pot three-component synthesis of functionalized novel benzo[g]benzo[4,5]imidazo[2,1-b]quinazoline derivatives[9]

I.2.14. One - pot three – component reaction of 3-(trifluoromethyl)isoxazol-5(4H)-one, malononitrile and aldehydes was carried out to synthesize functionalized trifluoromethylated isoxazolone-tethered trisubstituted methane derivatives, by Y. Zhang et al. in 2023 **(Scheme I.14.).** This reaction was mediated through catalytic amount of triethylamine. The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[10]



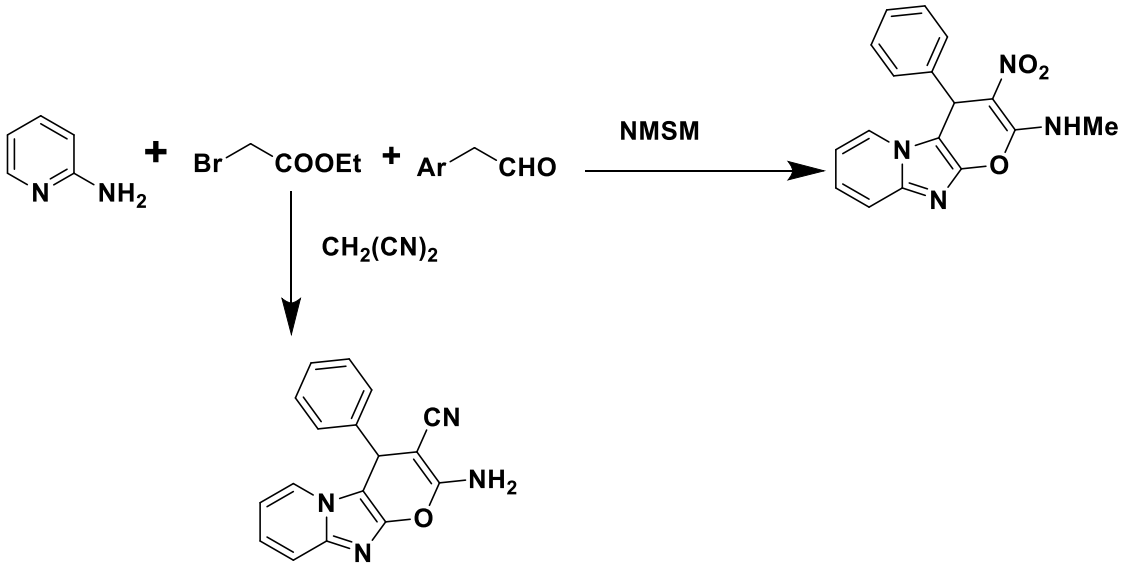
Scheme I.14. : One-pot three-component synthesis of functionalized trifluoromethylated isoxazolone-tethered trisubstituted methane derivatives[10]

I.2.15. One - pot multi – component sequential reaction of 2-nitrobenzaldehyde, aliphatic/aromatic amines, and homophthalic anhydride was carried out for telescopic synthesis of a nitrogen-fused heterocycle dihydrodibenzonapthyridinedione via imine formation, then the Castagnoli-Cushman reaction followed by nitro-reduction and intramolecular lactamization, by S.S. Deshmukh et al. in 2024 **(Scheme I.15.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[11]



Scheme I.15. : One - pot multi – component synthesis of nitrogen-fused heterocycle dihydrodibenzonapthyridinedione[11]

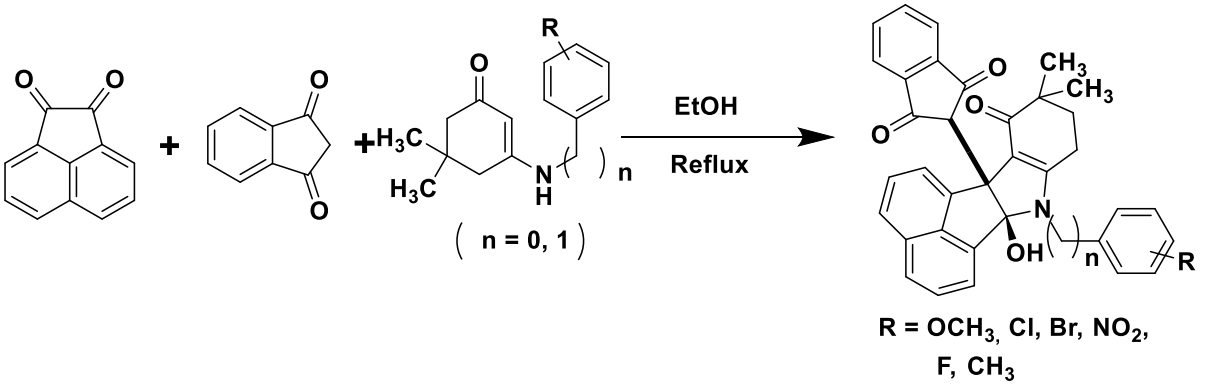
I.2.16. One - pot multi – component sequential reaction of 2-aminopyridine, ethyl 2-bromoacetate, ethanol and substituted benzaldehyde, followed by NMSM or malononitrile was carried out for synthesis of novel N-methyl-3-nitro-4-aryl-4H-pyrano[2′,3′:4,5]imidazo[1,2-a]pyridine-2-amine and 2-amino-4-aryl-4H-pyrano[2′,3′:4,5]imidazo[1,2-a]pyridine-3-carbonitrile respectively by R. Vediyappan et al. in 2023 **(Scheme I.16.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[12]



Scheme I.16. : One - pot multi – component synthesis of novel N-methyl-3-nitro-4-aryl-4H-pyrano[2′,3′:4,5]imidazo[1,2-a]pyridine-2-amine and 2-amino-4-aryl-4H-pyrano[2′,3′:4,5]imidazo[1,2-a]pyridine-3-carbonitrile[12]

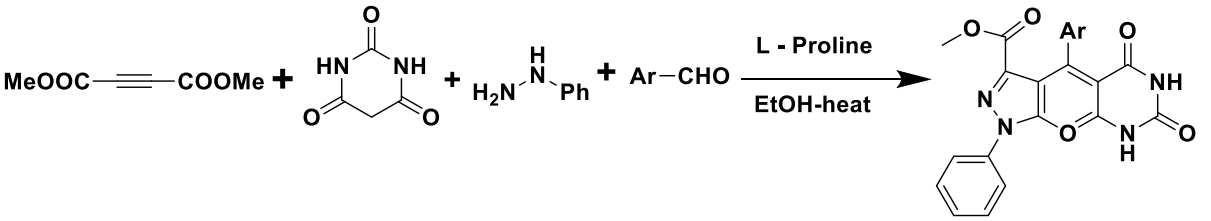
I.2.17. One - pot four – component reaction of dimedone, arylamines, acenaphthoquinone, and 1,3-indondione was carried out for synthesis of acenaphtho[1,2-b]indolindenedione derivatives

and acenaphtho[1,2-b]indolone derivatives by Z. Amiri et al. in 2023 **(Scheme I.17.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[13]



Scheme I.17. : One - pot four – component synthesis of acenaphtho[1,2-b]indolindenedione derivatives and acenaphtho[1,2-b]indolone derivatives[13]

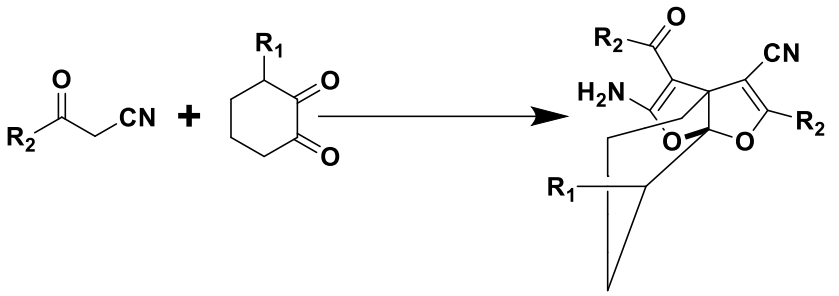
I.2.18. One - pot four – component L – Proline mediated condensation reaction of dimethyl but-2-ynedioate, Phenyl hydrazine, barbituric acid and aromatic aldehyde under Ethanol solvent was carried out for synthesis of methyl 4-(4-chlorophenyl)-5,7-dioxo-1-phenyl-1,4,5,6,7,8-hexahydropyrazolo [4′,3′:5,6] pyrano[2,3-d] pyrimidine-3-carboxylate derivatives by M. B. Yadav et al. in 2021 **(Scheme I.18.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[14]



Scheme I.18. : One - pot four – component synthesis of methyl 4-(4-chlorophenyl)-5,7-dioxo-1-phenyl-1,4,5,6,7,8-hexahydropyrazolo [4′,3′:5,6] pyrano[2,3-d] pyrimidine-3-carboxylate derivatives[14]

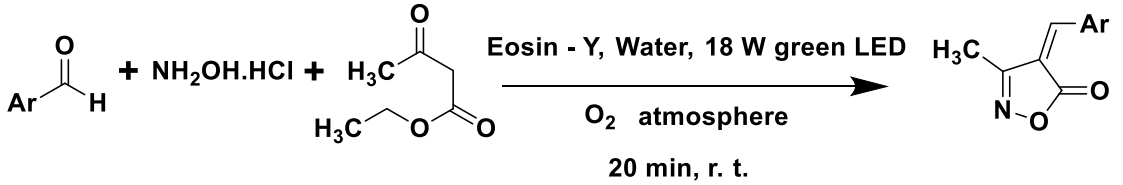
I.2.19. One – pot straightforward two – component effective base-catalyzed Knoevenagel, Michael and intramolecular/Paal-Knorr cyclization strategic reaction of cyclic α-diketones and α-cyanoketones was carried out for synthesis of heterocyclic [4.3.3] tetrahydro epoxyetheno

benzo-furan propellanes (TEBFs) by M. B. Yadav et al. in 2022 **(Scheme I.19.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[15]



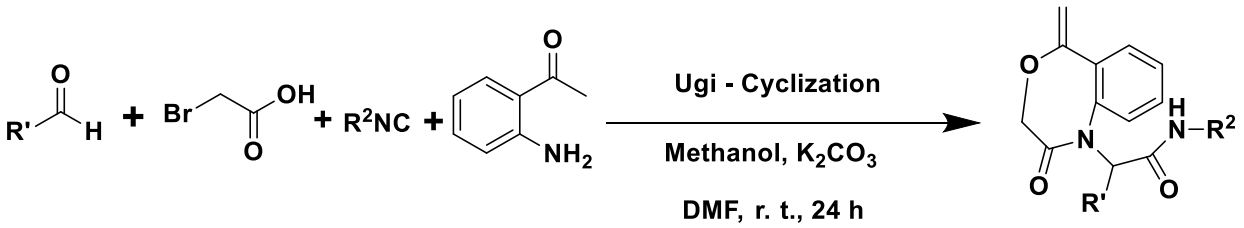
Scheme I.19. : One - pot four – component synthesis of heterocyclic [4.3.3] tetrahydro epoxyetheno benzo-furan propellanes (TEBFs)[15]

I.2.20. An eco-friendly green and metal-free visible light mediated, water solvent oriented one – pot three – component effective eosin-Y catalyzed reaction of aryl aldehydes, ethyl acetoacetate and hydroxylamine hydrochloride was carried out for synthesis of biologically potent 4-benzylidene-3-methylisoxazol-5(4H)-one by R. Kumar et al. in 2023 **(Scheme I.20.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[16]



Scheme I.20. : One - pot four – component synthesis of biologically potent 4-benzylidene-3-methylisoxazol-5(4H)-one[16]

I.2.21. An user-friendly, one – pot four – component effective base catalyzed Ugi - cyclization reaction of 2′-aminoacetophenone, aldehydes, bromoacetic acid, and isocyanides was carried out for synthesis of biologically potent 2-oxo-benzo[1,4]oxazepines by M. Mirfattahi et al. in 2024 **(Scheme I.21.).** The structures of the prepared products were characterized through their FT - IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.[17]



Scheme I.21. : One - pot four – component synthesis of biologically potent biologically potent 2-oxo-benzo[1,4]oxazepines[17]

I.3. Conclusion:

Thus, we can observe that several synthetic techniques are being developed to synthesize heterocyclic molecules with biological potency. It is evident from the analysis above that there is still much room for the development of novel response techniques in this area.

I.4. References:

References are displayed in **BIBLIOGRAPHY** under General Introductory part of **Chapter I,** that is, **A concise explanation about the perspective towards some production of biologically significant compounds with heterocyclic moiety** (pp. 197 - 198**).**

Section A

Humic Acid: A Rarely Explored, Robust, Green Catalyst for Solvent-Free Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and Benzo[*d*]thiazole

I.A.1. Introduction:

In the past several decades, research practices in chemistry are constantly evolving through overcoming the rigidities such as, fixed reaction patterns, systematic approaches inside the confines of a laboratory. In order to make any system sustainable, attempts should be made to keep the laboratory experimental conditions in accordance with the environment, surrounding us. Therefore, any alteration, innovation or discovery, made in the system must be handled with great care and consideration to ensure its suitability to the surroundings. The continuous environmental degradations and its already visible devastating impacts have made the researchers and scientists to be focused on to the suitability of their research like never before. As a consequence, like any other procedures, organic synthesis must look at the sustainability aspect through the application of innovative and greener protocols that avoid the use of hazardous solvents, toxic chemicals, poisonous catalysts, and harsh reaction conditions. Use of such substances can result in massive environmental pollution and damage to the nature, during the synthesis of chemical components, particularly organic molecules. For that reason, organic synthetic methodologies must attempt to replace the traditional solvents and catalysts (wherever possible) with appropriate alternatives. The need to keep the drug industry flourishing through maintaining the sustainable protocols makes it worthwhile to pursue chemical synthesis.

Solvent-free protocols are greener and one of the best solutions to these environmental issues, since they can eliminate most of the flaws like pyrophoric property of harmful and hazardous solvents with high volatility and poor recovery. There are ample scopes in future, for further more detailed inspection of the solvent-free pathway, basically, as a part for synthesizing of organic molecules through greener methodology. Due to such factors, solvent-free pathways of organic synthesis have become very much popular in recent years. The aim of this initiative is to enhance earthly consciousness above a number of hazardous chemicals and substitution of harmful solvents and substituting them using greener products to progress towards green chemistry [1–9].

Generally, high molecular weight materials are very much useful for organic synthesis because of their low toxicity, ease of separation, easy recovery and reusability. Among them humic acid is very rarely used, non toxic, easily accessible, inexpensive, environmentally benign, high molecular weight polymer with extraordinary catalytic activity. Humic acid is derived primarily from biodegradation of dead and decreased organic materials and obtained mostly in

peat, soil, coal, upland streams, dejected lakes and well water. It's interesting and essential catalytic activity is exhibited owing to the presence of wide range of most ample functional groups, e.g. carboxyl (-COOH) and phenolic hydroxyl (=CH-OH) group in its structure. However, a careful review of the literature reveals that, only a few articles have reported the application of catalyst. Therefore, there is an enormous scope of further detailed exploration of its catalytic venture in multidirectional protocols of biosynthesis. Low catalyst loading, outstanding yield and significant functional group toleration are some of the extraordinary characteristics of humic acid in its catalytic approach. Another important convenience about humic acid is its renewability. Structure of humic acid is given below **(Figure I.A.1.)** [10–12].

The previously reported humic acid mediated solvent-free production of multiple collection of functionalized bis(indolyl)methanes, bis(pyrazolyl)methanes, bis-coumarins and bis-lawsones by the reaction of vast range of aldehydes with Indole, 3-methyl-1-phenyl pyrazolone, 4-hydroxy coumarin and 2-hydroxy naphthalene-1,4-dione respectively [10]. Another previously reported humic acid catalyzed reaction was one pot, three components, water mediated preparation of 5-substituted 1*H*-tetrazoles, from a number of aldehydes, hydroxylamine hydrochloride in presence of sodium azide [11]. Again, humic acid was used as a support of Pd/Ni bimetallic catalyst for Heck coupling reaction, in one of the previous studies [12].

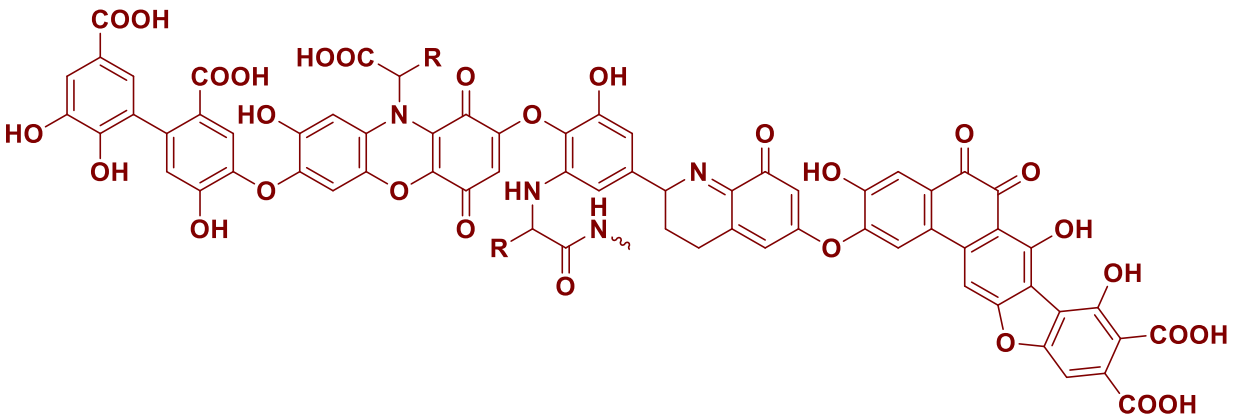


Figure I.A.1.: Structure of Humic Acid

4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine is a very essential compound under the highly important branch of fused heterocycles, with a vast pharmacological [13], pharmaceutical [14] and industrial [14] properties. It consists of a large number of biological activities, such as, antibacterial [14], anti-tumor [14], anti-inflammatory [14], antiviral [14], anticonvulsant [14],

anticancer [14], antifungal [14] or fungicidal [15], anti allergic [15], antimicrobial [15], anti mycobacterial [15], anti proliferative [15], anticoagulant [16], anti herbicidal [16], anti tuberculosis [17] – etc. It can be used as a salient synthon to design various modern medicinal drugs [18] for synthesizing a number of biologically active compounds [19] and natural products[5]. It's a remarkable optical liquid [8] with electronic properties [8] and used as dyes[20] and fluorescent [12] materials. This compound is so much useful for constructing medicines, associated with human and cattle contagious disorder such as, AIDS, hepatitis B and C, tuberculosis and bovine viral diarrhea, drug resistant cancers i.e. leukemia, carcinoma, melanoma and multi drug resistant tumors, which has no definite remedy or effective availability of vaccines till date [11].

It is very well known fact, that, heterocyclic and polycyclic compounds, containing nitrogen, sulfur and oxygen (N, S, and O respectively) are very much flexible and necessary framework for designing a variety of drugs [21]. Some basic skeletal structures of such bioactive drugs are represented below **(Figure I.A.2.).** Benzothiazole and its derivatives, the important part of heterocyclic [13] and polycyclic compounds [13], represent a number of biological [22], medicinal [23], pharmacological [14], pharmaceutical [24] significances like analgesic [15], anti epilepsy [25], anti lateral sclerosis [17], anti hypertensive [15], anti HIV [15], antiulcer [15], anti diabetic [26], anti Parkinson [27], antithrombotic [15], antihistamine [28], antiemetic [20], anti anxiety [29], anti stress [30], anti glutamate [19], anti parasitic [18], anti helminthic [31] – etc. They are used in auto immune diseases [17]. Benzothiazoles are extensive important class of pervasive heterocyclic moieties [32] and exist as molecules or molecular framework in many bioactive natural products [24], e.g. Vitamin B_{12} [12]. They have huge applications in material sciences [24] or material chemistry [24] as the primary components of materials with optical or electronic belongings [33] and also used as ligands of transition metals and intermediates of organic reactions [34]. They play an important role as ligands in asymmetric transformations [26]. It has great application prospect in synthesis of variety of agrochemical compounds [26]. They are pharmacophores and applied in variety of modern drug discovery and development like Omeprazol (proton-pump deterrence), Condesartan and Telmisartan (AT1 receptor nemesis), Mebendazole (drug to prevent parasitic worm infection), Dabigatran (direct thrombin inhibitor), Flunoxaprofen (NSAID) and Riluzole (sodium channel barricade and drug to fend off amyotrophic lateral sclerosis) – etc [27]. Benzothiazole derivatives are also present in Fanetizole

(anti-inflammatory agent), UDP-galacto-pyranose mutase inhibitor, κ and μ narcotic receptor and small molecular somatostatic receptor subtype 5 (SST5R) antagonists – etc [35]. It can act as efficient enzyme inhibitor, e.g. it is very popular inhibitor of Chemokin receptor ($CXCR_3$) [36], Lymphocyte Tyrosine kinase (LCK) [28], Glycinamide Ribonucleotide Transformylase (GARTfase) [37], Topo isomerase-1[15], Aldol reductase [38], HIV reverse transcriptase [15] - etc. Some derivatives of benzothiazole behave as plant growth regulators [39], photosensitizes, LTD_4 receptors [18], potent cataionic Trypsin receptor [30] and chemosensor[40] for a range of analytes. They are actively used in corrosion science [41]. These compounds are especially found in the moieties, which can conduct the life cycles in various cells [28]. They act a very significant role in metabolic process, taking place in living organisms [20]. They have vast industrial significances [6]. In industry, they are used as antioxidants [13], vulcanization accelerators [18], dopants in light emitting organic electroluminescent devices, i.e. nonlinear optical luminescent [13]. They can exhibit florescent properties [13] and so, they are used in designing sensor molecules of specific categories [13]. They can form the compounds with cytotoxic activities [15] and imaging agent for Ca^{2+} channel antagonist [13].

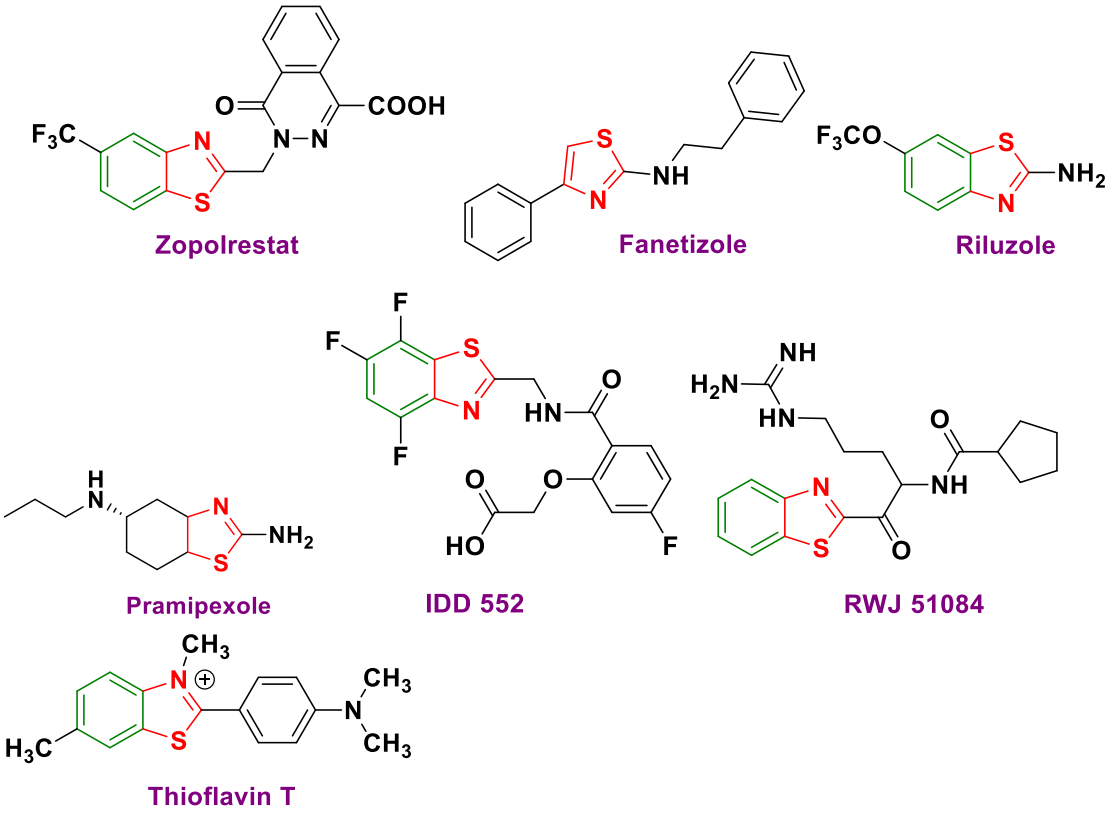


Figure I.A.2.: Some examples of biologically active drugs

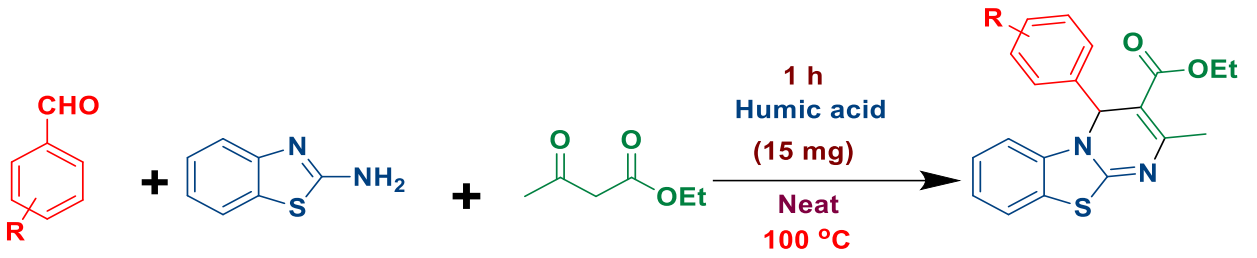
4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate was synthesized previously by using the catalysts like; magnetic nano catalyst (nano – kaoline or hydrated aluminium silicate Al_2O_3, $2SiO_2$, $2H_2O$)/Ti^{4+}/Fe_3O_4 [14], nano-Co-[4-chlorophenyl-salsylaldimine-pyranopyridine dione]Cl_2 or nano-Schiff base complex [42], DBU and CPB (cetyl pyridinium bromide) [15], phosphorus containing ionic liquids [13], Fe_3O_4@nano-cellulose/Cu(II) [43], Fe_3O_4@SiO_2-$TiCl_3$ nano particles [44], nano cellulose/BF_3/Fe_3O_4 [17], nano-$TiCl_2$/cellulose [16], L-proline [45], Lewis acid, covalently grafted over sulfonic acid functionalized carbon@titania composites [46], ager [47], ammonium chloride [19], microwave over *p*-TSA clay [48], MgO or 12-tungstophosphoric acid [49], chitosan [50], phosphoric acid supported on alumina (H_3PO_4-Al_2O_3) [51], Mg-Al-CO_3 and Ca-Al-CO_3 hydrotalcite [52], TBAHS [53] – etc.

Benzo[*d*]thiazole was synthesized previously by using the catalysts like; amino quinolate B,B-diphenyl complex as the photocatalyst [54], enzyme like Trypsin, Lipase, Bovin – etc.[22], H_2SO_4, HCl, H_3PO_4, HF – etc. traditional acid catalysts [23], Bronstead acid surfactant combined ionic liquids [32], I_2 in TBHP (Tert butyl hydroperoxide) [55], Cu(II)-Glycerol/MCM-41 (nanocatalyst) [20, 84], mesoporous titania - alumina mixed oxide [56], magnetic Co-doped $NiFe_2O_4$ [36], nano composite, mesoporous silica supported samarium [57], Ag_2O (in microwave) [58], epichlorohydrin cross linked β-cyclodextrin (β-CD polymer) [59], YCl_3 [60], UIO-66-NH_2 derived Bronstead acid catalyst [61], nano sealed UIO-66-NH-RSO_3H catalyst [53], ZnO nano particles [62], iron catalyst [37], ruthenium silicate zeolite [21], vanadium and molybdenum Schiff base complexes [28], flurescein (photocatalyst i.e. visible light in presence of O_2) [33], fluorinated phosphoric acid [34], camphore sulfonic acid [29], hydrotalcite, visible LED light in photosensitizer [63], laccase/DDQ [64], NH_2-MIL-125(Ti) metal-organic framework [65], tin modified mono ammonium phosphate fertilizer ($SnCl_2$ in MAP) or SnP_2O_7 in EtOH [66], hybrid crystal $H_3N(CH_2)_4NH_3SiF_6$ (monoalkyl ammonium hexafluorosilicate) [31], $NiFe_{2-x}Eu_XO$ nano structured catalyst [67], TiO_2 nano particle in H_2O_2(in P_{25} nanoparticles) [27], mesoporous poly(melamine-formaldehyde) [38], water(H_2O) [68], magnetic nano particles supported tungsto silicic acid [69], iron phthalocyanine [35], NaY zeolite functionalized by sulfamic acid/$Cu(OAC)_2$ or NaY zeolite-$NHSO_3H$/$Cu(OAC)_2$ as hybrid catalyst [25], oxalic acid: L-proline [40], solid acid supported on magnetic nano particles (solid acid catalyst [Fe_3O_4@SiO_2@$(CH_2)_3$NPC-SO_3H]Cl) [70], MIL-101(Fe)hexagonal microspindle [18], functionalized magnetic core shell nano particles, containing I_3^-, i.e. [Fe_3O_4@SiO_2@$(CH_2)_3NMe_3^+$]I_3^- [71], chitosan-SO_3H [72],

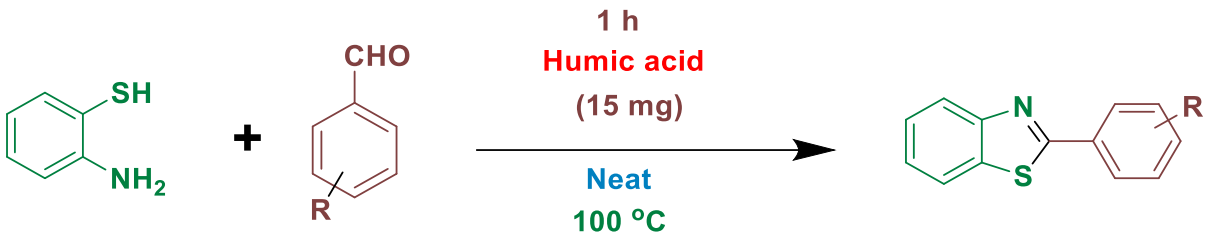
$H_3N(CH_2)_5NH_3BiCl_5$ [73], copper containing nano silica thioalated dendritic material [41, 85], two dimensional Bi_2WO_6 nano sheets as a sturdy catalyst (towards photocatalyzation) [39], phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) [51], CuI [74], $VOSO_4$ catalyst in ethanol [75], calcinized egg shell [26], copper(II)-diaminosarcophagine functionalized SBA-15 [30], proline-based ionic liquid catalyst [76], nano-titania-supported sulfonic acid catalyst (n-TSA) [77], tBuONa [78], visible light photo catalyst [79], i.e. CdSe nano composites, made by monmorillonitrile (MMT) [71], SiO_2-HNO_3 [80], Ag_2O_3/Celite [81], $Fe_3O_4/SiO_2/(CH_2)_3NMe_3^+ Br^-$ core shell nano particles [82], $CuFe_2O_4$ nano particle catalyst [83] – etc.

Metal catalysts are very much expensive, hazardous, dangerous, poisonous, fatal, toxic, and huge time consuming to be prepared. Ionic liquids are also very much expensive, auto toxic, especially for human and aquatic organisms. Moreover, Ionic liquids have their limited solubility and they cannot be removed by distillation. Therefore, we have chosen humic acid since; it is much superior in its catalytic approach with respect to the other mentioned catalysts. This makes the overall methodology of those reactions is superior in greener and environmentally more sustainable approach with respect to their previous studies.

The discussion, presented in the previous paragraphs, indicates the points of interests to synthesize compounds, containing benzothiazole moieties with a large no. of conveniences. The target compounds in this experiment, were functionalized 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine along with its derivatives in addition to functionalized benzo[*d*]thiazole and its derivatives. The present study utilized humic acid as significant greener catalyst and used some greener pathway like, solvent-free methodology **(Schemes I.A.1., I.A.2.). Scheme I.A.1.** represented here, the reaction of benzaldehyde, 2-aminobenzothiazole and ethylacetoacetate; along with the formation of functionalized 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine; on the other hand, Scheme 2 represented below, the reaction of benzaldehyde and 2-aminothiophenol; along with the formation of functionalized benzo[*d*]thiazole; in presence of humic acid catalyst, under absolute solvent – free condition.



Scheme I.A.1. : Humic acid mediated synthesis of functionalized 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine



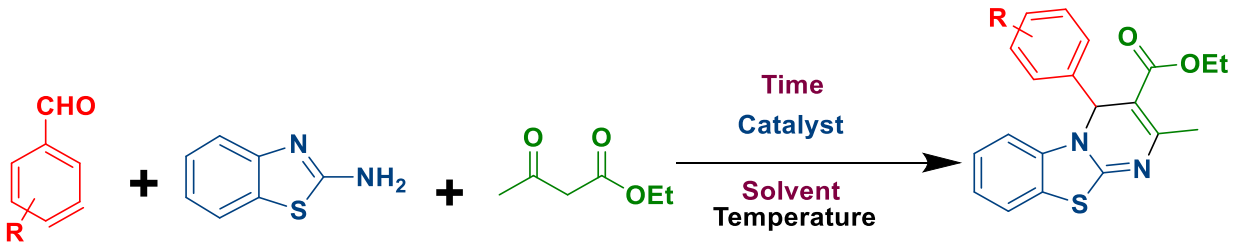
Scheme I.A.2. : Humic acid mediated synthesis of functionalized benzo[*d*]thiazole

I.A.2. Result and Discussion:

Catalyst, solvent and temperature are important driving components of any chemical reactions. So, it is necessary to maintain properly, the extent of catalyst, solvent and temperature throughout the target synthetic procedure. 1 mmol of benzaldehyde, 1 mmol of 2-aminobenzothiazole and 1 mmol of ethylacetoacetate were taken as reactants to undergo model reaction **(Scheme I.A.1.).** We started our optimization technique (Optimization procedure of **Scheme I.A.1.**, has been represented in Table I.A.1., below, in details), at first, with solvent, in presence of 30 mg of catalyst and next, it was observed that, refluxing with water, methanol and ethanol, the yield of the product was extensively low (Table I.A.1., entry 1, 2, 3). After that, by refluxing for 6 h continuously, the yield of the product was 50% with DMF (Table I.A.1., entry 4). When we carried out the same reaction, under neat condition, at 100 ^{o}C, with same amount of catalyst, then the yield of the product was enhanced up to 95% (Table I.A.1., entry 5). Then we started the optimization of catalyst by lowering the quantity as, 25 mg, 15 mg, 10 mg and 5 mg (Table I.A.1., entry 6, 7, 8, 9). As a result, we observed that, 15 mg of catalyst was enough to carry out this pathway and the yield of the product was 92% (Table I.A.1., entry 7). On the other hand, the

reaction could never be undergone in devoid of catalyst (Table I.A.1., entry 10). After that, by lowering the temperature up to room temperature, the yield of the product was reduced gradually (Table I.A.1., entry 11, 12, 13). Next, we kept track of the required time, for proceeding of the reaction and we found that, 1 h is sufficient for obtaining the maximum amount of product, under the indistinguishable reaction condition (Table I.A.1., entry 15).

Table I.A.1.: Optimization of reaction condition **(Scheme I.A.1.)**[a]



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield(%)[b]
1.	Water	30	reflux	6	trace
2.	Methanol	30	reflux	6	30
3.	Ethanol	30	reflux	6	42
4.	DMF	30	reflux	6	50
5.	Neat	30	100	6	95
6.	Neat	25	100	6	94
7.	Neat	15	100	6	92
8.	Neat	10	100	6	49
9.	Neat	5	100	6	43
10.	Neat	Nil	100	6	-
11.	Neat	15	70	6	77
12.	Neat	15	50	6	65
13.	Neat	15	rt	6	trace
14.	Neat	15	100	3	92
15.	**Neat**	**15**	**100**	**1**	**92**

The **bold** part signifies the optimized conditions;

[a]Reaction of benzaldehyde (1 mmol), 2-aminobenzothiazole (1 mmol) and ethylacetoacetate (1 mmol);

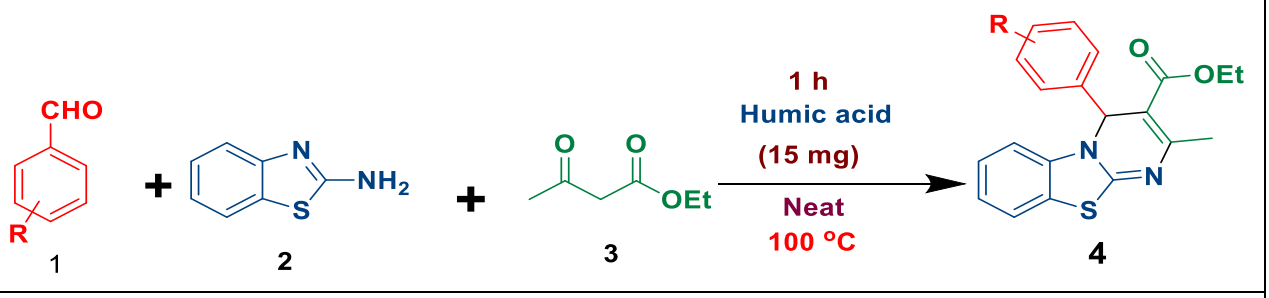
[b]Isolated yield was extracted through column chromatography.

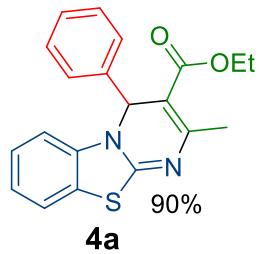
To perform in detailed study of our schemes, functionalized aldehydes were treated with 2-aminobenzothiazole and ethylacetoacetate **(Scheme I.A.1.)** under optimized condition and a variety of a number of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate derivatives were constructed. The resulted compounds have been listed below in Table I.A.2.

It was observed that, when electron withdrawing groups, especially nitro and trifluoromethyl were present in aldehyde, the product yield was very good (Table I.A.2., entry 4c, 4g respectively). But it was observed that, when aldehyde contained heterocyclic moiety, like thiophene, the product yield was not good (Table I.A.2., entry 4i). However, aldehyde with heterocyclic moiety, like pyridine, produced the products with medium yield (Table I.A.2., entry 4d). On the other hand, electron withdrawing groups like bromo, at ortho position, gave good yield (Table I.A.2., entry 4b). On the contrary, electron withdrawing group chloro at ortho position and that of fluoro at para position, gave poor yield of the product (Table I.A.2., entry 4f, 4h respectively).

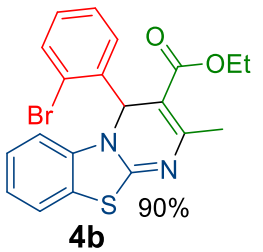
Table I.A.2.: Structural Representation of some synthesized compounds through the reaction pathway, mentioned in Scheme I.A.1.[a]

[a]**Table I.A.2.:** Synthesis of functionalized thiazolo[3,2-*a*]pyrimidine derivatives **(Scheme I.A.1.)**

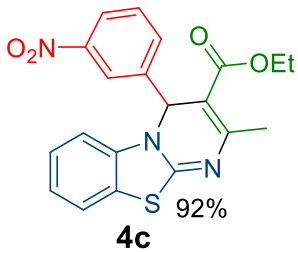




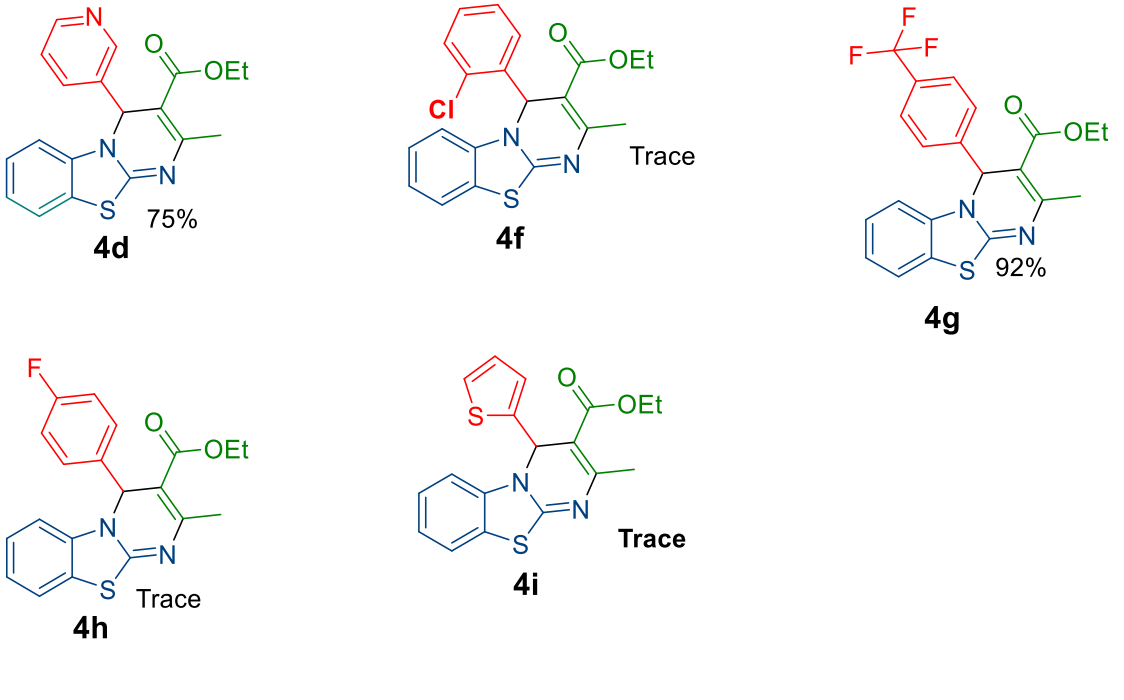
4a



4b



4c

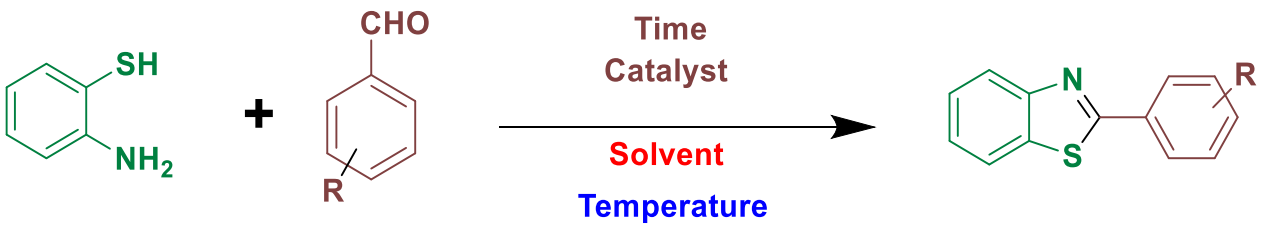


[a]Reaction of aldehydes (1 mmol), 2-aminobenzothiazole (1 mmol), ethylacetoacetate (1 mmol) and humic acid (15 mg), under solvent-free condition for 1 h.

In **Scheme I.A.2.**, we took 1 mmol of 2-aminothiophenol and 1 mmol of benzaldehyde as reactants to undergo model reaction **(Scheme I.A.1.).** In the screening method of this reaction, (Optimization procedure of **Scheme I.A.2.**, has been represented in Table I.A.3., below, in details), at first we choose solvent, in presence of 30 mg of catalyst, refluxing with water, DMF, methanol and ethanol the yield of the product was very low (Table I.A.3., entry 1, 2, 3, 4). By maintaining of 100 ^{o}C temperature continuously for 4 h, the yields of the product were 50% and 32% with PEG-200 and DMSO respectively (Table I.A.3., entry 5, 6).When we underwent the same reaction in neat condition, at 100 ^{o}C, with same amount of catalyst, then the yield of the product was enhanced up to 98% (Table I.A.3., entry 7). Then we initiated the optimization of catalyst, by reducing the amount of catalyst (Table I.A.3., entry 8, 9, 10, 11). Thus, it was observed that, 15 mg of catalyst was enough to carry out this procedure and the yield of the product was 97% (Table I.A.3., entry 9). On the other hand, the reaction could never be feasible to perform in devoid of catalyst (Table I.A.3., entry 12). After that, by lowering the temperature, the yield of the product was reduced frequently (Table I.A.3., entry 13, 14, 15). Next, we kept an eye on the required time for proceeding of the reaction and we discovered that, 1 h is sufficient for

gaining the maximum amount of product, under exactly the same reaction condition (Table I.A.3., entry 17).

Table I.A.3.: Optimization of reaction condition **(Scheme I.A.2.)**[a]



Entry	Solvent	Catalyst loading (mg)	Temperature (ºC)	Time (h)	Yield(%)[b]
1.	Water	30	reflux	4	-
2.	DMF	30	reflux	4	42
3.	Methanol	30	reflux	4	trace
4.	Ethanol	30	reflux	4	30
5.	PEG-200	30	100	4	50
6.	DMSO	30	reflux	4	32
7.	Neat	30	100	4	98
8.	Neat	25	100	4	98
9.	Neat	15	100	4	97
10.	Neat	10	100	4	88
11.	Neat	5	100	4	82
12.	Neat	Nil	100	4	-
13.	Neat	15	70	4	87
14.	Neat	15	50	4	81
15.	Neat	15	rt	4	Trace
16.	Neat	15	100	2	97
17.	**Neat**	**15**	**100**	**1**	**97**

The **bold** part signifies the optimized conditions;

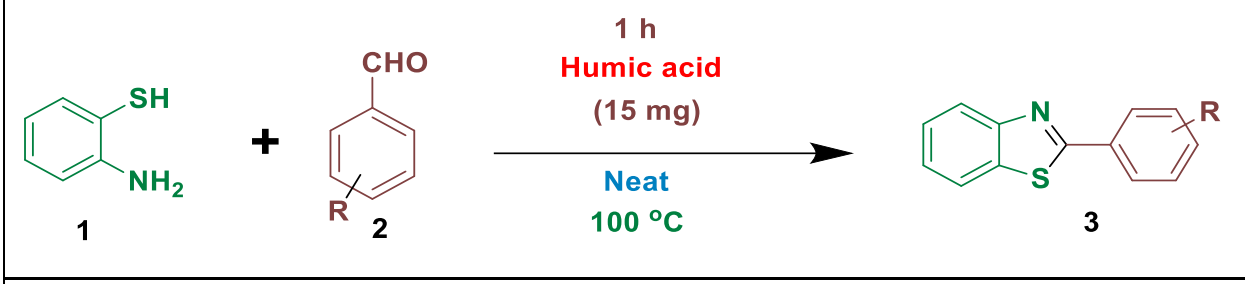
[a]Reaction of benzaldehyde (1 mmol) and 2-aminothiophenol (1 mmol);

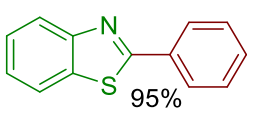
[b]Isolated yield was extracted through column chromatography.

To go through the detailed study of Scheme I.A.2., functionalized aldehydes were treated with 2-aminothiophenol (Scheme I.A.2.) under optimized condition and a variety of a number of benzo[*d*]thiazole derivatives were prepared. The resulted compounds have been listed below in Table-4. From this table, it was observed that, when electron withdrawing groups i.e. nitro at meta position, fluoro, chloro, trifluoromethyl and biphenyl at para position, were present in aldehyde, the product yield was excellent (Table I.A.4., entry 3b, 3k, 3m, 3h, 3l respectively). But it was also observed that, when an aldehyde contained electron withdrawing group i.e. fluoro at meta position, the yield was medium (Table I.A.4., entry 3i). When an aldehyde contained heterocyclic moieties like thiophene and furan, the product yield was medium to good (Table I.A.4., entry 3d, 3f respectively). Aldehyde, containing electron donating N, N dimethyl and methoxy groups, at para position, produced medium to good yield (Table I.A.4., entry 3e, 3o respectively). Vaniline and Salicylaldehyde gave very good yield (Table I.A.4., entry 3c, 3j respectively). Also, 2 naphthaldehyde produced a very good yield (Table I.A.4., entry 3n).

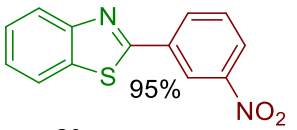
Table I.A.4.: Structural Representation of some synthesized compounds through the reaction pathway, mentioned in Scheme I.A.2. [a]

[a]**Table I.A.4. :** Synthesis of functionalized benzo[*d*]thiazole derivatives **(Scheme I.A.2.)**

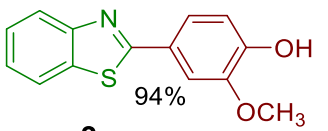




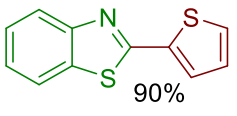
3a



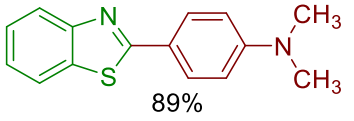
3b



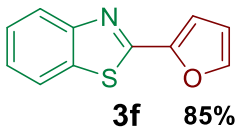
3c



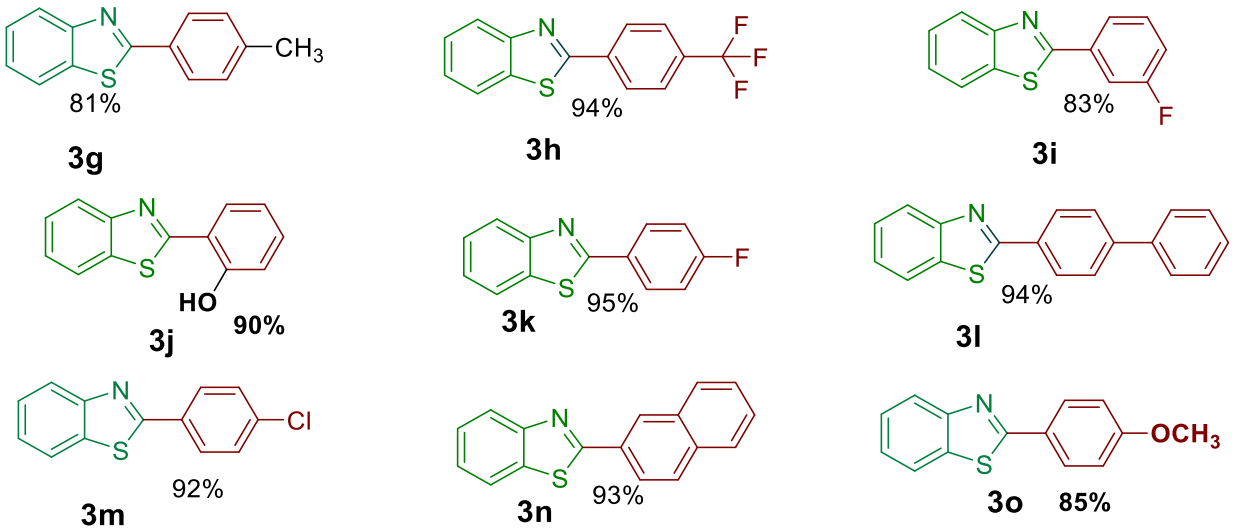
3d



3e



3f 85%



[a]Reaction of aldehydes (1mmol), 2-amino-thiophenol (1 mmol) and humic acid (15 mg) under solvent-free condition for 1 h.

I.A.3. Reusability Experiment:

Renewability of humic acid was confirmed through a model reaction, with benzaldehyde (5 mmol) and 2-aminothiophenol (5 mmol) in presence of 75 mg humic acid, under optimized reaction condition. After finishing of the first run, ethyl acetate (4 ml) was added to the reaction mixture. Catalyst was taken back smoothly from the reaction mixture by easy filtration procedure. Then the recovered catalyst was washed with ethyl acetate (3×4 ml) and next it was dried before being handed down for the next run. The filtrate of reaction mixture was shifted to another container and this method was done for two times repetitively. The catalyst was then washed with ethyl acetate again and after that, it was dried for affording the black coloured humic acid, which was used in the next run, with its dryness. Recuperation of humic acid was slightly lower than the amount used in the first run. However, the recuperated catalyst was used continuously for 4 runs with almost similar affinity and there was no noteworthy degradation in the transformation. This Recyclability test of humic acid catalyst has been represented in **Figure I.A.3.** below, through bar diagram. It signifies that, humic acid can expose its catalytic activity up to five successive runs without any considerable reduction in it and in lowering of the yield of the product.

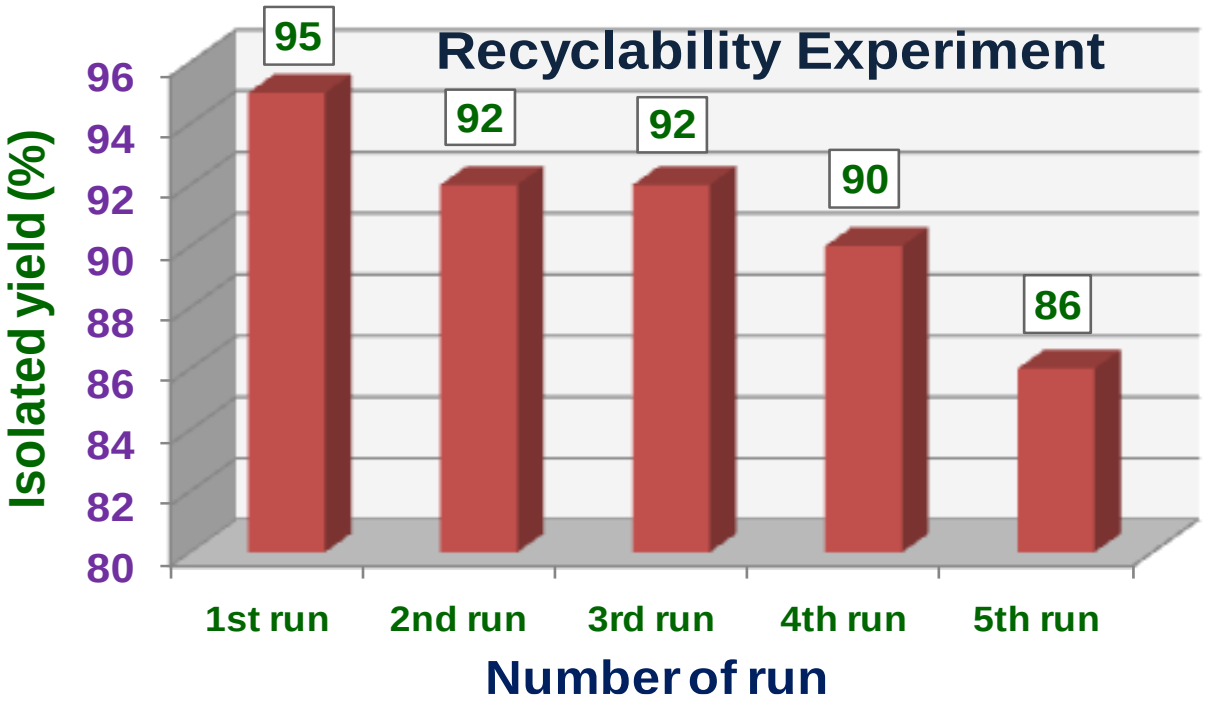


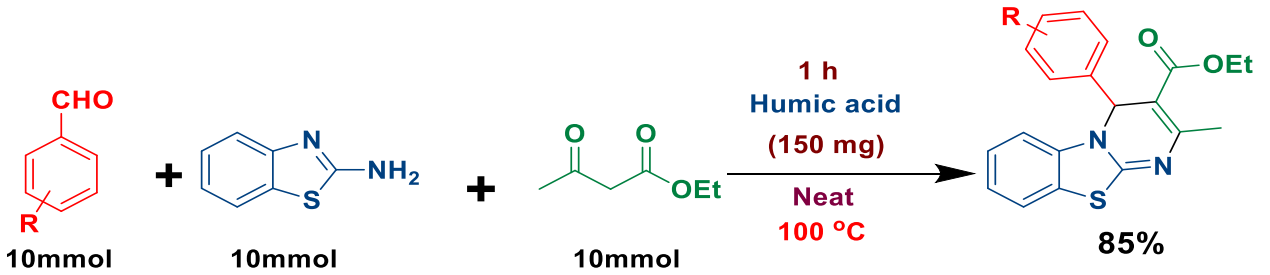
Figure I.A.3.: Reusability of Humic Acid catalyst

I.A.4. Gram - Scale Reaction:

The application of this methodology was examined in large scale, through carrying out the reactions in **gram-scale** (10 mmol scale) procedure. These also produced good yield, like the yield obtained in small scale reaction techniques. This Gram – Scale Reaction technique has been represented below, schematically, through **Figure I.A.4.**

Scale-up experiments:

Scheme I.A.1. :



Scheme I.A.2.:

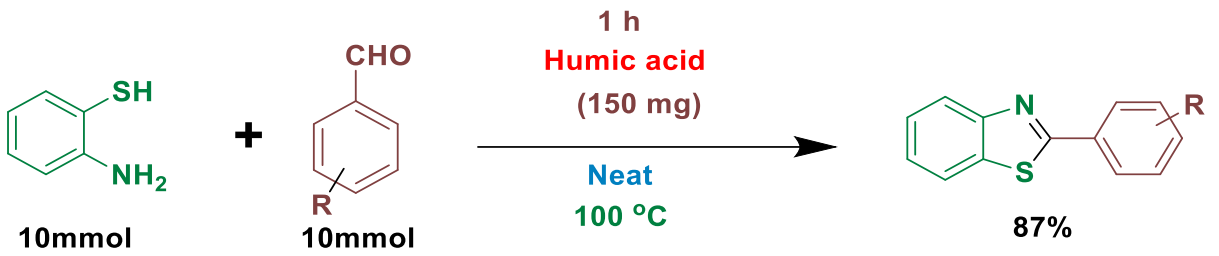
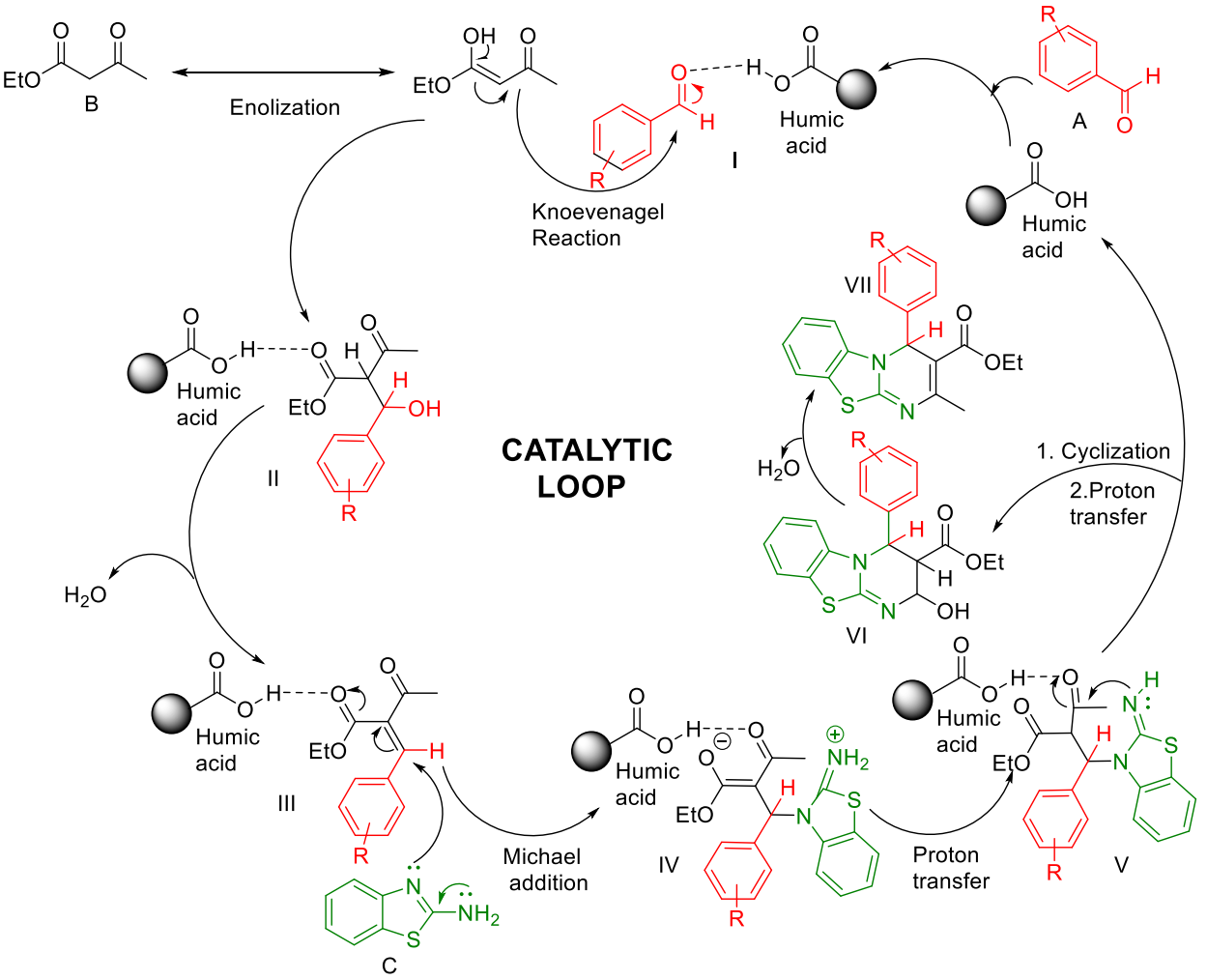


Figure I.A.4.: Gram – Scale Reaction

I.A.5. Plausible Mechanism for the Synthesis of 4H-benzo[4,5]thiazolo[3,2-a]pyridine-3-carboxylate and benzo[d]thiazole:

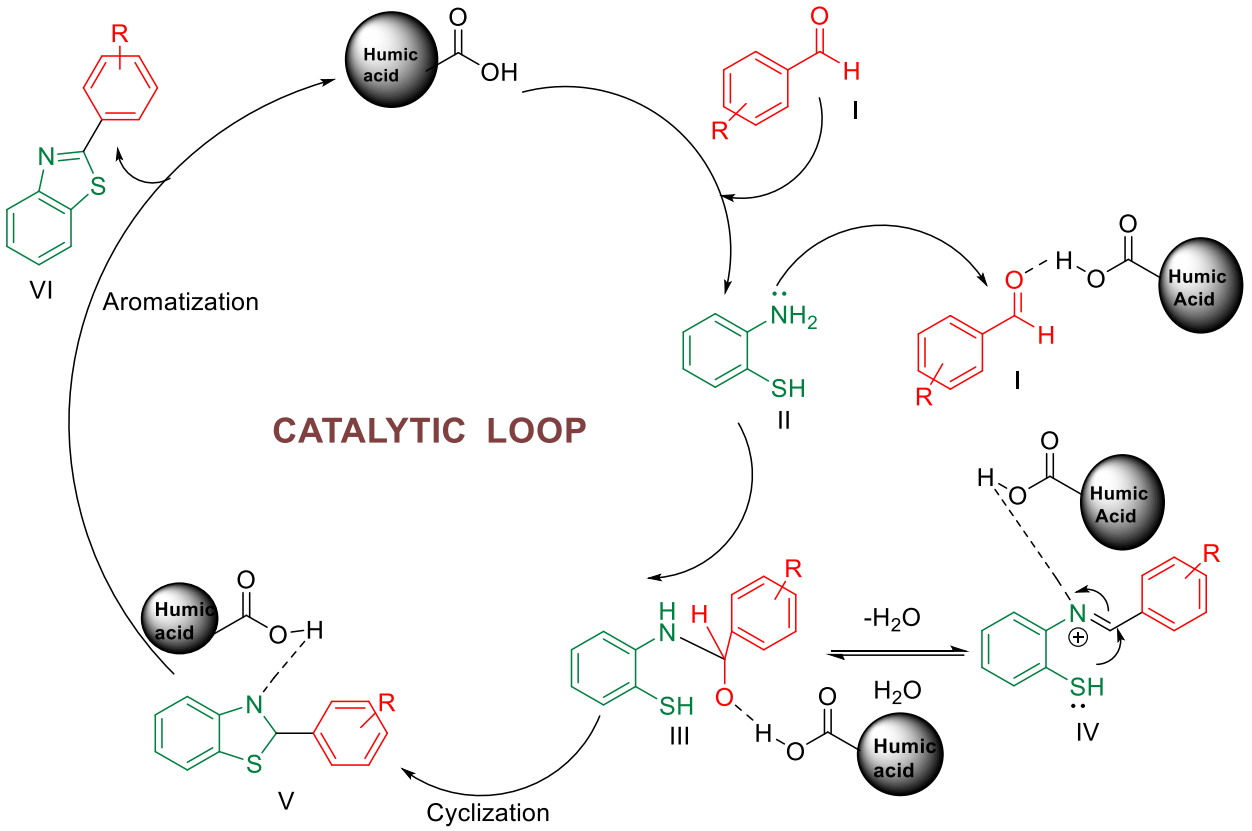
From the literature survey we have prepared the plausible mechanism for the synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate, which is designed in **Scheme I.A.3.** At first, the catalyst activates the aldehyde (A), through its acidic part (-COOH) to enhance the electrophilicity of the carbonyl group so that it can help the nucleophilic attack by enolised form of ethylacetoacetate (B), by simple nucleophilic addition pathway and the intermediate (II) is formed. Humic acid activates further, the carbonyl carbon of –COOEt in intermediate (II). Then after water elimination we get the intermediate (III), into which, the nucleophilic centre of 2-aminobenzohiazole (C) attacks through Michael addition pathway i.e. at the 4 position. Thus we get the intermediate (IV) in which carbonyl carbon is activated again by humic acid catalyst. After that, through proton transfer, we get the intermediate (V), which then undergoes cyclization, followed by proton transfer process. Thus, we get the compound (VI), which forms the final product 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (VII), by elimination of water and after that, the humic acid catalyst is restored. This reaction mechanism and pathway have been diagrammatically represented through the following **Scheme I.A.3.**



Scheme I.A.3. : Plausible mechanistic pathway for synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

From the surveying of literature, we have designed the plausible mechanism for the synthesis of benzo[*d*]thiazole, which is represented in **Scheme I.A.4.** At first, the catalyst activates the aldehyde (I) through its acidic part (-COOH), to increase the electrophilic nature of carbonyl group and so, it helps the nucleophilic attack by $–NH_2$ group of 2-aminothiophenol (II) by simple nucleophilic addition pathway and intermediate (III) is formed. This is transformed into intermediate (IV), by the loss of a water molecule. The enamine intermediate (IV) is activated again by the catalyst. Then nucleophilic attack occurs by –SH group of the same compound, followed by cyclization and aromatization. Through the formation of intermediate (V), the expected product benzo[*d*]thiazole (VI) is formed. After that the humic acid catalyst is restored.

This reaction mechanism and pathway have been diagrammatically represented through the following **Scheme I.A.4.**



Scheme I.A.4.: Plausible mechanistic pathway for synthesis of benzo[*d*]thiazole

I.A.6. Conclusion:

In conclusion, we have represented an environment friendly and feasible technique for synthesizing a number of functionalized 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and benzo[*d*]thiazole derivatives under the absence of any solvent, taking humic acid as catalyst to activate carbonyl oxygen of respective aldehydes and ester for enhancing the electrophilicity of carbonyl carbon, followed by nucleophilic addition onto that position. The overall mechanism proceeds through Cascade reaction, involving a well known Knoevenagel and Michael Addition pathway. Since, no metal was used here, so, the overall method was maintained as greener synthetic one. Again, the solvent-free condition, contributes a huge environmental sustainability to the protocol. Humic acid catalyst can be regained through easy filtration procedure and its recovery factor can proceed up to fifth run in devoid of any characteristic deviation of its extent of

activity. So, the basic uniqueness and creativity manifestation of this methodology, is, the utilization of environmentally benign, easily accessible and low priced humic acid catalyst, instead of any toxic, fatal, dangerous, exhaustive, hazardous and expensive metal catalyst. This methodology proposed in the present study can be considered as a part of the consistent effort of the scientists and researchers by creating a significant evolution within the chemical world of medicines, synthetic pathways of natural products and drug industries, in future endeavors.

I.A.7. Experimental Section:

I. General Information:

All the compounds were acquired from commercial suppliers and used without further purification. All the products were purified by column chromatography on silica gels (60−120 Mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were utilized. ^{1}H NMR,^{19} F and ^{13}C NMR were recorded using 400 MHz, 376 MHz and 100 MHz, respectively, on Bruker AV 400 NMR spectrometer using TMS as internal standard. Splitting manners of protons were explained as s (singlet), d (doublet), t (triplet) and m (multiplet).

II. General procedure for the synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine:

A mixture of 2-aminobenzothiazol (1 mmol), benzaldehyde (1 mmol), ethylacetoacetate (1 mmol) and humic acid (15 mg) was blended at 100 ^{o}C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept track of using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by easy filtration and was extracted with ethyl acetate twice (2×20 ml). Amalgamated extracts were cleaned with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate–petroleum ether). The products obtained were known compounds and were recognized by their color, melting point and NMR spectroscopy.

III. General procedure for the synthesis of benzo[*d*]thiazole:

A mixture of 2-aminothiophenol (1 mmol) benzaldehyde (1 mmol) and humic acid (15 mg) was blended at 100 ^{o}C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept an eye on using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by smooth filtration tecnique and was extracted with ethyl acetate twice (2×20 ml). Amalgamated extracts were washed with purified water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate–petroleum ether). The products obtained were known compounds and were recognized by their color, melting point and NMR spectroscopy.

IV. Spectroscopic data and Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of various benzo[*d*]thiazole and 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine derivatives :

2-Phenylbenzo[*d*]thiazole (Figure I.A.5.)

M.P.: 111 -113 ^{o}C; grey solid; yield : 93%; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 7.371 – 7.411 (m, 2H), 7.479 – 7.520 (m, 3H), 7.909 (d, *J* = 8 Hz, 1H), 8.078 – 8.113 (m, 3H) **(Figure I.A.6.).** **^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):** 116.685, 121.642, 123.250, 125.219, 126.346, 127.105, 127.585, 128.629, 129.047, 130.998, 133.628, 135.074, 154.148, 168.120**(Figure I.A.7.).**

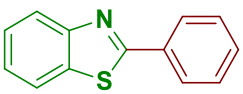


Figure I.A.5. Structure of 2-Phenylbenzo[*d*]thiazole

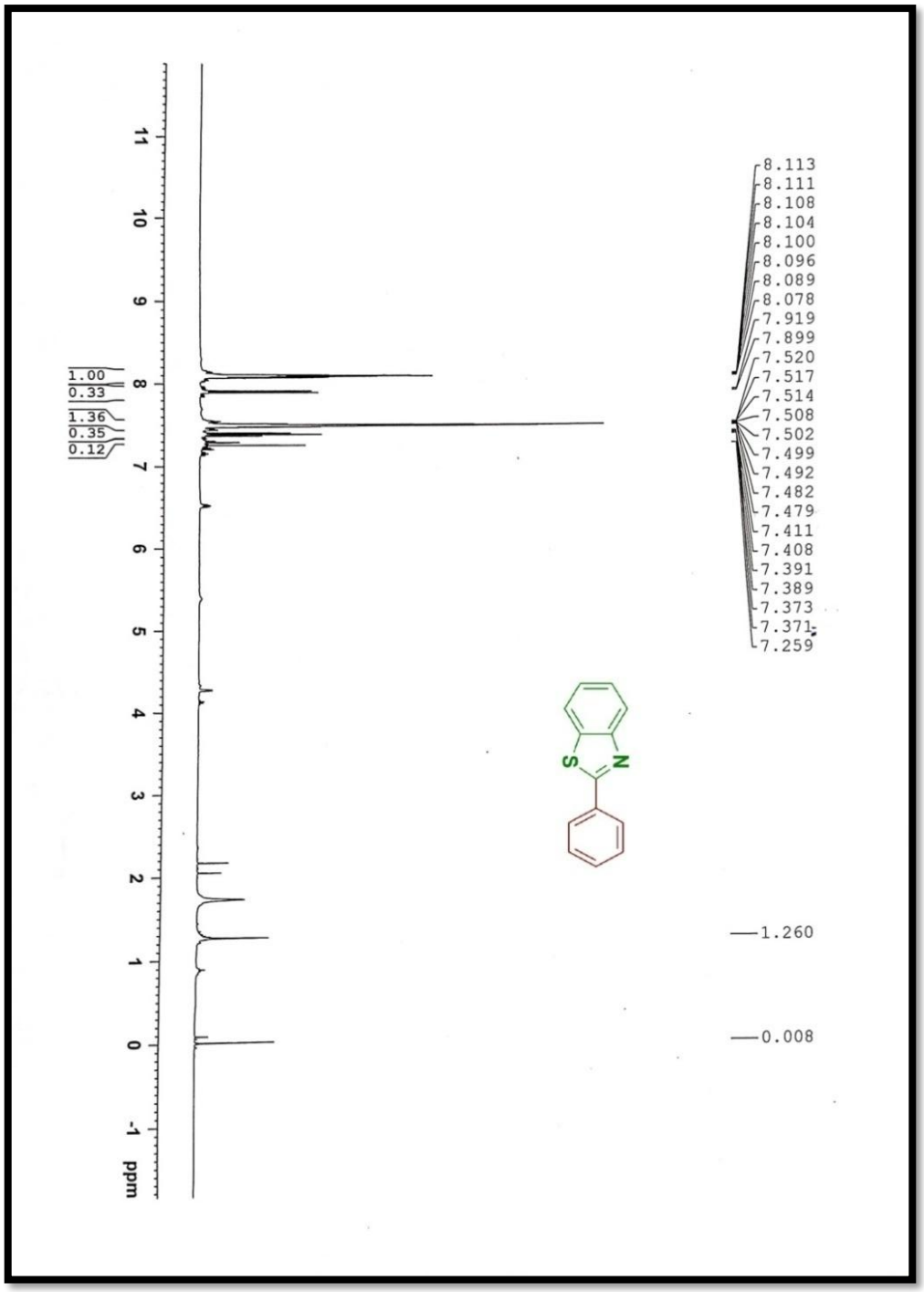


Figure I.A.6. ^{1}H Spectroscopical representation of 2-Phenylbenzo[*d*]thiazole

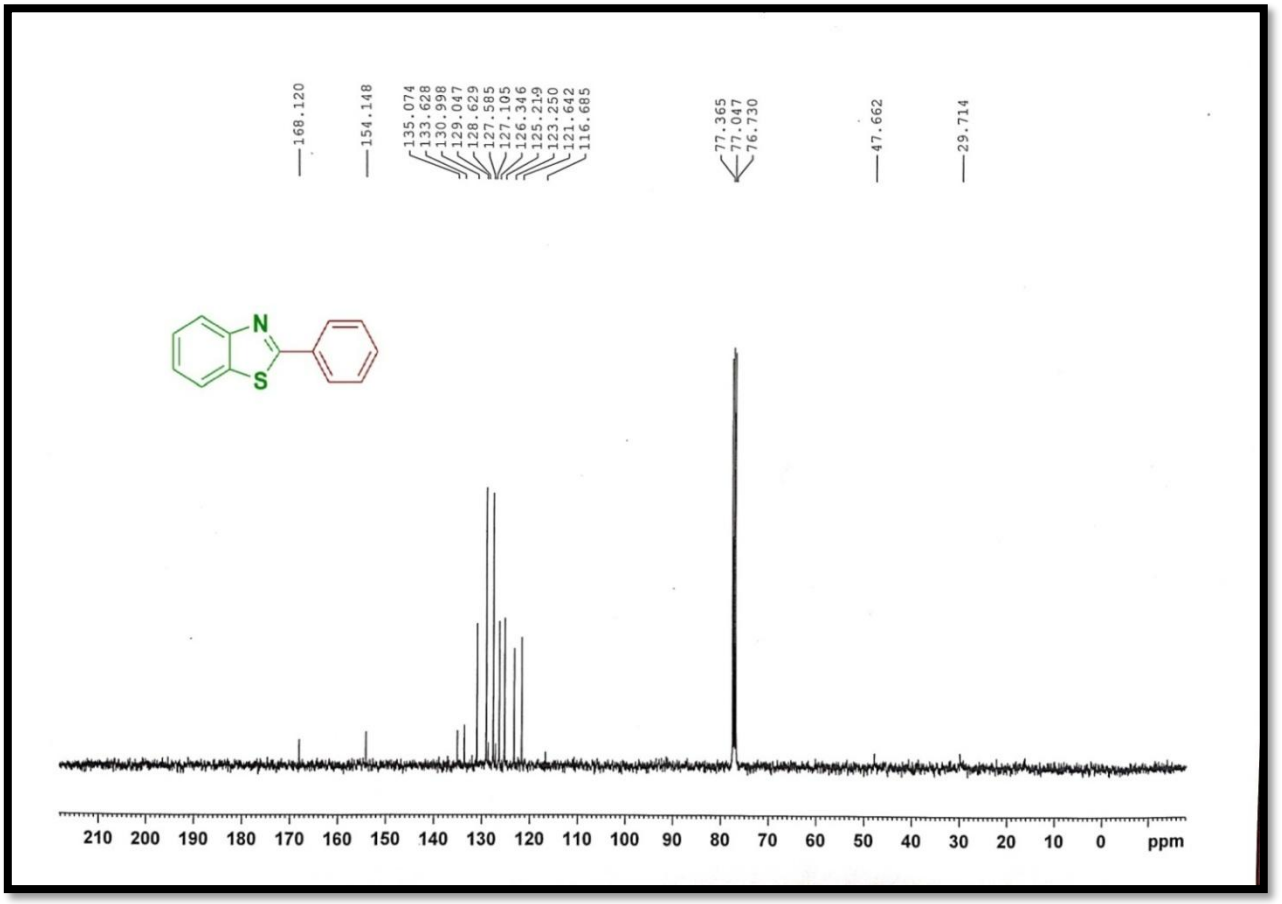


Figure I.A.7. ^{13}C Spectroscopical representation of 2-Phenylbenzo[*d*]thiazole

2-(3-Nitrophenyl)benzo[*d*]thiazole (Figure I.A.8.)

M.P. : 182.2 – 183.5 ^{o}C; off – white solid, yield : 95%; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 7.456 -7.476 (m, 1H), 7.551 (d, *J* = 0.8 Hz, 1H), 7.694 (t, *J* = 8 Hz, 1H), 7.954 (d, *J* = 8 Hz, 1H), 8.120 (d, *J* = 8 Hz, 1H), 8.325 (s, 1H), 8.424 (d, *J* = 8 Hz, 1H), 8.935 (m, 1H) **(Figure I.A.9.).**

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 121.840, 122.348, 123.761, 125.189, 126.041, 126.842, 130.113, 133.004, 135.187, 135.309, 148.773, 153.954, 164.899 **(Figure I.A.10.).**

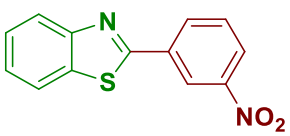


Figure I.A.8. Structure of 2-(3-Nitrophenyl)benzo[*d*]thiazole

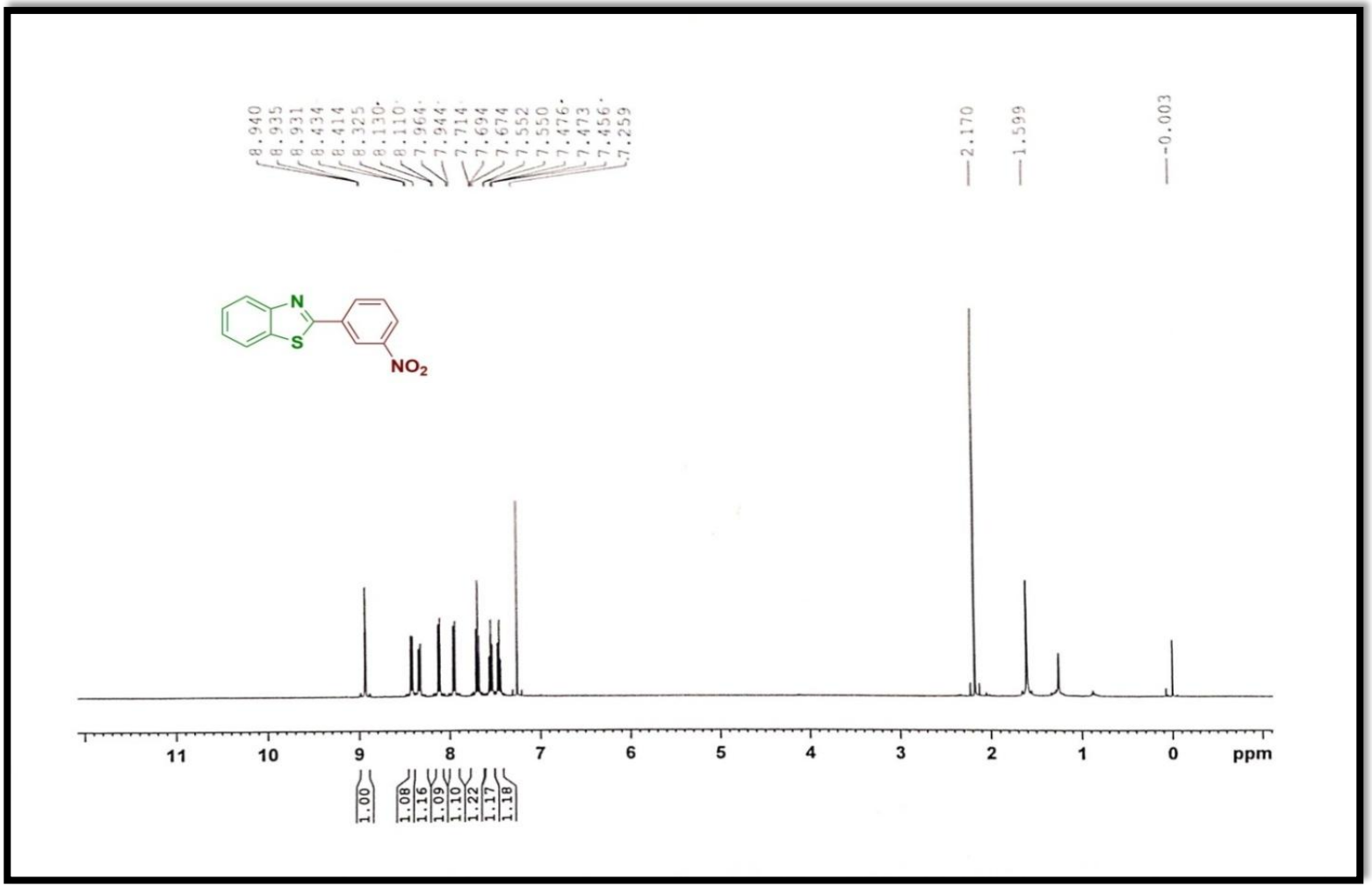


Figure I.A.9. ^{1}H Spectroscopical representation of 2-(3-Nitrophenyl)benzo[*d*]thiazole

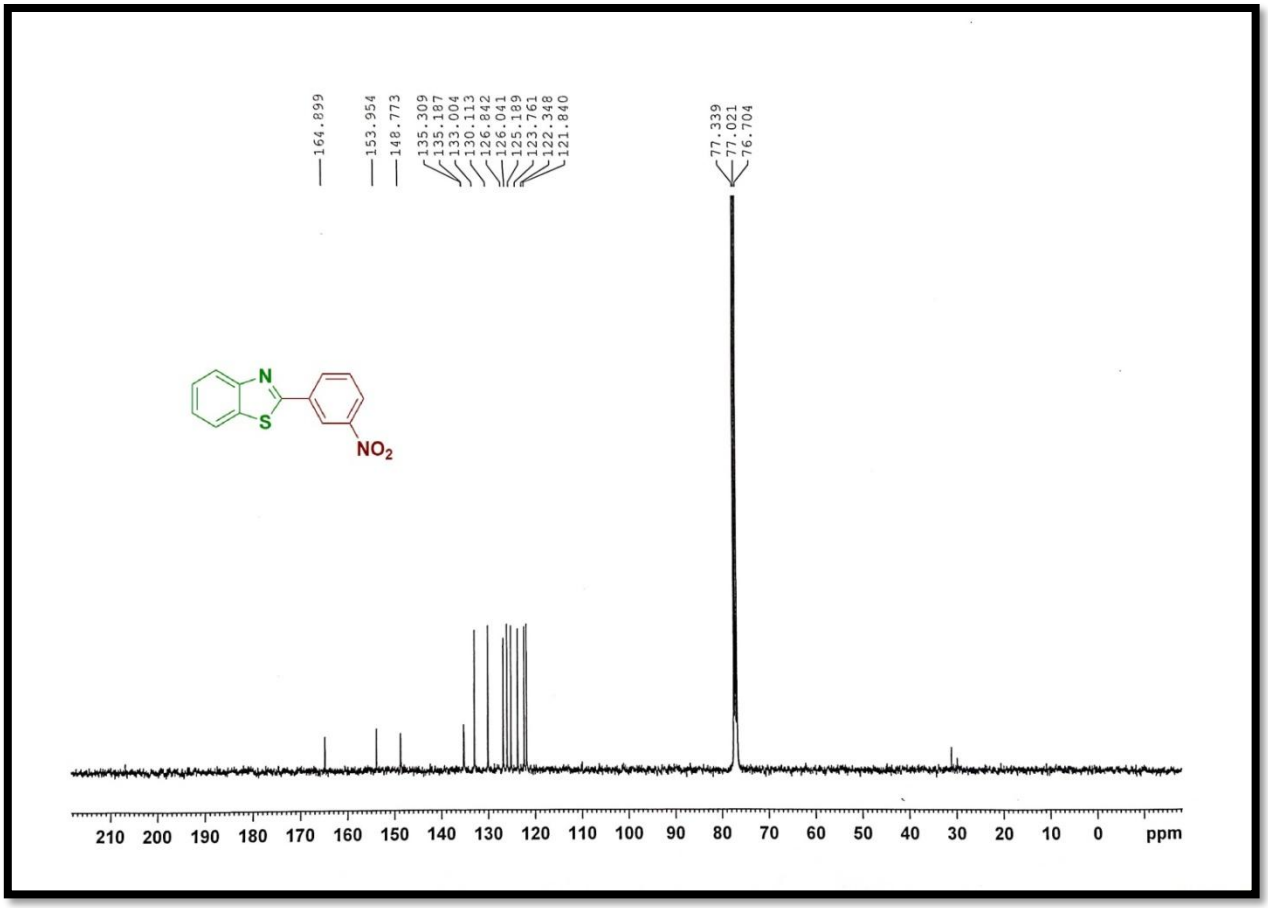


Figure I.A.10. ^{13}C Spectroscopical representation of 2-(3-Nitrophenyl)benzo[*d*]thiazole

2-(Thiophen-2-yl)benzo[*d*]thiazole (Figure I.A.11.)

M.P. : 99 ^{o}C; white solid; yield : 90%; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 7.142 (dd, *J* = 4 Hz; *J* = 4.8 Hz, 1H), 7.348 – 7.389 (m, 1H), 7.454 – 7.515 (m, 2H), 7.657 – 7.669 (m, 1H), 7.853 (d, *J* = 8 Hz, 1H), 8.03 (d, *J* = 8 Hz, 1H) **(Figure I.A.12.).**

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 121.642, 123.250, 125.219, 126.346, 127.105, 127.585, 128.629, 129.047, 130.998, 133.628, 135.074, 154.148, 168.120 **(Figure I.A.13.).**

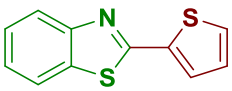


Figure I.A.11. Structure of 2-(Thiophen-2-yl)benzo[*d*]thiazole

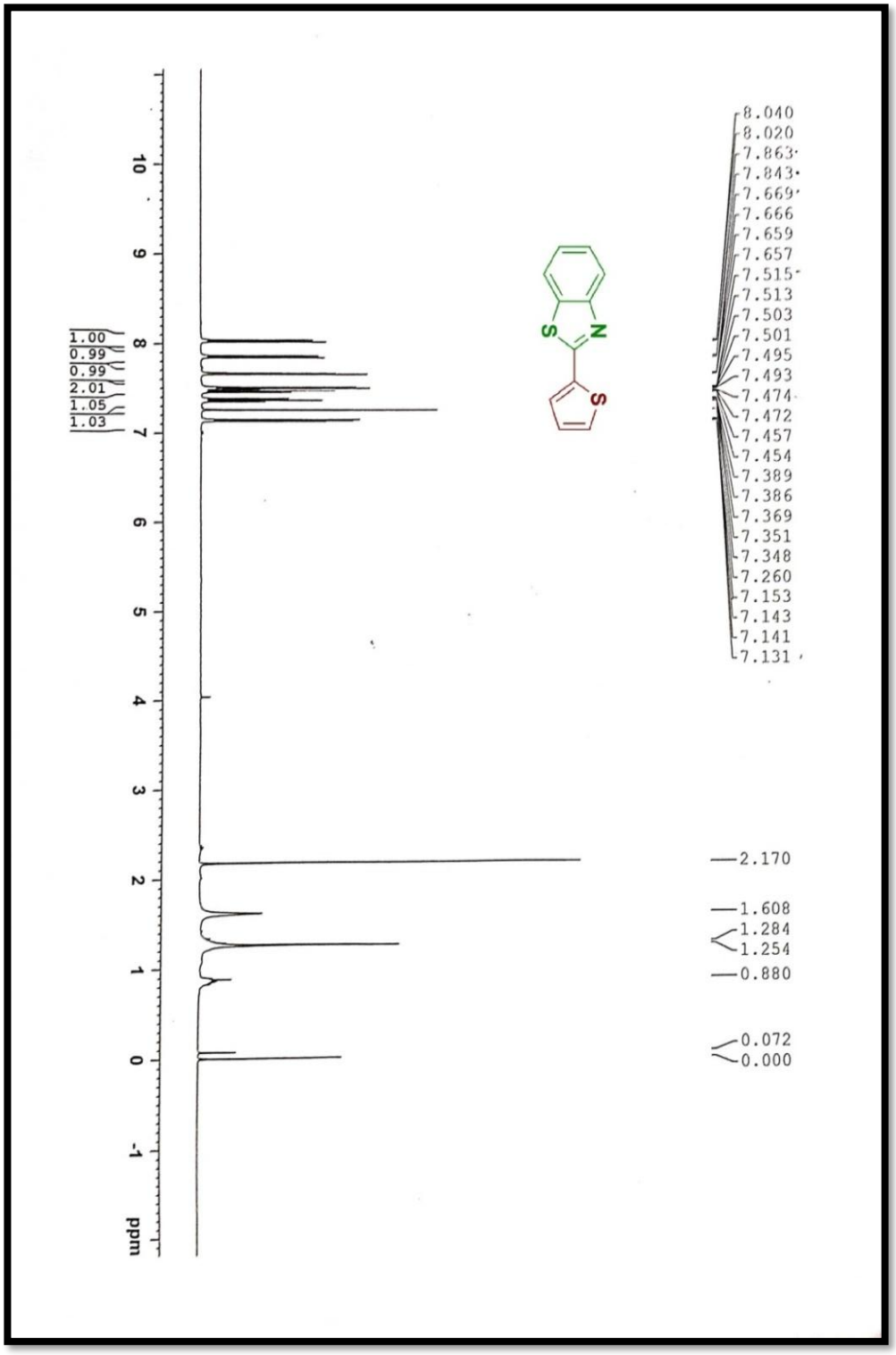


Figure I.A.12. ^{1}H Spectroscopical representation of 2-(Thiophen-2-yl)benzo[*d*]thiazole

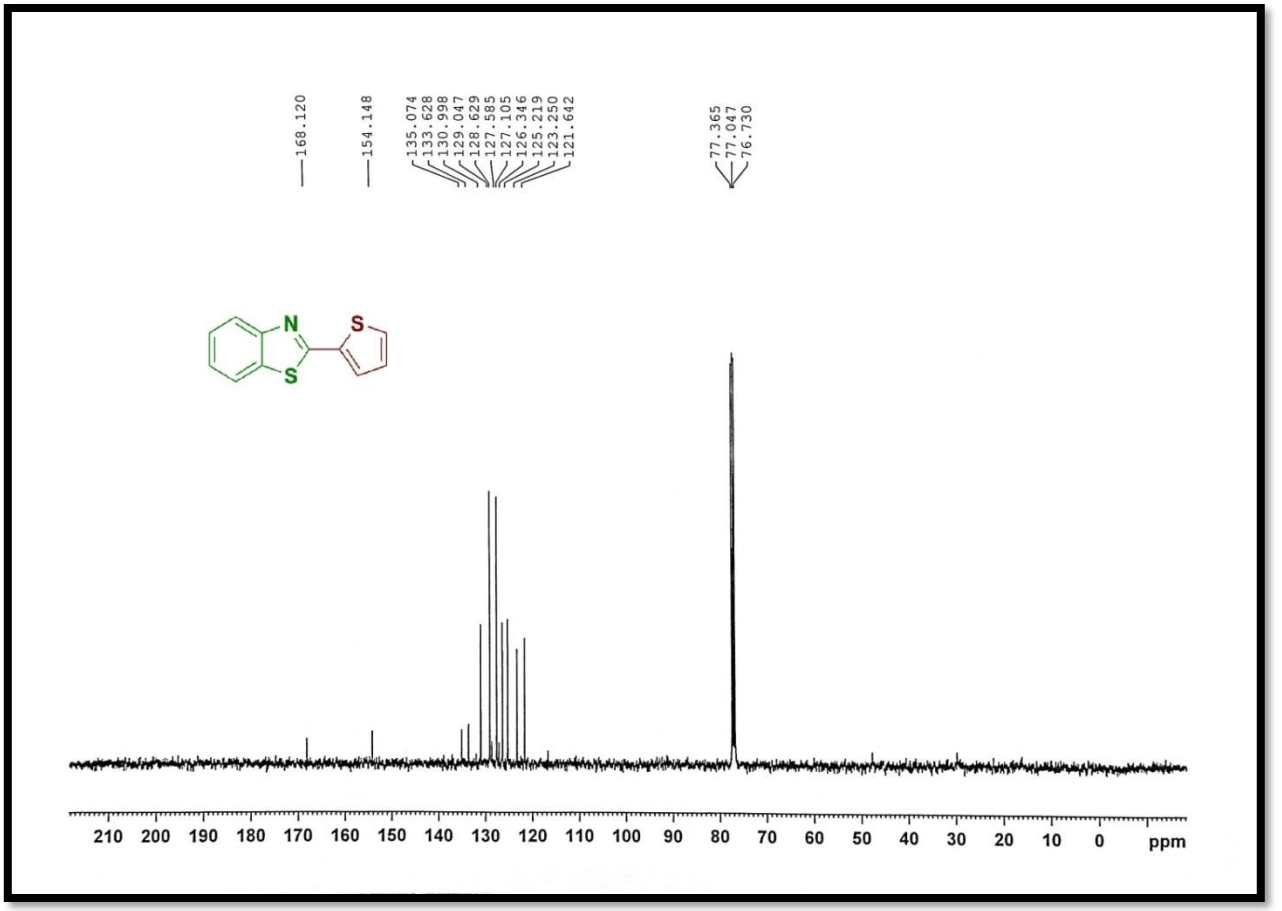


Figure I.A.13. ^{13}C Spectroscopical representation of 2-(Thiophen-2-yl)benzo[*d*]thiazole

4-(Benzo[*d*]thiazol-2-yl)-2-methoxyphenol (Figure I.A.14.).

M.P. : 168 – 169 ^{o}C; yellowish white solid, yield : 94%; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 2.170 (s, 1H), 4.037 (s, 3H), 5.960 (s, 1H), 7.006 (d, *J* = 8.4, 1H), 7.357 (s, 1H), 7.471 (s, 1H), 7.540 – 7.560 (m,1H), 7.724 (d, *J* = 2 Hz, 1H), 8.023 (d, *J* = 8 Hz, 1H) **(Figure I.A.15.).**

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 56.240, 109.285, 114.702, 121.512, 121.958, 122.759, 124.845, 126.223, 134.859, 146.933, 148.498, 154.104, 168.110 **(Figure I.A.16.).**

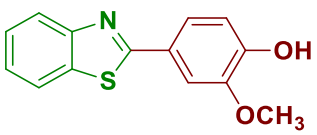


Figure I.A.14. Structure of 4-(Benzo[*d*]thiazol-2-yl)-2-methoxyphenol

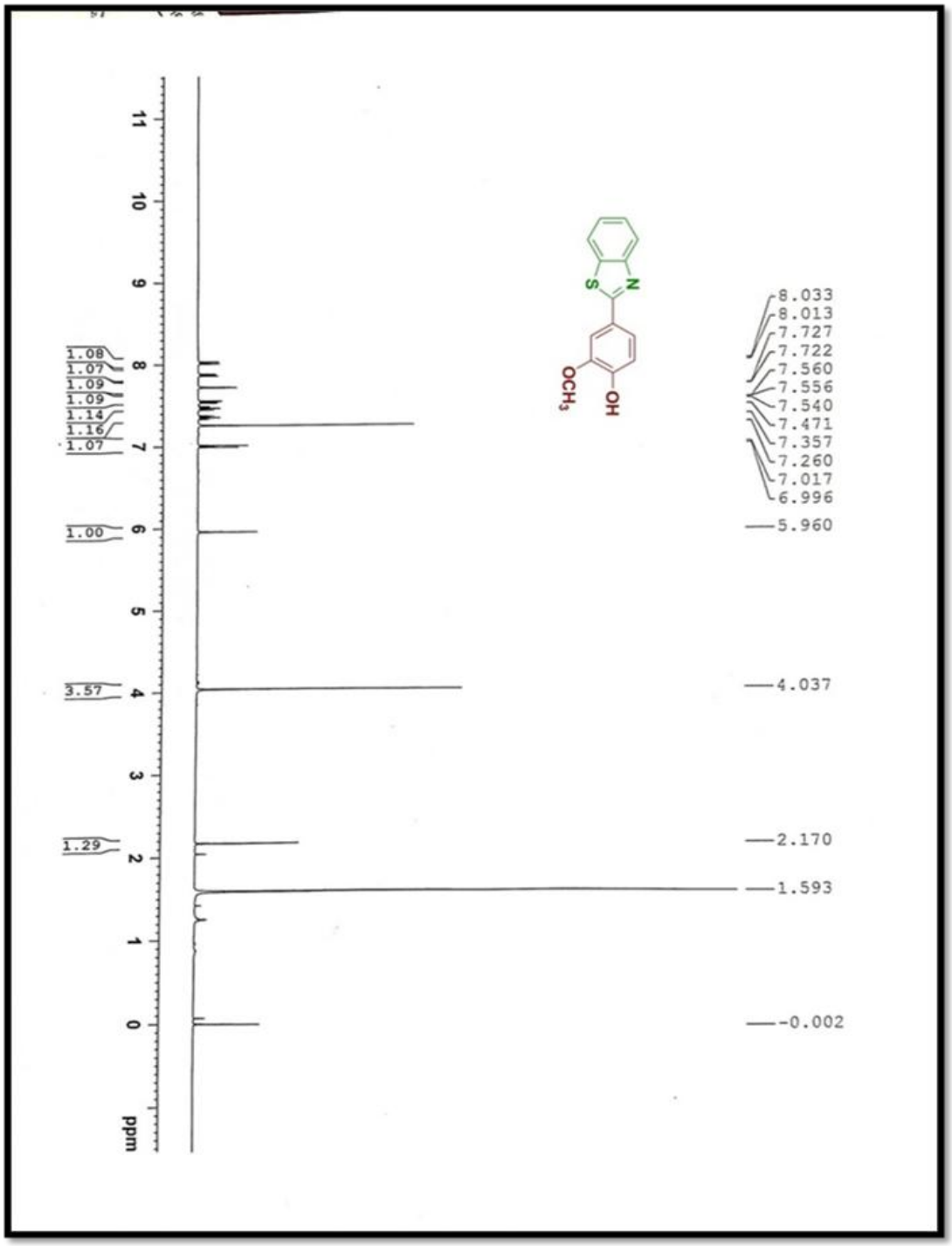


Figure I.A.15. ^{1}H Spectroscopical representation of 4-(Benzo[*d*]thiazol-2-yl)-2-methoxyphenol

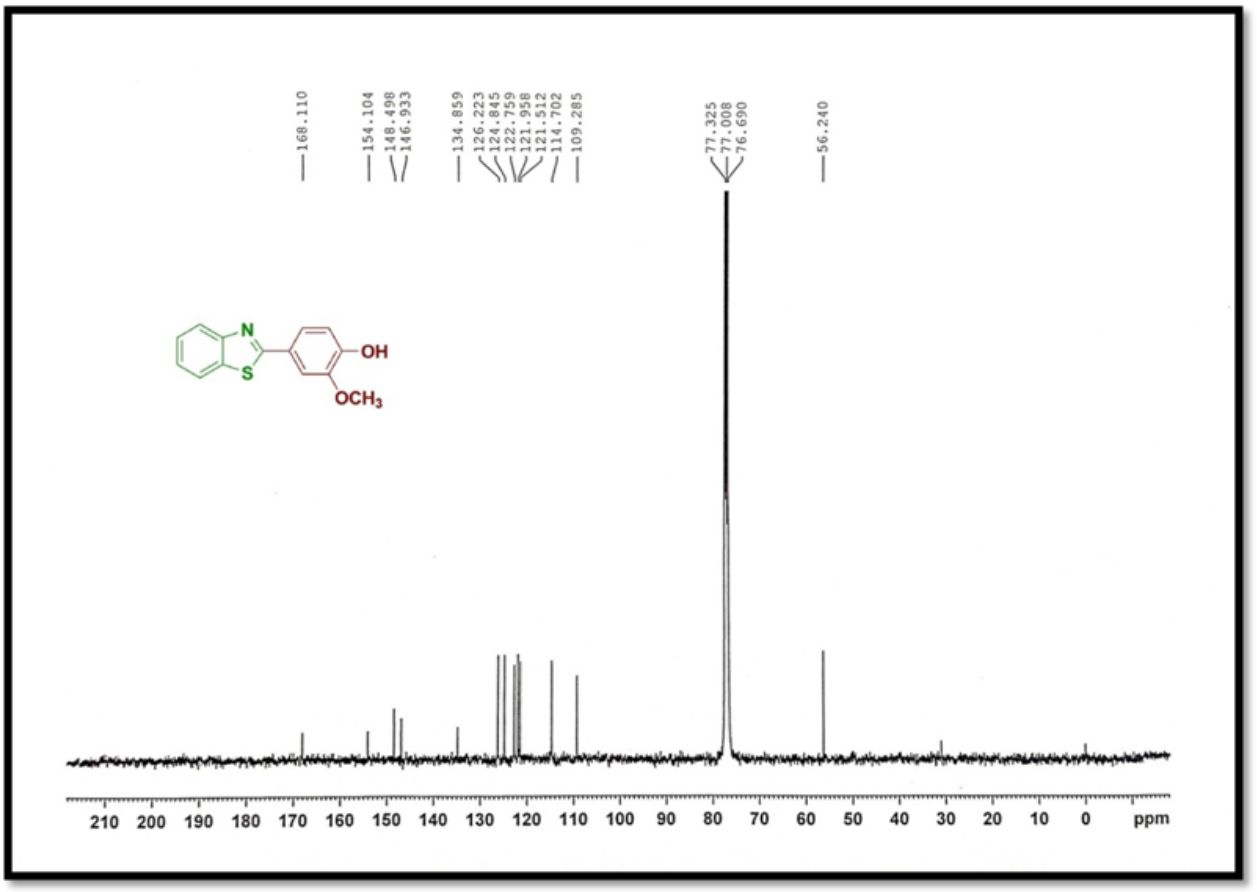


Figure I.A.16. ^{13}C Spectroscopical representation of 4-(Benzo[*d*]thiazol-2-yl)-2-methoxyphenol

4-(Benzo[*d*]thiazol-2-yl)-*N*, *N*-dimethylaniline (Figure I.A.17.).

M.P.: 160 – 162 ^{o}C; yellowish powder, yield : 89%; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 3.042 (s, 6H), 6.738 (dd, *J* = 2 Hz, *J* = 3.2 Hz, 2H), 7.282 -7.322 (m, 1H), 7.416 – 7.458 (m, 1H), 7.837 (d, *J* = 8 Hz, 1H), 7.951 – 8.001 (m, 3H) **(Figure I.A.18.).**

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 40.178, 111.693, 121.368, 122.282, 124.195, 125.988, 128.874, 134.560, 152.184, 154.433, 168.837 **(Figure I.A.19.).**

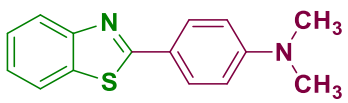


Figure I.A.17. Structure of 4-(Benzo[*d*]thiazol-2-yl)-*N*, *N*-dimethylaniline

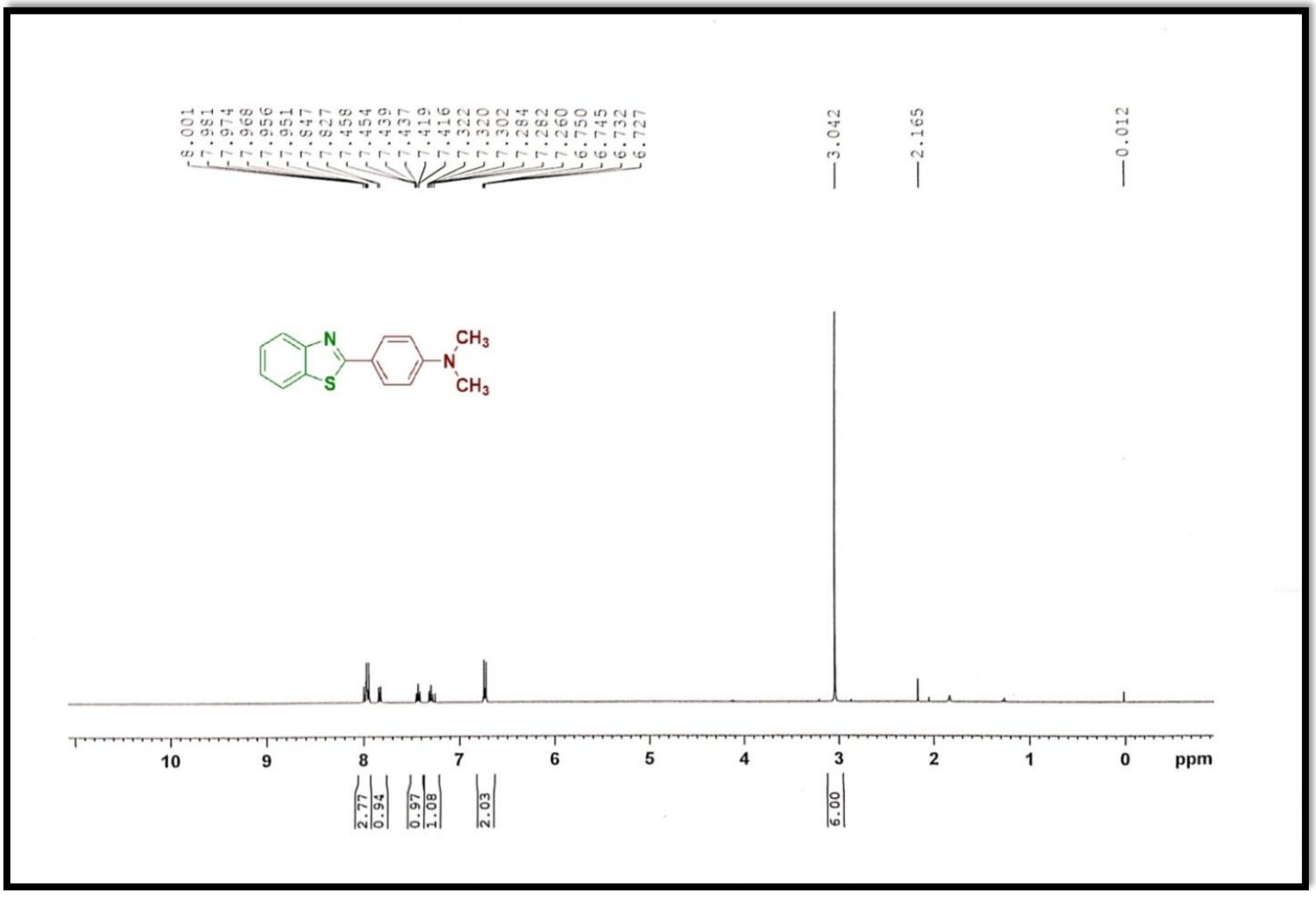


Figure I.A.18. ^{1}H Spectroscopical representation of 4-(Benzo[*d*]thiazol-2-yl)-*N*, *N*-dimethylaniline

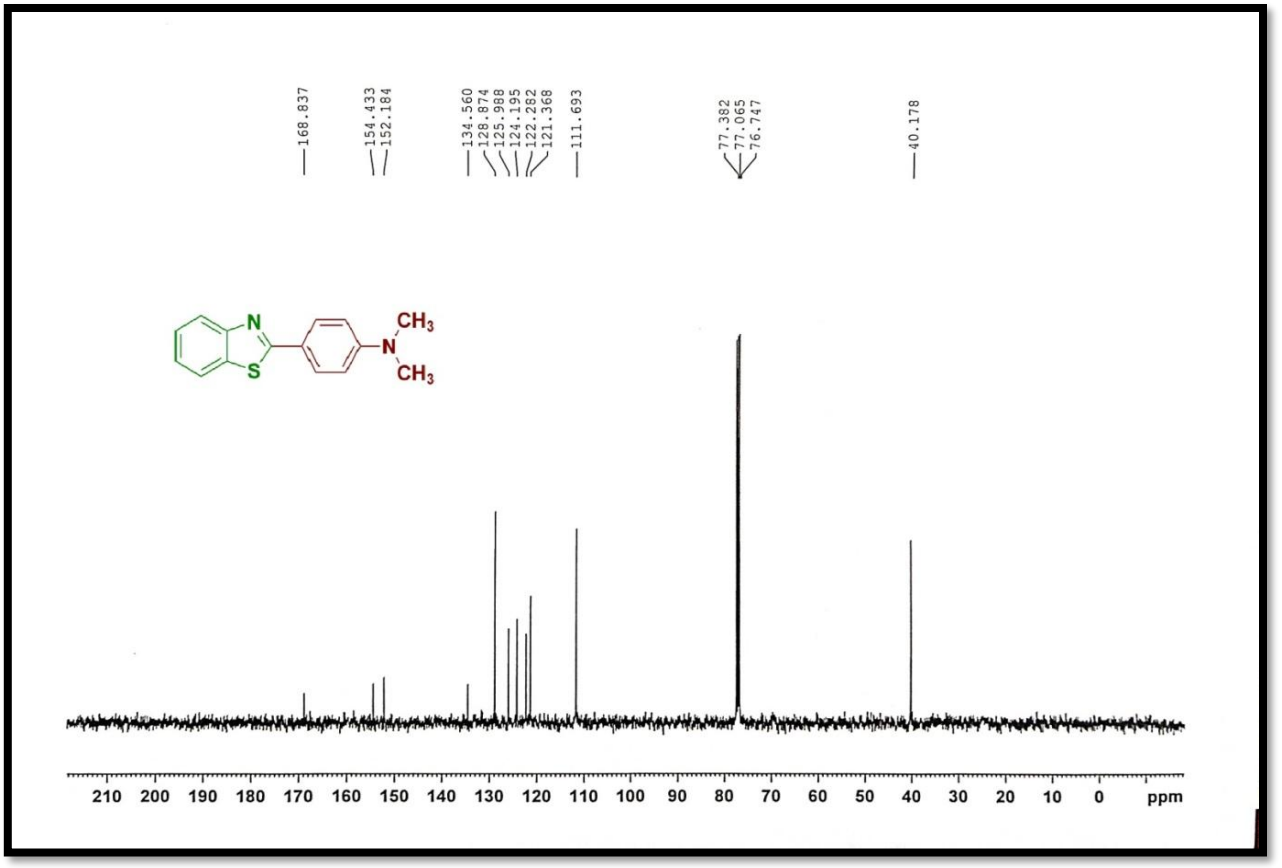


Figure I.A.19. ^{13}C Spectroscopical representation of 4-(Benzo[*d*]thiazol-2-yl)-*N*, *N*-dimethylaniline

2-(Furan-2-yl)benzo[*d*]thiazole (Figure I.A.20.).

M.P. : 102 -104 ^{o}C; yellowish powder; yield : 85%; **^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm):** 6.243 (s, 1H), 6.564 (q, *J* = 1.6 Hz, 1H), 7.180 (d, *J* = 3.2 Hz, 1H), 7.332 – 7.489 (m, 1H), 7.575 (d, *J* = 1.16 Hz, 1H), 7.845 – 7.865 (m, 1H), 8.051 (d, *J* = 8.16 Hz, 1H) **(Figure I.A.21.).**

^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 111.458, 112.558, 121.591, 123.128, 125.212, 126.497, 134.290, 144.717, 148.760, 153.760, 157.575 **(Figure I.A.22.).**

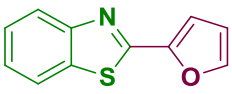


Figure I.A.20. Structure of 2-(Furan-2-yl)benzo[*d*]thiazole

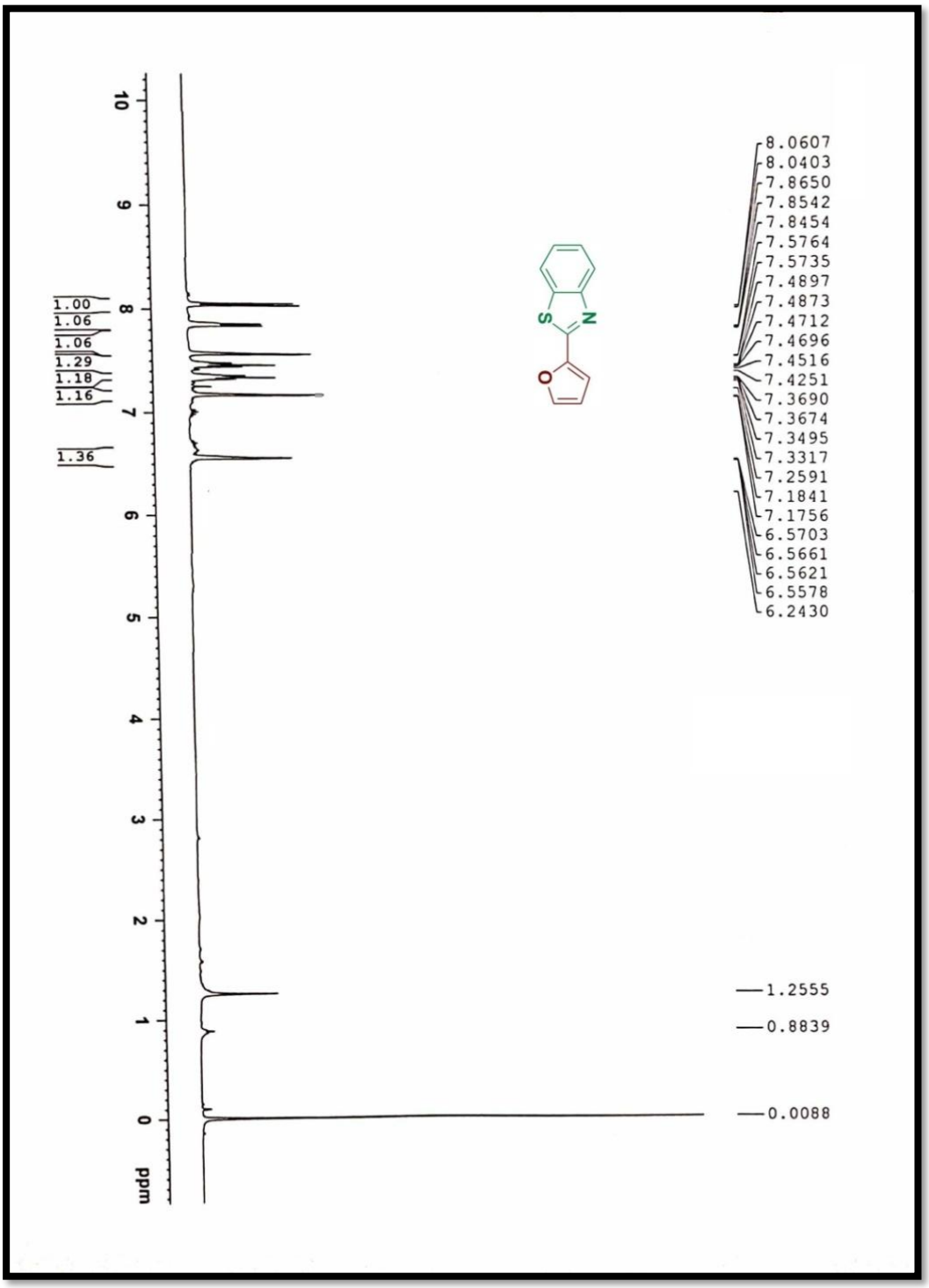


Figure I.A.21. ^{1}H Spectroscopical representation of 2-(Furan-2-yl)benzo[*d*]thiazole

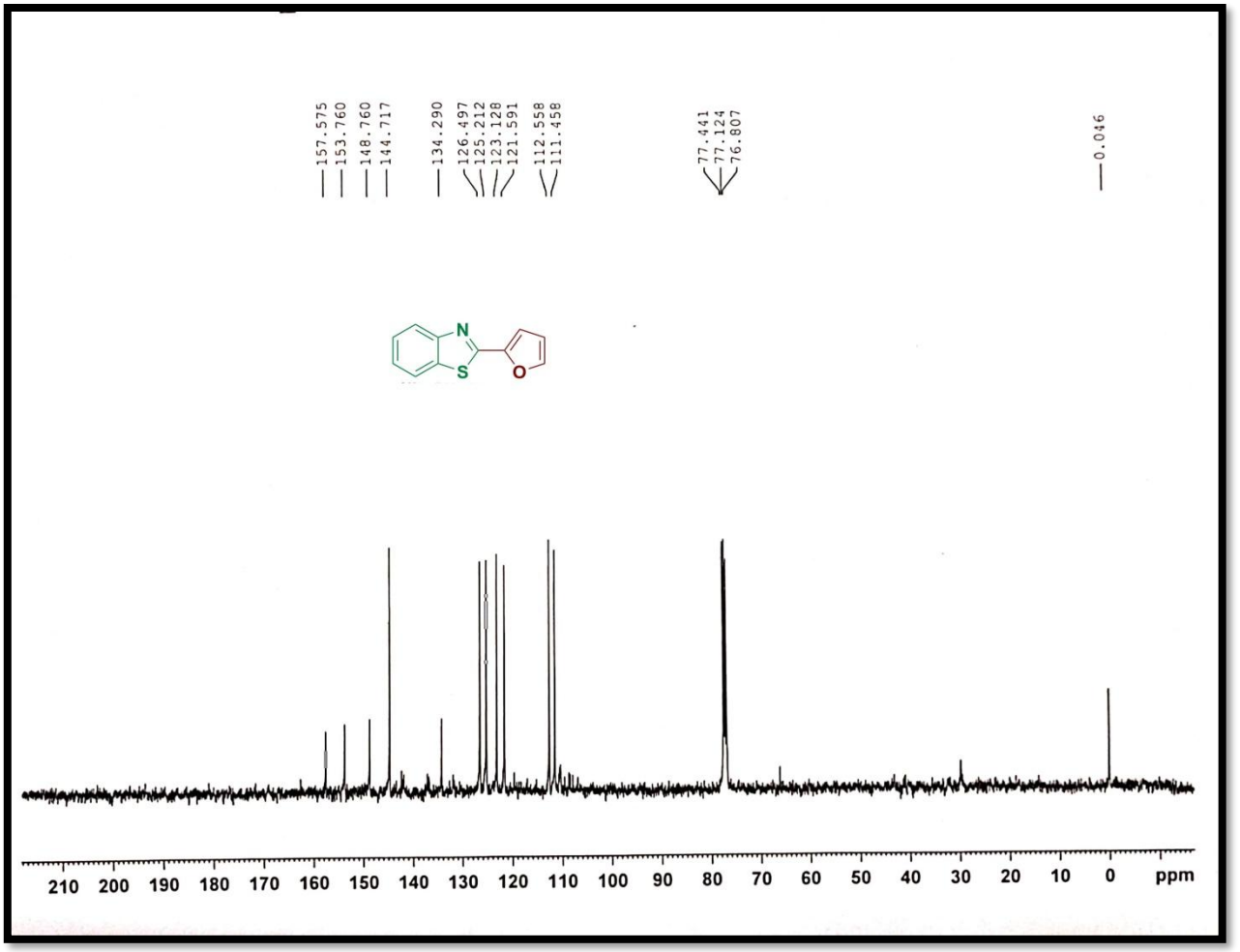


Figure I.A.22. ^{13}C Spectroscopical representation of 2-(Furan-2-yl)benzo[*d*]thiazole

2-(*p*-Tolyl)benzo[*d*]thiazole (Figure I.A.23.).

M. P.: 105 - 107 ^{o}C, white solid, yield : 81%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 2.374 (3H, d, *J* = 38 Hz), 7.284 – 7.351 (2H, m), 7.369 – 7.389 (1H, m), 7.465 – 7.506 (1H, m), 7.884 (1H, d, *J* = Hz), 7.990 (2H, d, *J* = 8 Hz), 8.074 (1H, d, *J* = 8 Hz) **(Figure I.A.24.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.089, 121.594, 123.057, 125.027, 126.269, 127.105, 128.856, 129.308, 129.741, 130.962, 134.957, 141.450, 154.176, 168.281 **(Figure I.A.25.).**

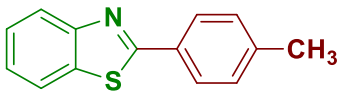


Figure I.A.23. Structure of 2-(*p*-Tolyl)benzo[*d*]thiazole

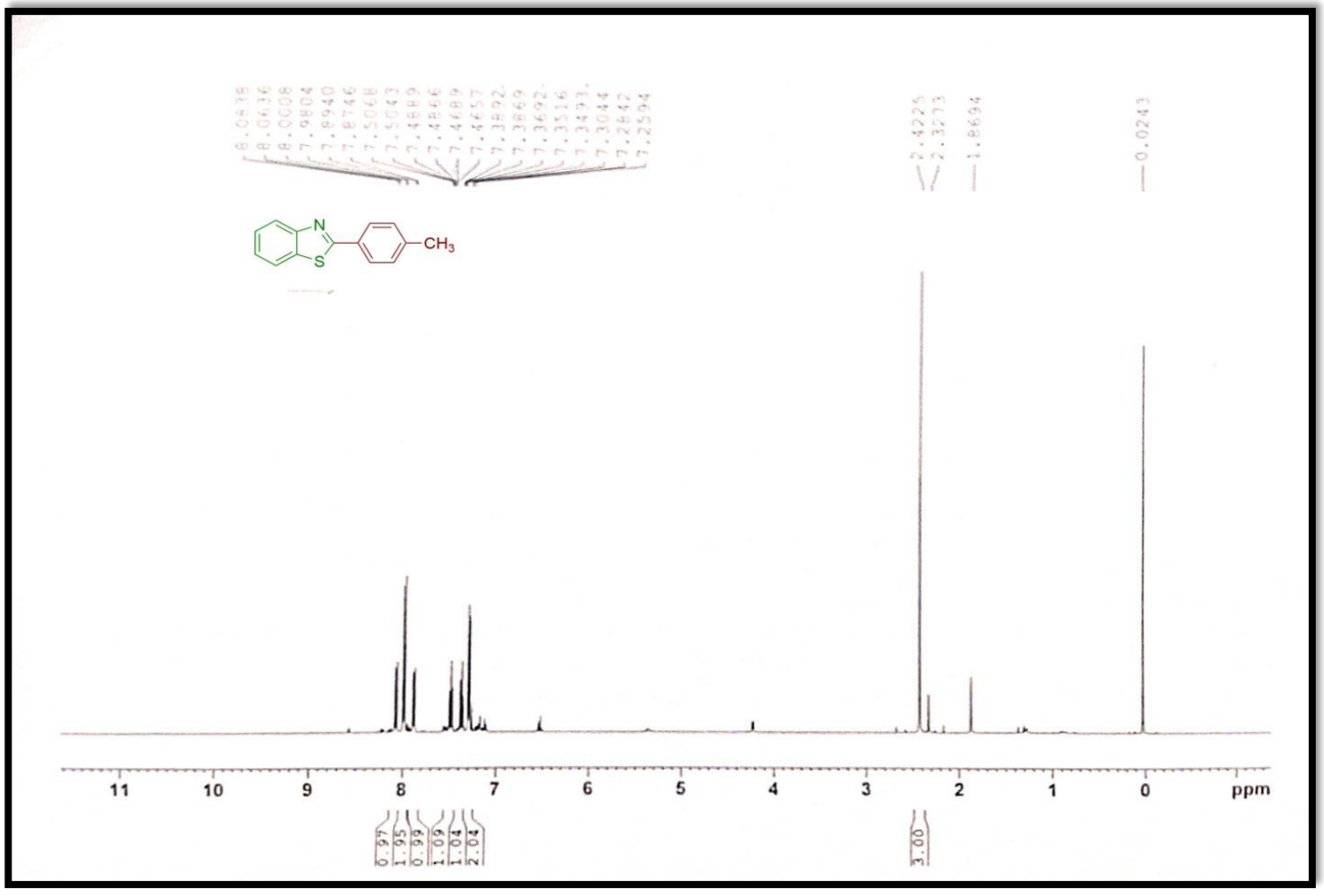


Figure I.A.24. ^{1}H Spectroscopical representation of 2-(*p*-Tolyl)benzo[*d*]thiazole

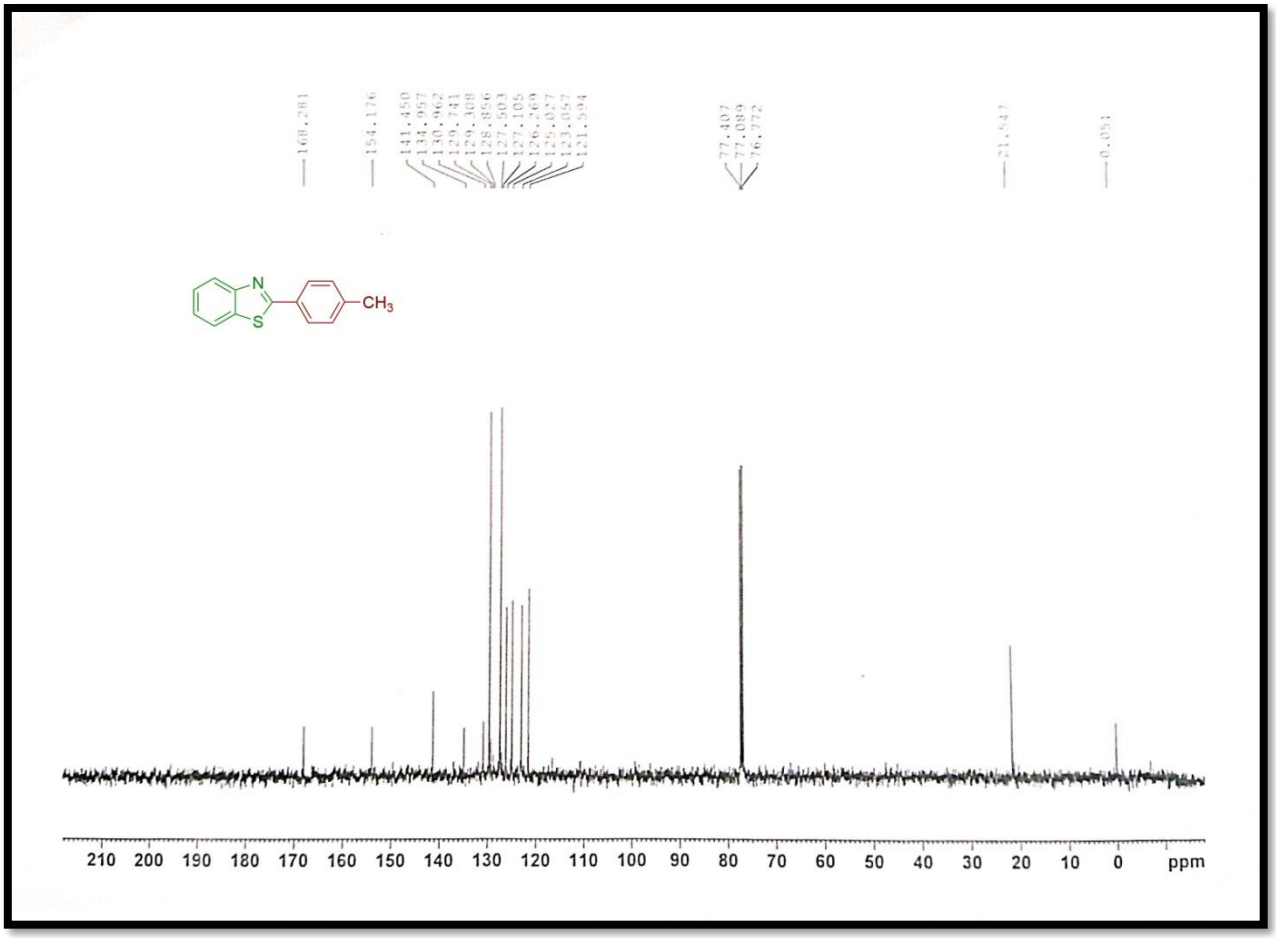


Figure I.A.25. ^{13}C Spectroscopical representation of 2-(*p*-Tolyl)benzo[*d*]thiazole

2-(3-Fluorophenyl)benzo[*d*]thiazole (Figure I.A.26.).

M. P.: 98 - 100 °C, white solid, yield : 83%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 7.189 (1H, dd, *J* = 0.4 Hz, *J* = 2 Hz), 7.392 – 7.532 (3H, m), 7.823 – 7.840 (2H, m), 7.842 – 7.923 (1H, m), 8.086 (1H, d, J = 8 Hz) **(Figure I.A.27.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.029, 114.330, 117.836, 121.693, 123.372, 125.561, 126.534, 130.635, 135.097, 135.651, 135.731, 153.983, 164.204 **(Figure I.A.28.).**

19F NMR (376 MHz, $CDCl_3$): δ (ppm): - 112.003 **(Figure I.A.29.).**

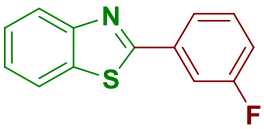


Figure I.A.26. Structure of 2-(3-Fluorophenyl)benzo[*d*]thiazole

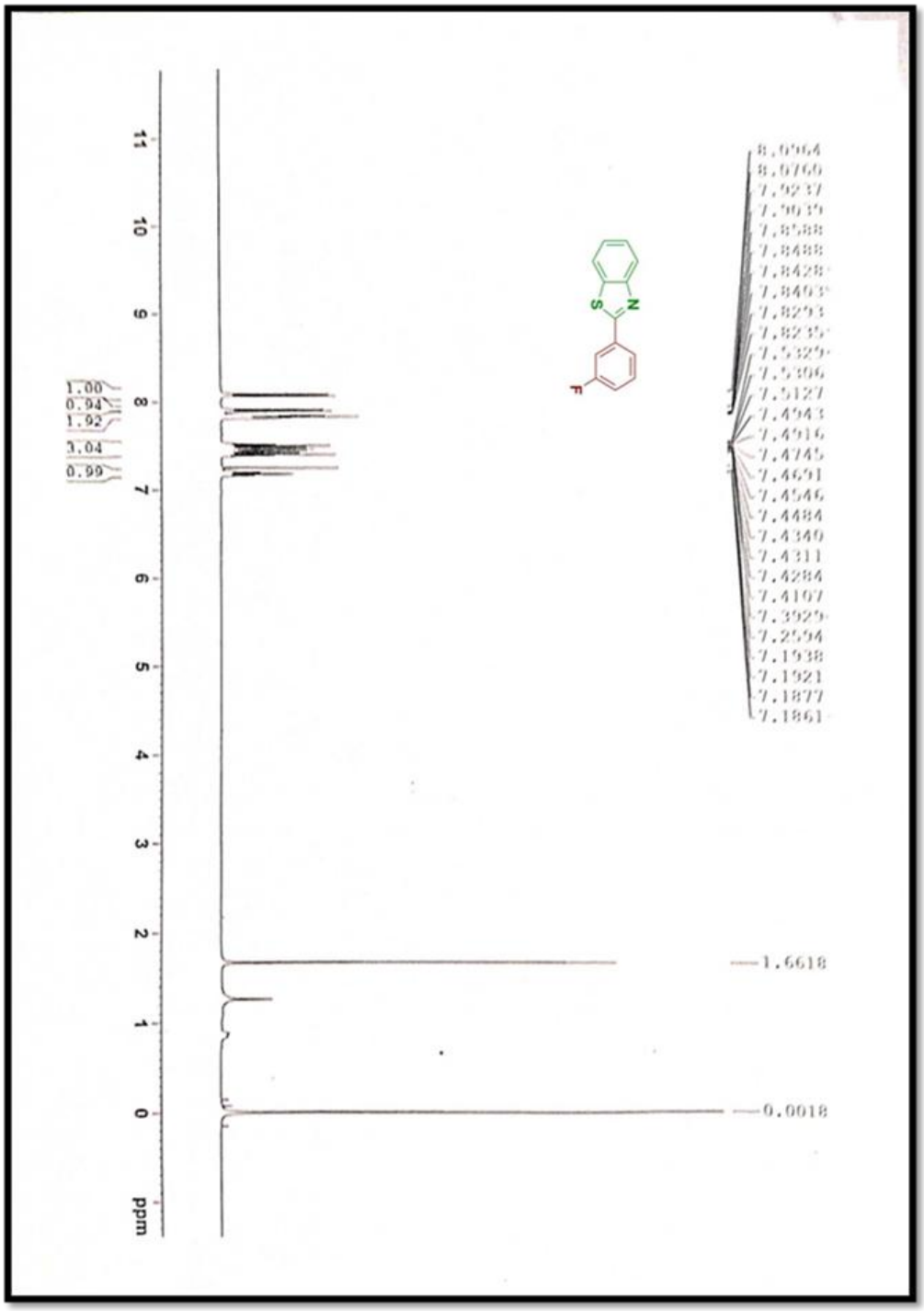


Figure I.A.27. ^{1}H Spectroscopical representation of 2-(3-Fluorophenyl)benzo[*d*]thiazole

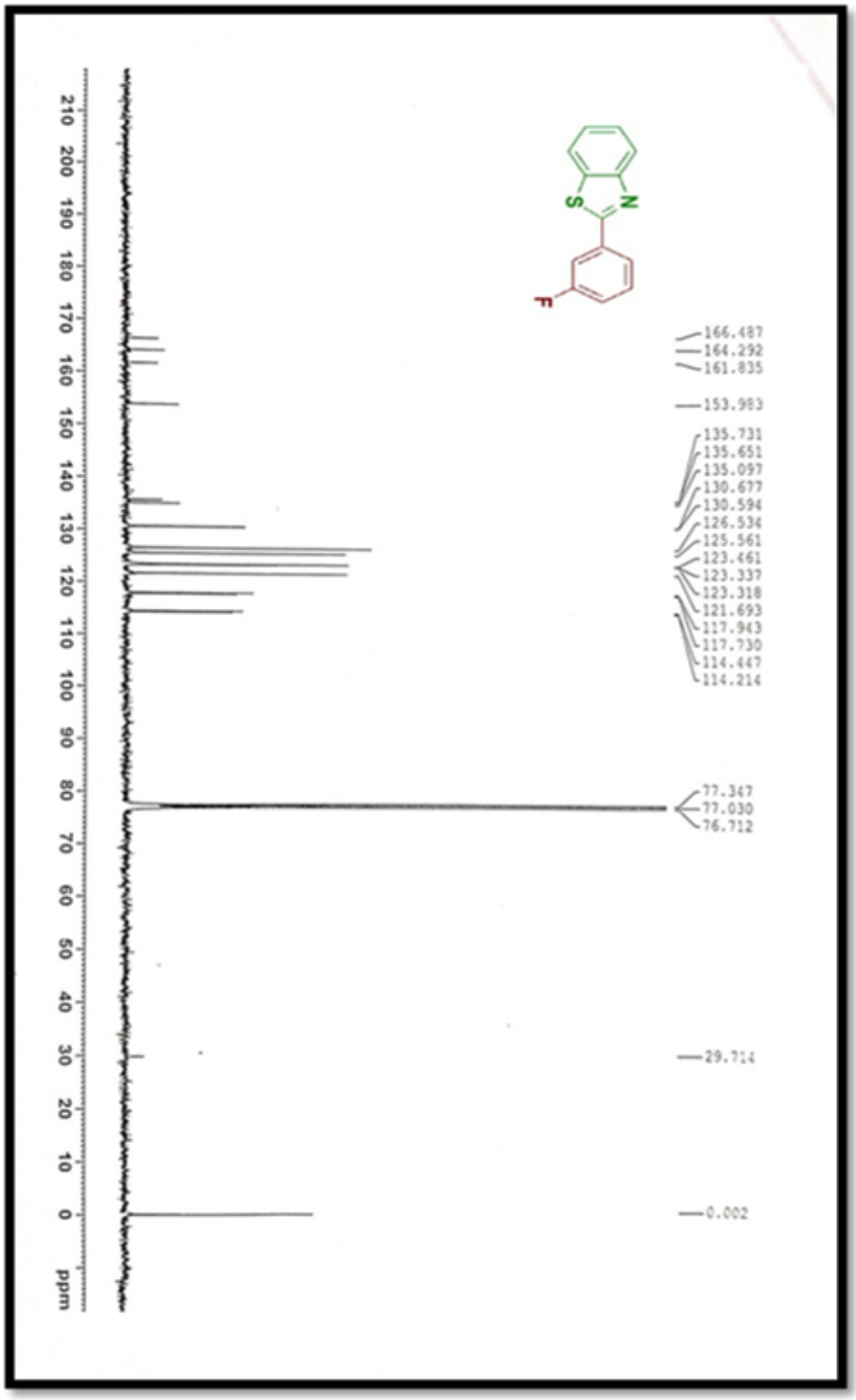


Figure I.A.28. ^{13}C Spectroscopical representation of 2-(3-Fluorophenyl)benzo[*d*]thiazole

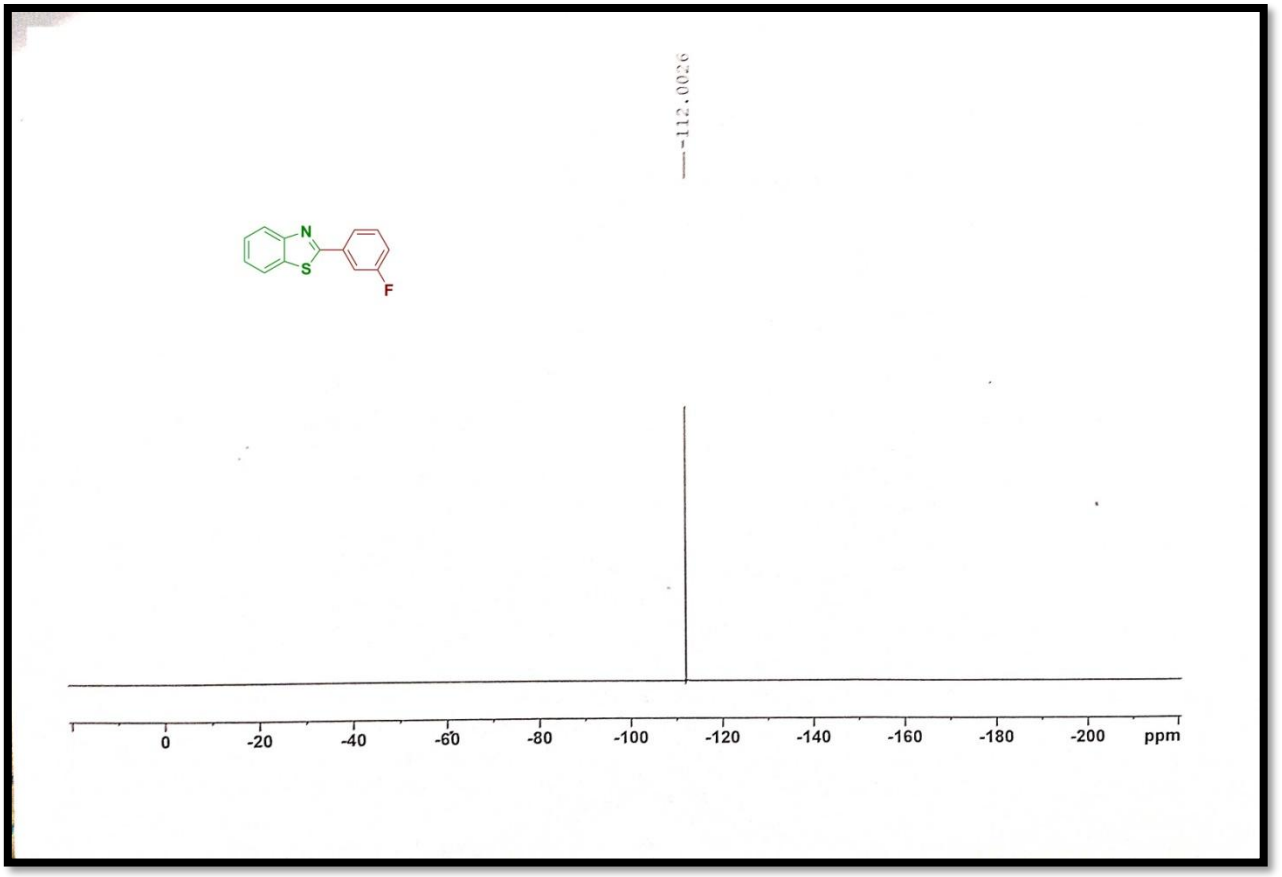


Figure I.A.29. ^{19}F Spectroscopical representation of 2-(3-Fluorophenyl)benzo[*d*]thiazole

2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole (Figure I.A.30.).

M. P.: 157–158 ^{o}C, white solid, yield : 94%, **^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm):** 7.485 – 7.596 (2H, m), 7.923 (2H, d, *J* = 8 Hz), 8.148 (2H, dd, *J* = 8 Hz), 8.294 (2H, d, *J* = 8 Hz) **(Figure I.A.31.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 123.066, 123.766, 126.601, 126.846, 127.449, 128.438, 135.250, 136.899, 153.896, 166.042 **(Figure I.A.32.).**

19F NMR (376 MHz, $CDCl_3$): δ (ppm): - 59.178 **(Figure I.A.33.).**

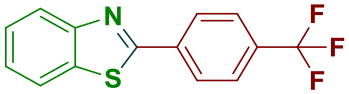


Figure I.A.30. Structure of 2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole

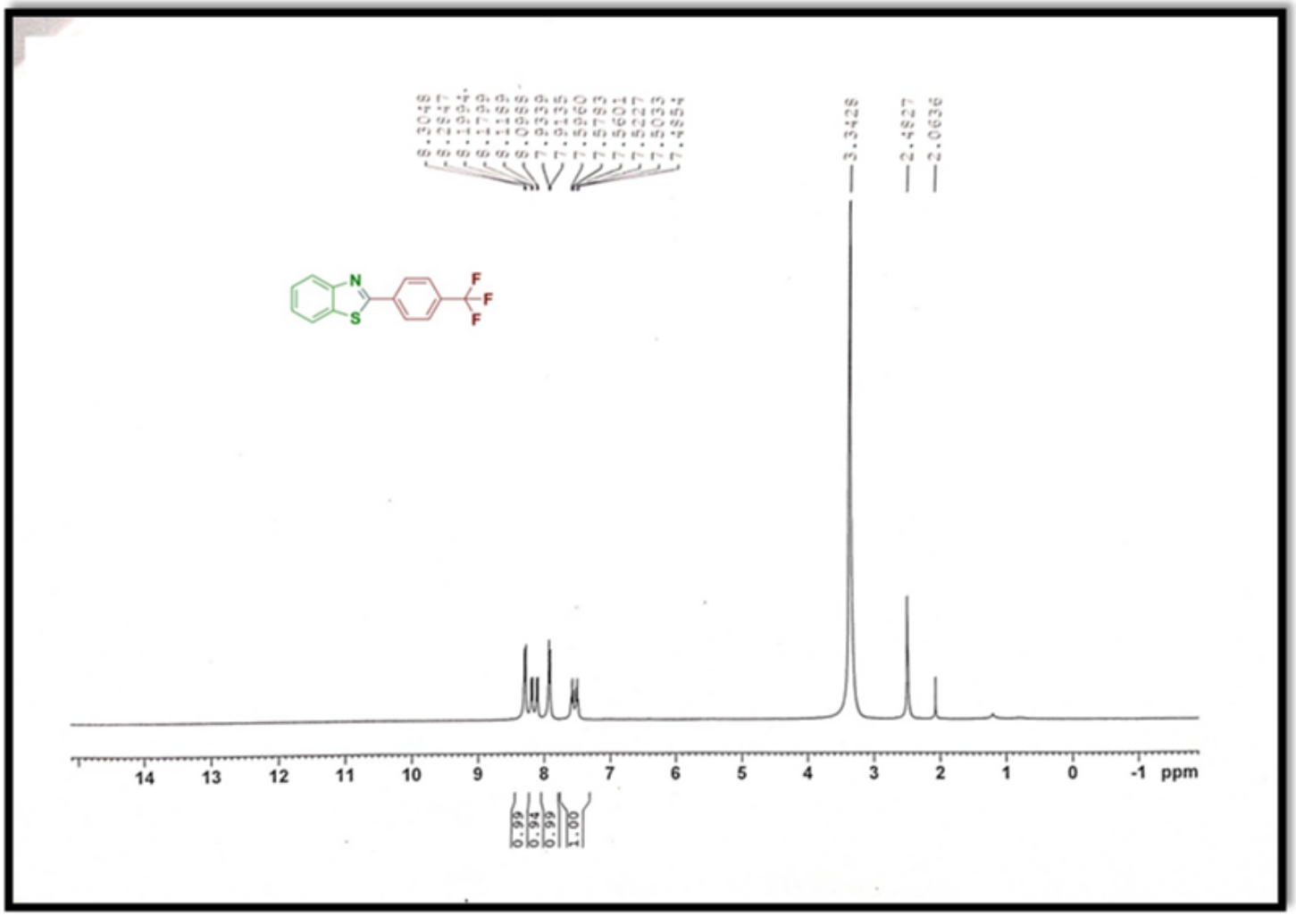


Figure I.A.31. ^{1}H Spectroscopical representation of 2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole

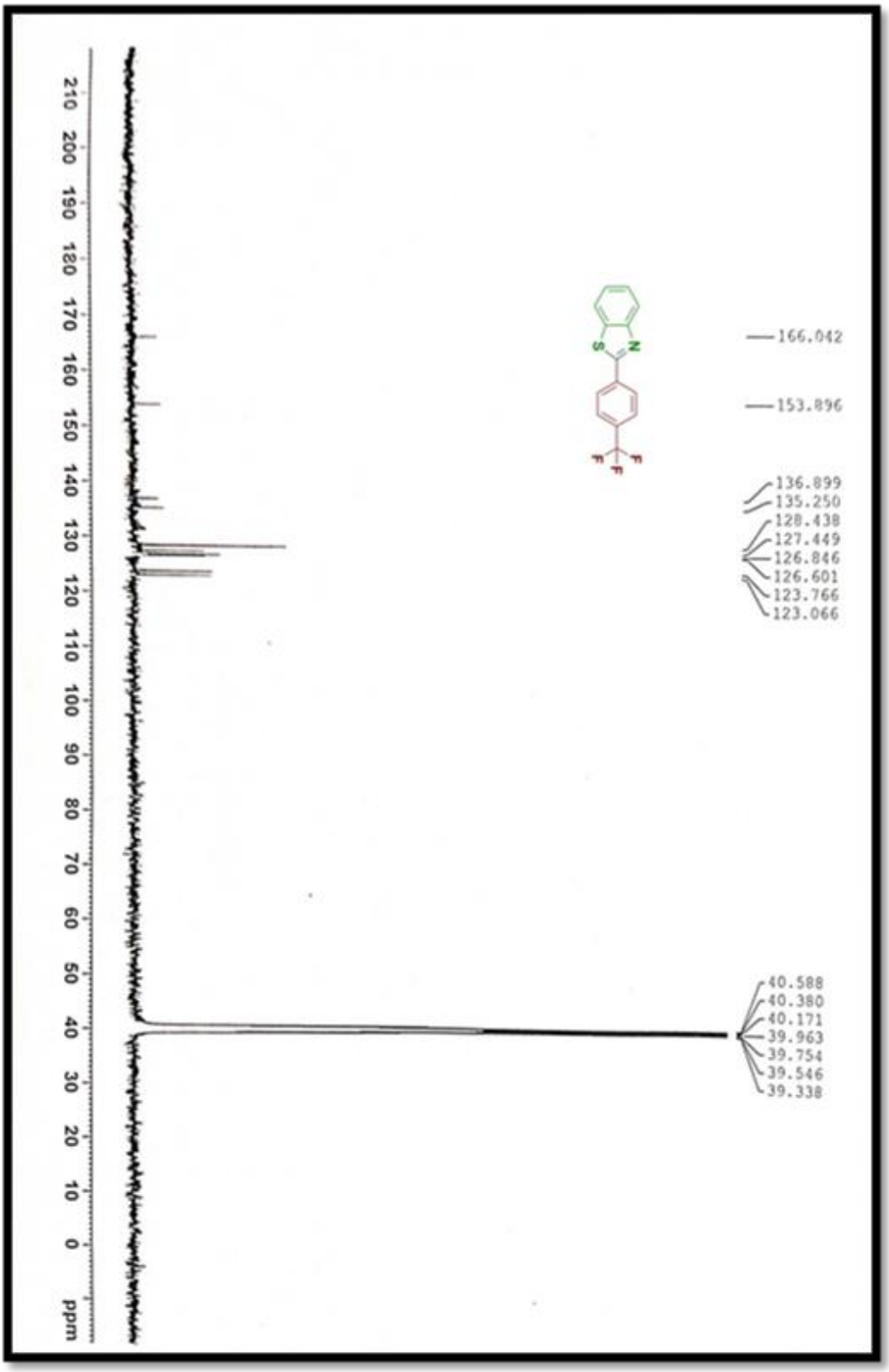


Figure I.A.32. ^{13}C Spectroscopical representation of 2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole

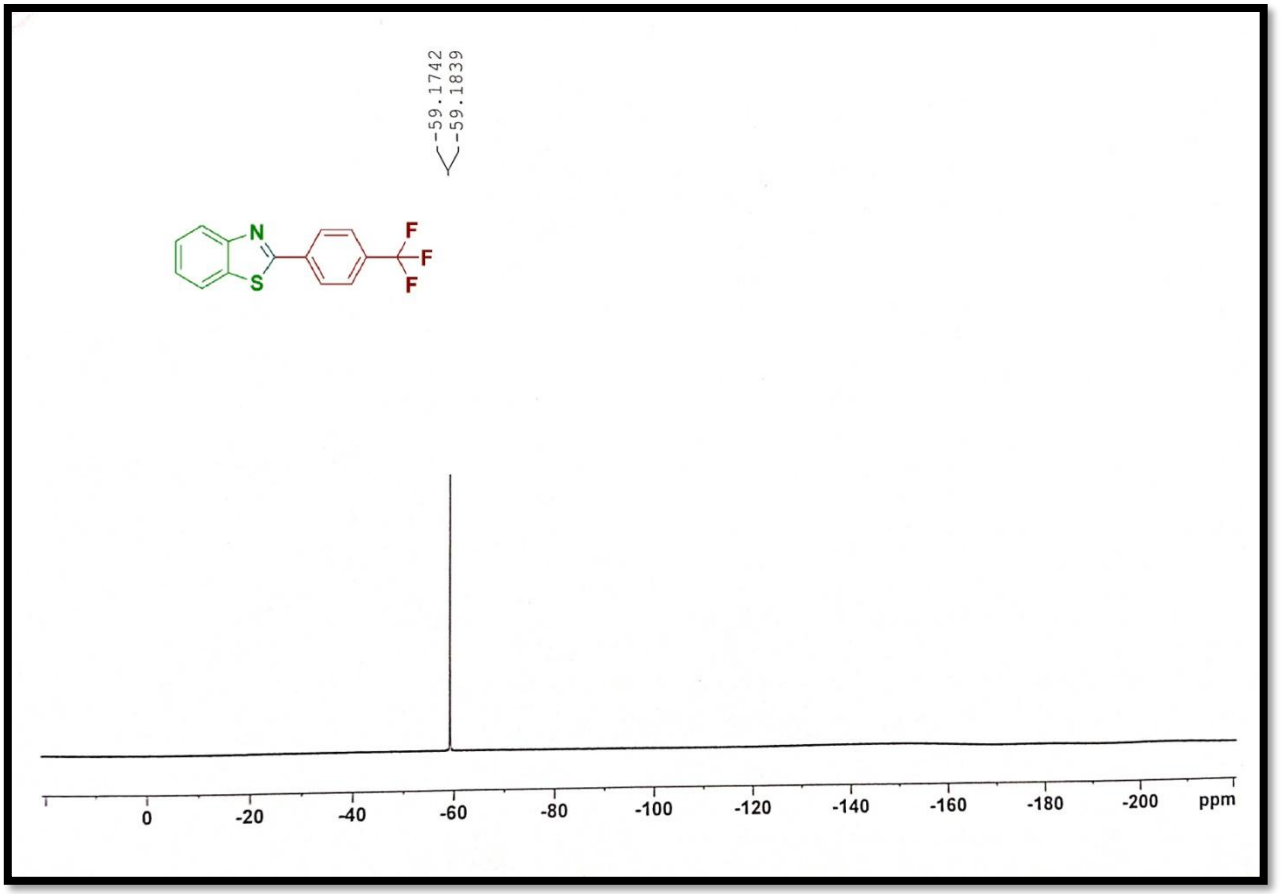


Figure I.A.33. ^{19}F Spectroscopical representation of 2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole

2-(2-Hydroxyphenyl)benzo[*d*]thiazole (Figure I.A.34.).

M. P.: 110 °C; yellow solid; yield : 90%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 6.926 – 6.966 (1H, m), 7.102 – 7.123 (1H, m), 7.358 – 7.510 (3H, m), 7.659 – 7.682 (1H, m), 7.861 – 7.997 (2H, m), 12.526 (1H, s) **(Figure I.A.35.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.091, 116.789, 117.874, 119.532, 121.511, 122.172, 125.542, 128.424, 132.590, 132.761, 151.827, 157.948, 169.377 **(Figure I.A.36.).**

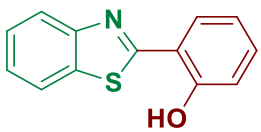


Figure I.A.34. Structure of 2-(2-Hydroxyphenyl)benzo[*d*]thiazole

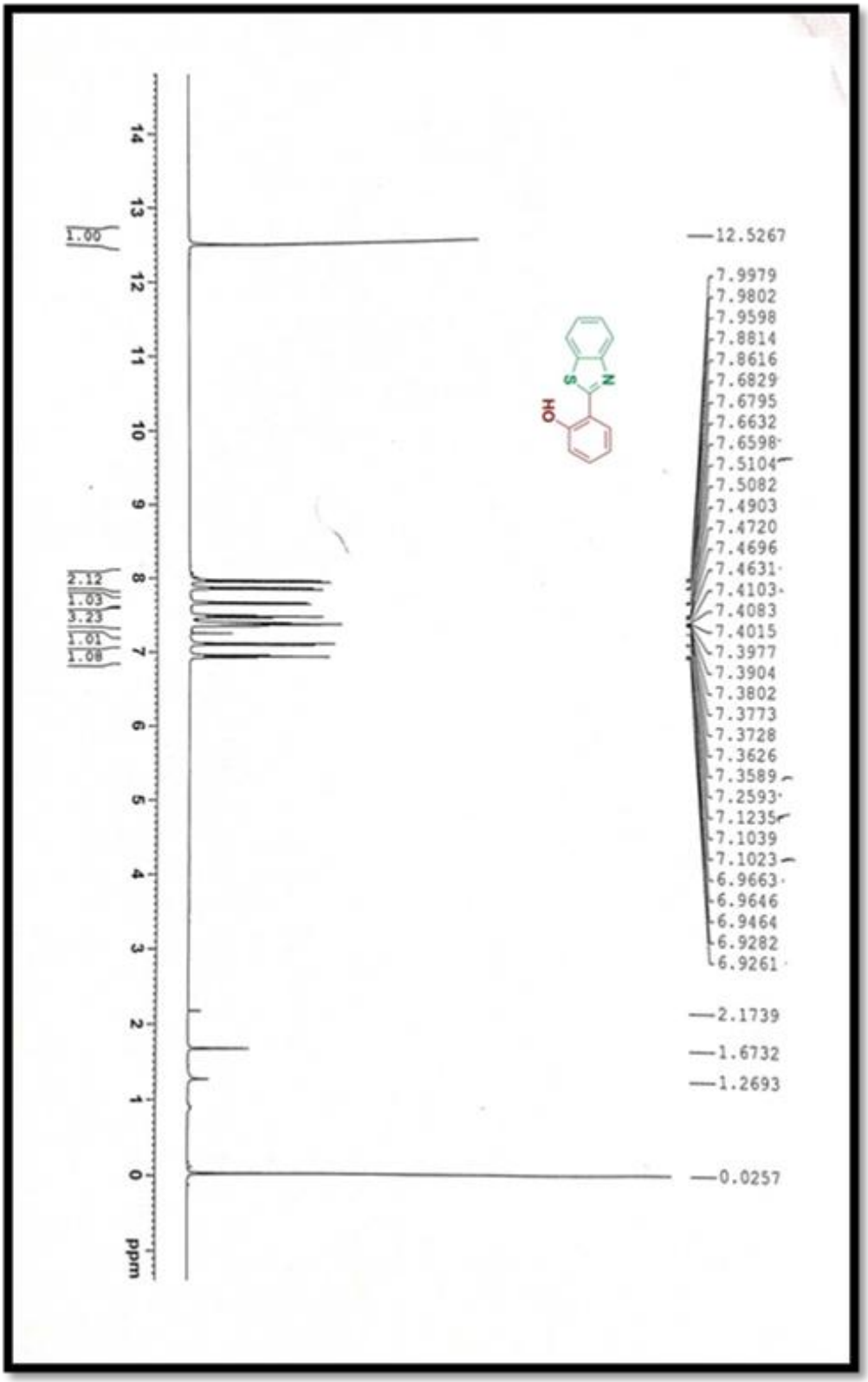


Figure I.A.35. ^{1}H Spectroscopical representation of 2-(2-Hydroxyphenyl)benzo[*d*]thiazole

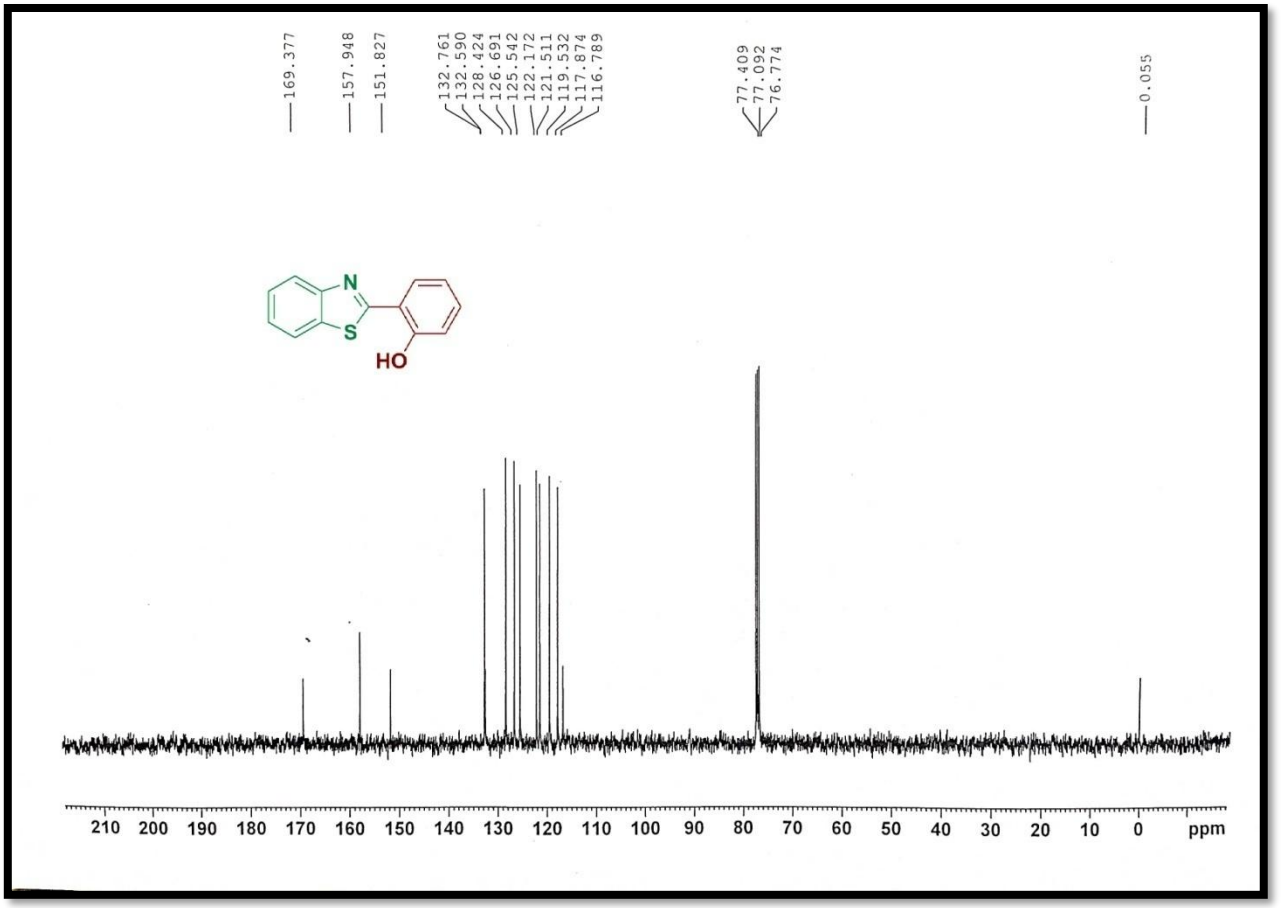


Figure I.A.36. ^{13}C Spectroscopical representation of 2-(2-Hydroxyphenyl)benzo[*d*]thiazole

2-(4-Biphenyl)benzo[*d*]thiazole (Figure I.A.37.).

M. P.: 248 °C, yellowish white solid, yield : 94%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 7.380 – 7.533 (5H, m), 7.696 (4H, dd, *J* = 8 Hz), 7.910 (1H, d, *J* = 8 Hz), 8.139 (3H, dd, *J* = 8 Hz, *J* = 17.6 Hz) **(Figure I.A.38.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.076, 121.660, 123.228, 125.223, 126.391, 127.137, 127.662, 128.019, 128.964, 132.512, 135.089, 140.068, 143.730, 154.236, 167.740 **(Figure I.A.39.).**

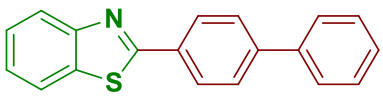


Figure I.A.37. Structure of 2-(4-Biphenyl)benzo[*d*]thiazole

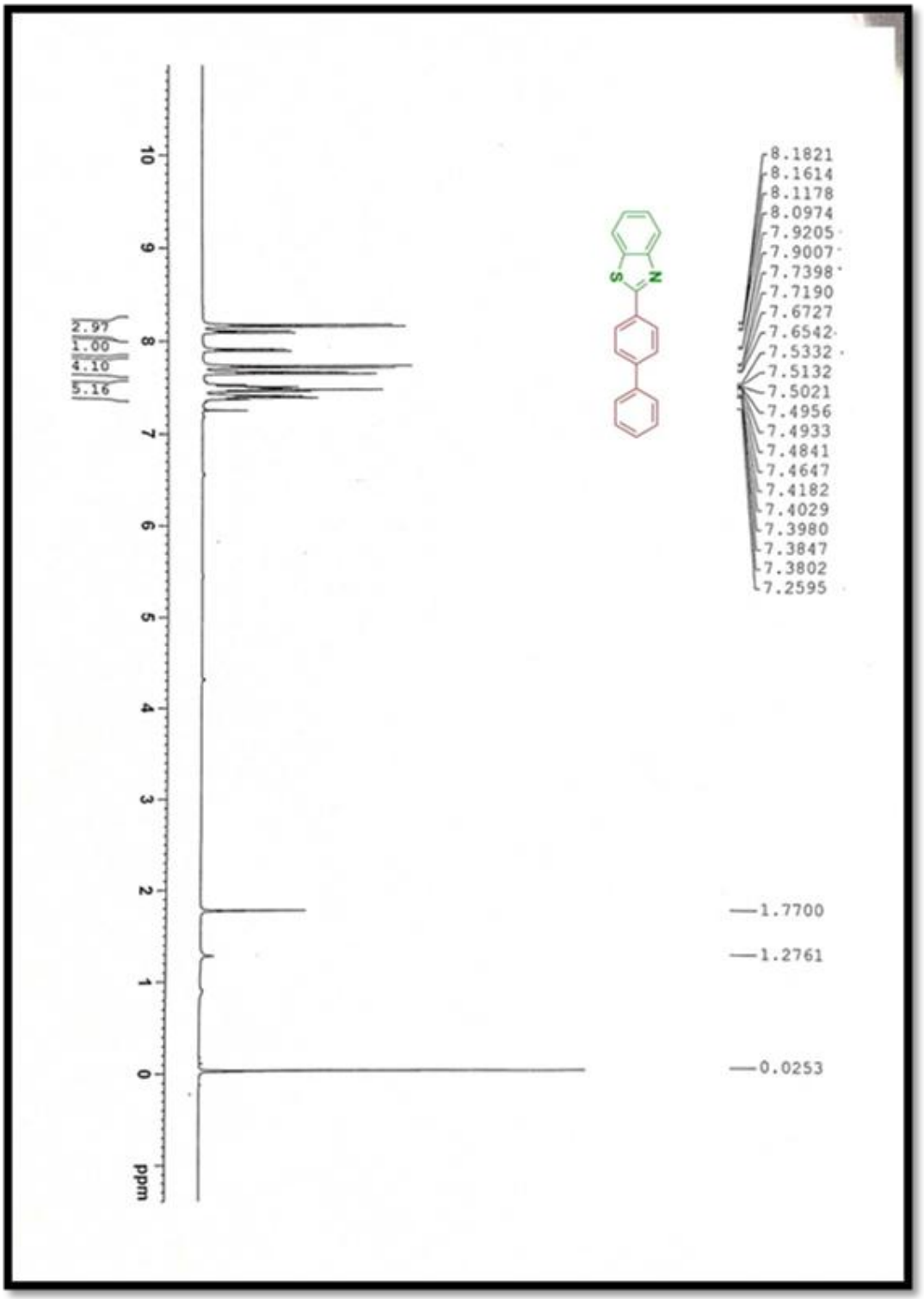


Figure I.A.38. ^{1}H Spectroscopical representation of 2-(4-Biphenyl)benzo[*d*]thiazole

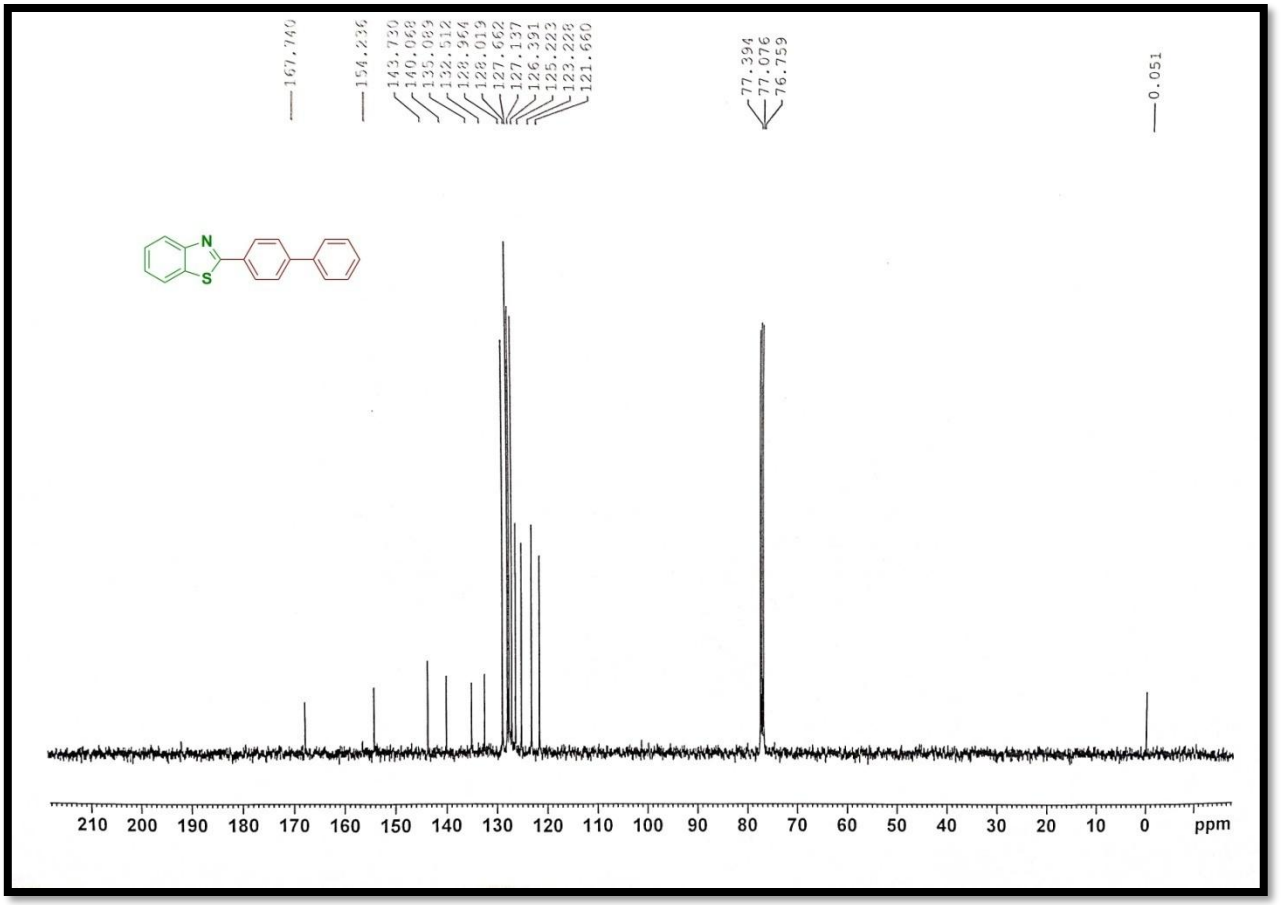


Figure I.A.39. ^{13}C Spectroscopical representation of 2-(4-Biphenyl)benzo[*d*]thiazole

2-(4-Chlorophenyl)benzo[*d*]thiazole (Figure I.A.40.).

M. P.: 105 °C, yellowish white solid, yield : 92%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 7.390 (1H, q, *J* = 0.8 Hz), 7.416 – 7.521 (3H, m), 7.897 (1H, d, *J* = 8 Hz), 8.076 – 8.004 (3H, m) **(Figure I.A.41.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.037, 121.667, 123.312, 125.433, 126.503, 128.351, 128.724, 129.289, 132.120, 135.063, 137.047, 154.072, 166.646 **(Figure I.A.42.).**

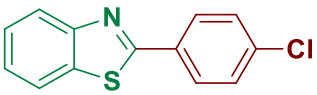


Figure I.A.40. Structure of 2-(4-Chlorophenyl)benzo[*d*]thiazole

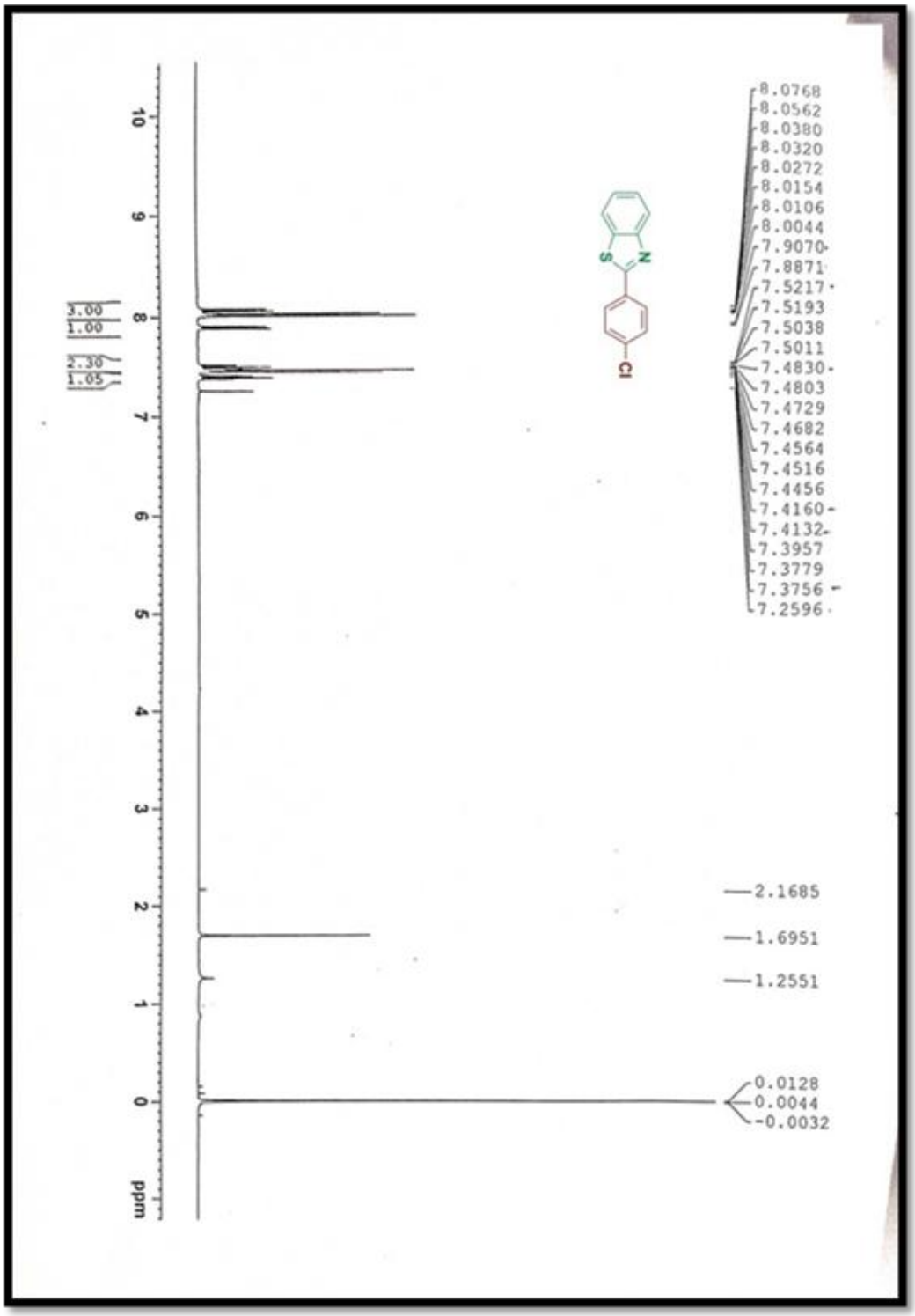


Figure I.A.41. ^{1}H Spectroscopical representation of 2-(4-Chlorophenyl)benzo[*d*]thiazole

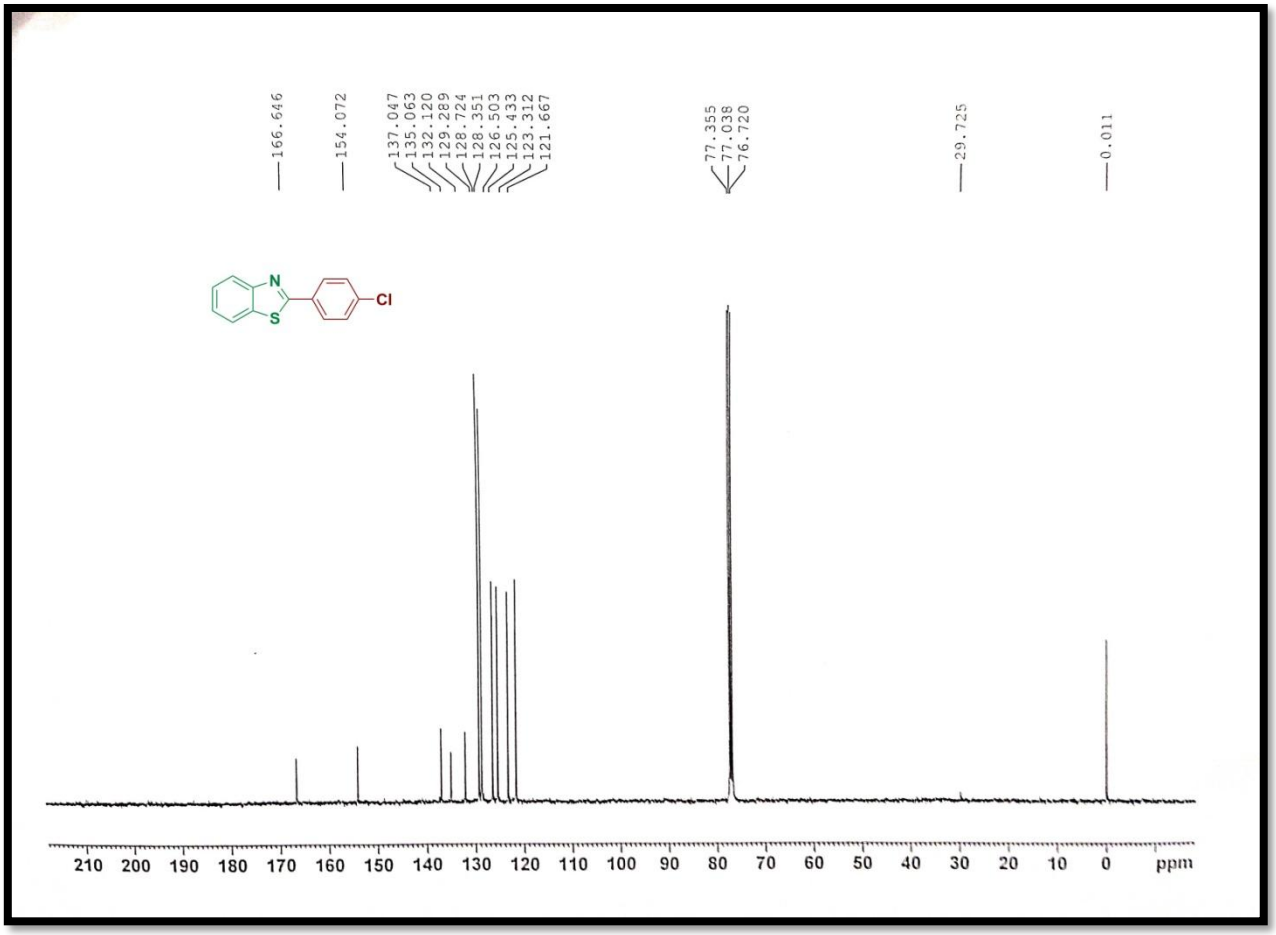


Figure I.A.42. ^{13}C Spectroscopical representation of 2-(4-Chlorophenyl)benzo[*d*]thiazole

2-(2-Naphthyl)benzo[*d*]thiazole (Figure I.A.43.).

M. P.: 245 - 248 °C, white solid, yield: 93%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 7.392 (1H, t, *J* = 8 Hz), 7.495 – 7.565 (3H, m), 7.852 – 7.965 (4H, m), 8.125 – 8.220 (2H, m), 8.559 (1H, s) **(Figure I.A.44.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.109, 121.673, 123.263, 124.454, 125.268, 126.416, 126.897, 127.478, 127.604, 127.896, 128.846, 130.993, 133.203, 134.628, 135.163, 154.260, 168.135 **(Figure I.A.45.).**

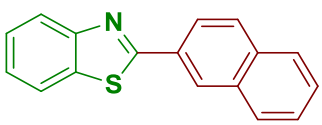


Figure I.A.43. Structure of 2-(2-Naphthyl)benzo[*d*]thiazole

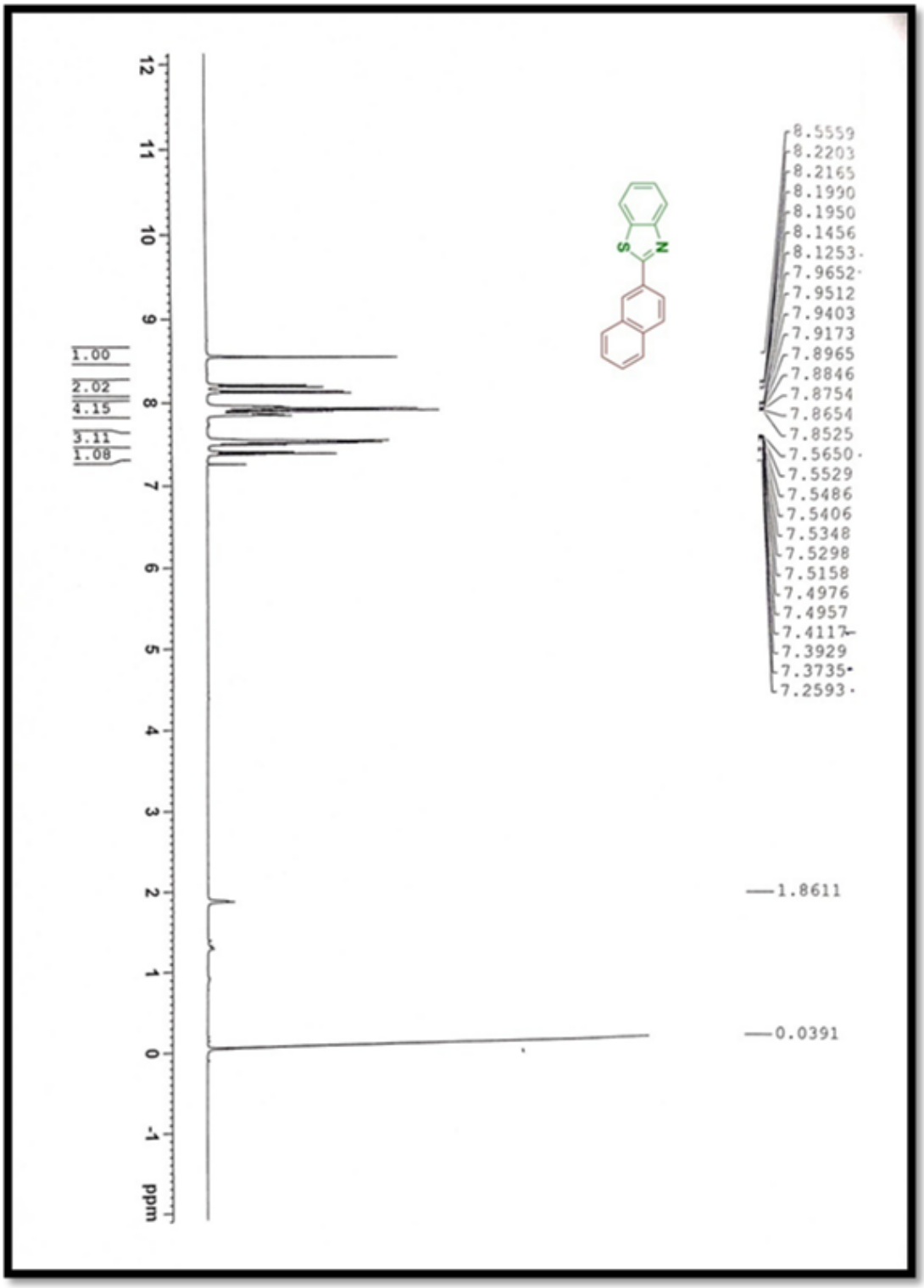


Figure I.A.44. ^{1}H Spectroscopical representation of 2-(2-Naphthyl)benzo[*d*]thiazole

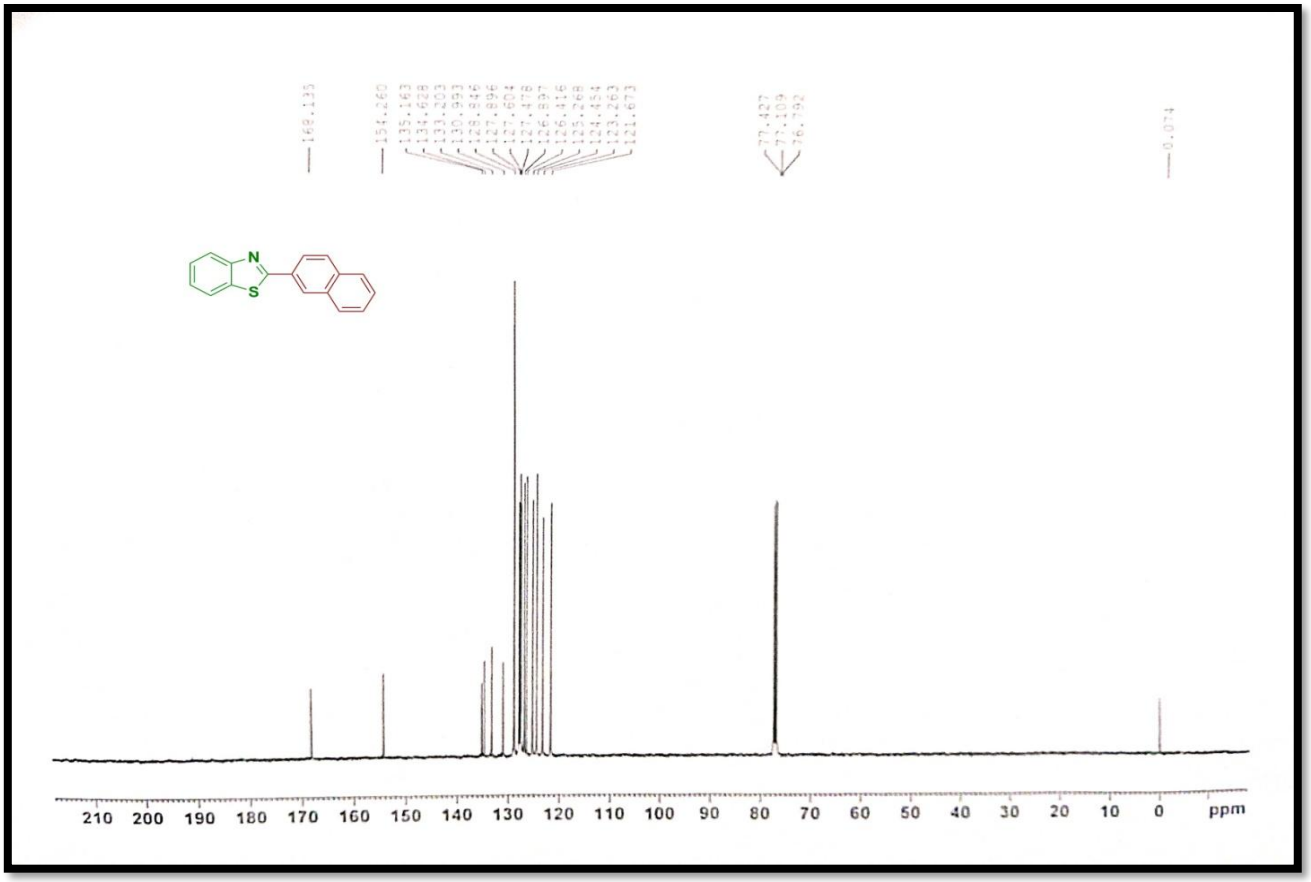


Figure I.A.45. ^{13}C Spectroscopical representation of 2-(2-Naphthyl)benzo[*d*]thiazole

2-(4-Fluorophenyl)benzo[*d*]thiazole (Figure I.A.46.).

M. P.: 102–103 °C, white solid, yield: 95%, **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm): 7.150 – 7.207 (2H, m), 7.364 – 7.405 (1H, m), 7.474 – 7.515 (1H, m), 7.891 (1H, d, *J* = 8 Hz), 8.052 – 8.106 (3H, m) **(Figure I.A.47.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 77.036, 116.051, 116.270, 121.621, 123.211, 125.258, 129.491, 129.576, 129.971, 135.068, 154.118, 163.215, 166.230 **(Figure I.A.48.).**

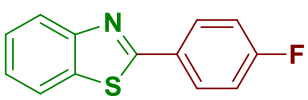


Figure I.A.46. Structure of 2-(4-Fluorophenyl)benzo[*d*]thiazole

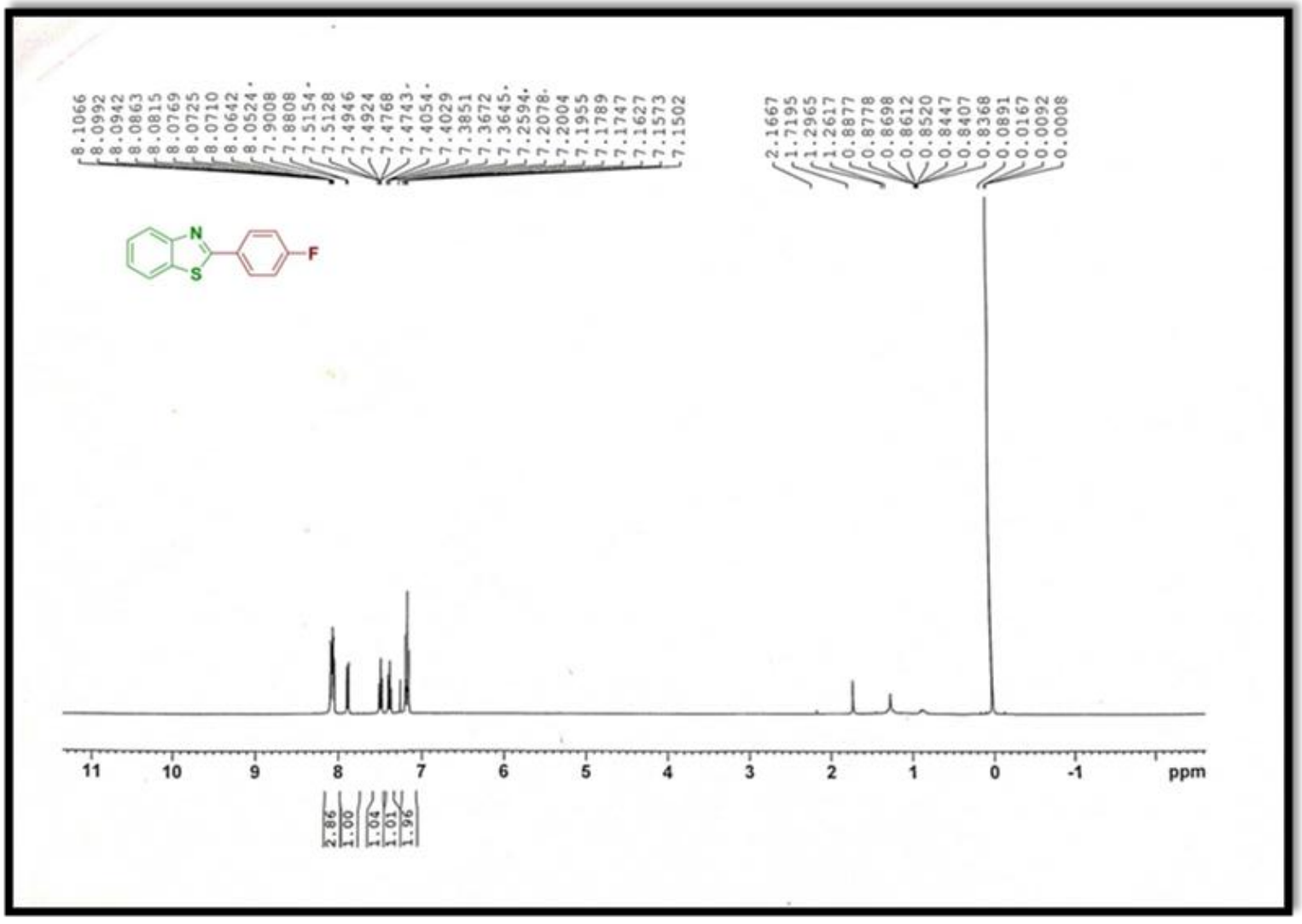


Figure I.A.47. ^{1}H Spectroscopical representation of 2-(4-Fluorophenyl)benzo[*d*]thiazole

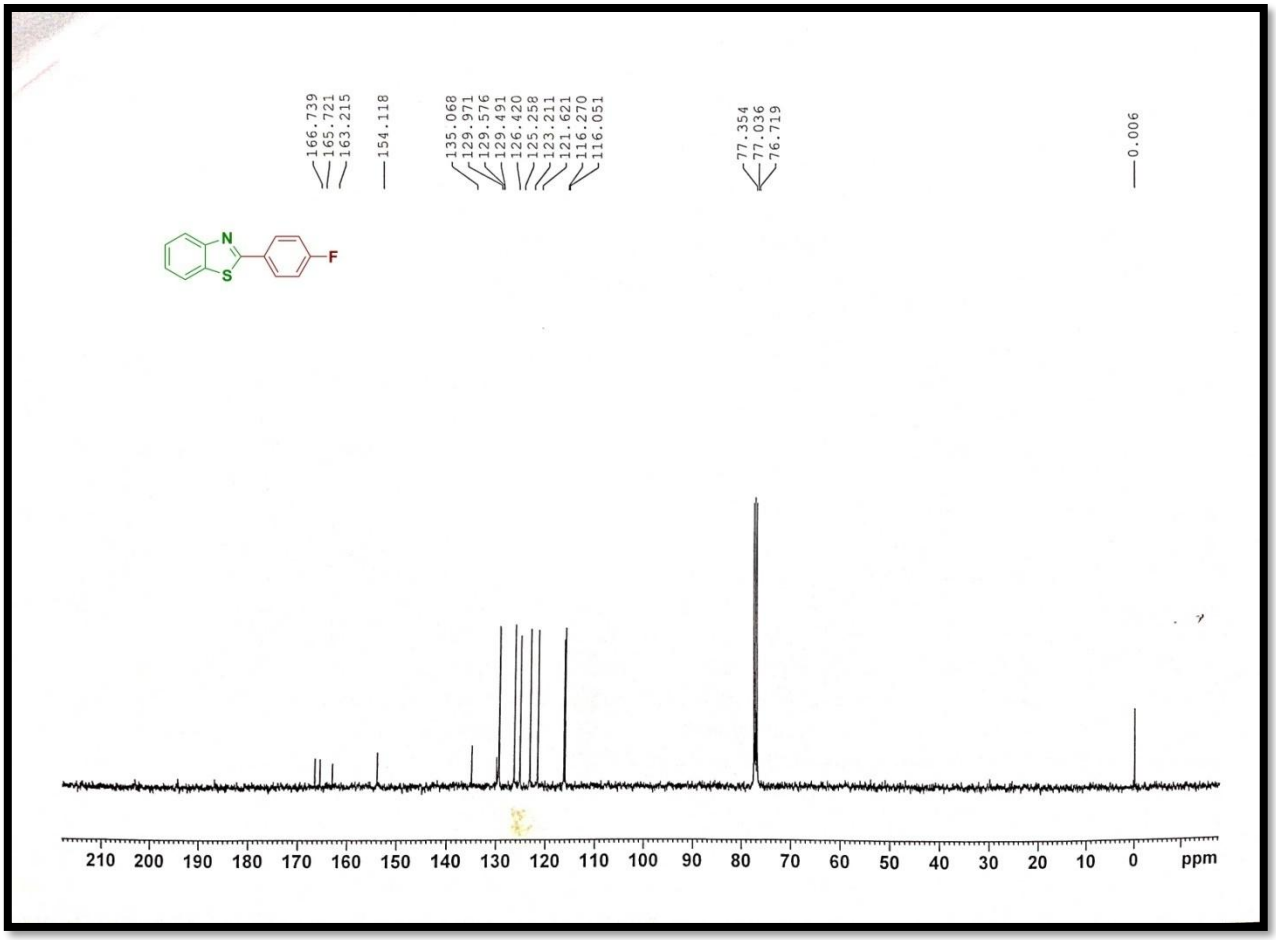


Figure I.A.48. ^{13}C Spectroscopical representation of 2-(4-Fluorophenyl)benzo[*d*]thiazole

2-(4-Methoxyphenyl)benzo[*d*]thiazole (Figure I.A.49.).

M.P.: 125–126 ^{o}C ^{o}C, white solid, yield : 85%, **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 3.888 (3H, s), 6.988 – 7.024 (2H, m), 7.334 – 7.374 (1H, m), 7.449 – 7.490 (1H, m), 7.879 (1H, d, J = 8 Hz), 8.021 – 8.057 (3H, m) **(Figure I.A.50.).**

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 55.470, 77.003, 114.386, 121.505, 122.834, 124.794, 126.203, 126.466, 129.126, 134.876, 154.242, 161.948, 167.875 **(Figure I.A.51.).**

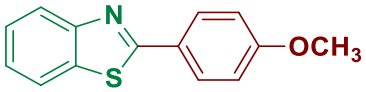


Figure I.A.49. Structure of 2-(4-Methoxyphenyl)benzo[*d*]thiazole

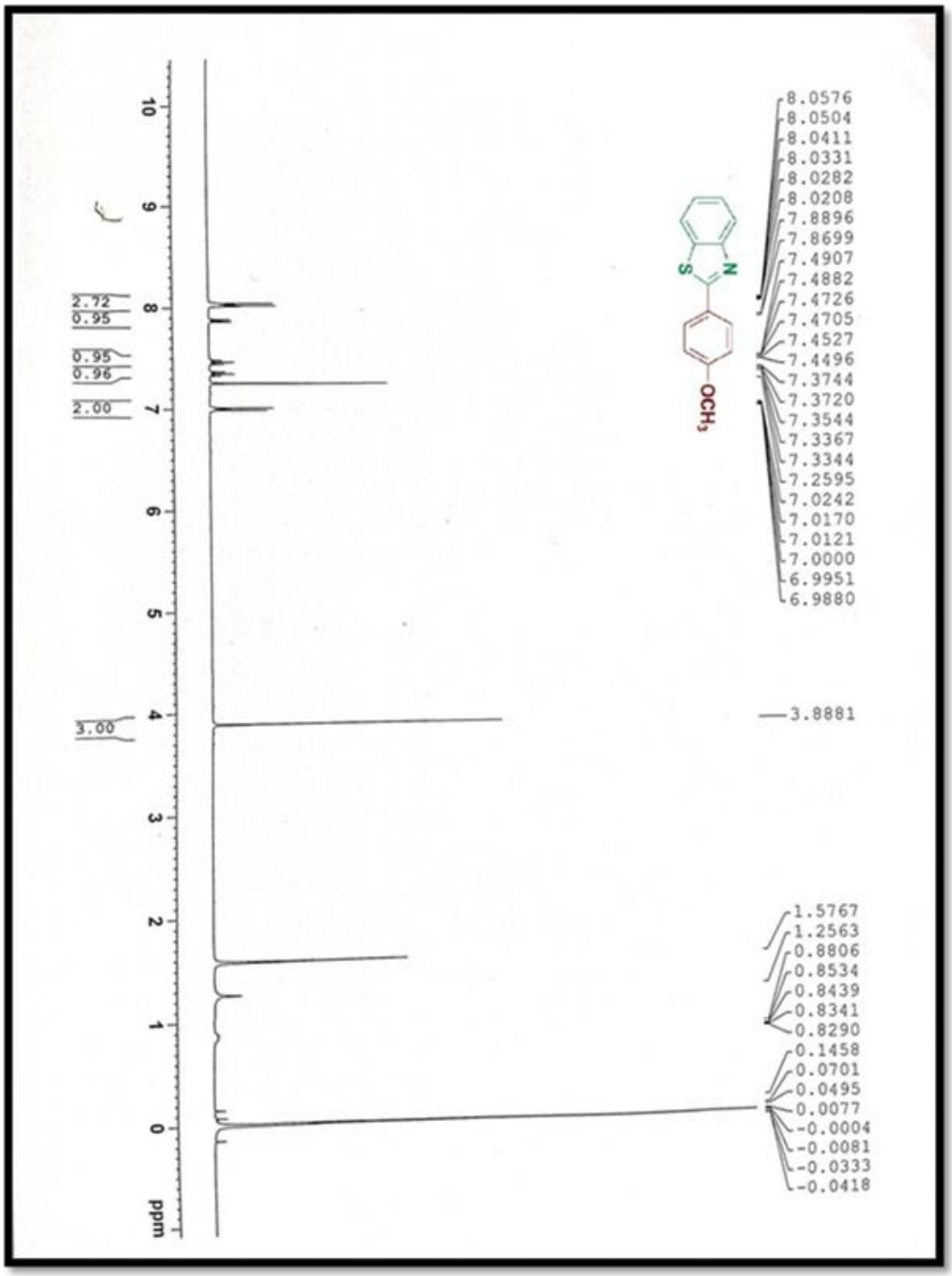


Figure I.A.50. ^{1}H Spectroscopical representation of 2-(4-Methoxyphenyl)benzo[*d*]thiazole

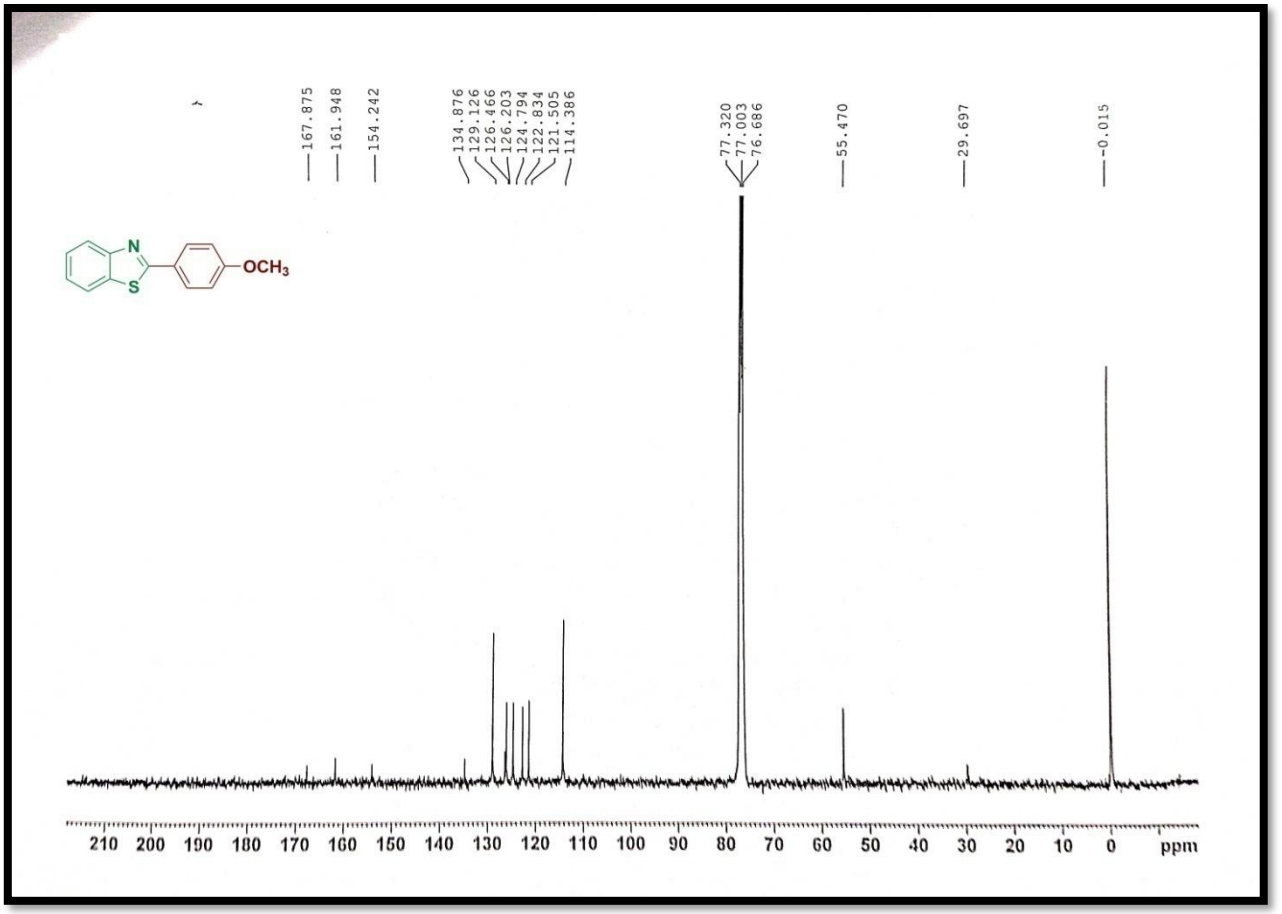


Figure I.A.51. ^{13}C Spectroscopical representation of 2-(4-Methoxyphenyl)benzo[*d*]thiazole

Ethyl 2-methyl-4-phenyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.52.)

M.P. : 174 - 176 ^{o}C; pale yellow crystal; yield : 90%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.157, (t, *J* = 7.2 Hz, 3H), 2.469 (quintet, *J* = 1.7 Hz, 3H), 4.018 (t, *J* = 7.2 Hz, 2H), 6.431 (s, 1H), 7.174 (s, 5H), 7.256 (quintet, *J* = 1.28 Hz, 3H), 7.391 (t, *J* = 5.6 Hz, 1H) **(Figure I.A.53.).**

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm): 14.005, 23.128, 57.018, 60.045, 102.594, 112.391, 122.268, 126.784, 129.006, 137.559, 141.960, 154.267, 162.887, 165.504

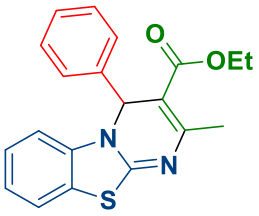


Figure I.A.52. Structure of Ethyl 2-methyl-4-phenyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

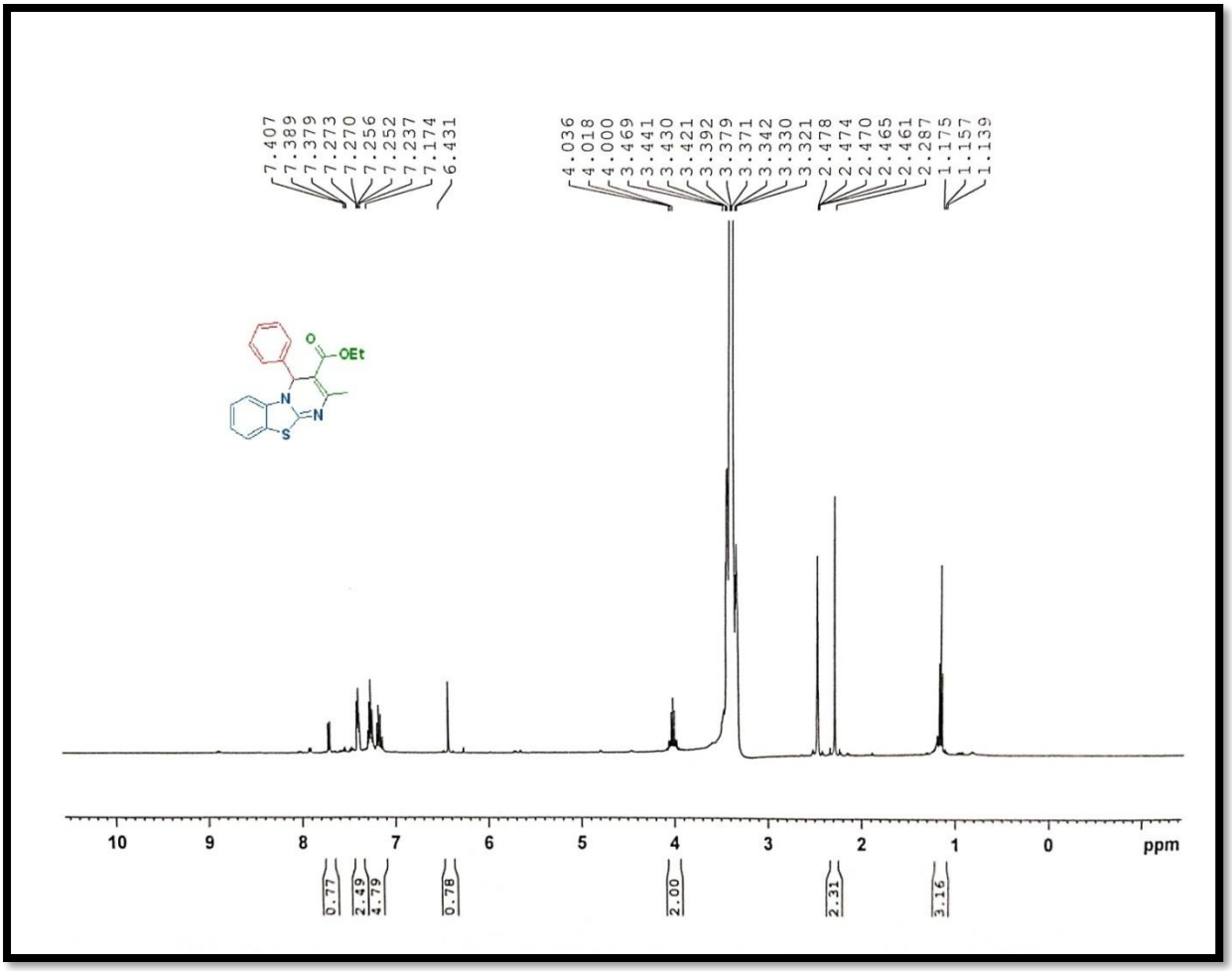


Figure I.A.53. ^{1}H Spectroscopical representation of Ethyl 2-methyl-4-phenyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.54.).

M.P. : 261 – 262 ^{o}C; off - white solid; yield : 92%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.085 (t, *J* = 7 Hz, 3H), 2.419 (s, 3H), 4.026 (q, *J* = 6.8 Hz, 2H), 6.662 (s, 1H), 7.175 (t, *J* = 7.6 Hz, 1H), 7.282 (t, *J* = 7.6 Hz, 1H), 7.511 (d, *J* = 8 Hz, 1H), 7.576 (t, *J* = 8 Hz, 1H), 7.737 (d, *J* = 7.6 Hz, 1H), 7.827 (d, *J* = 7.6 Hz, 1H), 8.058 (d, *J* = 8 Hz, 1H), 8.315 (s, 1H) **(Figure I.A.55.).** **^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm):** 14.448, 23.774, 56.338, 60.227, 102.428, 112.873, 122.225, 123.246, 123.478, 123.809, 124.861, 127.510, 130.956, 133.875, 137.646, 143.997, 148.160, 155.598, 163.556, 165.707 **(Figure I.A.56.).**

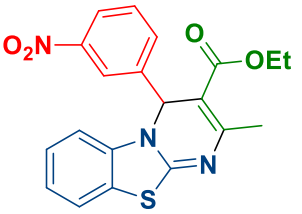


Figure I.A.54. Structure of Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

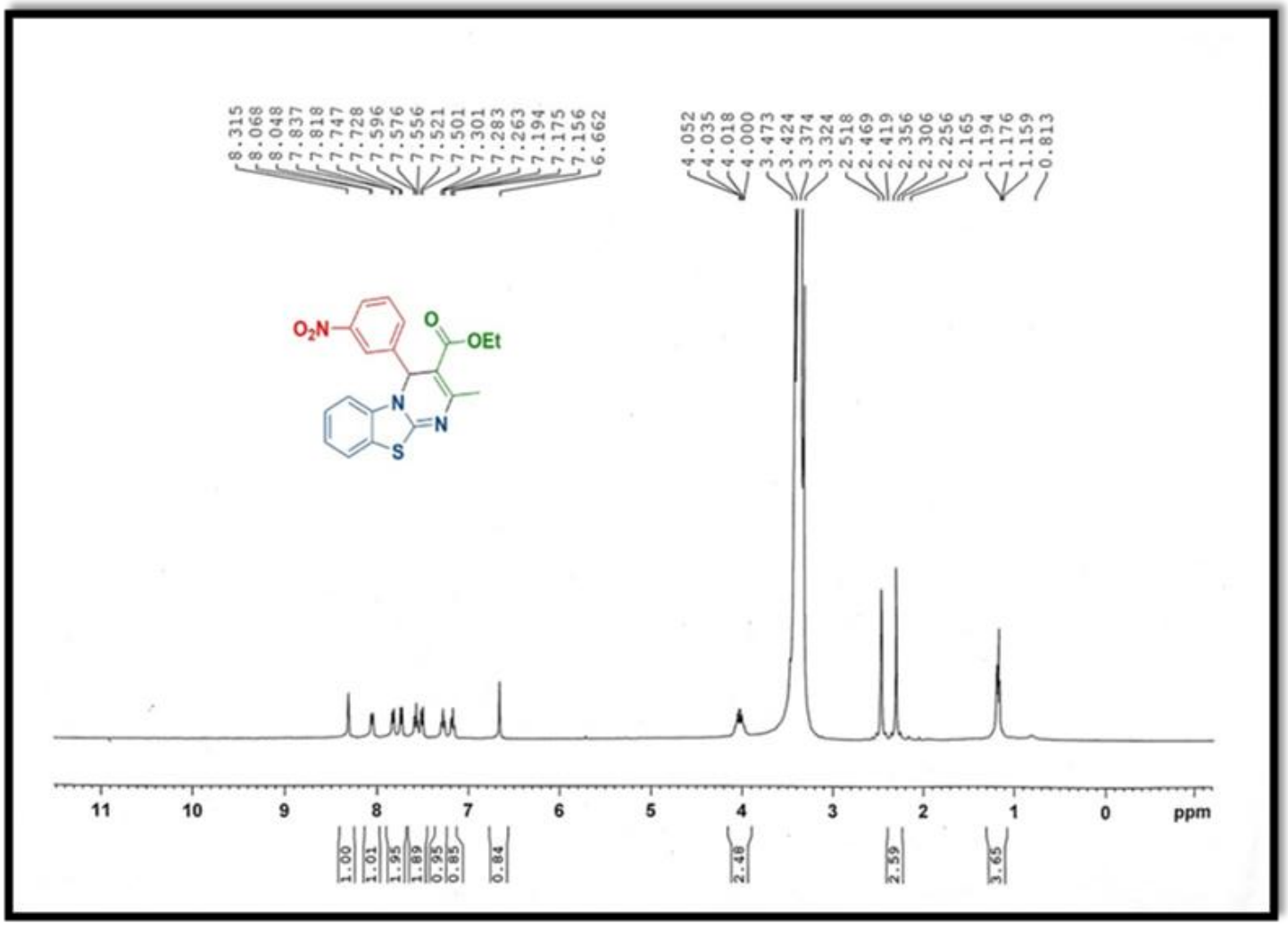


Figure I.A.55. ^{1}H Spectroscopical representation of Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

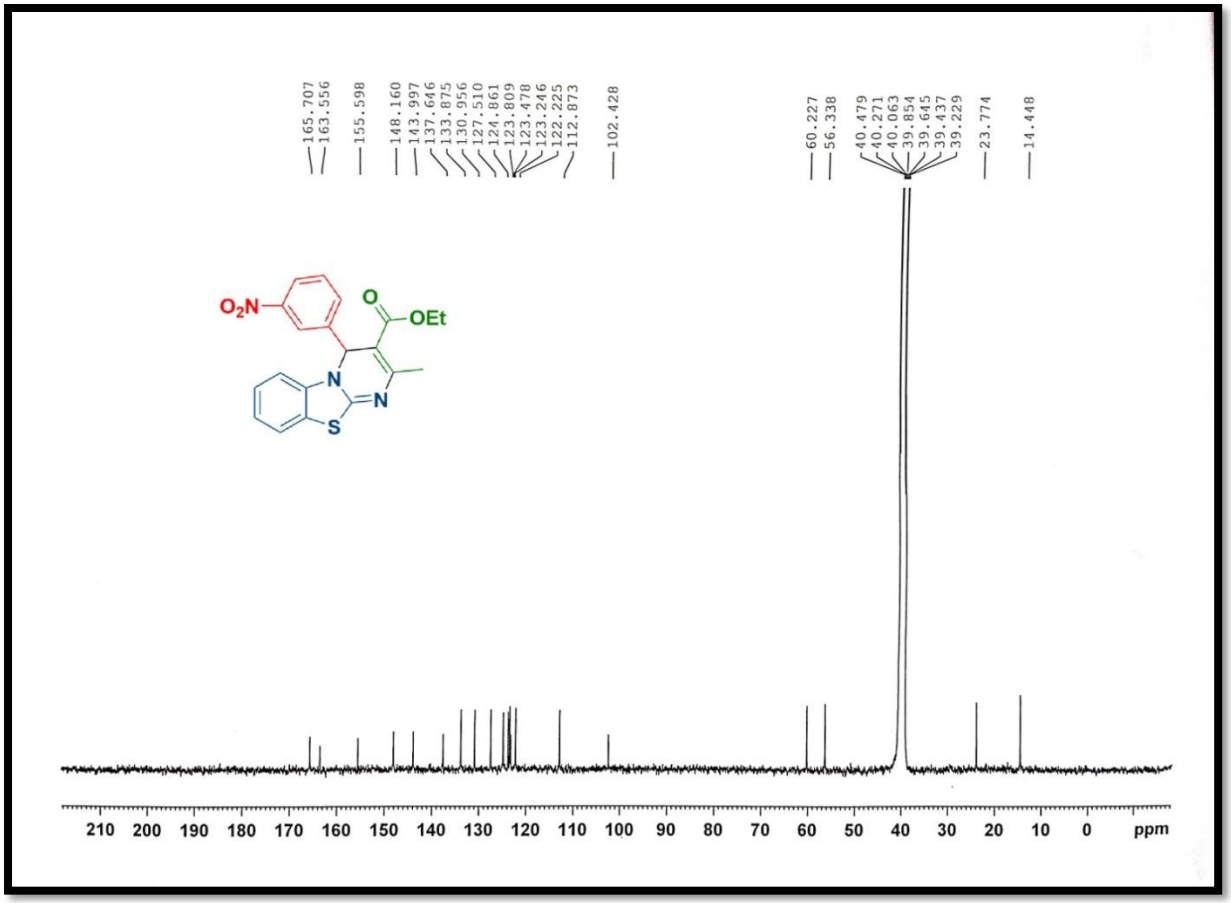


Figure I.A.56. ^{13}C Spectroscopical representation of Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.57.).

M.P. : 169 – 172 ^{o}C; yellow powder, yield : 92%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.154 (t, *J* = 7 Hz, 3H), 2.301 (s, 3H), 3.986 - 4.066 (m, 2H), 6.547 (s, 1H), 7.145 (t, *J* = 7.4 Hz, 1H), 7.259 (t, *J* = 7.6 Hz, 1H), 7.404 (d, *J* = 8.4 Hz, 1H), 7.635 - 7.718 (m, 5H) **(Figure I.A.58.).**

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm): 14.497, 23.784, 56.614, 60.126, 102.575, 112.687, 123.156 (d, *J* = 25.8Hz, 1C), 123.401, 124.692, 125.729, 126.076, 127.366, 128.396, 129.040, 129.355, 137.750, 146.258, 155.258, 163.395, 163.808, (**Figure I.A.59.).**

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ (ppm): -61.211 (s) **(Figure I.A.60.).**

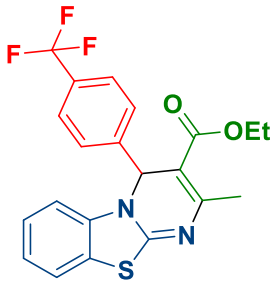


Figure I.A.57. Structure of Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

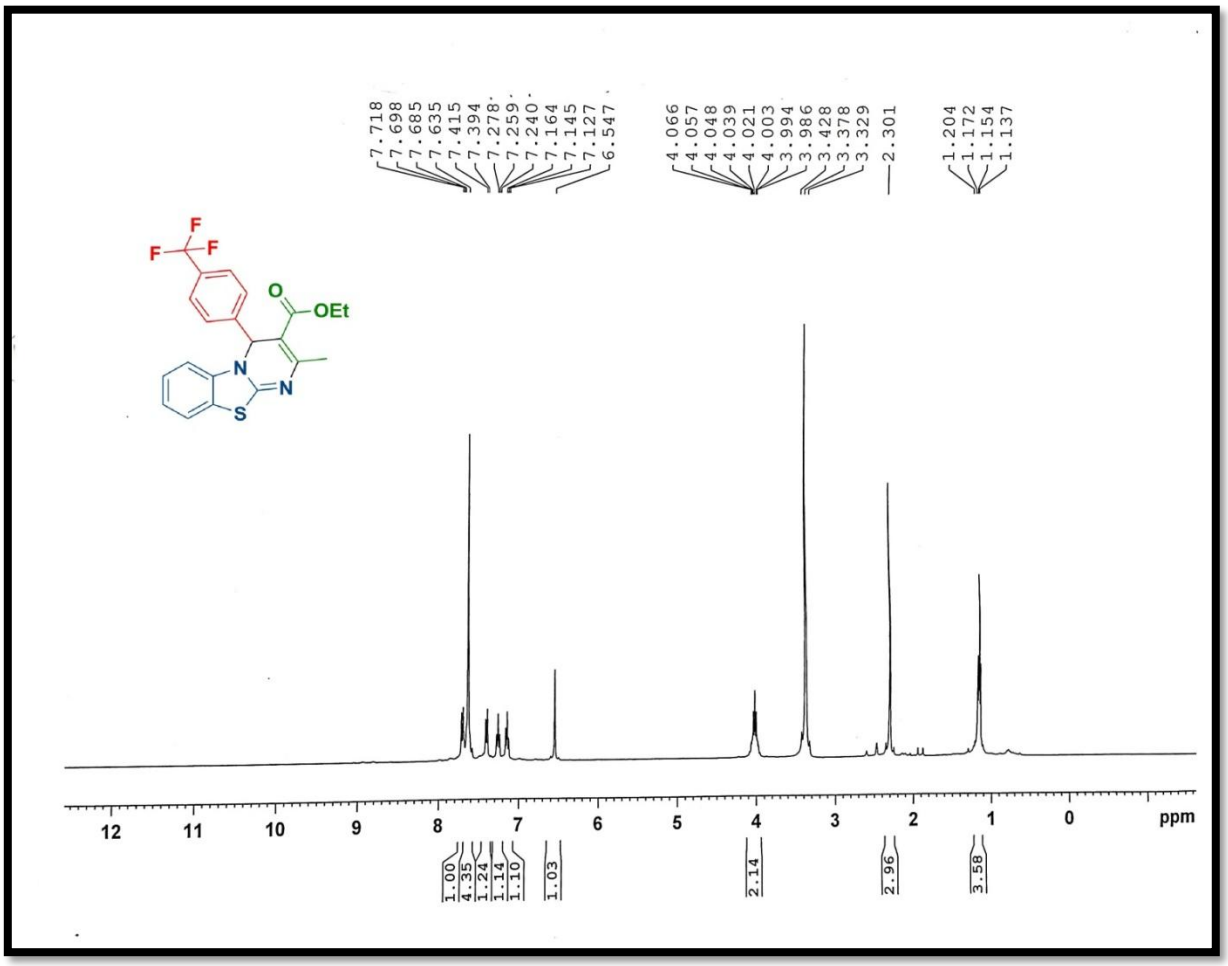


Figure I.A.58. ^{1}H Spectroscopical representation of Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

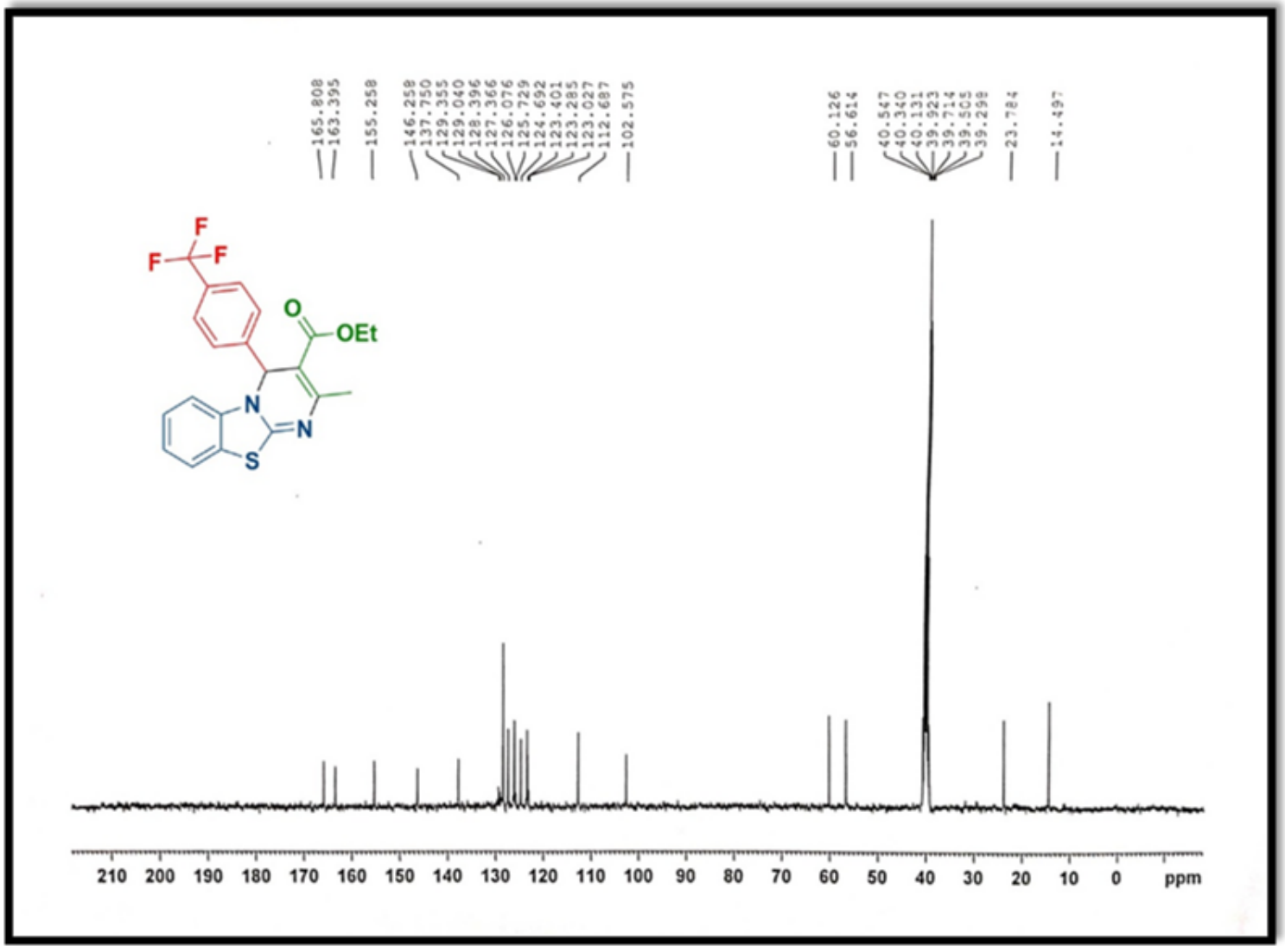


Figure I.A.59. ^{13}C Spectroscopical representation of Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

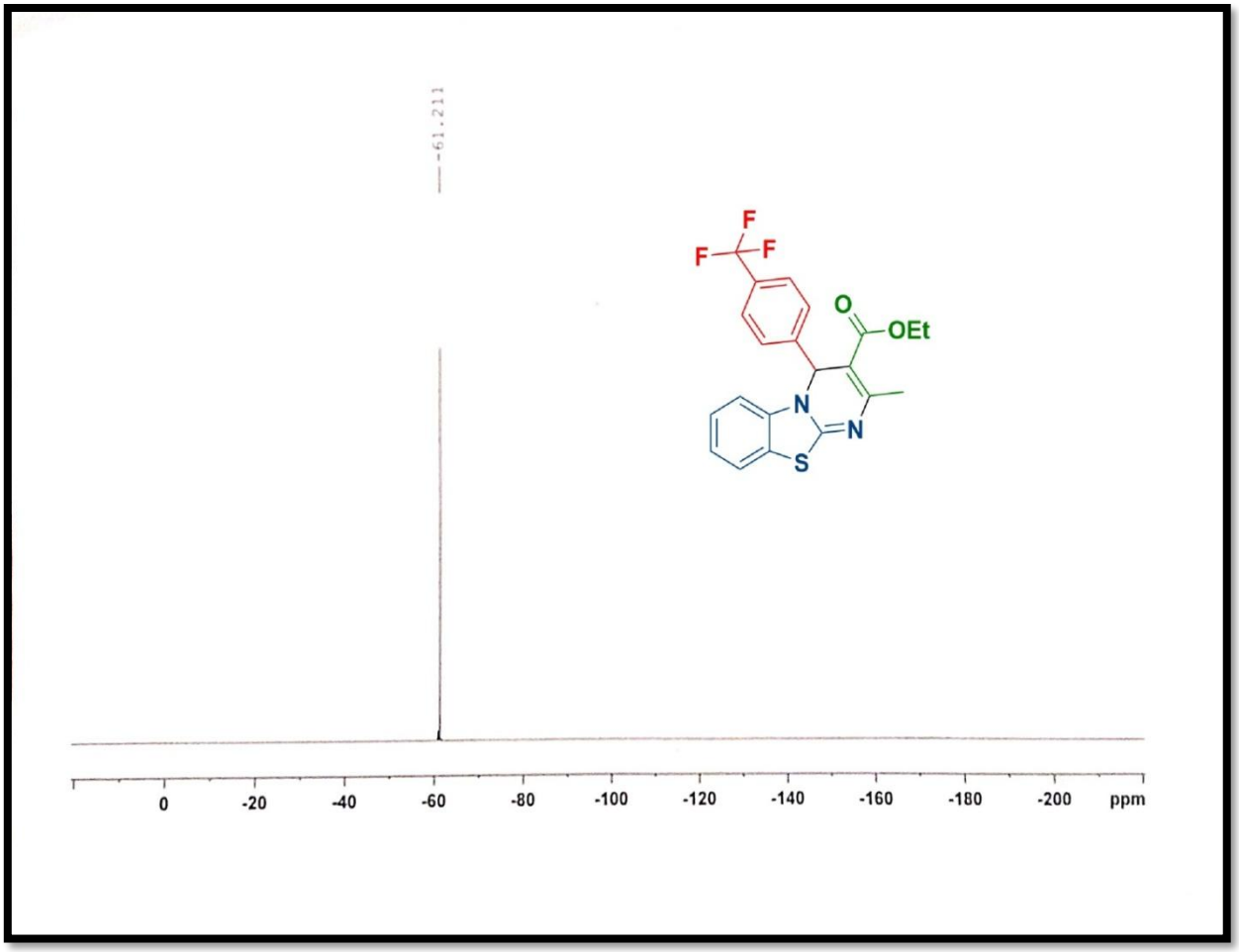


Figure I.A.60. ^{19}F Spectroscopical representation of Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Ethyl 4-(2-bromophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.61.).

M.P. : 168 – 170 ^{o}C; yellowish powder; yield : 85%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.095 (t, *J* = 7 Hz, 3H), 2.274 (t, *J* = 2.19 Hz, 3H), 4.022 (d, *J* = 6.8 Hz, 2H), 6.630 (s, 1H), 7.139 (d, *J* = 8.4 Hz, 2H), 7.276 - 7.322 (m, 2H), 7.386 (s, 1H), 7.522 (m, 2H), 7.683 (s, 1H) **(Figure I.A.62.).**

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm): 14.725, 23.679, 57.225, 59.908, 102.625, 106.887, 112.227, 119.253, 121.799, 122.947, 123.398, 124.685, 127.202, 127.476, 129.315, 130.888, 131.286, 133.511, 138.175, 140.956, 154.738, 163.107, 165.824 **(Figure I.A.63.).**

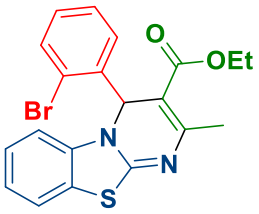


Figure I.A.61. Structure of Ethyl 4-(2-bromophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

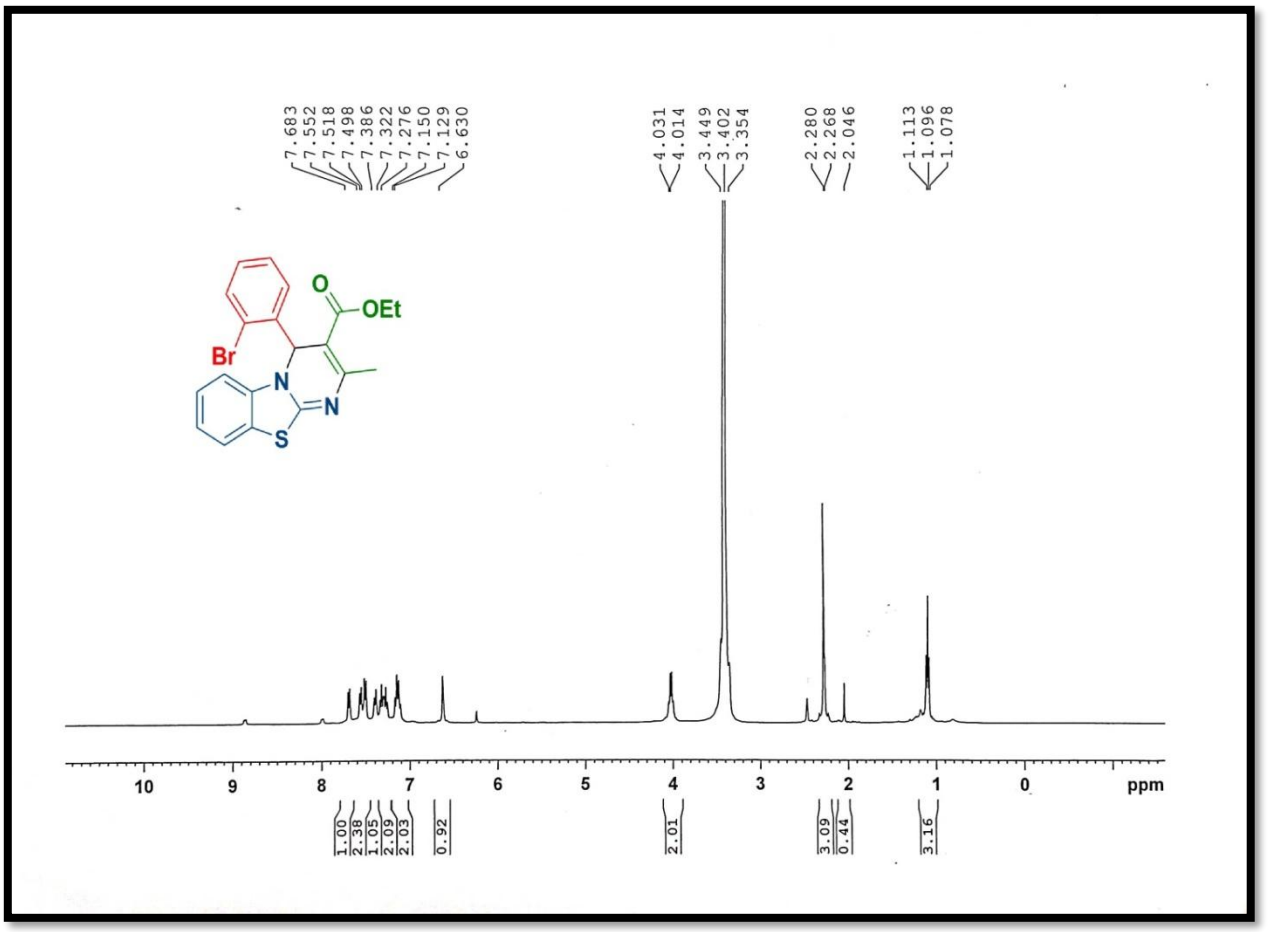


Figure I.A.62. ^{1}H Spectroscopical representation of Ethyl 4-(2-bromophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

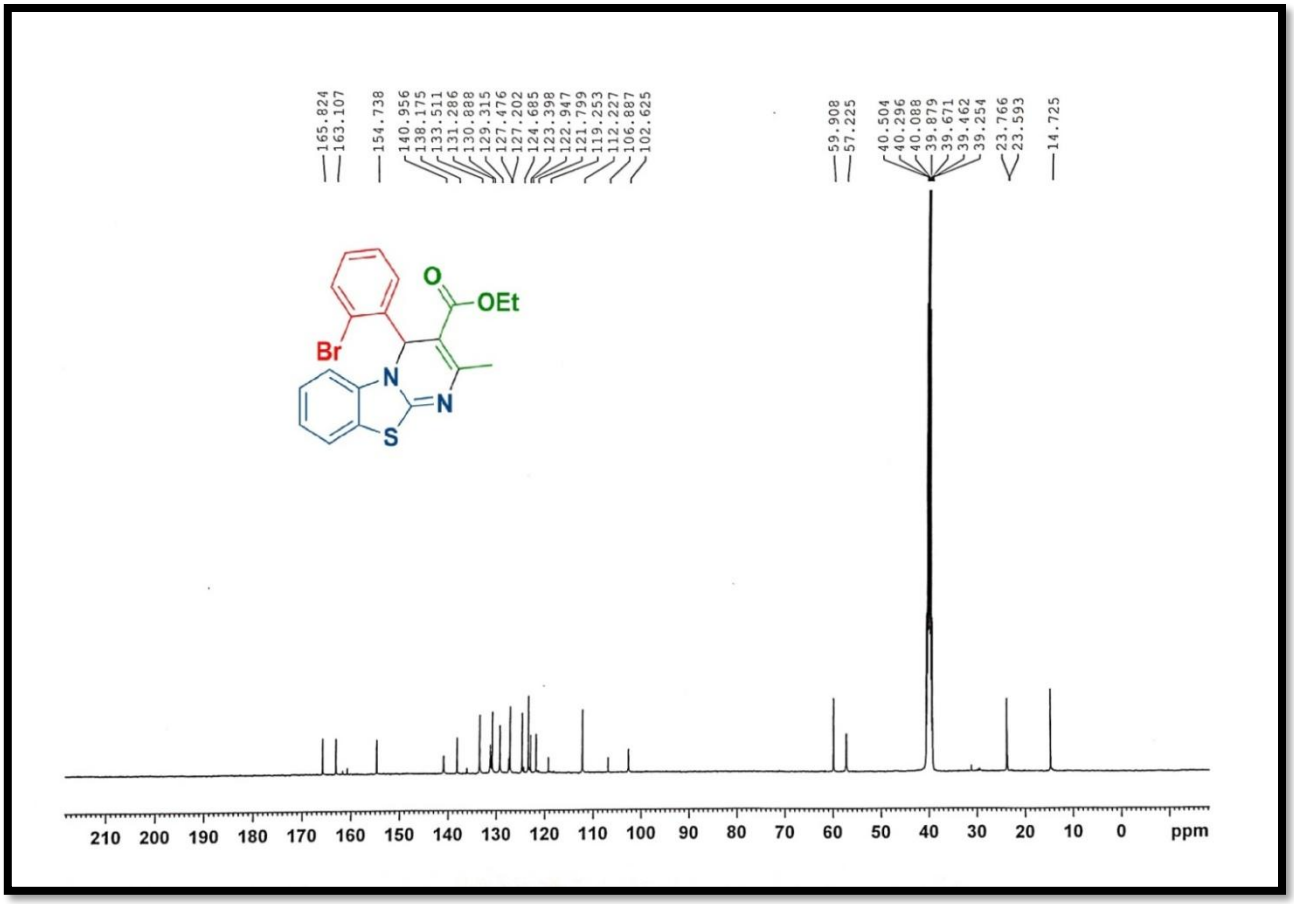


Figure I.A.63. ^{13}C Spectroscopical representation of Ethyl 4-(2-bromophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Ethyl 2-methyl-4-(pyridine-3-yl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.64.).

M.P. : 175 – 176 ^{o}C; yellowish solid; yield : 90%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.131 – 1.196 (m, 3H), 2.461 - 2.478 (m, 3H), 4.026 (q, *J* = 7.2 Hz, 2H), 6.513 (s, 1H), 7.175 (s, 1H), 7.301 (d, *J* = 8 Hz, 2H), 7.486 (d, *J* = 8 Hz, 1H), 7.727 (d, *J* = 7.6 Hz, 2H), 8.382 (d, *J* = 3.2 Hz, 1H), 8.678 (d, *J* = 1.6 Hz, 1H)

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm): 14.374, 23.355, 54.878, 60.442, 102.289, 112.628, 123.229, 123.420, 124.904, 125.056, 127.628, 135.512, 137.364, 137.524, 148.137, 149.807, 155.343, 165.927 **(Figure I.A.65.).**

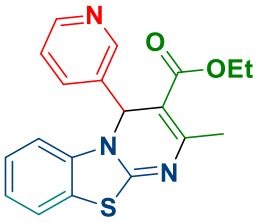


Figure I.A.64. Structure of Ethyl 2-methyl-4-(pyridine-3-yl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

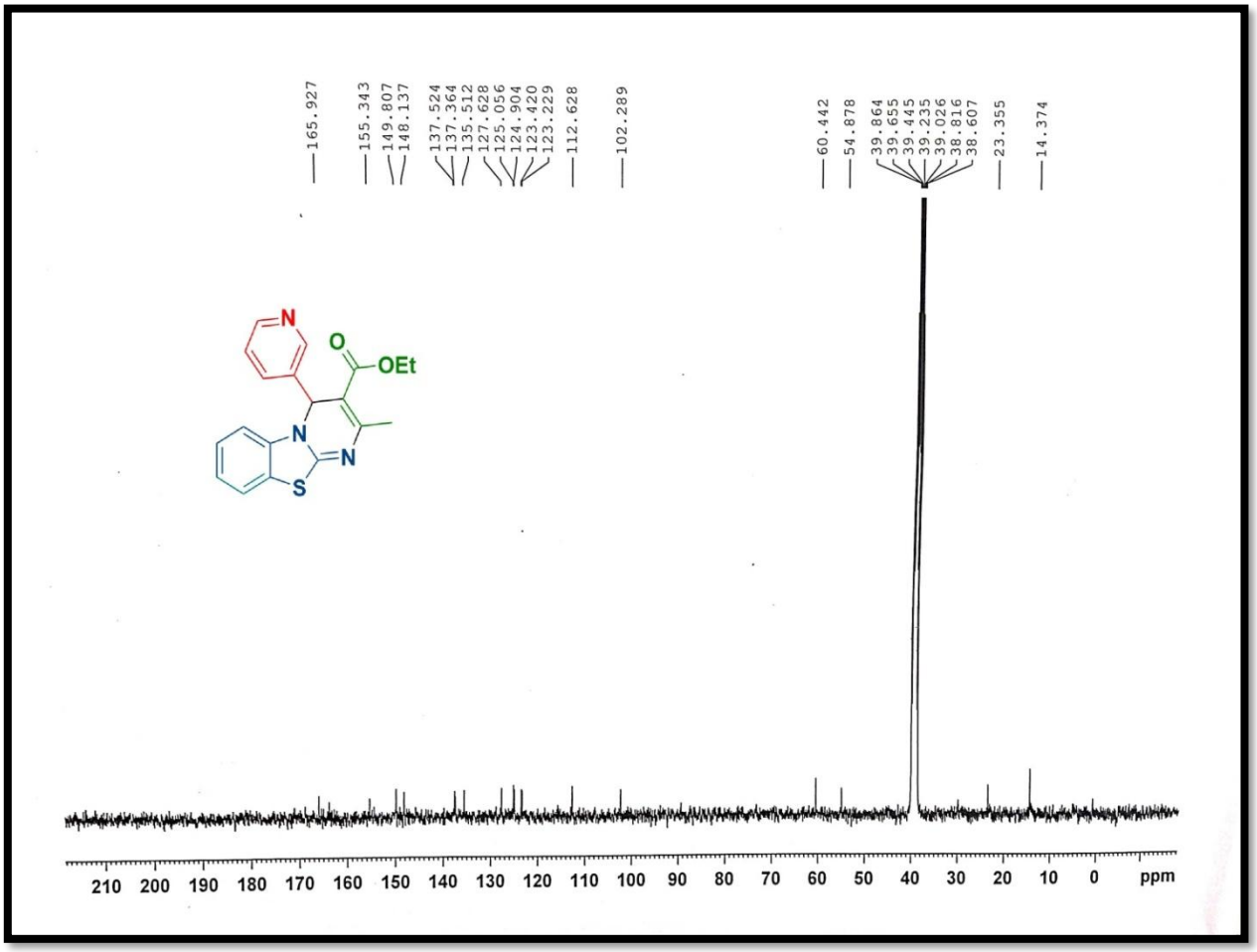


Figure I.A.65. ^{13}C Spectroscopical representation of Ethyl 2-methyl-4-(pyridine-3-yl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Ethyl 2-methyl-4-(4-fluorophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (Figure I.A.66.).

M.P. : 165 – 167 ^{o}C; yellowish solid; yield : 90%; **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm):** 1.136 – 1.197 (m, 3H), 2.316 – 2.483 (m, 3H), 4.042 (d, *J* = 7.2 Hz, 2H), 6.517 (s, 1H), 7.185 (s, 1H), 7.304 – 7.323 (m, 2H), 7.468 (s, 1H), 7.725 (d, *J* = 7.6 Hz, 2H), 8.383 (s, 1H), 8.677 (s, 1H) **(Figure I.A.67.).**

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm): 14.494, 23.663, 54.908, 60.170, 102.393, 112.713, 123.281, 123.444, 124.695, 124.800, 127.464, 135.166, 137.428, 137.633, 148.539, 149.955, 155.426, 163.442, 165.767. **(Figure I.A.68.).**

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ (ppm): -108.796 (s) **(Figure I.A.69.).**

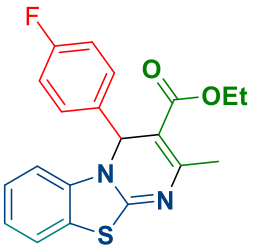


Figure I.A.66. Structure of Ethyl 2-methyl-4-(4-fluorophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

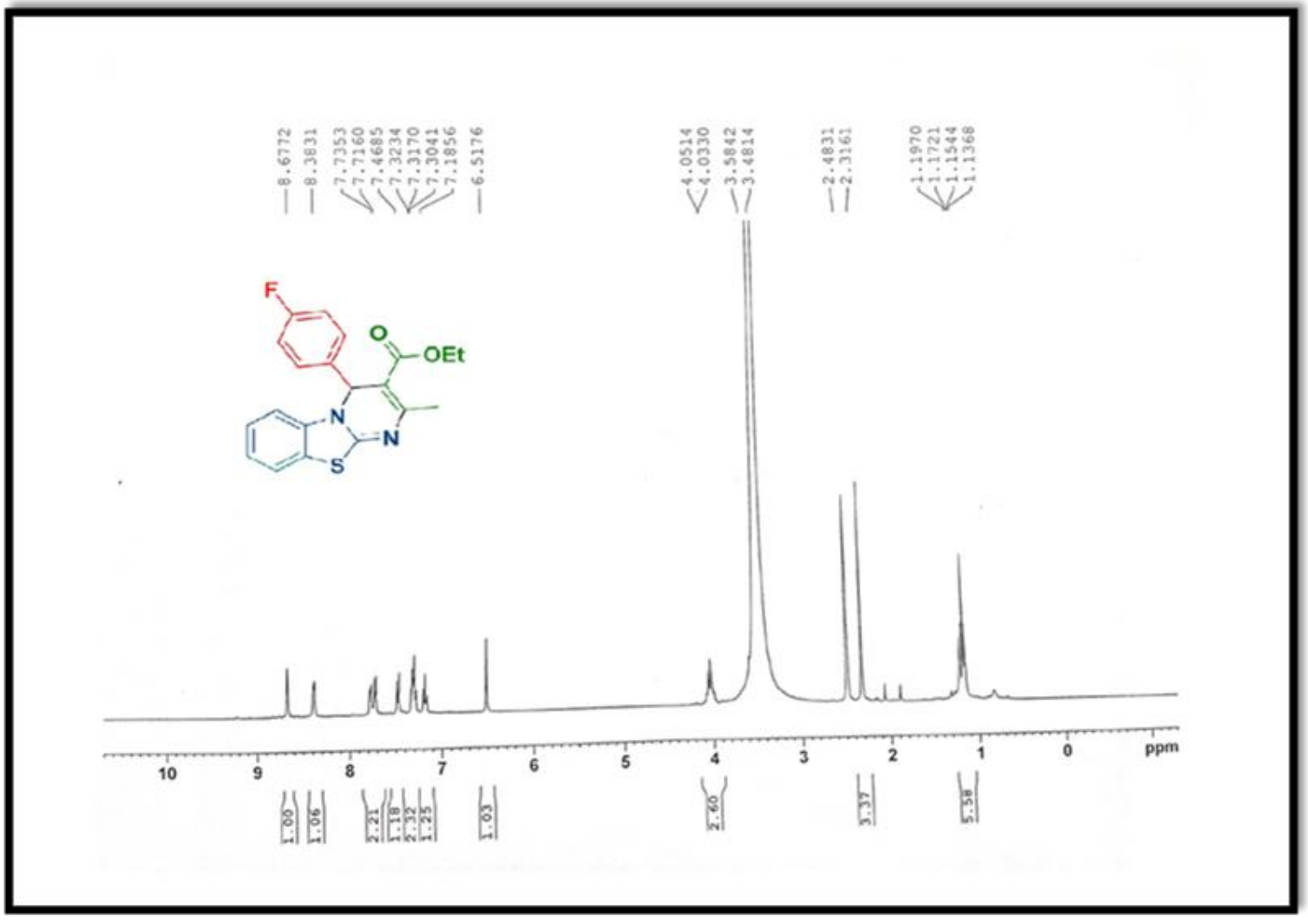


Figure I.A.67. ^{1}H Spectroscopical representation of Ethyl 2-methyl-4-(4-fluorophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

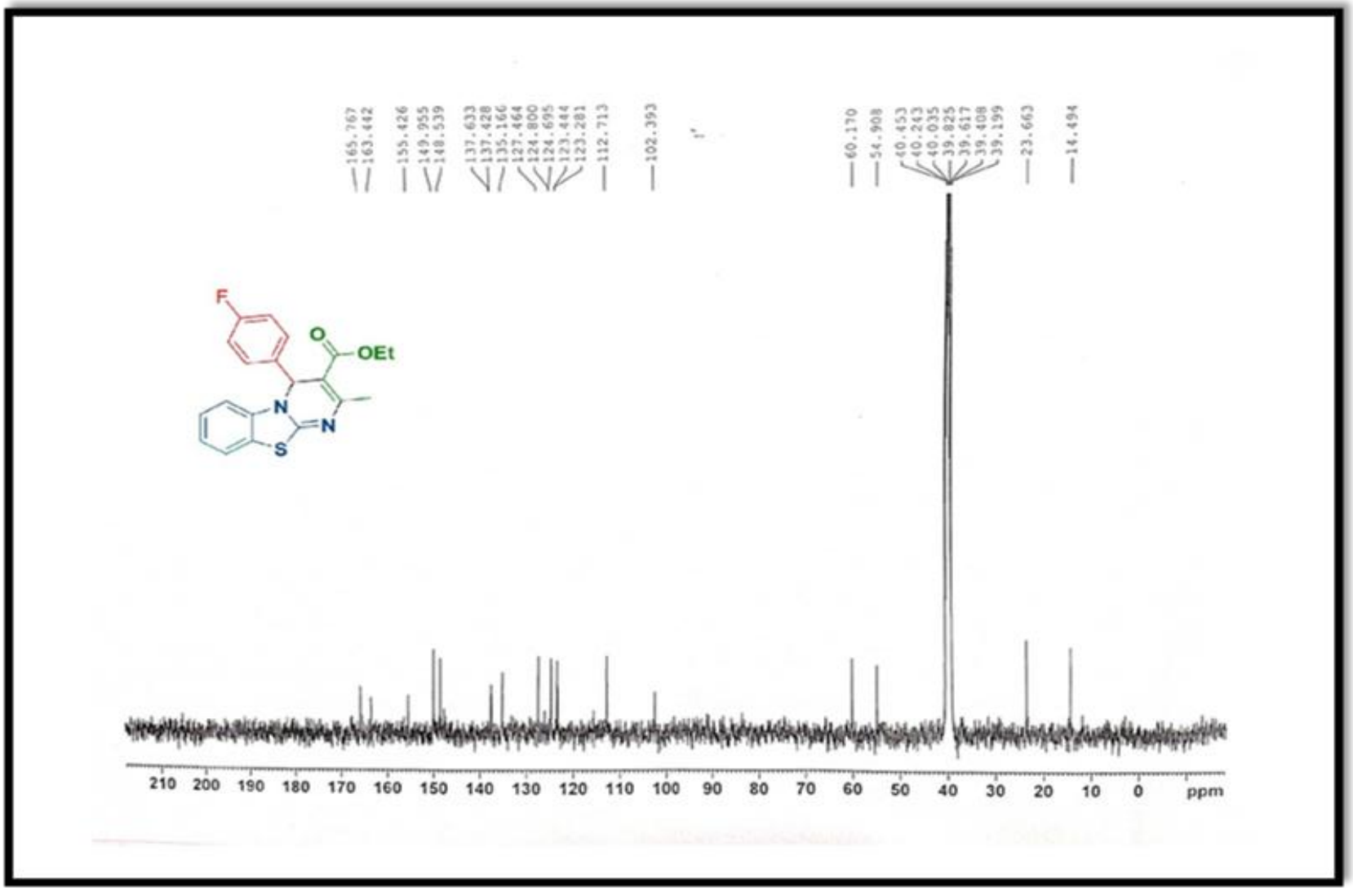


Figure I.A.68. ^{13}C Spectroscopical representation of Ethyl 2-methyl-4-(4-fluorophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

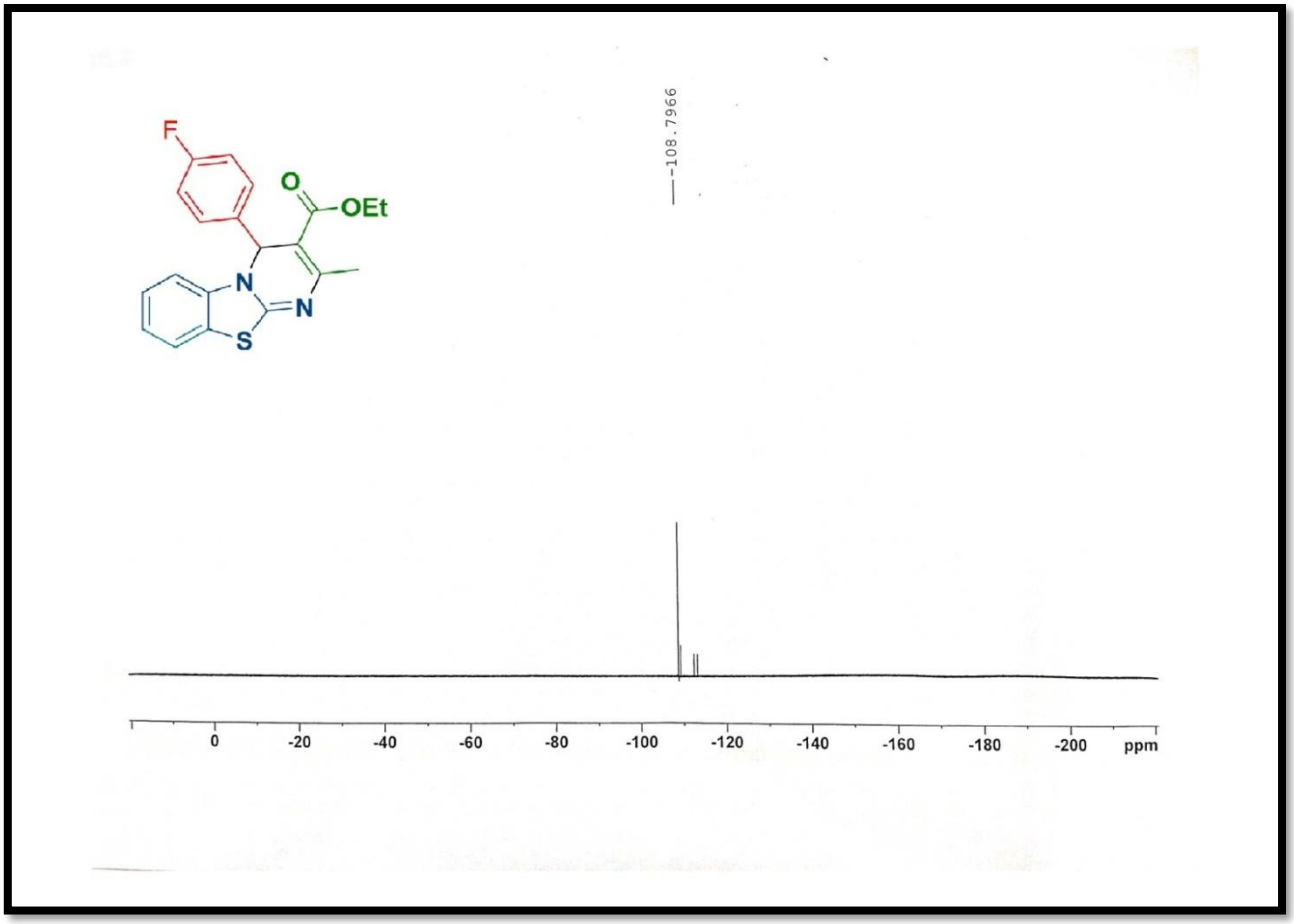


Figure I.A.69. ^{19}F Spectroscopical representation of Ethyl 2-methyl-4-(4-fluorophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

I.A.8. References:

References are displayed in **BIBLIOGRAPHY** under **Chapter I, Section A,** that is, "**Humic Acid: A Rarely Explored, Robust, Green Catalyst for Solvent-Free Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and Benzo[*d*]thiazole"** (pp. 199-206**).**

Section B

Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent-Free Synthesis of 3,3'-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

I.B.1. Introduction:

One of the main concerns in organic conversions is with catalysts and solvents. The main drawbacks of solvents are their ignitable properties and their dangerous character, which includes excessive volatility and inadequate recuperation. The primary drawback of the metal catalyst is that, at the conclusion of the chemical reaction, it causes metal infection, which is harmful to the ecosystem. Any environmentally friendly solvent and biocatalyst could be used to address these drawbacks. By employing β - cyclodextrin in the form of a supramolecular catalyst, we have created a metal-free protocol[1]. Water[2] is an extremely beneficial reaction system in terms of both environmental friendliness and nature of small atomic consumption. The development of homogeneous catalysis and supramolecular chemistry has made the supramolecular catalyst a valuable device in the synthesis of organic heterocyclic compounds[3]. A significant enzyme model amongst the variety of supramolecular organisms is cyclodextrin (CD)[4–7]. Since cyclodextrins are hydrophobic cavities found in cyclic oligosaccharides, they are capable of binding with targets in selective ways, allowing them to facilitate chemical procedures along with a large selectivity [8–12]. Using non-covalent bonding, CDs can reversibly attach to a host-guest complex formed by the supporting materials throughout the reaction. This complex is what changes the spatial arrangement of products throughout organic reactions. Because the guest molecules are incorporated to the CD hole, the features are associated with the formation of morphological limitations in the guest molecules. It employs the hydrophobic chamber, just like β - cyclodextrin, to encapsulate physiologically beneficial substances from aqueous solutions, thereby improving biological availability and the stability of medicinal compounds. Because of these qualities, CDs are now a valuable resource for pharmaceutical firms. Additionally, CDs are inexpensive, widely accessible, non-virulent, and consequently recyclable [13, 14].

β - Cyclodextrin, a key category of cyclodextrins, is an assortment of cyclic oligosaccharides comprised of a macrocyclic ring of seven glucose subunits attached through a-1,4 glycosidic bonds and is a crucial enzyme simulation [16]. Like other cyclodextrins, β - cyclodextrin also utilizes its inner hydrophobic chamber to trap molecules that function biologically, from water solution and to selectively fasten the organic substrates. In modern times, there is growing curiosity in the employing of homogeneous catalysts and supra molecular chemistry as significant players in the synthesis of organic heterocyclic materials [15] and pharmaceutically significant elements. By non-covalent supra molecular bonding and the reversible generation of host-guest

complexes, as observed in enzymes, β - cyclodextrin catalyzes organic reactions with great selectivity[17]. This slowly boosts the stability and biological accessibility of therapeutic molecules. Numerous chemical molecules, including aldehydes, ketones, anhydride, oximes, amines, and nitriles, are activated by β - cyclodextrin, which also speeds up reactions[18]. These characteristics of β - CD make this a valuable tool for synthetic chemistry and pharmacological manufacturers. In addition, β - CD is a benign and non hazardous supramolecule that is readily attainable, able to be recycled, affordable, and dissolves in water smoothly because of its hydrophilic exterior part [19]. Here, **Figure I.B.1.** is representing the Structure of β – Cyclodextrin.

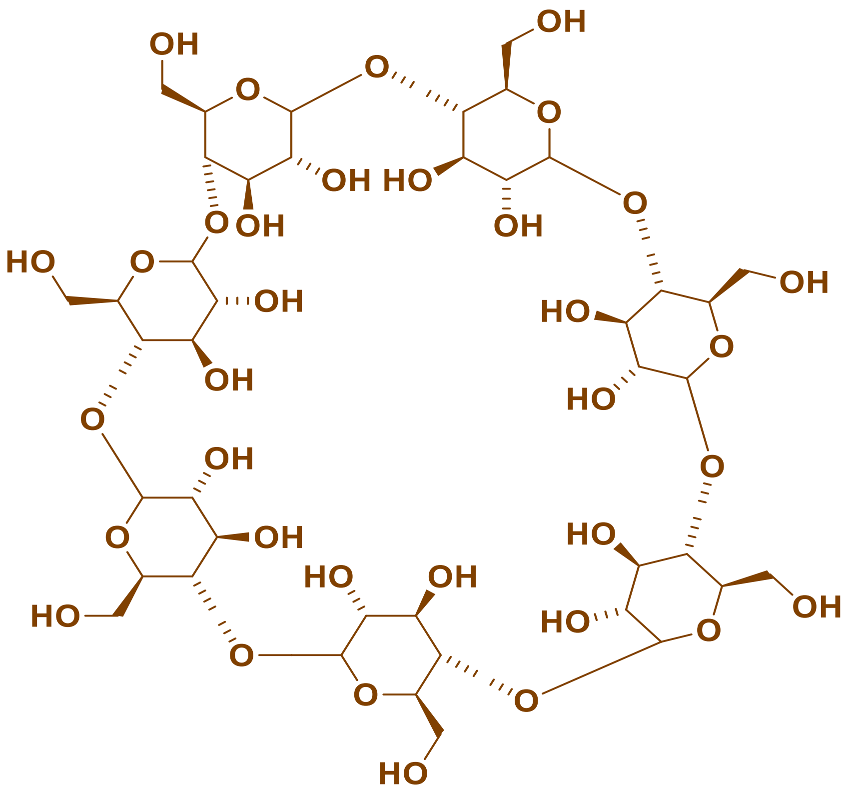


Figure I.B.1.: Structure of β – Cyclodextrin

Because of their several distinct bio capabilities, pyrazolone derivatives, one class of N-accommodating heterocycles, are a vital component of many fields in the sciences, including materials science and pharmaceuticals. Nowadays, pyrazolone derivatives are included in many commercially available medications for myocardial ischemia [69] and brain ischemia [70]. Among these, bis(pyrazolyl)methanes are widely employed as drugs that stimulate gastric secretion[71],

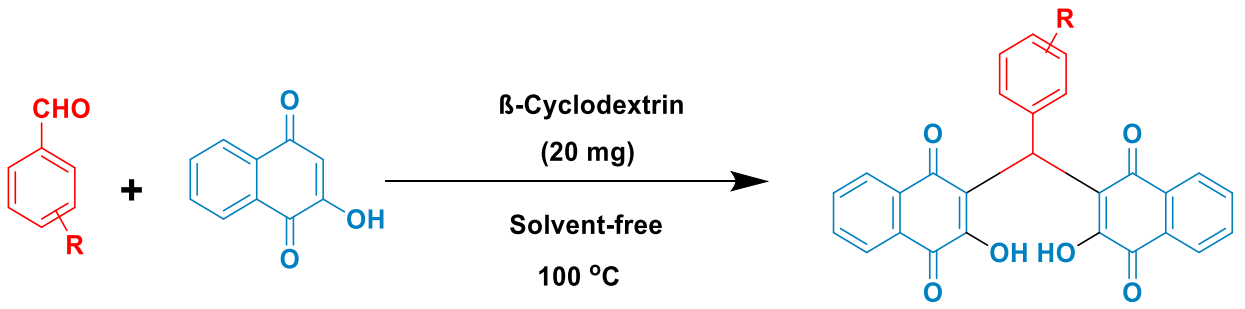
have been shown to have permissive biological activity, and are antibacterial [72], antipyretic [73], anti-inflammatory [74], antidepressant [75], and antifilarial [22–27]. Additionally, such substances are found in a large number of insecticides [28], fungicides [29], dyes, and the chelating and extraction agents for different metal ions [30], in addition to pesticides [31]. Pyrazoles that have been appropriately functionalized can be identified as sodium channel inhibitors and HIV-1 reverse transcriptase antagonists [32, 33]. The most popular technique for creating 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) is combining the Knoevenagel-Michael reaction in one pot with a variety of catalysts, including sodium dodecyl sulfate [34], electrocatalytic approach [35], SDBS [36], silica-SO_3H [37], PEG-SO_3H [38], phosphomo lybdic acid [39], biological surfactant [40], 3-aminopropylatedsilica gel [41], Caffein-H_3PO_4 [42], 1,3-disulfonic acid imidazolium tetrachloroaluminate [43], and metal complexes [44]. Many protocols have been developed recently based on this component [45]. Nonetheless, a number of limitations plague the majority of techniques, including the utilization of poisonous solvents and harsh catalysts, poor yields, extended reaction durations, unfavorable reaction circumstances, and laborious work-up protocols. For this reason, creating an efficient and ecologically friendly technique for the production of bis(pyrazolyl)methanes is essential.

In the domain of heterocyclic chemistry, 3,3'-(aryl/alkyl-methylene)bis(2-hydroxynaph thalene-1,4-dione), additional physiologically significant compound known as bis-Lawson derivatives, has become extremely significant. It is readily made using the Lawson substance (2-hydroxy-1,4-naphthoquinone), a renowned endogenous red-orange dye that is produced through the leaves of the henna plants (Lawsonia inermis Linn.) and is one of the medicinal plant's most essential ingredients [46]. Because of its biological adaptability, various portions of which have been employed conventionally for over 5000 years in the form of cosmetics (body paint, tattoo color, and hair dye) all throughout the world [47]. Because of its all-natural origin, it is a suitable herbal cure for multiple diseases and useful in the creation of partially long - lasting hair dyes [48]. It has a miscellaneous application in the pharmaceutical industries including diuretic, CNS depressing, anti-inflammatory, antipyretic, hepatoprotective, antimicrobial, wound healing, hypoglycaemic, analgesic, tuberculostatic and antiparasitic actions of the plant [49-63]. This substance has also been shown to have several important pharmacological and biological properties, including anti-oxidant [64], cytotoxic [65], anticoagulant [66], anti-acute pancreatitis [67], antibacterial [68], trypsin inhibitor [69], antifungal [70], inhibitory agent of the accumulation of advanced glycated

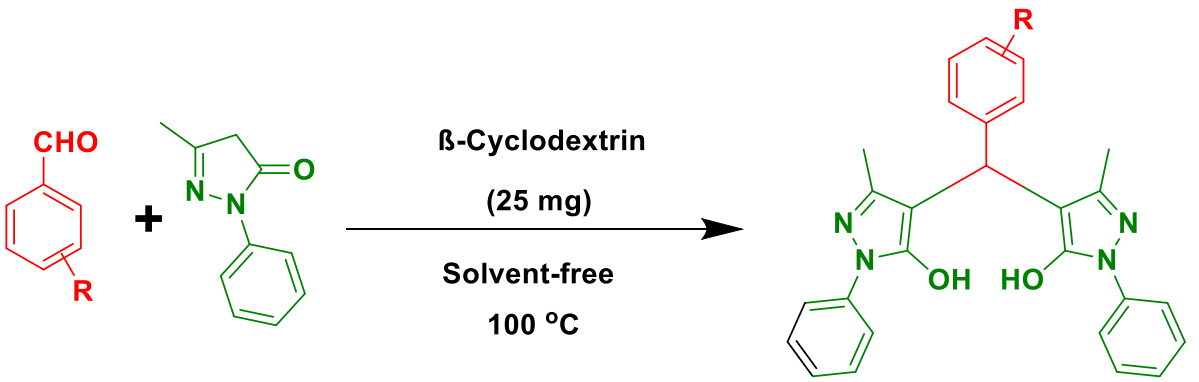
end products (AGEs) [71], and many more. Because it has the ability to provide ligands for metal complexations, it is also helpful in coordination chemistry [72]. The simple reaction of 2-hydroxy-1,4-naphthoquinone with aromatic aldehyde may be used to create bis-Lawson. β-alanine and acetic acid [73], TFA [74], O-carboxymethyl chitosan [75], Sulfamic acid [76], H_2SO_4 or ionic liquid [77], LiCl [78], and lipase [79] are a few previously published methodologies. Still, compared to the others, such domain has not been fully investigated. Therefore, there is a significant chance that this strategy can be investigated subsequently for advancements.

β - Cyclodextrin is a cheap, safe, non-toxic, readily available, and ecologically relevant catalyst. In light of such considerations, we have chosen β-cyclodextrin in the form of a catalyst in the development of a environmentally sustainable approach for the One – Pot, Solvent - free synthesis of 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) from number of aldehydes and 2-hydroxy-1,4-naphthoquinone (Lawson Reagent) and for the One – Pot, Solvent - free synthesis of 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) from a number of aldehydes and 3-methyl-1-phenyl-1H-pyrazol-5-ol **(Scheme I.B.1., I.B.2)**.

Scheme I.B.1. represented here, the reaction of a number of aldehydes and 2-hydroxy-1,4-naphthoquinone (Lawson Reagent) via simple Nucleophilic Addition Reaction along with the formation of functionalized 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione); on the other hand, **Scheme I.B.2.** represented below, the reaction of a number of aldehydes and 3-methyl-1-phenyl-1H-pyrazol-5-ol via simple nucleophilic addition (Knoevenagel Michael addition) Reaction; along with the formation of functionalized 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol); in presence of β - Cyclodextrin catalyst, under absolute solvent – free condition.



Scheme I.B.1. : β - Cyclodextrin mediated synthesis of functionalized 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione)



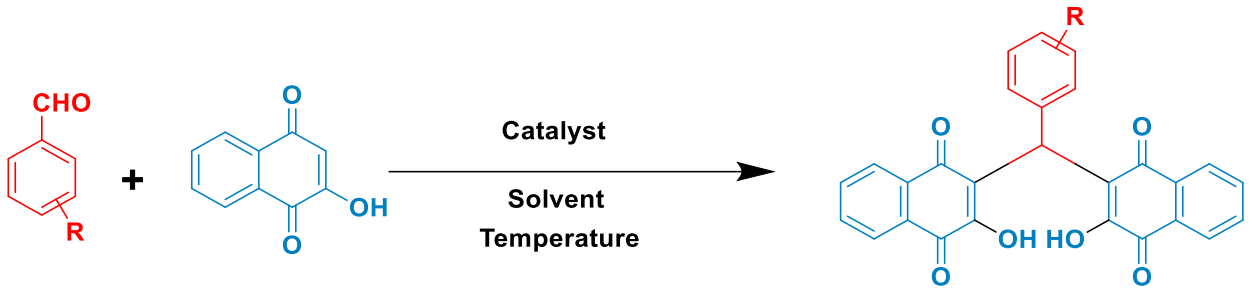
Scheme I.B.2. : β - Cyclodextrin mediated synthesis of functionalized 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

I.B.2. Result and Discussion:

The most crucial factors are Solvent, Temperature and Catalyst for propelling chemical reactions. For this reason, during the intended synthetic process, it is essential to preserve the appropriate levels of these three cores of such systems. 1 mmol of benzaldehyde and 1 mmol of 2-hydroxy-1, 4-naphthoquinone were considered here in the form of reactants to undertake target reaction **(Scheme I.B.1.).** We started our optimization performance (Optimization technique of **Scheme I.B.1.,** has been depicted in **Table I.B.1.**, here, in broader way) initially, with the solvents, by using of 40 mg amount catalyst and then, it was scrutinized that, doing reflux with methanol DMF and water, the yield of the product was comprehensively small (Table I.B.1., entry 1, 2, 3). Next, by applying PEG – 200, at 100 ^{o}C for continuous 5 hours, the yield of the product was 30% only (Table I.B.1., entry 4). After that, employing of DMSO and water along with constant 5 hours application of reflux procedure, the yield was 33% and 54% respectively (Table I.B.1., entry 5, 6). When we carried out the similar reaction, under neat condition, at 100 ^{o}C, with similar quantity of catalyst, then the yield of the product was enriched up to 97% (Table I.B.1., entry **7**). Then we commenced the optimization of catalyst by reducing the amount as, 35 mg, 30 mg, 25 mg, 20 mg, 15 mg, 10 mg and 5 mg, by maintaining the same 100 ^{o}C temperature and time as 5 hours; as a result, we saw the yield trend, like, 97%, 95%, 95%, 93%, 88%, 82% and 75% respectively (Table I.B.1., entry 8, 9, 10, 11, 12, 13, 14). Thus, we observed that, 20 mg of catalyst was sufficient to undergo this approach and the yield of the product was 93% (Table I.B.1., entry 11). On the other hand, the reaction could never be possible to run in devoid of catalyst (Table I.B.1., entry 15).

After that, by lowering the temperature up to room temperature, the yield of the product was reduced gradually (Table I.B.1., entry 16, 17, 18). Subsequently, we reserved record of the requisite time, for proceeding of the reaction and we found that, 1 h is adequate for reaching towards the highest quantity of product, under the indistinguishable reaction circumstances (Table I.B.1., entry 21).

Table I.B.1.: Optimization of reaction condition **(Scheme I.B.1.)**[a]



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield (%)[b]
1.	Methanol	40	reflux	5	-
2.	DMF	40	reflux	5	trace
3.	Ethanol	40	reflux	5	trace
4.	PEG - 200	40	100	5	30
5.	DMSO	40	reflux	5	33
6.	Water	40	reflux	5	54
7.	Neat	40	100	5	97
8.	Neat	35	100	5	97
9.	Neat	30	100	5	95
10.	Neat	25	100	5	95
11.	Neat	20	100	5	93
12.	Neat	15	100	5	88
13.	Neat	10	100	5	82
14.	Neat	5	100	5	75
15.	Neat	Nil	100	5	-
16.	Neat	20	70	5	87

17.	Neat	20	50	5	81
18.	Neat	20	r. t.	5	trace
19.	Neat	20	100	3	93
20.	Neat	20	100	2	93
21.	**Neat**	**20**	**100**	**1**	**93**

The **bold** part signifies the optimized conditions;

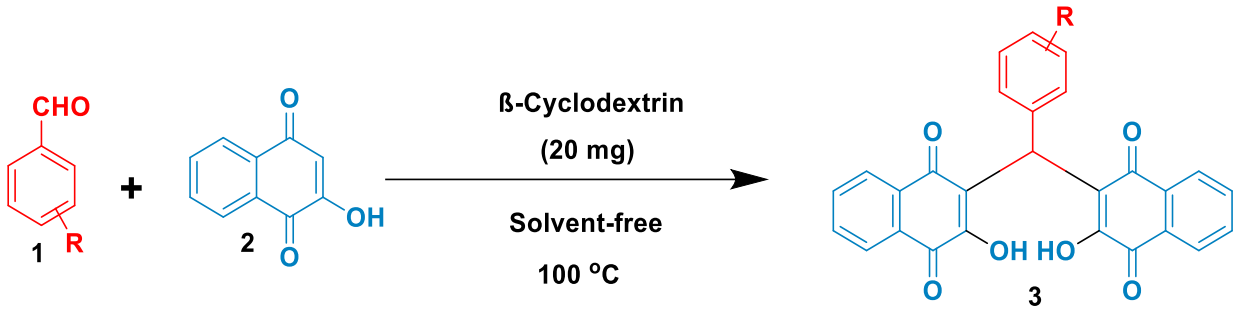
[a]Reaction of benzaldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (1 mmol) ;

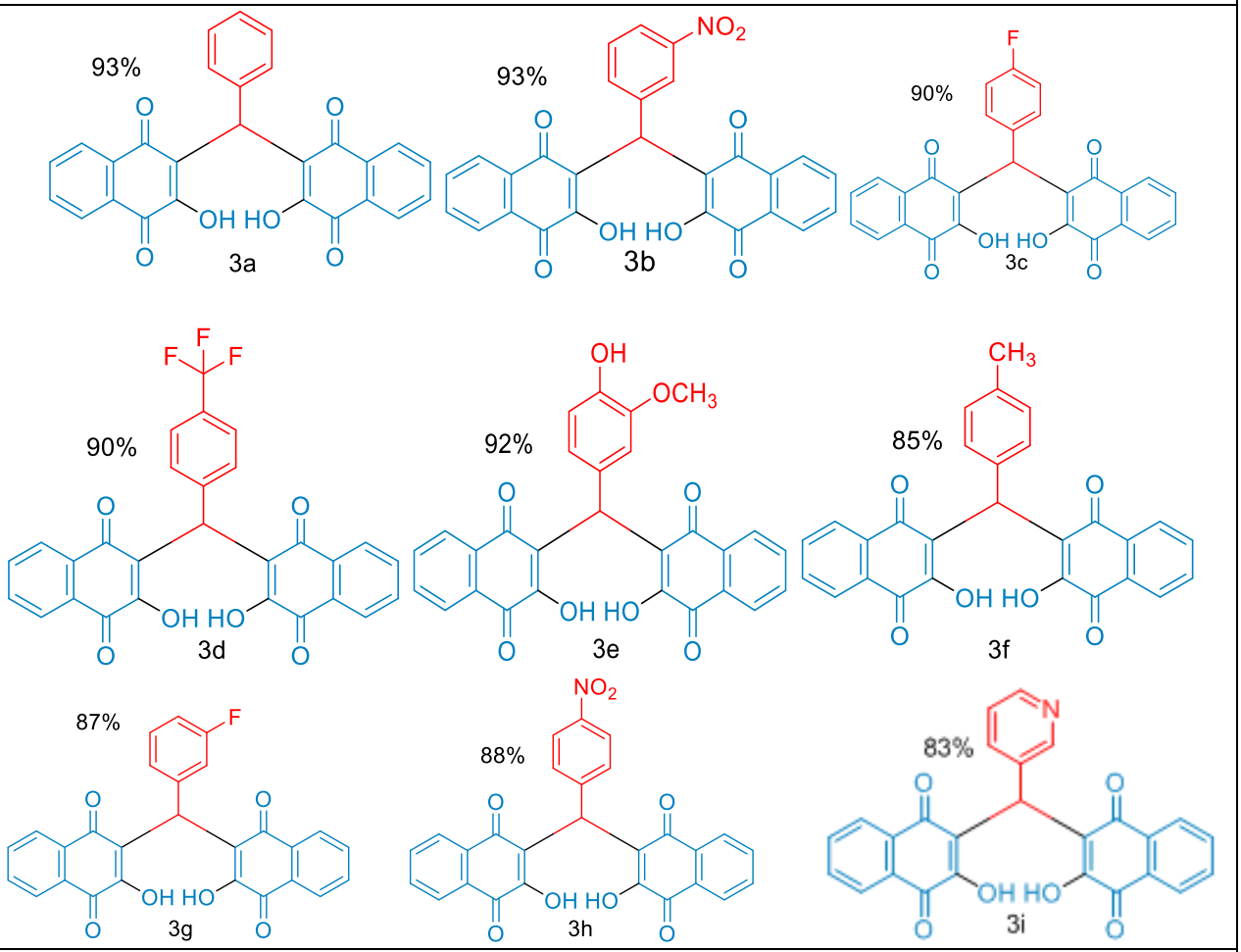
[b]Isolated yield was extracted through column chromatography.

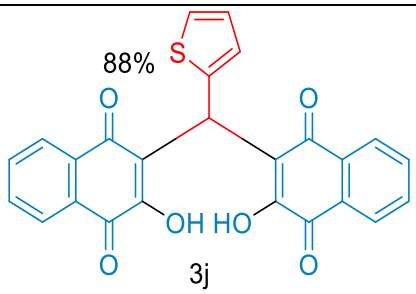
To perform in detailed study of our schemes, functionalized aldehydes were treated with 2-hydroxy-1,4-naphthoquinone **(Scheme I.B.1.),** under optimized condition and a variety of a number of 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) derivatives were constructed. The resulted compounds have been listed below in Table I.B.2.

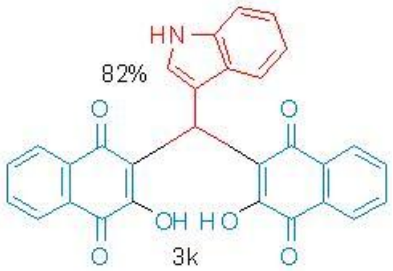
It was observed in this table that, when electron withdrawing groups, especially nitro, trifluoromethyl, fluoro, biphenyl and 2-naphthaldehyde were present in aldehyde, the product yield was highly satisfactory (Table I.B.2., entry 3b, 3c, 3d, 3l, 3n respectively). However, when electron withdrawing nitro group was at four positions, the yield was medium and well (Table I.B.2., entry 3h). But it was observed that, when aldehyde contained hydroxy and methoxy groups at ortho position with each other, or in case of vaniline, the yield of the product is so much good although these were not typical electron withdrawing groups except the presence of some negative inductive effect (Table I.B.2., entry 3e). In case of the presence of heterocyclic moiety, like thiophene, 3-pyridine and 3-indole, the product yield was medium to good (Table I.B.2., entry 3j, 3i, 3k respectively). However, aldehyde with positive inductive effect at para position produced the product with medium yield (Table I.B.2., entry 3f). On the other hand, aliphatic group at para position gave very poor yield of the product (Table I.B.2., entry 3m).

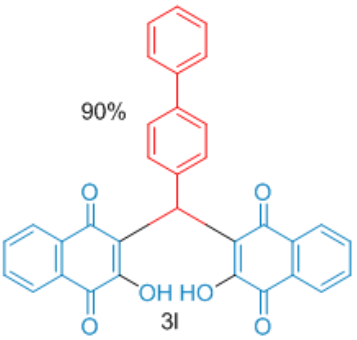
[a]**Table I.B.2.:** Synthesis of functionalized 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione)derivatives **(Scheme I.B.1.)**

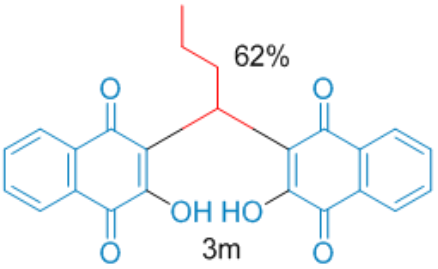


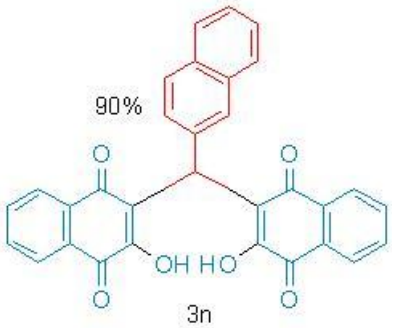








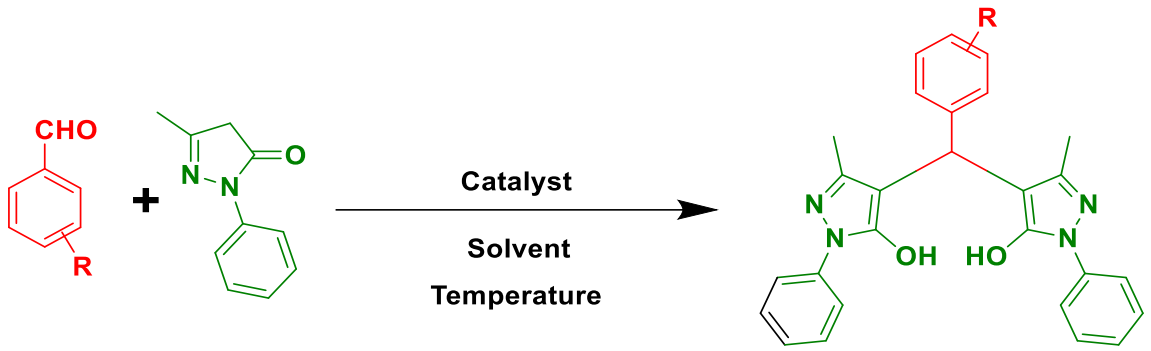




[a]Reaction of benzaldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (1 mmol) and β - Cyclodextrin (20 mg), under solvent-free condition for 1 h.

In Scheme I.B.2., we took 1 mmol of 3-methyl-1-phenyl-1H-pyrazol-5-ol and 1 mmol of benzaldehyde as reactants to undergo model reaction (Scheme I.B.2.). In the screening method of this reaction, (Optimization procedure of Scheme I.B.2., has been represented in Table I.B.3., below, in details), at first we choose solvent, in presence of 40 mg of catalyst, refluxing with methanol, ethanol, water and DMF, the yield of the product was considerably small (Table I.B.3., entry 1, 2, 3, 4). By maintaining of 100 ^{o}C temperature consistently for 4 h, the yield of the product was 95% under neat condition (Table I.B.3., entry 5). Then we commenced the optimization of catalyst, by dropping the quantity of catalyst (Table I.B.3., entry 6, 7, 8, 9, 10, 11). Thus, it was observed that, 25 mg of catalyst was enough to carry out this procedure and the yield of the product was 90% (Table I.B.3., entry 8). On the other hand, the reaction could never be feasible in devoid of catalyst (Table I.B.3., entry 12). After that, by reducing the temperature up to room temperature, the yield of the product was reduced frequently (Table I.B.3., entry 13, 14, 15). Next, we kept an eye on the mandatory time for happening of the reaction and we exposed that, 1h is adequate for gaining the maximum amount of product, under exactly the same reaction condition (Table I.B.3., entry 17).

Table I.B.3.: Optimization of reaction condition **(Scheme I.B.2.)**[a]



Entry	Solvent	Catalyst loading (mg)	Temperature (ºC)	Time (h)	Yield (%)[b]
1.	Methanol	40	reflux	5	trace
2.	Ethanol	40	reflux	5	20
3.	Water	40	reflux	5	50
4.	DMF	40	reflux	5	40
5.	Neat	40	100	5	95
6.	Neat	35	100	5	93
7.	Neat	30	100	5	92
8.	Neat	25	100	5	90
9.	Neat	15	100	5	88
10.	Neat	5	100	5	47
11.	Neat	Nil	100	5	40
12.	Neat	25	100	5	-
13.	Neat	25	70	5	75
14.	Neat	25	50	5	60
15.	Neat	25	r. t.	5	trace
16.	Neat	25	100	3	90
17.	**Neat**	**25**	**100**	**1**	**90**

The **bold** part signifies the optimized conditions;

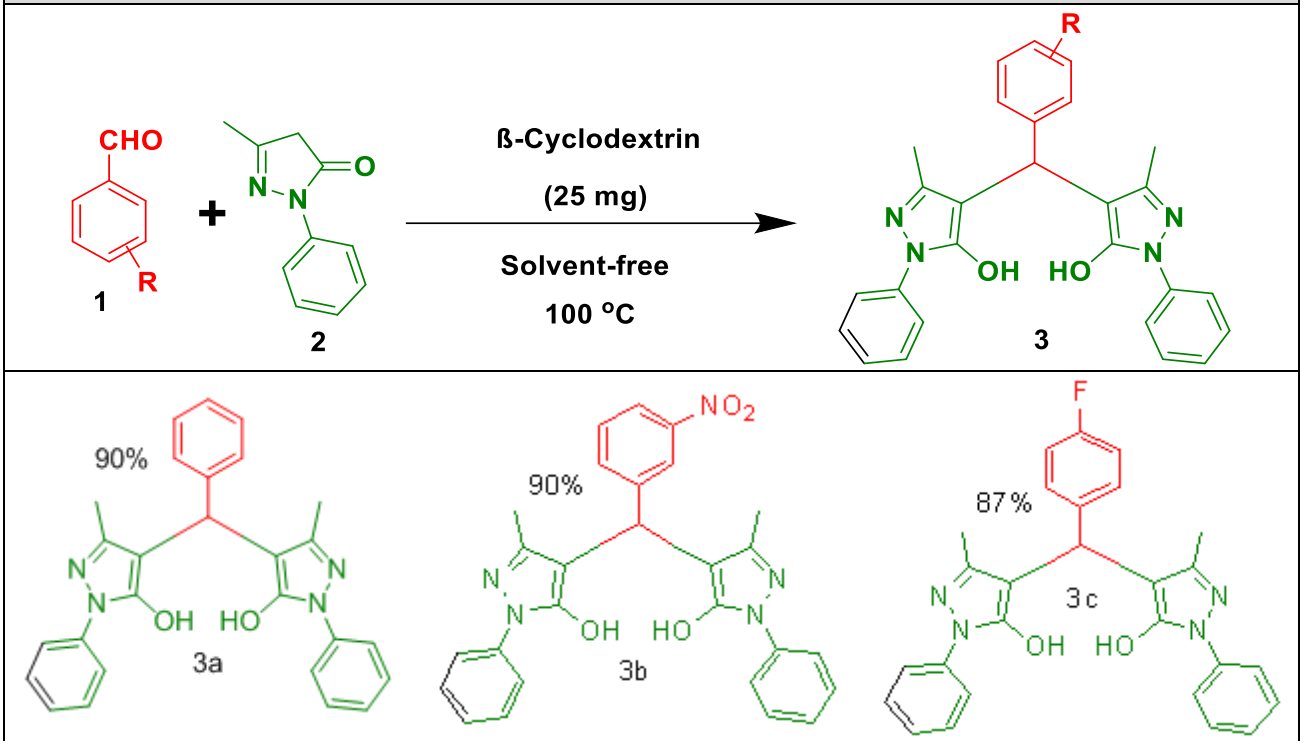
[a]Reaction of benzaldehyde (1 mmol) and 3-methyl-1-phenyl-1H-pyrazol-5-ol (1 mmol) ;

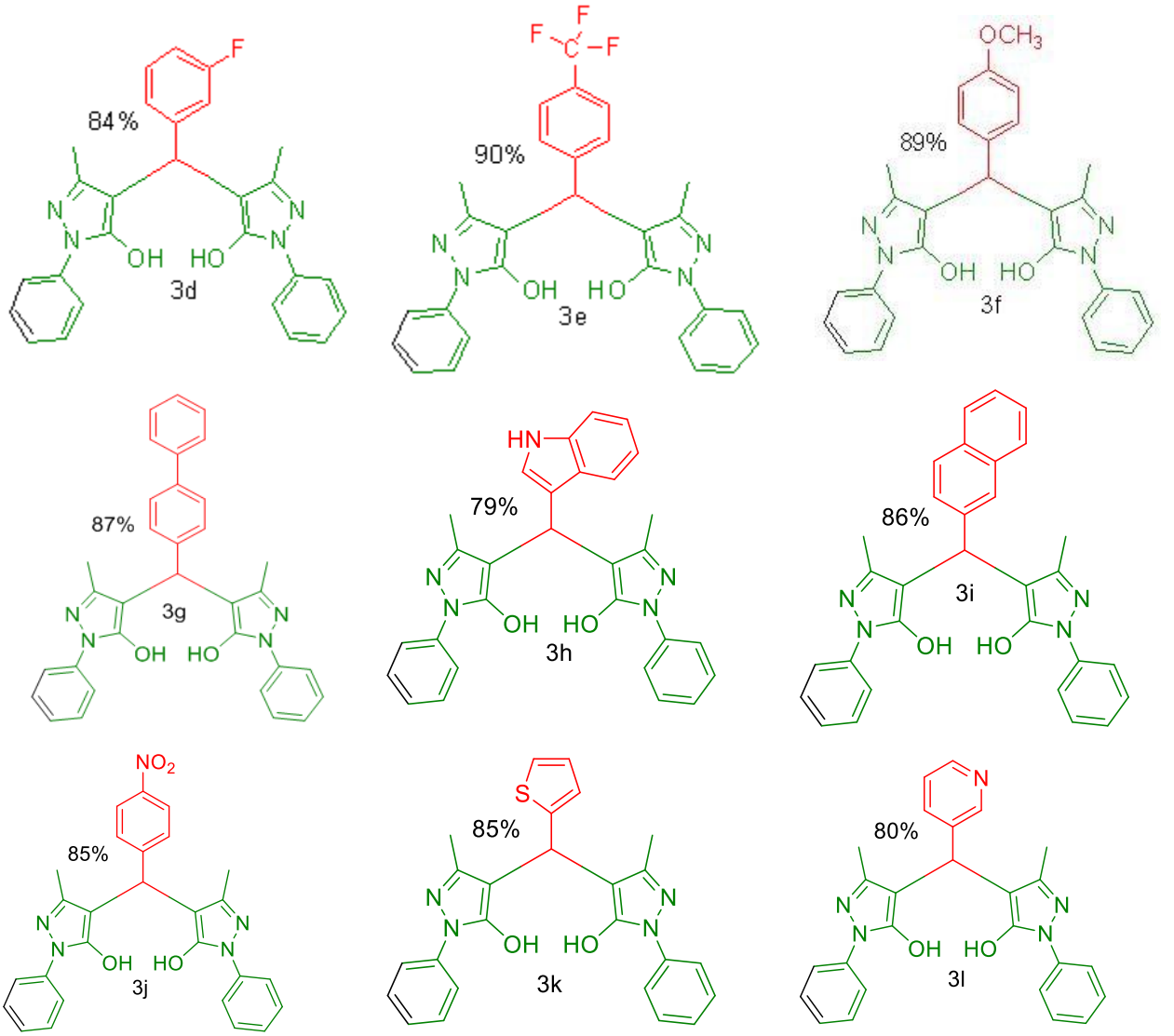
[b]Isolated yield was extracted through column chromatography.

To go through the detailed study of scheme 2, functionalized aldehydes were treated with 3-methyl-1-phenyl-1H-pyrazol-5-ol **(Scheme I.B.2.)** under optimized condition and a variety of a number of 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives were prepared. The resulted compounds have been listed below in Table I.B.4.

From this table, it was observed that, when electron withdrawing groups i.e. nitro at meta position and trifluoromethyl at para position, were present in aldehyde, the product yield was excellent (Table I.B.4.**,** entry 3b, 3e respectively). But it was also observed that, when an aldehyde contained electron withdrawing group i.e. fluoro at para and meta positions, the yield was medium (Table I.B.4., entry 3c, 3d respectively). When an aldehyde contained electron withdrawing groups like, nitro at para position, biphenyl and 2-naphthaldehyde, the product yield were medium (Table I.B.4., entry 3j, 3g, 3i respectively). Heterocyclic moieties like 3- indole, thiophene and 3-pyridine, the product yield were medium to low (Table I.B.4., entry 3h, 3k, 3l respectively). Aldehyde, containing negative inductive effect methoxy group, at para position, produced a satisfactory yield of the product (Table I.B.4., entry 3f).

[a]Table I.B.4.: Synthesis of functionalized 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives **(Scheme I.B.2.)**





[a]Reaction of aldehydes (1mmol), 3-methyl-1-phenyl-1H-pyrazol-5-ol (1 mmol) and β - Cyclodextrin (25 mg) under solvent-free condition for 1 h.

I.B.3. Reusability Experiment:

Renewability of β - Cyclodextrin was established through a replica reaction, with benzaldehyde (5 mmol) and 2-hydroxy-1, 4-naphthoquinone (5 mmol) in occurrence of 75 mg β - Cyclodextrin, underneath optimized reaction circumstance. After finishing of the first run, ethyl acetate (4 ml) was added to the reaction mixture. Catalyst was taken back effortlessly, from the reaction mixture, by straightforward work – up, followed by filtration procedure, after the first run. Then the recovered catalyst was sponged down with ethyl acetate (3×4 ml) and next it was dried before being passed down for the next run. The filtrate of reaction mixture was shifted to another

container and this method was done for two times repetitively. The catalyst was then cleaned with ethyl acetate again and after that, it was dried for affording the white coloured β - Cyclodextrin, which was used in the next run, with its dryness. Recuperation of β - Cyclodextrin was slightly lower than the amount used in the first run. However, the recuperated catalyst was used continuously for 3 runs with almost similar affinity and there was no notable degradation in the conversion. This Recyclability test of β - Cyclodextrin catalyst has been depicted in **Figure I.B.2.**, below, by the way of bar diagram. It signifies that, β - Cyclodextrin can expose its catalytic efficacy up to four succeeding runs without any substantial lessening in it and in reducing of the yield of the product.

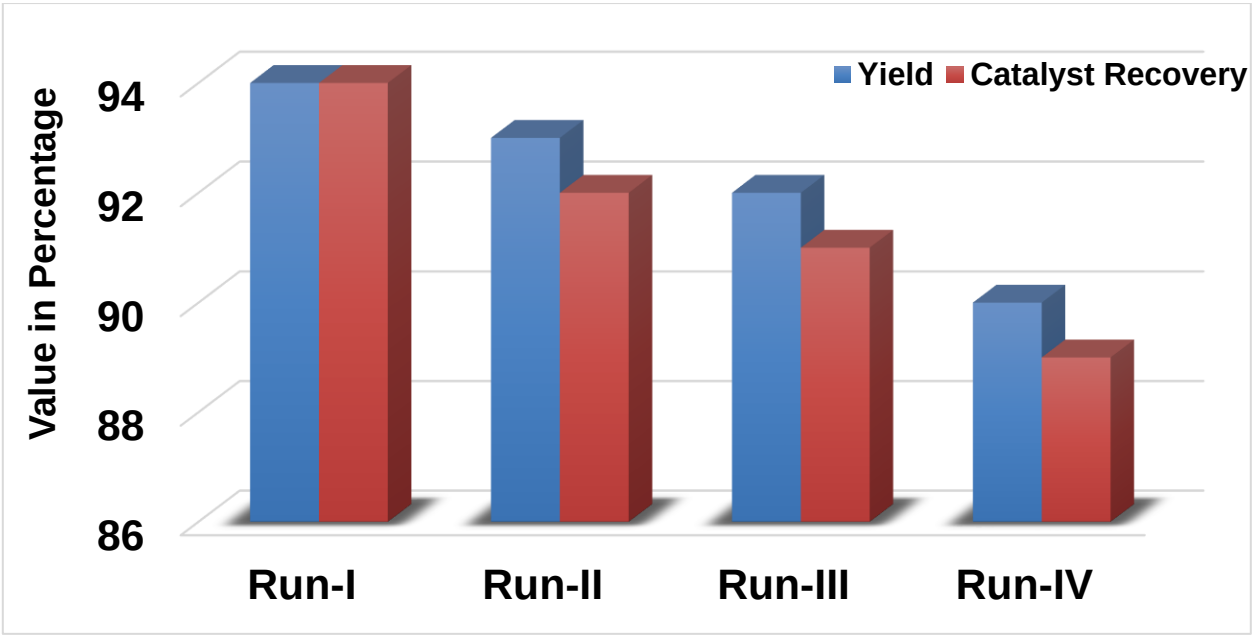


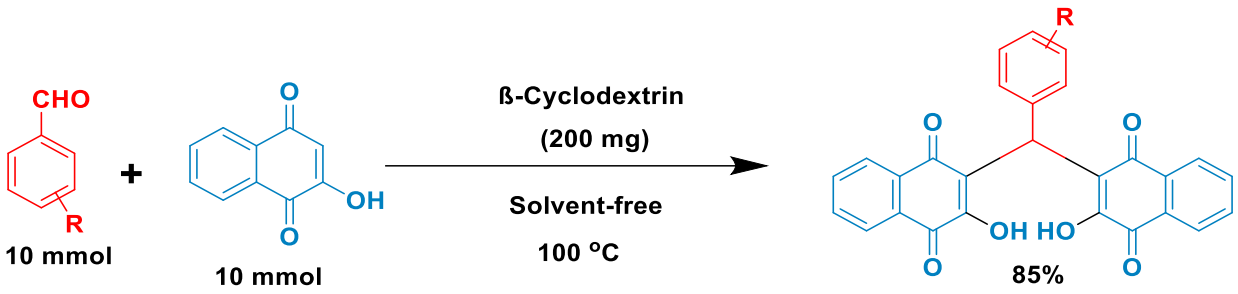
Figure I.B.2.: Reusability of β – Cyclodextrin

I.B.4. Gram - Scale Reaction:

The application of this methodology was examined in large scale, through carrying out the reactions in **gram-scale** (10 mmol scale) procedure. These also produced good yield, like the yield obtained in small scale reaction techniques. This Gram – Scale Reaction technique has been represented below, schematically, through **Figure I.B.3.**

Scale-up experiments:

Scheme I.B.1.:



Scheme I.B.2.:

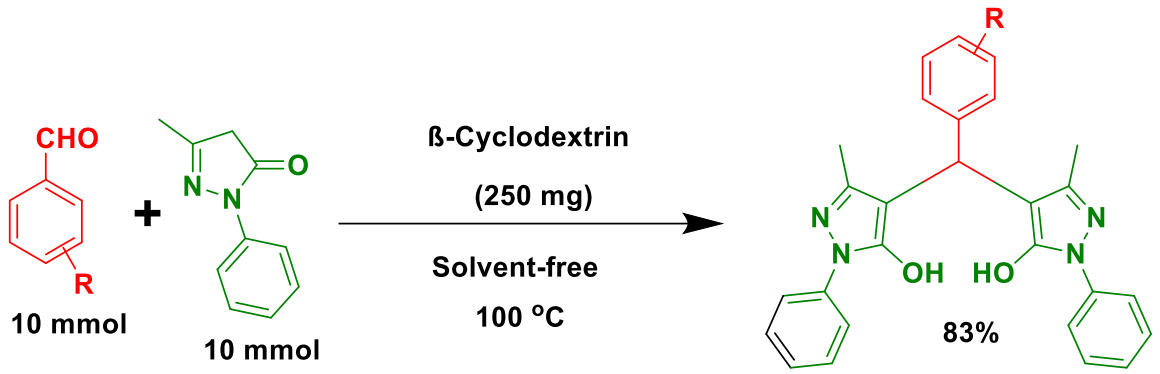
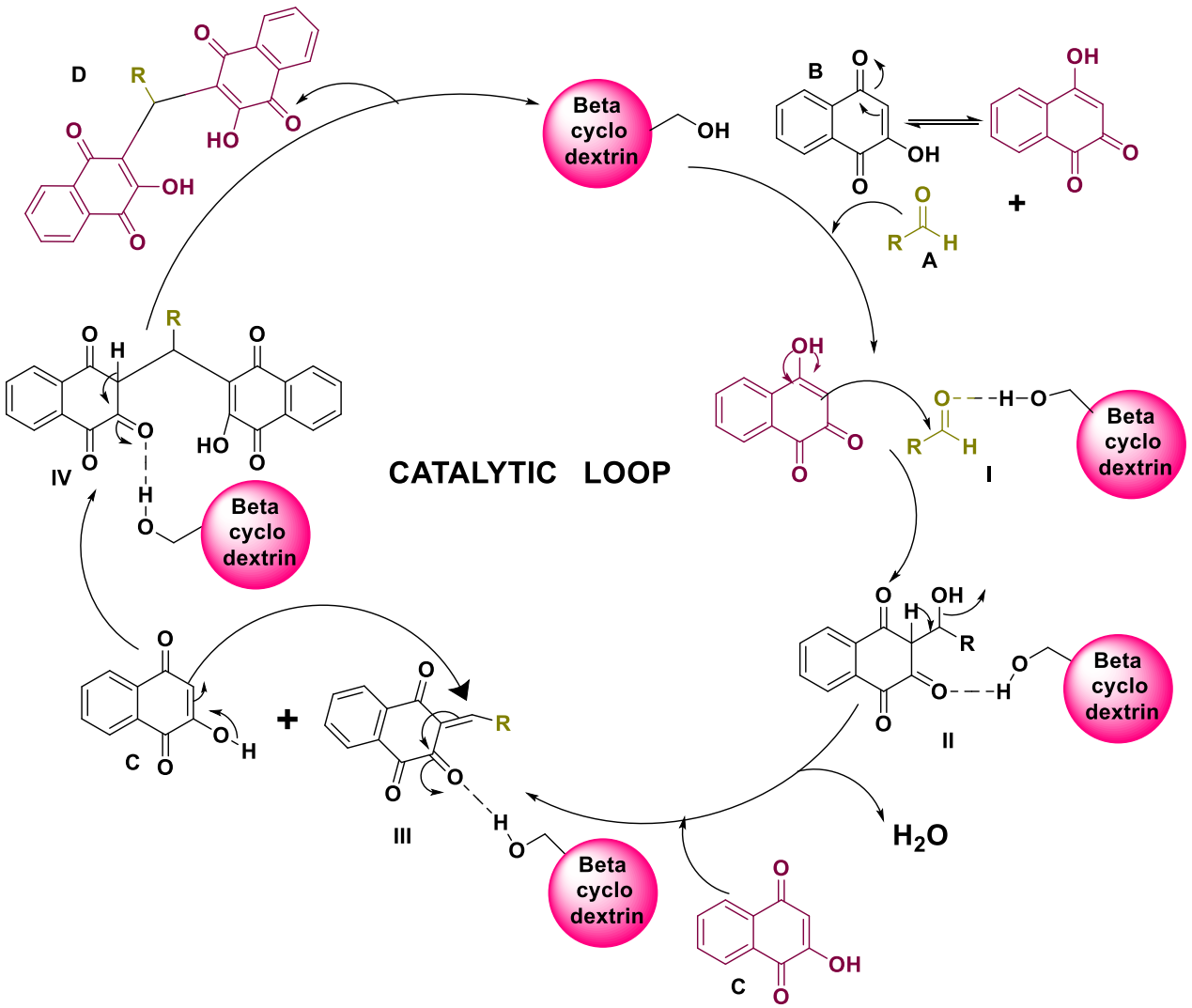


Figure I.B.3.: Gram – Scale Reaction

I.B.5. Plausible Mechanism for the Synthesis of 3, 3'-(phenylmethylene)bis(2-hydroxynaphthalene 1,4-dione) and 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol):

From the literature investigation we have prepared the plausible mechanism for the synthesis of 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene 1,4-dione), which is depicted in scheme I.B.3. At first, the catalyst stimulates the aldehyde (A), by the way of its acidic hydrogen (-OH) to augment the electrophilicity of the carbonyl portion so that it may facilitate the nucleophilic attack by enolized form of the first mole of 2-hydroxy-1,4-naphthoquinone (Lawson Reagent) (B), through straightforward nucleophilic addition manner and the intermediate (II) is constructed. β – Cyclodextrin activates further, one of the carbonyl carbons of intermediate (II). Then after water elimination we get the intermediate (III), into which, the nucleophilic centre of another mole of 2-

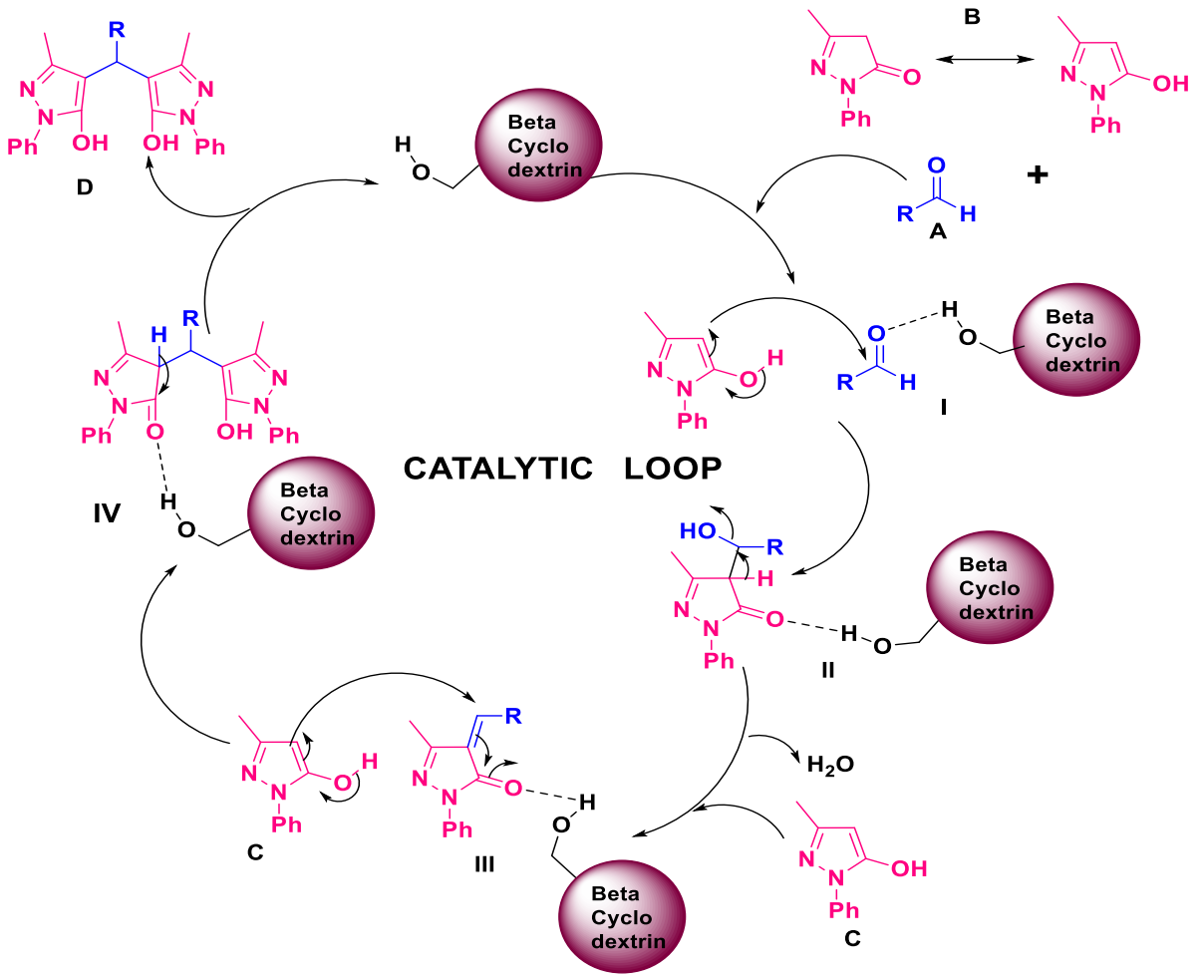
hydroxy-1, 4-naphthoquinone (C) attacks by following Michael addition pathway i.e. at the 4 position of activated intermediate (III). Thus we get the intermediate (IV) in which carbonyl carbon is activated again by β – Cyclodextrin catalyst. After that, through aromatization, we get the ultimate product (D). With this approach, the β – Cyclodextrin catalyst is restored at the last step of such mechanism. This reaction mechanism and pathway have been diagrammatically represented through the following **Scheme I.B.3.**



Scheme I.B.3.: Plausible mechanistic pathway for synthesis of 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene 1,4-dione)

From the literature survey we have prepared the plausible mechanism for the synthesis of 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol), which is designed in **Scheme I.B.4**. At first, the catalyst activates the aldehyde (A), through its acidic hydrogen (-OH) to enhance the

electrophilicity of the carbonyl group so that it can help the nucleophilic attack by enolised form of the first mole of 3-methyl-1-phenyl-1H-pyrazol-5-ol (B), by simple nucleophilic addition pathway and the intermediate (II) is formed. β – Cyclodextrin activates further, one of the carbonyl carbons of intermediate (II). Then after water elimination we get the intermediate (III), into which, the nucleophilic centre of another mole of 3-methyl-1-phenyl-1H-pyrazol-5-ol (C) attacks through Michael addition pathway i.e. at the 4 position of activated intermediate (III). Thus we get the intermediate (IV) in which carbonyl carbon is activated again by β – Cyclodextrin catalyst. After that, through aromatization, we get the ultimate product (D). With this approach, the β – Cyclodextrin catalyst is restored at end. This reaction mechanism and pathway have been diagrammatically represented through the following **Scheme I.B.4.**



Scheme I.B.4.: Plausible mechanistic pathway for synthesis of 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

I.B.6. Conclusion:

Using supramolecular β-cyclodextrin as an organocatalyst, we triggered the carbonyl oxygen of the corresponding aldehydes to strengthen the electrophilicity of the carbonyl carbon, subsequently performing nucleophilic addition into that location. In summary, we can demonstrate an environmentally sound and achievable strategy for generating numerous examples of functionalized 3, 3'–(phenylmethylene)bis(2-hydroxynaphthalene 1,4-dione) and 4, 4'–(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives with no involvement of any solvent. The general process encompasses the Cascade reaction, comprising the well-known Michael Addition and Knoevenagel route. Since no metal was utilized in this process, the entire synthetic approach remained more environmentally friendly. Once more, the protocol's solvent-free requirement greatly enhances its ecological viability. The β-cyclodextrin catalyst can be retrieved using a simple filtration process, and its restoration aspect can continue without any typical deviations in its level of effectiveness until the fourth run. Therefore, the fundamental innovation and inventiveness of this technology is the adoption of supramolecular β-cyclodextrin catalyst, which is inexpensive, readily available, and secure for the environment in place of any detrimental, deadly, perilous, extensive, hazardous, and overpriced metal catalyst. The currently underway study's technique ought to be viewed as an integral component of the scientists' and researchers' ongoing efforts, contributing to a notable advancement in the chemical realm of medicines, natural product synthesis, and the drug industry in subsequent years.

I.B.7. Experimental Section:

I. Common Information:

All the compounds were acquired from commercial suppliers and used without doing further decontamination process. All the products were purified by column chromatography on silica gels (60−120 Mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were utilized. ^{1}H NMR,^{19} F and ^{13}C NMR were recorded using 400 MHz, 376 MHz and 100 MHz, respectively, on Bruker AV 400 NMR spectrometer using TMS as internal standard. Splitting manners of protons were explained as s (singlet), d (doublet), t (triplet) and m (multiplet).

II. General course of action for the production of 3, 3'-(phenylmethylene)bis(2-hydroxynaphthalene 1,4-dione):

A mixture of 2-hydroxy-1,4-naphthoquinone (1 mmol), benzaldehyde (1 mmol) and β – Cyclodextrin (20 mg) was blended at 100 ^{o}C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept track of using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was exterminated to room temperature and ethyl acetate (5 mL) was employed to the reaction mixture and the catalyst was kept separated by straightforward filtration and was extracted with ethyl acetate twice (2×20 ml). Amalgamated extracts were cleaned with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The primeval product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate–petroleum ether). The products obtained were known compounds and were recognized by their color, melting point and NMR spectroscopy.

III. General procedure for the synthesis of 4, 4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol):

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-ol (1 mmol) benzaldehyde (1 mmol) and β – Cyclodextrin (25 mg) was blended at 100 ^{o}C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept an eye on using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was exterminated to room temperature and ethyl acetate (5 mL) was employed to the reaction mixture and the catalyst was kept separated by straightforward filtration and was extracted with ethyl acetate twice (2×20 ml). Amalgamated extracts were cleaned with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The primeval product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate–petroleum ether). The products obtained were known compounds and were recognized by their color, melting point and NMR spectroscopy.

IV. Spectral Data of some compounds:

3,3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

(Chapter **I**, Section **B**, Table **I.B.2**, entry **3b) (Figure I.B.4.).**

M.P.: 215-217 ^{o}C; **^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm):** 6.796 (s, 1H), 7.498 - 7.723 (m, 1H), 7.768 - 7.809 (m, 6H), 7.907 - 8.009 (m, 6H) **(Figure I.B.5.).**

^{13}C NMR (75 MHz, DMSO-d6) δ (ppm): 33.573, 120.737, 121.728, 121.949, 125.754, 126.298, 129.819, 131.402, 132.570, 133.610, 134.423, 134.531, 144.632, 148.325, 165.003, 182.819, 183.933. **(Figure I.B.6.).**

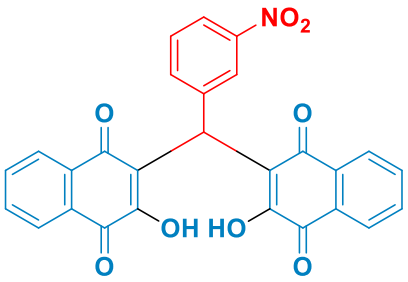


Figure I.B.4.: Structure of 3,3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

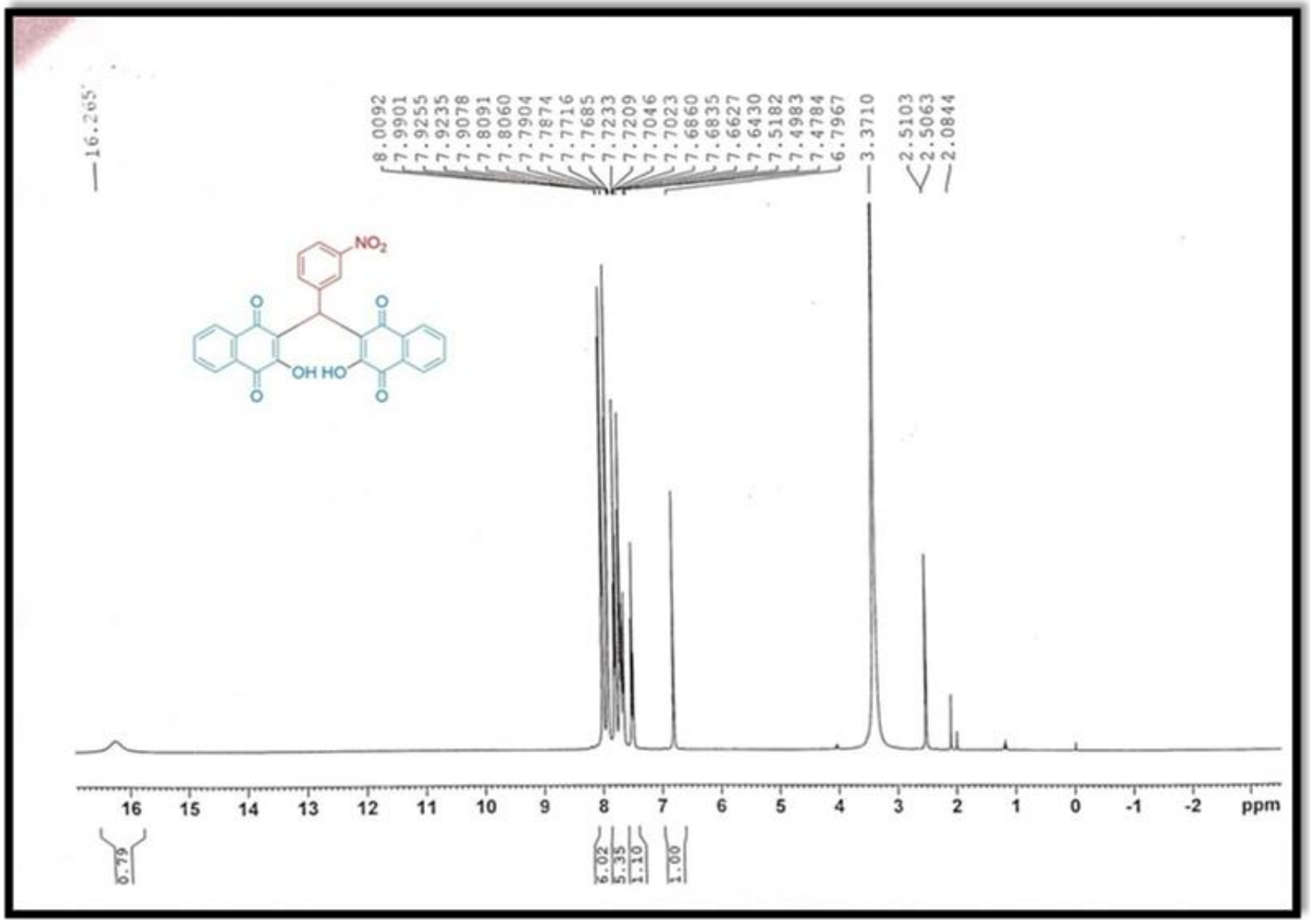


Figure I.B.5.: ^{1}H NMR spectroscopic representation of 3, 3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

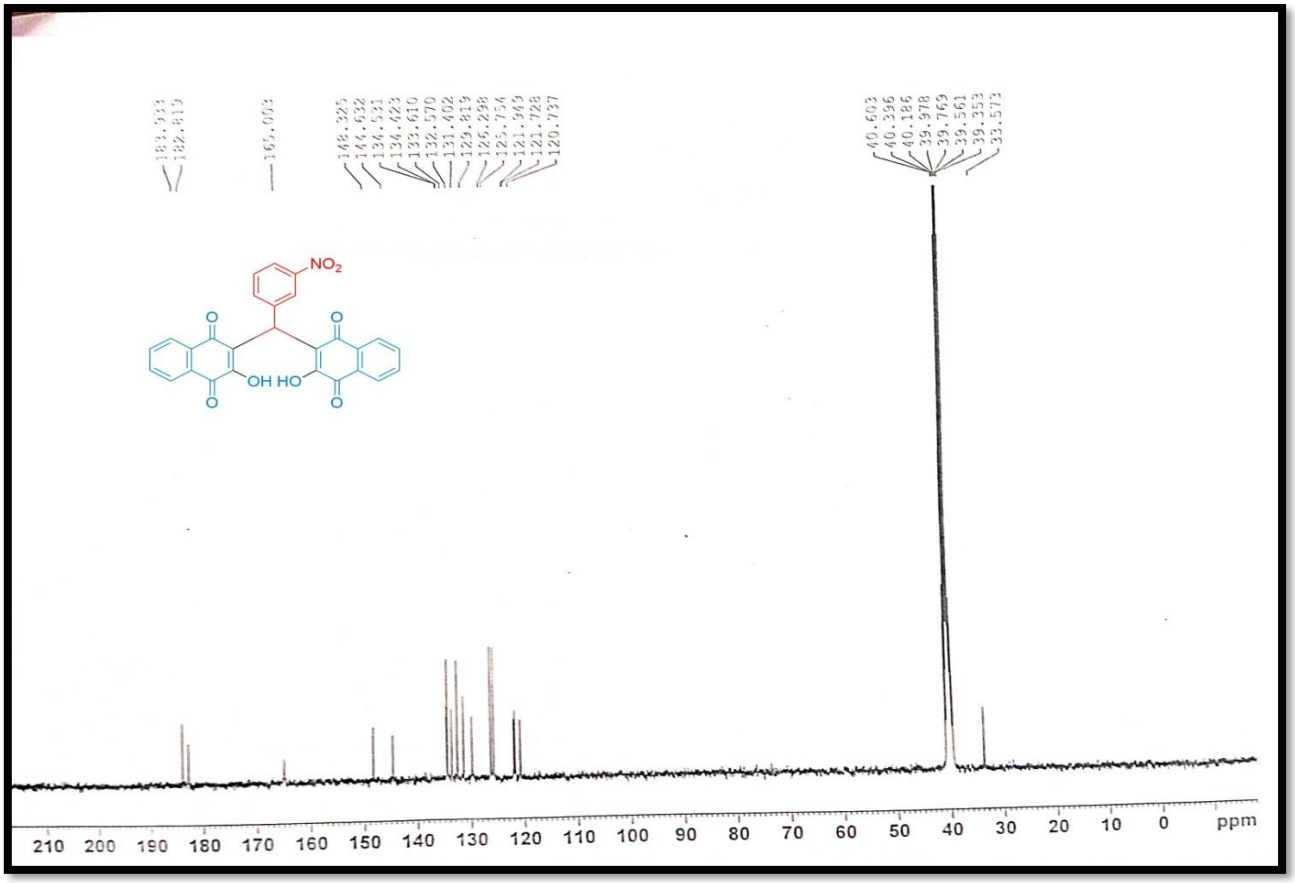


Figure I.B.6.: ^{13}C NMR spectroscopic representation of 3,3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

3,3'-((4-trifluoromethyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

(Chapter **I**, Section **B**, Table **I.B.2**, entry **3d) (Figure I.B.7.).**

^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm): 6.754 (s, 1H), 7.356 (d, 2H, *J* = 8 Hz), 7.523 (d, 2H, *J* = 8 Hz), 7.692 – 7.778 (m, 5H), 7.903 (d, 2H, *J* = 7.2 Hz), 7.985 (d, 2H, *J* = 7.6 Hz) **(Figure I.B.8.).**

^{13}C NMR (75 MHz, DMSO-d6) δ (ppm): 33.682, 122.263, 123.723, 125.118, 125.689, 126.023, 126.255, 126.434, 128.023, 131.398, 132.509, 133.643, 134.375, 147.161, 165.042, 182.858, 184.018. **(Figure I.B.9.).**

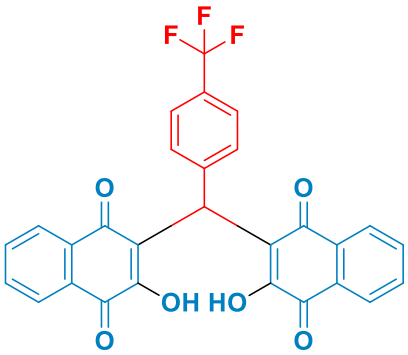


Figure I.B.7.: Structure of 3, 3'-((4-trifluoromethyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

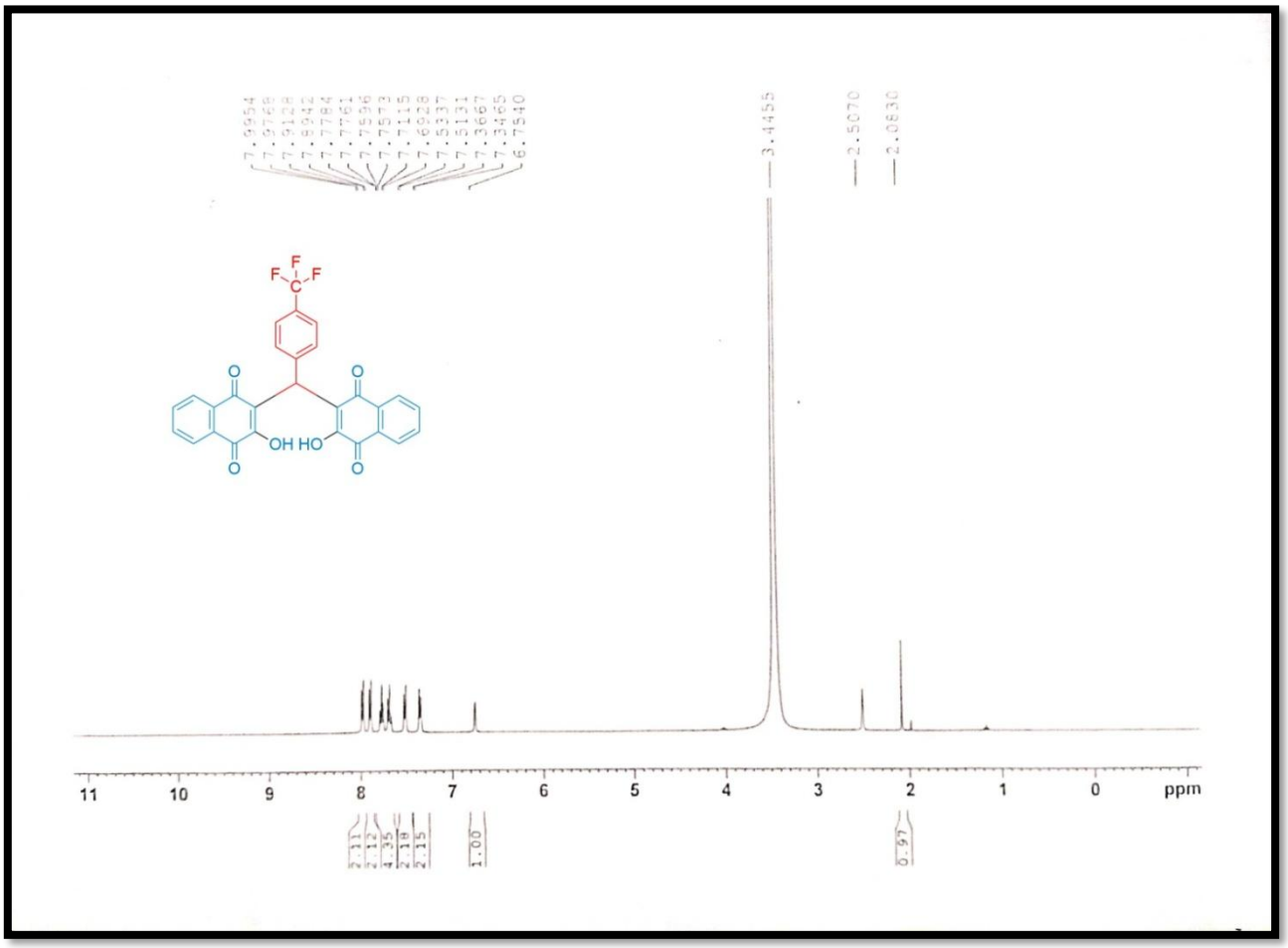


Figure I.B.8.: ^{1}H NMR spectroscopic representation of 3, 3'-((4-trifluoromethyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

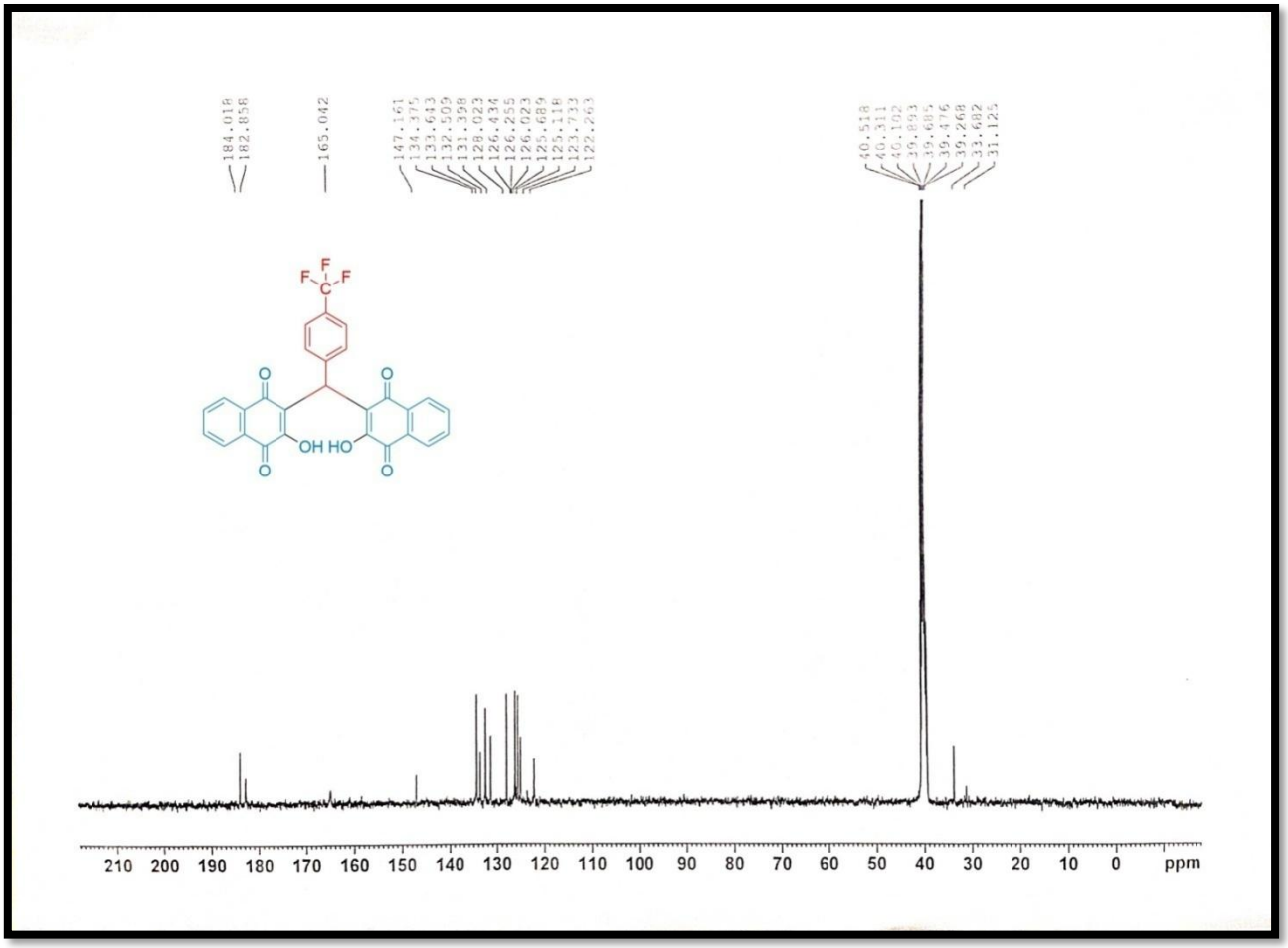


Figure I.B.9.: ^{13}C NMR spectroscopic representation of 3, 3'-((4-trifluoromethyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

4,4′-[(4-Methoxylphenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

(Chapter **I**, Section **B**, Table **I.B.4**, entry **3f) (Figure I.B.10.).**

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 2.34 (s, 6H), 3.70 (s, 3H), 4.90 (s, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 8.0 Hz, 4H), 7.71 (d, J = 8.0 Hz, 4H); **(Figure I.B.11.).**

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 12.2, 32.9, 55.5, 114.0, 121.0, 126.1, 128.7, 129.4, 134.5, 146.7, 158.0. **(Figure I.B.12.).**

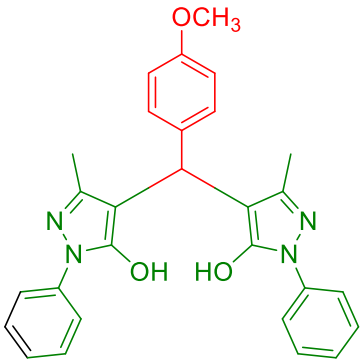


Figure I.B.10.: Structure of 4,4′-[(4-Methoxylphenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

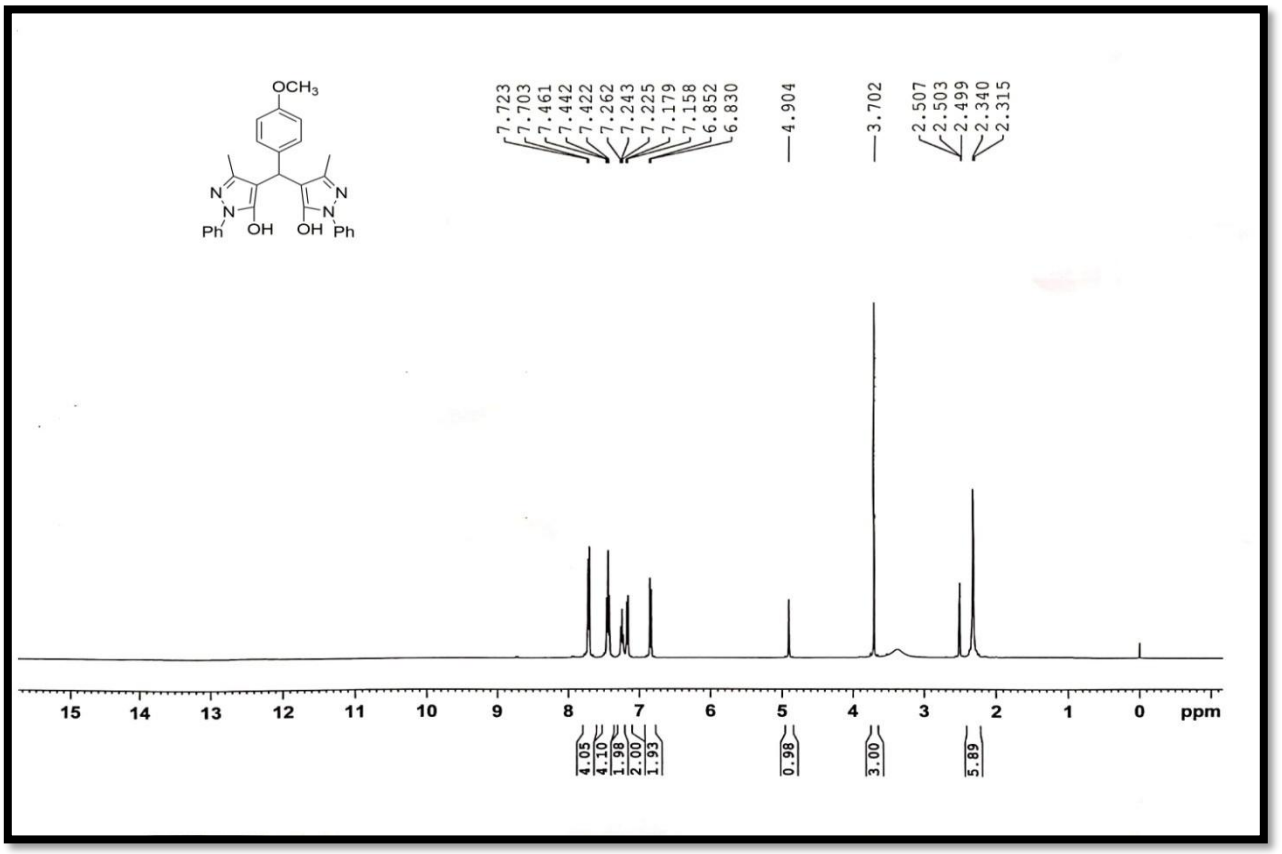


Figure I.B.11.: ^{1}H NMR spectroscopic representation of 4,4′-[(4-Methoxylphenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

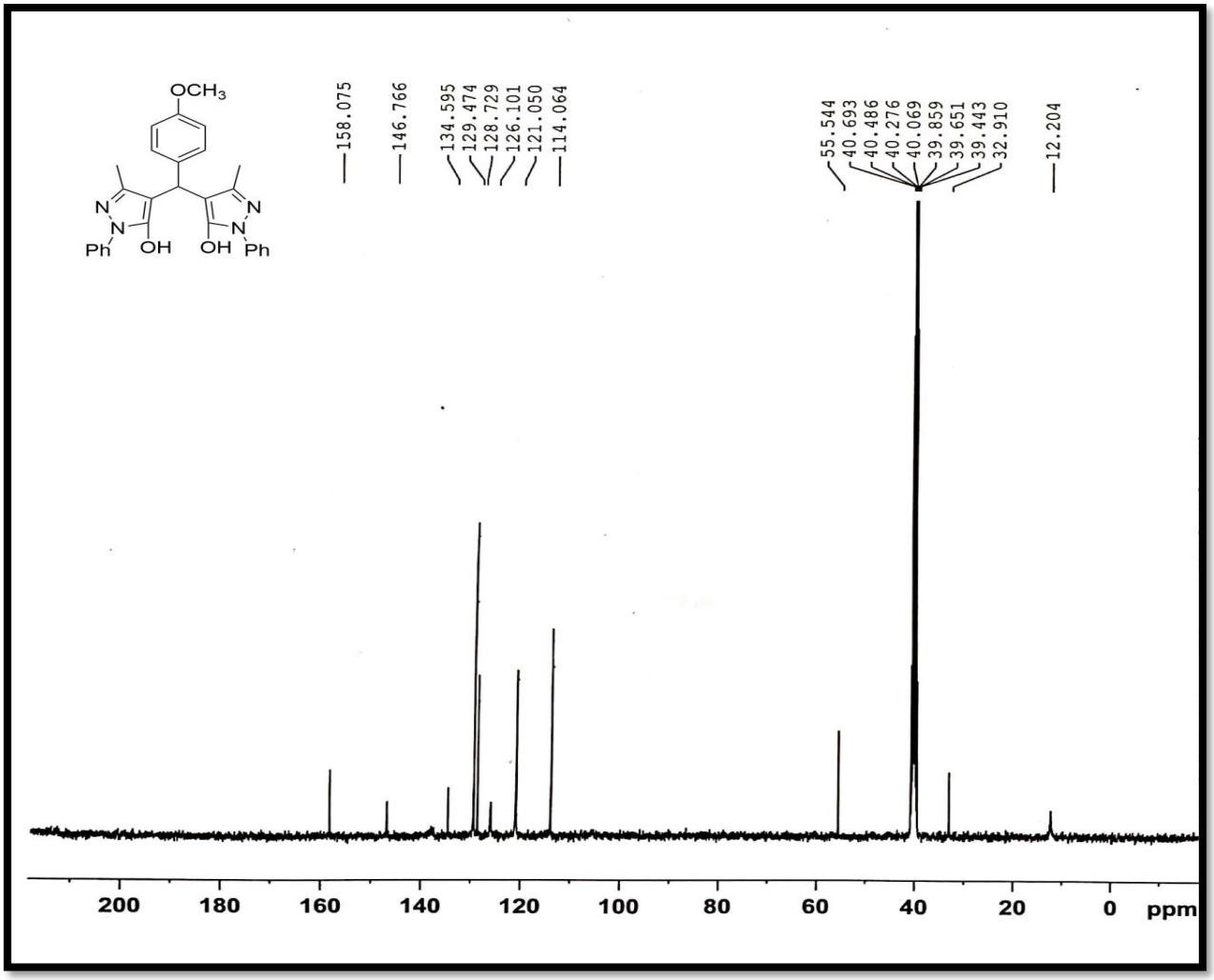


Figure I.B.12.: ^{13}C NMR spectroscopic representation of 4,4′-[(4-Methoxylphenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

I.B.8. References:

References are displayed in **BIBLIOGRAPHY** under **Chapter I, Section B,** that is, "**Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent–Free Synthesis of 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)"** (pp. 207-216**).**

Chapter II

Wide-ranging analysis of polymeric exploration, synthesis and evaluation

General Introductory portion

II.1. Introduction:

A lubricant's main component is lubricating oil, sometimes referred to as base oil or lube oil. They are an intricate combination of aromatic, naphthenic, and paraffinic hydrocarbons with a broad variety of molecular weights, viscosities, densities, and other properties. The primary purpose of lubricating oils is to lessen the friction between metal surfaces when an engine is operating. Lube oil has many different tasks to do in an engine in addition to reducing friction, such as reducing temperature-related variations in viscosity of oil, facilitating the low-temperature circulation, reducing the consumption of fuel, inhibiting corrosion, and so forth. Due to the extreme workload, productivity suffered, necessitating regular oil changes. The need for technologically sophisticated lubricant oil is growing due to advancements in technology and the variety of contemporary engines available. This includes increased expectations for multimodal effectiveness, cost effectiveness, and safeguarding the environment. Natural lubricants made of petroleum cannot meet all of the demands of a contemporary engine. As a consequence, lubricating oil has a significant amount of functional additives [1-6] to improve its already-existing qualities and provide new functionality. Such substances are known as lubricating oil additives, and commercialized lubricant refers to lubricant that has been loaded with additives. In base oil, the additives are added as just one substance or in mixtures of two or more chemicals at varying concentrations based on the requirements and field maintenance capability. In order to be dissolved in base oil, the majority of additives are biologically composed of extended-chain hydrocarbon units.

Generally, lubricating oil additives fall into three groups:

a) **Surface – level additives:** Such chemicals provide a barrier of protection on the metal surfaces, preventing corrosion and wearing. Some examples of this type include excessive pressure [1], friction modifiers, substances that inhibit corrosion [2], anti-wear (AW) [3], etc.

b) **Additives for lubricant protection:** The additives in lubricant oil are shielded by lubricant protection additives from oxidation, elevated temperatures, fracture, etc. This class includes antioxidants [4] and foam inhibitors [5].

c) **Additive that improves performance:** Such additives are incorporated to improve the base oil's current qualities or add new ones. Viscosity modifiers (VM) [6], pour point depressants (PPD) [7], detergents, dispersants, demulsifiers, and so forth are examples of frequently used additives [8].

The current study involves synthesizing a few polymeric VM, PPD, and AW additives, then characterizing and assessing their efficacy in base oils. The concise histories of these all three categories of additives are shown here.

➢ **Modifiers of viscosity:** Materials that withstand viscosity alteration with temperature are known as viscosity modifiers (VM) or viscosity index improvers (VII). They preserve a favorable relationship within viscosity and temperature by increasing lubricating oil viscosity at higher temperatures and reducing it at lower ones. A hypothetical metric used to indicate how viscosity changes with temperature is the viscosity index (VI) [9]. The viscosity of the oil changes less with temperature the higher the viscosity index, and the other way around. **Figure II.1**. is representing here, the general procedure of enhancement of volume of Viscosity Modifiers.

The viscosity fluctuates in lubricating oil as a function of temperature is represented by VI. The soluble capacity of the additive in base oil, chemical behavior, molecular weight, and shear stability all affect VM's efficacy. In base oil, the VM stays wrapped at low temperatures [10]. As the temperature rises, the lubricating oil causes the spiral to swell and split up into a larger, chain-like structure [11].

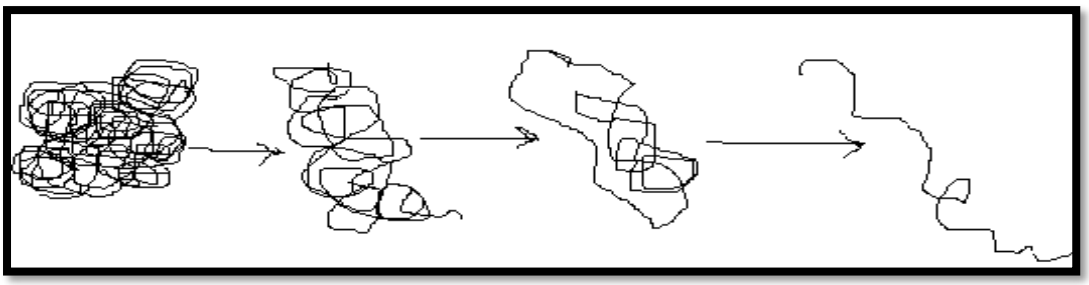


Figure II.1. : Expansion of Viscosity Modifier with temperature

Base oil's viscosity increases as a result of the additives' increased volume, offsetting the natural decrease in base oil viscosity with increasing temperature [12]. In addition to increasing efficient volume in oil solution, VMs exhibiting greater molecular weights additionally display increased

viscosity indices. When the viscosity of the base oil grows, an effective VM should become less efficient at raising the viscosity of low viscosity oils.

An engine lubricant that meets both the low and elevated temperature requirements of the SAE viscosity categorization system can be made with the right design. **Figure II.2.** is representing the structures of Polyisobutylene (PIB) [13], olefin copolymer (OCP), hydrogenated styrene isoprene copolymer (SIP), polyacrylates, polybutadiene rubber (PBR), and other VMs are among the most frequently documented VMs.

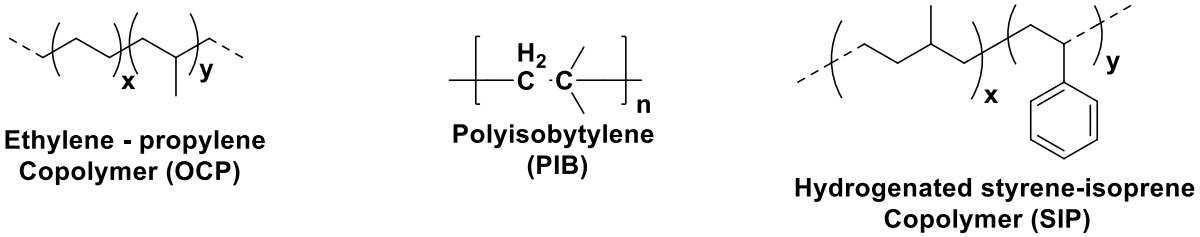


Figure II.2. : Structure of frequently utilized Viscosity Modifiers

- **Pour point depressant:**

There is usually a certain wax in organic base oils, which is a linear high molecular weight hydrocarbon that starts to crystallize at a particular temperature known as the cloud point. The crystals having a needle shape imprison the oil by forming a solid, grease-like matrix with minimal wax. The procedure of crystal development intensifies as the temperature drops, and the oil ultimately ceases streaming at that point.

Pour point is the smallest temperature at which oil is permitted to flow. Lube oil flow enhancers, also known as pour point depressants (PPDs), are additives that lower the pour point of oil to increase its low-temperature mobility. In colder locations, lubricants must function well, and this requires a lower pour point. The majority of PPDs are polymethacrylates [15], polyacrylates [16], vinyl acetate/fumerate copolymers [14] etc. have been represented in **Figure II.3.**



Figure II.3. : Frequently utilized Pour Point Depressant

The oil's wax crystal networks also contribute to a boost in viscosity. This impact is usually only momentary since the shear force produced by a typical combustion engine is enough to cause the wax to break. However, this may put the engine under additional strain and shorten its lifespan. Chains of long hydrocarbons are present in polymeric substances that decrease the pour point. Their morphological linearity hinders the formation of crystals and helps them coordinate with the oil wax matrix.

➢ Anti wearing additives:

Anti-wear additives are lubricant additives that stop attachment between the metals amongst gear component parts directly. Over time, wear on metal surfaces from consistent friction between metal components reduces the efficiency of the engine. By creating a barrier, AW additives lessen wear across the surfaces of metals. Powerful AW additives chemisorb or adsorb onto metal surfaces. Occasionally electron transfer happens in between the absorbed molecule and the metal surface in the event of chemisorptions [11]. This phenomenon has been depicted here in **Figure II.4.**

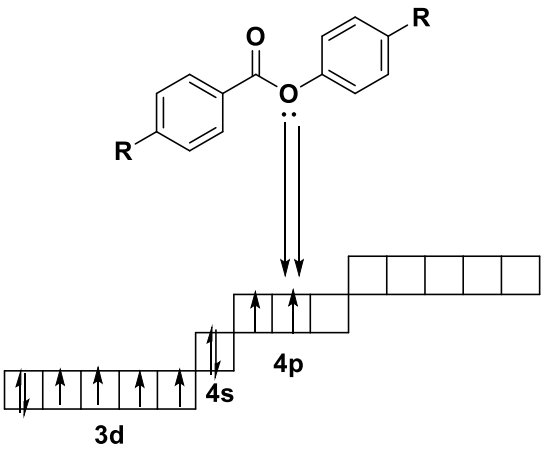


Figure II.4. : Diagramatic representation of donor accepter bond between AW additive and metal (Fe) surface

Organosulfur and organophosphorus materials, such as phosphates, dithiocarbamates, and organic polysulfide, are commonly utilized additives for severe pressure [17] and AW applications. As an antioxidant and corrosion inhibitory agents, zinc dialkyl dithio phosphate (ZDDP) is arguably the most popular AW addition found in engine oil formulations [18]. Tricresyl phosphate (TCP) is added to various crankcase oils, hydraulic fluids, and turbine engine lubricants for elevated

temperatures usage as an AW and EP addition. Stearic acid works well as an AW addition in colder temperatures (below 150 °C). The utilization of liquid crystals [3] and nanoparticles [19] as AW additives has increased a little while back due to the harmful characteristics of the aforementioned chemicals. Due to their favorable structures, they can both encapsulate surfaces of metals through chemisorption or absorption. Structure of some AW components have been represented in **Figure II.5.**

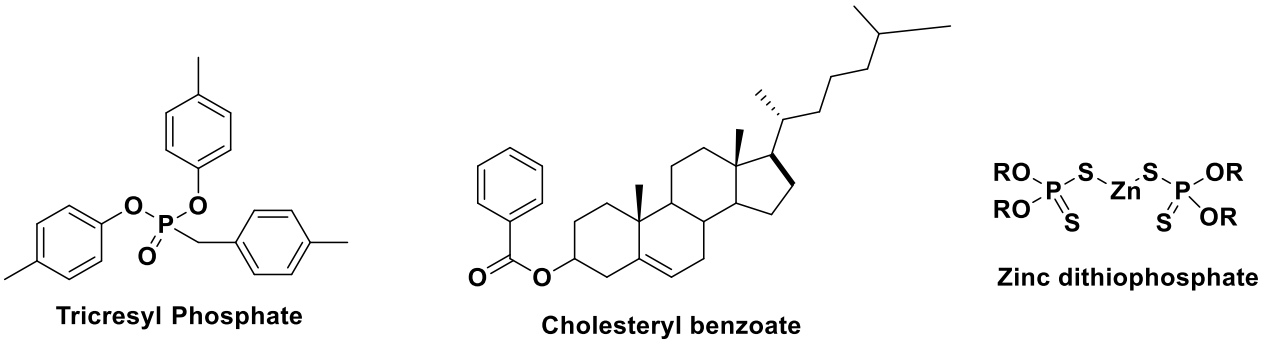


Figure II.5. : Some Antiwear Additives

Extensive research has been conducted to elucidate the mechanism underlying anti-wear chemicals. Additives for tremendous pressure interacts thermochemically with the metal surfaces to generate robust, long-lasting protective coatings. This movie can tolerate harsh safeguarding the metal surface from heat and mechanical pressure. There is a dearth of scientific research on organisms with multifaceted qualities, despite the fact that several additions have been examined and claimed to perform either solely as VM [20], PPD [21], or AW [22] additives or in combination with one or more of these additives offering dual-functioning features as VM-PPD [23] or VM-AW [24], among others. Contemporary engines and cutting-edge technology have increased the requirement for affordable, environmentally friendly additives [25 - 27] with versatile efficacy. In order to satisfy the aforementioned requirements, efforts were undertaken to incorporate multidimensional capability into an individual additive device. Networks of liquid crystallization merged polyacrylate were created and their multifaceted additive capabilities assessed. To guarantee cost-effectiveness, a significantly smaller volume of liquid crystal was used. The current study examines the idea of greener technologies by synthesizing and assessing their efficacy of multimodal additives constructed from vegetable oil alongside additional green monomers. Peanut oil, rice bran oil, and olive oil are examples of vegetable oils employed in the

current research work. The experiment also utilized organically produced α and β pinene as ecological subunits. In addition to exhibit high biodegradability, the additive-doped lubricating fluids demonstrated good multidimensional additive functionality. The study, in summary, covers the preparation, characterization, and assessment of efficiency of several additives for lubricating oils. FT-IR and NMR were used for spectroscopic characterization, and TGA (thermogravimetric analysis) was used to determine thermal stability. The gel permeation chromatographic method (GPC method) or viscometric measurement was used for determining the molecular weight of the polymers. Ultimately, using conventional ASTM procedures on various base oils, the additives' effectiveness in the form of viscosity modifiers (VM), pour point depressants (PPD), and anti-wear agents (AW) were assessed. A few of the produced additives' oil hardening and degrading stability (measured by means of shear stability) were also identified and documented. According to ISO 846: 1997 guidelines, a biodegradability research was conducted utilizing the disc diffusion method with a variety of fungal pathogens and a soil burial test. Some possible additives that can be developed for usage in commerce have been identified by current research, and we will be pursuing these in the not too distant future. Furthermore, the study has made a significant contribution to the relatively unknown chemistry of lubricant additives and will undoubtedly encourage new scientists to pursue lubrication technologies as a topic of study.

II.2. References:

References are displayed in **BIBLIOGRAPHY** under General Introductory part of **Chapter II,** that is, **Wide-ranging analysis of polymeric exploration, synthesis and evaluation** (pp. 216-219**).**

Background of the Present Study

II.3. Background and Objectives:

Part – 1:

A material added to surfaces in touch with one another to lessen frictional force is called a lubricant. Liquid or semi-liquid property can be situated in lubricants. Base oil and an additive bundle are both present in the lubricant. Chemically speaking, base oils are the interconnected blend of aromatic, paraffinic, and naphthenic hydrocarbons with a broad variety of molecular weights. They exist within the environment in a variety of density levels, viscosities, and distillation curves.

Base oils are anticipated to have a variety of additional functions, including temperature resistance, low temperature flow ability, fuel economy, cost effectiveness, and engine lifetime enhancement, along with to their fundamental role of smoothing the edges of metal to minimize friction. But due to their limitations in terms of improving their qualities, traditional base oils typically do not match modern technological standards. The needs of outstanding lubricants are typically beyond the capabilities of base fluids mineral oil in devoid of the use of contemporary additive expertise. Some additives are incorporated into basic oils with the goal of improving their lubricating characteristics. Lube oil additives [1] are compounds that either give base oils fresh capabilities or enhance their current qualities. Additives are selected based on the attribute that has to be added to base oil. Compounds' physical and chemical characteristics are important factors in how well they work together. Chemicals that fall under the category of additives include plain organic molecules, polymers, inorganic compounds, etc. In base oil, they are utilized as a single ingredient or as a combination of chemicals.

The sorts of additives can vary based on their effectiveness. Below is a list of some of the most significant in this discipline. Multidirectional approach of Lube Oil Additives has been depicted through **Figure II.6.**

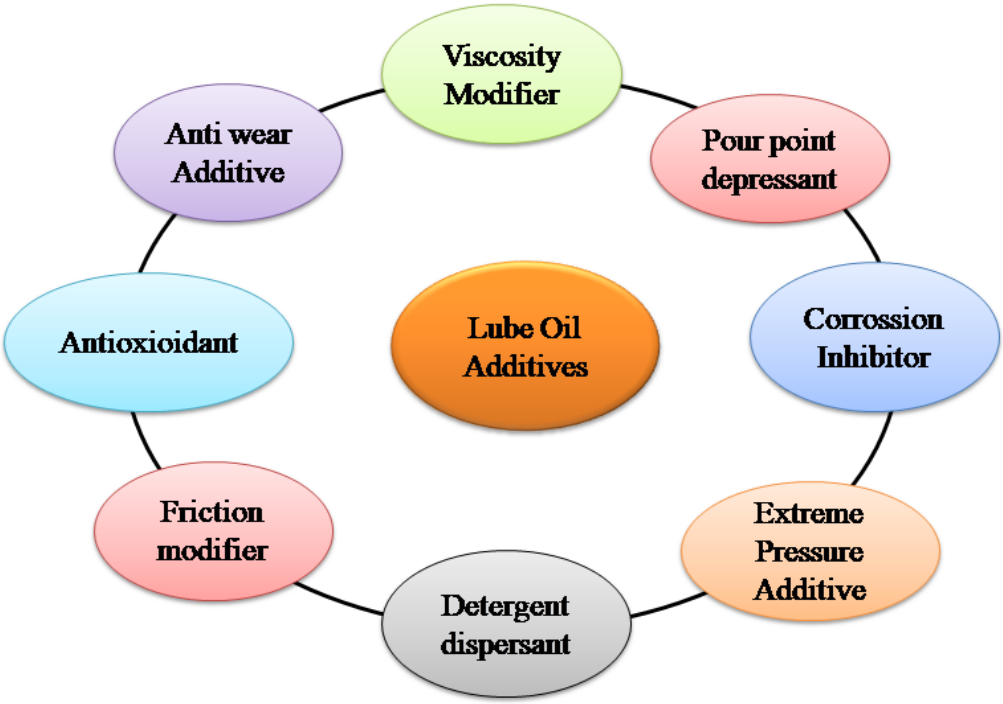


Figure II.6. : Various types of Lube Oil Additives

When added to basic lubricating the fluid such additives enhance its inherent qualities and enhance field service longevity in current usage. The need for multifaceted additives is growing in light of the high cost and potentially dangerous features of the chemicals employed in this industry. In the modern engine oil industry, multimodal additives are crucial to technological advancement. Global research efforts are progressively concentrating on creating additives with several functions [2-6]. As per the prior research, a single system can exhibit several additive capabilities in the context of multidimensional additive systems [7-10]. Thus, adding several functionalities to a single platform has grown increasingly important in the modern world. In light of this, the current study combines the three primary additive efficacies—VM, PPD, and AW—into a single additive scheme. It will be extremely relevant to provide a quick discussion of the VM, PPD, and AW lubricating oil additives in light of the current inquiry. The creation of multifunctional polymeric additives with both PPD and VII capabilities is becoming more feasible owing to a number of studies and the experience gained from using high molecular weight molecules in the form of additives.

A viscosity modulator is explained by means of viscosity index (VI), an arbitrary value that represents a lubricant's durability against viscosity variation with temperature, as stated in the basic introductory part. Compounds known as viscosity moderators (VM) alter how quickly

viscosity changes with temperature. The VI of base oil is raised in a specific temperature spectrum by the incorporation of VM. Increased VI indicates a stronger durability to oil viscosity to temperature changes. Once more, the kind and concentration of the additive affect a VM's efficacy. When multiple grades motor oils are used, this property is the most noticeable.

VM [12] is often made up of long chain, large molecular weight polymer compounds. The the ability to dissolve, molecular weight, and sensitivity to shear breakdown [13] of the polymer compounds in the oil determine how well the VM performs. When the temperature rises, the soluble capacity of polymers often rises because the molecules of the polymer shift from having tight coils to an open configuration, which has a larger volume. The viscosity of the oil increases as a result of this volume grows, offsetting the viscosity's natural decrease as temperature rises [14, 15].

A larger molecular weight polymer has a greater viscosity index with respect to a smaller molecular weight polymer of the identical category[17], because polymers with greater molecular weights additionally improve the effective volume in an oil solution[16]. The minimum temperature at which lubricating oil can circulate when chilled underneath particular circumstances is known as the pour point[18]. For an engine to operate in a cold area, base oil must have a low pour point. Most mineral oils typically comprise slightly dispersed wax, which starts to break out as crystals when the oil cools down. These crystals create a stiff architecture that locks the oil in tiny enclaves[19]. The oil lacked all capacity for circulation during testing circumstances when the wax's crystal framework became sufficiently powerful. Eliminating all wax components from the oil throughout refinement is one way to get minimal pour points. However, the procedure leads to an upsurge in carbon deposition accumulation and a reduction in base oil's stability during oxidation. Preventing the production of a wax crystal framework in the oil at reduced temperatures is a different approach for achieving a lesser pour point. The polymer components in the base oils can help accomplish this. These polymers, also referred to as pour point depressants or flow improvers, stop wax from crystallizing and enhance flow characteristics. Pour point depressants' alkyl chain length, structural characteristics, and composition of chemicals all affect how effective they are. PPD's mode of functioning is a topic of great curiosity. PPD chemicals were thought to wrap the wax crystal and stop them from growing any more. After that, further acknowledged pathway engages polymer’s co operative crystallization of the polymer with wax materials. Such process prevents the manufacture of three dynamical frameworks and

conserves wax materials in the form of an extensive little entity inside the oil and secures their circulations [20-22].

The elimination of even a little bit of wax from oils is a challenging, pricey, and time-taking technique. Pour point depressants convey an affordable way to easily facilitate the right amount circulation of oil in an engine at lower temperatures. Light microscopy demonstrates that wax crystals resemble thin sheets. The PPDs constitute the crystals of wax larger as well as branching by co operative crystallization and more robust crystals can establish an advantageous framework solely at a reduced temperature, which results minimal pour point.

The subsequent sentences provide a specific presentation of the findings made by earlier studies relating VM and PPD. The manufacture and assessment of acrylate copolymers as a PPD in lubricant oil formulations were covered by U.S. Patent No. 5834408. According to U.S. Patent No. 4867894, petroleum oil's pour point characteristics were demonstrated by copolymers of methyl methacrylate with an average molecular weight between 50,000 and 500,000.

The usage of polymethacrylate polymers alongside an average alkyl group chain length that varies in between 12.6 to 13.8 is described in U.S. Patent No. 4956111. These polymers can lower the pour point to 35 ^{0}C and in accordance with detergents and other additives, such as VII.

The olefin copolymer of conjugated carboxylic acid ester as PPD for lubricating oil is disclosed in U.S. Patent No. 4906702.

A lubricating oil formulation with seven amounts of a polymer layout, soluble in oil, including a particular quantity of ethylene α-olefin copolymer, exhibiting multiple-purpose qualities such as PPD and VII characteristics, is disclosed in U.S. Patent No. 4088589.

The production of a dispersing agent VII and a pour point depressant of a terpolymer of maleic anhydride, lauryl methacrylate, and stearyl methacrylate can be obtained in U.S. Patent No. 4668412. The manich base of amino ethyl pyparazine, paraformaldehyde, and 2, 6-ditertiarybutyl phenol have been combined with dimethyl amino propyl amine and can formulate the above agents.

A lubricating component with hydrogen containing butadiene-isoprene copolymers and PPD, VII characteristics is also disclosed in U.S. Patent No. 4032459.

Acrylate and methacrylate oriented copolymers alongwith unsaturated dienes show good shear resistance and could be especially helpful as a VII, according to U.S. Patent No. 4073738.

A methacrylate co operative polymer with outstanding low temperature capabilities in lubricating oils is disclosed in U.S. Patent No. 5955405. It consists of 5 to 15 weight percent butyl methacrylate, 70-90 weight percent C-10 to C-15 alkyl methacrylate, and 5-10 weight percent C16 –C30 alkyl methacrylate.

A terpolymer consisting of an alkyl ester of a conjugated monocarboxylic acid, an unsaturated olefin containing homo and heterocyclic nitrogen compound, and either an allyl acrylate or methacrylate or a perflouro alkyl ethyl acrylate or methacrylate is added to an oil formulation that includes mineral oils and exhibits enhanced PPD and VII features (U.S. Patent No. 4886520). The polymerization of a mixed methacrylate consisting of alcohols with carbon atoms comprising C16–C24 is disclosed in U.S. Patent No. 6458749. This type of methacrylate is exceptionally efficient when it comes to meeting various low temperature fluidity qualities for a wide variety of base oils.

A polymeric additive based upon an octadecene-methacrylate copolymer was published by Azim et al. in 2005 as a multipurpose additive (VM, PPD, Dispersancy - detergent) [23].

It has been determined that the manufactured substances' effectiveness as VM grows with rising alkyl chain size and additive dosage, but their efficacy as PPD improves with minimizing manufactured polymer content. Another copolymer framework constructed around styrene-methyl methacrylate in the form of a multipurpose functioning (VM, PPD, and detergent-dispersant) additive for lubricant oil was discovered by Azim et al. in 2009 [24].

Another comparable paper detailed a procedure for making a number of alkyl acrylate and maleic anhydride copolymer and terpolymer derivatives. They looked into how PPD attributes were affected by the copolymer and terpolymer structures [25].

The majority of PPD and VM additives are acrylate-oriented. The effectiveness of poly alkyl acrylate and poly alkyl methacrylate as VM and PPD has been the subject of numerous publications [26 -28].

In the 1930s, pour point depressants were officially documented for the first time [29].

Ruehrwein described the effect of n-alkyl poly methacrylate as PPD in the sequence dodecyl, tetradecyl, hexadecyl, and octadecyl over 20 years afterwards [30].

According to an article, briefer alkyl polymers worked well on low-temperature pour oils, whereas longer polymers were successful at lowering the pour point of elevated temperature pour oils. The

creation and characterization of a viscosity index enhancer for naphthenic and paraffinic base oils were examined by Bataille et al. in 1994 [28].

Though tribological functionality in this kind of an assembly is relatively unusual, the literature accessible through VM and PPD indicated wide utilization of poly acrylate and poly methacrylate as homo or copolymer [31].

The continuous rubbing created when two sliding metallic elements coming into proximity causes scarring on the metal exteriors, which impairs the performance of components in engines. Several additives that can promote lubricity and resist rusting are included in lubricating oil to reduce the friction between them. A substance's lubricity cannot be evaluated precisely because it is not a physical attribute. Assessments are conducted to measure a lubricant's effectiveness in a particular platter. This is frequently accomplished through calculating the quantity of wear that a specific wear-inducing component causes onto a surface over a specified period of time. There are other specifications for other variables including surface area, temperature, and pressure. When two liquids have the identical viscosity, the fluid exhibiting less wear damage is said to be more lubricating. Because of this, lubricity is also known as a materials' antiwear characteristic. Via creating a layer of protection, anti-wear additives are utilized to stop straight metal-to-metal interaction amongst gear component portions.

Every single anti-wear additives work fundamentally by forming a barrier of protection at the bearing surface, mostly during commencement and in borderline and elastohydrodynamic lubrication regimes. The primary source of wear in such areas is asperity communication [32].

The framework of lubricants determines their tribological characteristics. Solid lubricants, such as graphite, tungsten disulfide (WS_2), or titanium disulfide (TiS_2), are typically employed as multilayered compositions. The crystal lattice's assembled atom structure allows an opening field of protective functionality to emerge. It has been widely recognized that wear behavior is determined by the chemistry of the surface, but that the existence of an adhered closely packed molecule single layer may prevent immediate interaction across the two surfaces and result in an enormous decrease in friction. The identical task can be performed by liquid crystalline materials, which are distinguished by both a certain kind of spatial hierarchy and a sequential orientation of components.

Since mesogenic chemicals contain polar counterparts, which improve adhesion on the steel exterior, they may be much more beneficial. Such impact makes it significantly simpler for a slipping layer to develop in fact, such a plane could potentially function as a barrier [33].

Various research have documented the usage of Schiff bases, azoxys, cyanoaryls, and esters in the form of the source of lyotropic and thermotropic liquid crystals with nematic, smectic, and cholesteric mesophases to be lubricant additives. MLCs were employed like lubricant additives, mixes, and pure forms [34 – 38].

In a shear stream across parallel plates, Nakano[39] investigated the cellular alignment of the nematic liquid crystal 4-pentyl-4' cyanobiphenyl (5CB). The combination of the sheet's width and the sliding speed determined the molecular orientations. Since cholesteric MLCs are found in naturally occurring bio lubricants, they have also drawn a lot of interest. Atomic force microscopy (AFM) revealed that the liquid crystal formed barrier layers on the counterpace exteriors, high-nitrogen stainless-steel femoral heads, and Ultra - High Molecular Weight Polyethylene (UHMWPE). Waters et al.[40] discovered that cholesterol palmitate liquid crystal lubricant drastically lowered wearing. It was determined that adding liquid crystal lubricant to hip replacement pieces could significantly reduce wear.

The findings of studies on the lubrication property of liquid crystals and their corresponding solutions in petroleum and artificially produced oils as an indicator of MLC intensity were reported by Kupchinov et al. [41]. The wear and friction index are reduced by the MLCs in the lubricant. A number of research [42–46] have been conducted to determine the connection in among the molecular structure and tribological properties of MLCs in order to justify the construction of novel MLC lubricants. Because of their accessibility and electro optical uses, cyanophenyls and cyanobiphenyls are two of the most researched MLC lubricants. Using a two-roller friction testing tool, Mori and Iwata [47] investigated the tribological behavior of nematic and smectic fluid crystals, specifically alkyl cyanobiphenyl (CB), alkoxycyanobiphenyl (ECB), and alkylcyanophenyl cyclohexane (CPC).

As commercialized oil additives, a number of thermo tropic MLC genera have been investigated [48].

The research investigation found that temperature and the bulk viscosity fluctuations had no appreciable impact on frictional levels. For every liquid crystal examined, the coefficient of

friction of steel is reduced when one weight percent of the liquid crystals is added to each of the two base oils.

Liquid crystals with different morphologies and structures have good tribological qualities, but they are ineffective for any other type of additive execution, according to a review of the literature on anti-wear additives. From this, we developed the concept of combining fluid crystals with polyacrylate to produce multimodal (VM, PPD, and AW) capabilities. In order to maintain the lowest possible manufacturing expenses, the author's mixture of innovation contains a very little proportion of crystal into the liquid.

Once more, the functionality of the specimens was examined after various crystals of fluid were combined in the similar polyacrylate to associate architecture with efficacy. This section uses homo polydecyl acrylate and homo polydodecyl acrylate as homo polymers. In similar fashion, a mixture of acrylate combined with liquid crystals was examined in greater depth. Taking into account the current requirements and the attention provided by OEMs, it was decided to carry out the current study in an effort to create an effective multifaceted additive with VM, PPD, and AW qualities for lubricating oils.

II.3. Background and Objectives:

Part – 2:

With the introduction of new technology and constantly evolving concepts, the automotive sector is thriving daily. The primary areas of research in this sector have continued to be the use of polymeric additives, their modification to achieve maximum efficacy with lowest dosage, or the introduction of new prospective lubricating additives.

However, in the last ten years, environmental issues have taken center stage, forcing these sectors to confront the difficult task of implementing somewhat greener ideas. Therefore, there has been a significant increase over the years in the substitution or reduction of traditional chemicals or additives with biodegradable ones. Non-traditional forms of energy are receiving a lot of concern for maintaining the natural world; as a result, using bio-lubricant to decrease the usage of fossil fuels and boost their sustainability is highly appealing. There is a significant amount of research being conducted on animal and plant-based oils[1]. For industrial purposes, vegetable oils and their modified counterparts have replaced petroleum-based products with sustainable options

because of their easy availability, low toxicity, lack of volatile organic compounds, biodegradability, and affordability[2].

95–97% of Triglycerides as well as mono and diacylglycerides make up vegetable oils. Tri-esters are formed with glycerol in varied ratios by saturated fatty acids such as stearic acid (18:0), palmitic acid (16:0) and tetradecanoic acid (14:0) and unsaturated fatty acids (MUFA or PUFA) such as oleic acid & ricinoleic acid in 18:1 ratios, linoleic acid in 18:2 ratios and linoleic acid in 18:3 ratios.

A wide range of industrial products, including printing inks [7], water-thinnable primers [6], electrodeposition paints [5], paints [4] and wall finishes [3] have been made using vegetable oils.

When contrasted with mineral oil, the viscosity index of the majority of vegetable oils is often higher. The elevated flash point of vegetable oils is additional significant characteristic. Above all, vegetable oils are more environmentally friendly since they are less harmful, reusable, and biodegradable. They can also help lessen reliance on foreign petroleum oils in the future. However, the large amount of unsaturation in the structural framework of natural vegetable oils makes them less stable against oxidation, meaning that if left untreated, the oil will rapidly oxidize, thicken, and polymerize into a consistency similar to plastic[8].

However, various adjustments such selective hydrogenation, epoxidation, transesterification, and radical polymerization can get around this[9-10].

There are two types of plant oil: non-edible and edible. The main producers of vegetable oils include some perennial plants like corn, palm, olive and coconut, as well as annual species like peanuts, cottonseed, linseed, corn and soybean[11].

Soybean oil has emerged as a leading contender due to its composition and accessibility for the manufacturing of biodegradable lubricant additives. Now, soybean oil and linseed oil have comparable triglyceride contents, while linolenic acid content is significantly higher in linseed oil, which is a colorless to yellowish oil derived via the dried, ripened seeds of the flax plant (Linum usitatissimum) (18:2). As a result, compared to soybean oil, the degree of unsaturation for the triglyceride in linseed oil is slightly higher[12].

From an economic perspective, India produces adequate linseed oil seeds to be considered worthy of consideration. The main benefit of using linseed oil is that it may be utilized as an impregnator in its natural state or combined with other oils, resins, or solvents to create a blend. It may also be

employed as a plasticizer and the hardener in putty, as well as a pigment binder in oil paints, wood finishing, and linoleum manufacturing[13].

Below is a summary of some previous research on the alteration of vegetable oil as a possible lubricant additive.

1. Linseed oil and its peroxidation in air or oxygen flowing at room temperature were studied by B. Cakmakli in 2004. It was researched how these polymeric peroxides might be used in tissue engineering and swell management[1].
2. Reduced erucic rapeseed oil's antioxidant effectiveness as an oxidation inhibitor was examined by Becker, R., and Knorr, A. in 1996[8].
3. Epoxy vegetable oil was studied by Ashraf, M., S., and Ahmed (2007) for mixing with PMAA polymers to enhance mechanical and physical qualities. In this instance, dehydrated epoxy castor oil was utilized[13].
4. Using BZP and performance analysis, Ghosh, P., and Karmakar, G. (2014) studied biodegradable multifunctional lubricant additive based on sunflower oil in a solvent-free polymer synthesis process employing thermal or MW irradiation[14].
5. In 2020, Ghosh, P., and Talukdar, S., studied the multifunctional additive properties of rice bran oil co and its homo polymer with dodecyl acrylate and styrene[15].
6. Using AIBN as a radical initiator, Ghosh, P., and Saha, D. (2018) synthesized a castor oil homo and copolymer with alpha-pinene and examined the additive efficacy[16].

   Vegetable oil has so many useful applications, and its advantageous qualities—like its high degree of unsaturation, ready to polymerize propensity, accessibility, and other qualities—have encouraged us to investigate its potential for creating environmentally benign polymeric additives. Using acrylate and alpha-pinene as potential lube oil additives, we prepared castor oil and acrylate-based copolymers, rapeseed oil styrene-based homo and copolymers, and rice bran oil based homo and copolymers. Their effectiveness in terms of VII, PPD, TGA, biodegradability, and antiwear property were tracked during the characterization process using FT-IR, NMR, and GPC.

II.3. Background and Objectives:

Part – 3:

It is commonly known that while crude oil reserves are depleting, there is a growing possibility of both oil price increases and the eventual depletion of current reserves[1]. Because traditional mineral lubricants are hazardous and have a moderate biodegradable properties they are typically not appropriate for surroundings[2, 3]. These oils have a significant negative impact on both human life and plant by contaminating the air, soil, and drinking water. Consequently, in some particular places, stringent requirements are needed regarding a variety of ecological challenges, including toxicity, biodegradability, safety, health and emissions[4]. Therefore, as public worries about pollution-free environments grow, so does the need for ecologically sound lubricants[2, 3]. The lubricant industry has been working to create recyclable lubricants that are of higher quality compared to those comprised of petroleum oil due to growing environmental concerns[5].

Sustainable development[6], which is commonly understood as "functioning" reasonably to satisfy the requirements of the present while safeguarding the potential of future generations to fulfill their own demands, can be greatly aided by the utilization of raw materials that are recyclable[7].

It is clear that using regenerative raw materials wherever and whenever feasible is a crucial step regarding sustainable growth in a span of diminishing fossil oil sources and rising greenhouse gas emissions. Specifically, by reducing CO_2 emissions, this can prevent additional contributions to greenhouse effects and continuously supply a raw material basis for everyday products. Additionally, using recyclable raw materials and harnessing nature's synthetic aptitude can (in certain situations) satisfy additional green chemistry criteria, such an inherent degradation design or anticipated reduced toxicity of the final products[6].

The chemical industry uses wood, sugars, plant oils, polysaccharides (mostly cellulose and starch) and different regenerative raw materials extensively to acquire non-fuel operations. Packaging materials, coatings, pharmaceuticals and specialty chemicals are just a few of the numerous items made from these naturally occurring substances. Plant oils are currently the chemical industry's most significant sustainable raw material. They are widely utilized as raw materials for surfactants, cosmetics and lubricants[8].

Vegetable oils are a possible source of environmentally favorable (ecologically sound) lubricants because of their exceptional lubricating efficiency, biological degradation, and ecological sustainability[9-14]. Monoesters and Triesters are the two primary chemical groupings that make up almost every kind of vegetable oils. Triesters (triglycerides), which are glycerol molecules with three long- chains of fatty acids joined at the hydroxy groups by esters, make up the majority of vegetable oils. Monoesters of long-chain fatty acids and fatty alcohols with distinct chemistry make up a tiny portion of vegetable oils[13, 14]. All of the fatty acids in vegetable oil triglycerides have carbons between 14 to 22 numbers, and their degrees of unsaturation vary[13, 15, 16]. The majority of vegetable oils have distinct polar and non-polar group areas within one single molecule. Vegetable oil is specifically amphiphilic due to the existence of polar groups, which enables it to be utilized to be a hydrodynamic and boundary lubricant[11, 17].

The elevated molecular weight triglyceride molecule in vegetable oils reduces volatility, the polar ester group and high viscosity index provide good boundary lubrication properties, the vegetable oils have a high solubilizing power for polar contaminants and additive molecules, and they are less expensive than synthetic oils[4, 10, 12, 18-24].

The triglycerides (tri-esters of glycerol along with extended chain fatty acids, **Figure. II.7.**), containing changeable composition of fatty acids based on the crop, the plant, the season, and the growing circumstances[25].

Triglycerides that are liquid at room temperature are referred to as "oil" in this context. The stereochemistry of the fatty acid chains' double bonds, the extent of unsaturation, and the span of the fatty acids' carbon chain are the most significant factors influencing the physical and chemical characteristics of these oils.

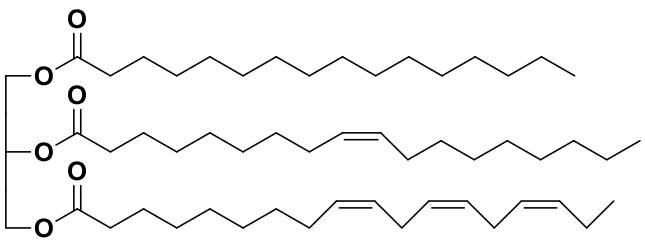


Figure II.7. : Common structure of triglyceride ester situated in vegetable oil

The intrinsic limitations of vegetable oils as lubricants are also caused by their triglyceride frameworks. Unsaturated double bonds in fatty acids serve as active sites for a variety of processes. Vegetable oils have two main issues because functional fluids have limited low-

temperature characteristics [28,29,33,35-38] along with poor durability against thermal oxidative stability [12,26-34], which causes quick decline, clogging, and deposition growth when used. The skeletal "double bond" components in the "-CH group" of the alcoholic components and the fatty acid are what cause the oxidative and thermal instability of plant-oriented oils [10, 38]. Swift reactions at the double-bond functional groups are the source of a vegetable oil's inadequate oxidative stability[39]. Numerous vegetable oils are prone to oxidation and contain significant levels of unsaturated fatty acids. The oil is more vulnerable to oxidation the higher the unsaturation grade[23, 24]. The raised viscosity caused by oxidative deterioration shortens the usable life of fluids made from vegetable oil[30]. Following extended exposure to low temperatures (–10 to 0°C), vegetable oil exhibits solidification and cloudiness [40, 41]. Additionally, vegetable oils don't do well in preventing corrosion[42]. These oils are vulnerable to hydrolytic disintegration because of the ester functionality included in the triacylglycerol molecule[43].

Consequently, it is necessary for preventing water from being contaminated in the form of emulsions at all stages. Yet, their capability to serve as industrial lubricants is limited by their low oxidation and thermal stability as well as their inadequate low-temperature characteristics[44]. Because the entire base oil is highly polar, it can interact strongly with the lubricated surfaces, making vegetable oils very good boundary lubricants. Both the lubricant molecules' affinity to the surface and any potential reactions related to it have an impact on boundary lubrication functionality.

Vegetable oil's oxidative stability can be increased by converting its alkene groups into other stable functional groups, while its thermal efficiency can be enhanced by decreasing the oil's structural homogeneity by adding alkyl side chains[45]. The problems surrounding the use of plant oils in lubricants have been resolved by the adoption of a number of contemporary technologies. Chemical alteration, additive therapy, and genetic modification are a few examples[19].

When utilized as lubricant base oils at temperatures of about 120 °C, Joseph and Sharma's [46] combination of aminic and phenolic antioxidants may be used to increase the thermo-oxidative stability of vegetable oils. A thermo-oxidatively stable base lubricant oriented on methyl-12-hydroxystearate, a castor oil derivative featuring 70% recoverable carbon, has been recommended by Vinci et al. [47].

Mendoza et al. [48] created a sunflower base oil to use in hydraulic agricultural tractor mechanisms that has an 89% biological degradation rate, an enhanced pour point of -27 °C (the base oil's pour point is -3 °C), and enhanced oxidation stability (its oxidation induction time is 71 minutes as opposed to 8 minutes to feed the base oil). The oil's formulation satisfies the specifications of the benchmark mineral oil for excessive pressure tribological testing and prevents the production of microwelds. The ability to compress and viscosities of vegetable oils have been investigated by Regueira et al. [49] in order to use them as lubricants and hydrolytic fluids. It is clear from the aforementioned literature that chemically altered vegetable oils have a wide range of applications to be base fluids.

Using green sources as lube oil performance additives rather than just like base oils or base fluids is an additional consideration. Research in this area is creating fresh opportunities as the lubricant industry has been working to develop sustainable lubricants with superior technological properties than traditional lubrication oil additives. The application of polymeric additives and sunflower oil bio fuels, such as styrene butadiene and ethylene vinyl acetate copolymer, in lubricant manufacturing has been documented by Franco et al.[50] Triglycerides are anticipated to be crucial in the 21st century for the synthesis of polymers from resources that are renewable, according to a new evaluation of their use in polymer research that focused onto cross-linked frameworks for wrapping and resin usage.[51] Additionally, plant oils may supply linear polymer chains in addition to those cross-linked frameworks.

The manufacture and testing of a lubricating additive composed of vegetable oil that may be employed to increase thermal endurance and viscosity is disclosed in US Patent No. 5229023.

The manufacture and application of an additive based on jojoba oil have been described in US Patent No. 48730008. Classes of vegetable oil equivalents that have been sulfurized and have improved lubricating qualities are detailed in US Patent No. 4970010. Once more, the tribological and anti-wear attributes of certain vegetable wax ester are described in US Patent No. 4152278. The chemical structure of recyclable vegetable oil for lubricants was covered in US Patent No. 6534454 B1. The use of meadow foam oil and its derivatives as lubricant additives was asserted in US Patent No. 4925581.

Using several types of soybean and sunflower oils, Erhan et al. [12] have found outstanding oxidation and low temperature stability of vegetable oil-oriented lubricants. Certain triglyceride vegetable oils' friction qualities have been characterized by Biresaw et al. [11]. Boshui et al. [52]

investigated the effects of two fatty acidic diethanolamide borate additions onto the lubricity and ability of biological degradation of indigestible mineral lubricating oil, demonstrating tribological performance.

II.3. Background and Objectives:

Part – 4:

Vegetable oils are typically added to enhance base oils' tribological effectiveness and thermal stability. However, it is not particularly common to utilize those products like pour point depressants and viscosity modifiers. As previously mentioned, the additive capabilities of vegetable oils alone are not particularly promising. Therefore, the author polymerized several vegetable oils with alkyl polyacrylate to employ them as LOA. This resulted in a system that combined the high viscometric capacity of vegetable oil together with the outstanding lower-temperature flow capability of poly alkyl acrylate, as well as significant biodegradable properties

With rising oil prices, global warming, and other environmental issues (including waste), switching from fossil fuels to energy from renewable sources may significantly promote future environmentally friendly development. There has previously been significant commercial application for the production of polymers and monomers from oils and plant fats and fresh advancements in such fields present encouraging prospects.

A popular technique for heating and drying materials in both commercial and residential settings, exposure to microwaves is also used in many environmentally friendly procedures. When juxtaposed with traditional heating, microwave irradiation significantly accelerates both inorganic and organic processes. The quick and immediate heating of the reacting substances themselves has also been shown to result in notable increases in selectivity and yield.

Moreover, closed-vessel operations can readily employ high-pressure manufacturing, which opens the door to ecologically friendly conditions for reaction by enabling the utilization of low-boiling solvents. In light of this perspective, the author used microwave conditions to synthesize the current vegetable oil-based lubricating oil additive.

A steady supply of oil sources is necessary for the ever-expanding lubricant industry, but regrettably, petroleum crude is the most common source of base stock or base lubricant, and its sources are finite and steadily declining. Regardless of this, lube has certain significant drawbacks, such as,

- They emit harmful compounds into our surroundings through residue and have inadequate biodegradable properties.
- Their rheological and tribological qualities are subpar.
- There are few and non-renewable sources [5].

Although synthetic lube base stock is thought to be a substitute, there are some significant problems with it, including as,

- When contrasting them with mineral lube, they are more costly [4].
- They are linked to more dangerous environmental conditions.
- Biodegradability doesn't look good.
- They cannot cooperate since they are less dispersed with mineral lube.

Petroleum-based additives, including zinc-diethyl dithiophosphate (ZDDP) as a tribo improver and polyacrylate to be a rheo improver, pose major environmental risks due to their sulfur and heavy metal content [1-2]. Heavy metals and sulfur compounds are released by friction modifiers, molybdenum dithiocarbamate complexes employed as solid lubricants, and their action diminishes with fluid age [3]. As a result, bio-oriented lubricant additives are gaining more attention in research. Because of their low aquatic toxicity, high biocompatibility, superior friction qualities, high viscosity index and high flash point, lubricants made from vegetable oils are a promising substitute for mineral and synthetic oil-oriented lubricants, despite being more expensive compared to the latter [5-7]. Vegetable oils have an oleophobic and oleophilic portion in their composition due to their long fatty acid chain and polar end groups. As a result, they can be utilized as the both hydrodynamic and boundary lubricants and as a base stock for mixing various ecologically sound additives [3]. As we saw in our earlier chapters, additives made from castor oil, rapeseed oil, and rice bran oil had outstanding tribological and rheological qualities on this front. Additionally, research was conducted on the preparation of alternative lubricant additives and base stock.

1. The application of poly (hydroxy thioether) vegetable oil derivatives to be antiwear additives for eco-friendly industrial oils in automotive applications received a patent by Erhan et al. (2008–2014). Erhan et al. have previously described various techniques for converting unsaturated fatty acids into fatty acid ester derivatives by forming their epoxides [9–11].

2. A new method of creating chemically amended triglycerides has been granted patents by Doll et al. (2014). It involves reacting phosphorus-oriented acid hydroxide or esters along with epoxidized triglyceride oils or alkyl esters. The phosphorus-containing triglyceride derivatives that are so generated are useful as antiwear and anti-friction additives on behalf of industrial and automotive oils [12].
3. Biswas et al. (2014) copyrighted a process that involves interacting amines of cyclic or aromatic hydrocarbons alongside epoxidized fatty acids, their esters, or triglyceride oils to produce nitrogen-containing fatty acid derivatives. These fatty acid derivatives are utilized in automotive and industrial oils as antiwear or anti-friction additives [13].
4. The antiwear additive functionality of vegetable oil incorporating boron was produced and examined by Heise, G.L.; Sharma, B.K.; and Erhan, S.Z. (2015) in accordance with U.S. Patent 9156859 B2[14].
5. Multipurpose additives composed of polymers from castor oil, sunflower oil, and soybean oil were studied by Ghosh, P., and Karmakar, G. (2013–2015)[17–19].
6. In 2007, Fox, N.J. and Stachowiak, G.W. conducted an evaluation of lubricants based on vegetable oil [24].

The poor thermal oxidative stability, low volatility, and high viscosity of vegetable oils make them unsuitable for direct use as lubricants in comparison to mineral lubricants. There are two methods for doing this: either reactions at the olefinic functionalities of the fatty acid chain or reactions at the carboxyl groups of fatty acids, esters, or triglycerides of vegetable oils (transesterification). The next section discusses many research initiatives in certain fields.

- **TRANSESTERIFICATION:**

1. Sukjit et al. revealed that adding 5% rapeseed oil methyl esters to diesel fuel significantly reduced the wear scar diameter [25]. Blending palm oil methyl esters with diesel base oils was found to enhance their lubricating capabilities [26, 27].

2. When palm oil methyl ester was added to the base oil lubricant, Masjuki and Maleque (1997) reported a low wear rate of steel ball bearings [28].

3. By transesterifying castor oil along with different alcohols while trimethylchlorosilane (TMSCl) acts in the role of acidic mediator, Malavolti et al. have produced biodiesels [29].

4. Madankar et al. [30] described the possible application of castor oil methyl esters to be lubricants due to their good lubricity, low pour point and high viscosity.

5. The resulting glycerol has various uses in the diverse chemical industry, such as a water-oriented lubricant [31].

- **REACTION WITH THE VEGETABLE OIL'S OLEFINIC PART:**

Fatty acid or ester epoxidation and its use as a biolubricant: The epoxidation of vegetable oils' olefinic properties is an essential phase in creating an organic lubricant (the base stock and/or additive). Peracid can be used to make vegetable oil epoxide [32–34]. Due to their increased reactivity, various reagents, including amines, thiols, alcohols and acids can readily un obstruct the oxirane rings of epoxides to produce a variety of value-added compounds, including bio-plasticizers, lubricants (base stocks/additives), and other chemicals with industrial applications. Epoxidized vegetable oils and fatty esters are used to make lubricant additives that reduce wear and friction due to the fact that they dissolve better in vegetable oils.

1. The creation of corrosion-protective additives using an epoxidized methyl ester of an unsaturated fatty acid and a sulfuric acid was reported by Schafer et al. [35].
2. To lessen lead corrosion in fuels and lubricants, Rowland et al. revealed various antifriction additives made from an epoxidized fatty acid [36].
3. As environmentally friendly antiwear and anti-friction additives for lubricants, hydroxy thioether derivatives of vegetable oils made by breaking apart the epoxy rings of epoxidized soybean oil with common organic thiols are utilized [37–38].

Sulfur added to the triglyceride framework gives the molecule polar functions that increase the derivatives' ability to adsorb on the metal surface, lowering the coefficient of friction and wear.
Better cloud point and pour point readings were demonstrated through ester hydroxy derivatives of methyl oleate, which were produced via unlocking the epoxy rings of epoxidized methyl oleate using different organic acids (propionic, octanoic, hexanoic, or 2-ethyl hexanoic acid) [28]. As lubricant additives, they also demonstrated enhanced tribological, lubricating, and thermo-oxidation stability.

Given that linseed oil has numerous uses in both the petroleum and polymer industries, some studies based on it was quite intriguing in this respect. In one work, polymethyl methacrylate was mixed with linseed oil polyesteramide and dehydrated castor oil to create a bioartificial polymer with enhanced physical and mechanical characteristics [40–41]. In a different

study, polyvinyl chloride (PVC) and triethylene glycol ester of gum resin were combined with epoxidized linseed oil to create an organic viscosity-enhancing substance [42].

Epoxidized linseed oil is frequently utilized to serve as a supplementary stabilization device for polymers containing halogens as well as a plasticizer or lubricant [43]. Linseed oil biodiesel was created through the method of transesterification and its impact on engine operation and exhaust emissions was examined in a study. The results indicated that while linseed biodiesel and fuel blends behaved fairly similarly to regular diesel fuel, the former's exhaust emissions were generally better [44]. In their study, V A Markov et al. found that a mixture of 90% diesel fuel and 10% linseed oil has chemical and physical characteristics that are fairly comparable to those of petroleum diesel fuels. They also found that using such a mixture as motor fuel reduced the emissions of exhaust harmful substances like unburned hydrocarbons, nitric oxides and carbon monoxide [45]. A combination of linseed oil, P. P. Chahande has effectively created a novel polymeric surfactant that is both bios recyclable and environmentally benign [46]. Because of their cell adhesion and growth, Birten Cakmakli et al. have created a number of naturally decomposing synthetic branching graft copolymers of linseed oil with methyl methacrylate and described their possible use in tissue engineering [47]. Polyvinyl alcohol and epoxidized linseed oil have been combined by S. M. Ashraf et al. to create a plasticizer and anti-corrosive covering layer with low water absorption, flexibility and high endurance [40–41].

II.3. Background and Objectives:

Part – 5:

Copolymers comprising ethylene, propylene, and occasionally a diene make up olefin copolymers (OCP). In oil, smaller polymeric side chains have fewer impacts on viscosity modification [12, 13]. On the other hand, polymers having lengthy ethylene sequences have a more crystalline framework. Because crystalline polymers are less soluble in oil compared to amorphous ones, OCP polymers may separate from the oil and clog engine filters, reducing their ability to modify viscosity. Once more, the crystalline form of OCP increases the likelihood that the polymer is going to interact with oil waxes at reduced temperatures, leading to a substantial rise in lower-temperature oil viscosity and in the worst situations, lubricant oil gelling. In lower temperature engine conditions of operation, this is absolutely unacceptable.

Star polymers are known to offer better shear stability than OCPs because of their molecular structure [14, 15]. These types of viscosity modifiers, which are produced by hydrogenating isoprene that has been anionically polymerized, are sold commercially. A comparatively low molecular weight distribution (Mw/Mn) is the outcome of anionic polymerization. Because star-shaped polymers have smaller hydrodynamic and gyrational radii than their linear counterparts, they typically have lesser internal viscosities. This renders them ideal for application in lubricating lubricants on automobile engines and other fluids that need to have minimal viscosity. They have high shear stability and a superior thickening impact.

The chemical makeup of lubricating oil and techniques for running internal combustion engines to increase engine performance were covered in U.S. Patent No. 8415284 B2. The majority of the lubricating composition was made up of lubricating viscosity oil, with a small amount of at least one olefin copolymer with an average molecular weight ranging from more than 10,000 to 300,000. A vinyl-substituted aromatic substance (A) and an element chosen from the category comprising a C5–C30 olefin, a polyalkylene compound, and their combinations (B) are grafted onto the olefin copolymer. The reaction mixture's mole ratio of A/B varied roughly from 0.25:1 to 5:1. A small quantity of at least one non-grafted olefin copolymer, styrene isoprene copolymer, methacrylate copolymer, or styrene butadiene copolymer with an average molecular weight ranging from more than 50,000 to 300,000 was selectively added to the lubricating mixture.

The manufacture of olefinic polymer combinations and their use as a viscosity index enhancer with improved lower-temperature properties were claimed in U.S. Patent No. 6753381. The performance of two polymer samples—a polymer blending which includes an ethylene-propylene copolymer with an elevated ethylene load and one with minimal ethylene content—was compared in the patent. For various compositions, the polymer combinations' molecular weights ranged from 20,000 to 3,00,000.

The viscosity index enhancer and dispersion qualities for certain ethylene copolymers were detailed in U.S. Patent No. 4517104. Polyamines alongside two or more primary amine groups and a carboxylic acid component, preferably alkylene polyamine and alkenyl succinic anhydride, including polyisobutenyl succinic anhydride, combined with ethylene copolymers, like as copolymers of ethylene and propylene, ethylene, propylene, and diolefin, etc., were fused together or reacted with ethylenically unsaturated carboxylic acid associations. By preventing cross-

linking, these processes added varnish inhibition and dispersancy to the ethylene copolymer, which led to a raise in viscosity, haze, or gelling.

Certain stabilized imide grafts of ethylene copolymeric lubricant additives were created by U.S. Patent No. 4137185. The oil-soluble, derivatized ethylene copolymers were made from roughly 2 to 98 weight percent ethylene and one or more C3 to C28 alpha-olefins, such as propylene, which were transplanted with an ethylenically-unsaturated dicarboxylic acid substance and ideally solution-grafted at elevated temperatures and in the presence of a high-temperature decomposable free-radical initiator. The polyamine then reacted with an alkylene polyamine, such as diethylene triamine, to produce carboxyl-grafted polymeric imide, typically maleimide.

An oil-soluble stable amide of the polyamine was then produced via treating the derivatives with an anhydride of a C1–C30 hydrocarbyl substituted acid, preferably acetic anhydride. Oil solutions of the amide derivative showed little variation in viscosity throughout an extended duration of time. The most effective polymers as multifunctional viscosity index enhancers were those with molecular weights between 10,000 and 500,000.

Some oleaginous formulations with a unique ethylene alpha-olefin polymer as a viscosity index improver addition were detailed in U.S. Patent No. 5151204. The ethylene alpha-olefin polymers are made up of monomer units made from ethylene and at least one alpha-olefin, which can be expressed by the formula $H_2C=CHR^1$. The polymer's average molecular weight ranges from above 20,000 to roughly 500,000, and at least 30% of its chains typically contain terminal ethylidene unsaturation. R^1 is an alkyl group with 1–18 carbon atoms.

There are styreneisoprene (SIP) polymers and styrene-butadiene (SBC) depending on the kind of diene employed. When utilized in engine oils, their optimal molecular weight prevents shear strains [10]. Copolymers of isoprene and styrene exhibit favorable high and low temperature characteristics. Styrene-isoprene polymers have molecular weights ranging from 50,000 to 100,000 g/mol [10, 16]. Engine oils are the most common application for them. They can also be utilized in different sectors where shear stability demands are stricter, including as oils for aviation piston engines and tractor propagation fluids.

Isoprene and styrene block copolymers are also used commercially as lubricant additives. There have been reports of both diblock (A-B) and triblock (A-B-A) polymers, where A stands for polyisoprene and B for polystyrene. For optimal thickening effectiveness, an increased isoprene production is preferred. These block polymers behave as associative thickeners since the

polystyrene regimes are oil insoluble during the majority of the temperature region that matters for engine oils. Therefore, the molecular weight of the individual molecules is generally modest, with the isoprene blocks having a molecular weight of 50,000 to 1,000,000 and the styrene block having a molecular weight of 30,000 to 50,000.

It has been further claimed that SIP polymer kinds perform better in star polymer structures. Star polymers made of triblock copolymer arms of hydrogenated polyisoprene/polybutadiene/polyisoprene are proposed in U.S. Patent No. 5460739. The thickening efficiency is enhanced by the higher ethylene proportion provided by the hydrogenated polybutadiene unit. According to the patent, the negative impact on low temperature qualities could be reduced by positioning the hydrogenated polybutadiene block closer to the nucleus. Comparing these polymers to the tapered arm polymers of U.S. Patent No. 4,116,917, it was discovered that they offered better low temperature qualities. In contrast to pure polyisoprene polymers, a debit in low temperature performance persisted when such polymers were given a hydrogenated polybutadiene block large enough to offer a credit in thickening functionality.

Several star polymers made of hydrogenated poly (styrene/isoprene) are described as efficient viscosity index improvers in U.S. Patent No. 4116917. According to the inventors, the polymers have very good low temperature viscosity characteristics in addition to great thickening performance at elevated temperatures. Once more, such polymers had much better "temporary shear loss" in addition to having far better oxidative and persistent shear stability. Temporal shear loss is the term used to describe the transient decrease of viscosity under excessive shear circumstances brought on by the polymeric VI improvers' non-Newtonian nature.

The application of three-block copolymers as a viscosity index enhancer is described in U.S. Patent No. 3668125. Certain polymers contain a hydrogenated styrene-isoprene-styrene unit in their structure. The degree of active unsaturation for both the isoprene and styrene monomer fragments was decreased to 50% or higher. The terpolymers exhibited reduced shear stability at high temperatures but appropriate low temperature viscosity properties. Once more, they demonstrated thickening power at 210° F in spite of their modest molecular weights.

In a lubricant base stock with a viscosity index of at least 85, U.S. Patent No. 3772196 examined an assembly of two-block copolymers consisting of a first polymer block of an alkenyl arene, such as styrene, and a second nearly fully hydrogenated polymer block of isoprene and specific pour

point depressants. The formulations could be made to meet several ASTM and SAE engine oil productivity and engine service classes and had good shear stability.

A solid, cyclone-finishable polymer with surprising viscosity balance that improved qualities for oil compositions and did not display cold flow was claimed by U.S. Patent No. 5278252. A copolymer made up of a homopolymer block of isoprene joined to a copolymer block of isoprene and a monoalkenyl aromatic hydrocarbon was hydrogenated to create the polymer.

Star polymers with tetra block copolymer arms of hydrogenated polyisoprene-polybutadiene-polyisoprene along with polystyrene are revealed in U.S. Patent No. 6034042. These polymers were said to have better thickening and viscosity-modifying qualities. The viscosity improver performance of hydrogenated styrene butadiene star copolymer was detailed in a relatively recent U.S. Patent 20120101017 A1. According to the study, between 3 and 25% of the star copolymer and between 97 and 75% butadiene could be present. In comparison to base oil, the star copolymer may also be added to lubricants in a lubricant additive in a quantity of roughly 12 weight percent.

The three primary types of viscosity modifiers—poly methacrylate (PMA), olefin copolymer (OCP), and hydrogenated styrene isoprene copolymer (SIP)—are also utilized as thickeners and are recognized for their exceptional shear stability, according to the literature review. Their viscometric characteristics have been the primary subject of research. However, little research has been done on their tribological characteristics. They may nevertheless have some anti-wear benefits because of various structural features, even though they lack the particular qualities needed to be a good anti-wear addition. In light of this expectation, the author chose to look at the anti-wear qualities of a few well-known viscosity modifiers.

II.4. References:

References are displayed in **BIBLIOGRAPHY** under **Background of the Present Study,** oriented five parts of **Chapter II**, that is, **Wide-ranging analysis of polymeric exploration, synthesis and evaluation** (pp. 219-235**).**

Section – A

Synthesis and Performance Evaluation of Castor oil – Styrene Co-polymer: an Outstanding Multipurpose Directional Lubricant Additive

II.A.1. Introduction:

There are many different base fluids and chemical additives used in the formulation of sophisticated lubricants. The moving surfaces are kept separated from one another by the basal liquid, which creates a fluid zone between them to reduce friction. It reduces the amount of heat generated during operating condition and gets rid of the wear particles. Without sophisticated lubrication, additive chemistry and lubricant conceptualization, it would have been difficult to develop advanced engine and gearbox technologies. Contemporary engine oils are made up of a variety of additives that are combined with base oils to create a comprehensive product that can meet even the most rigorous performance standards.The compounds, known as additives, satisfy the desired properties of lubricating and repelling the same. In most cases, they are chemical compounds with a non-polar hydrocarbon chain and a polar head group. Numerous lubricating oil additives are employed, including detergent-dispersants, corrosion inhibitors and substances for usage under extremely high pressures, viscosity index improvers (VIIs), antioxidants (AOs), and pour point depressants (PPDs).

The least temperature at which lubricating oil flows without interruption when refrigerated within defined parameters is known as the pour point. Paraffinic wax, a component of petroleum oils, crystallizes into stiff lattice-like frameworks at lower temperatures, obstructing flow. Hindering the production of wax crystal formations that would block passage of oil at low temperatures is how some high molecular weight polymers work. These chemical additives are also known as pour point depressants, flow improvers, paraffin antagonists, or wax moderators. Pour point depressants have no impact on the temperature or quantity of crystals that developed. The adsorption, co-crystallization, aggregation, and enhanced wax dissolution rate of these compounds are among their most generally acknowledged modes of action. Pour point depressants allow flowing at temperatures underneath the pour point of unaltered lubricant, because they co-crystallize along with paraffinic wax; alter the development of the lattice-like organization. Chlorinated polymers, wax alkylated phenol polymers, wax alkylated naphthalene polymers and polymethacrylates are examples of popular pour point depressants.

Another crucial lubricant property, viscosity is assessed using the arbitrary Viscosity Index (VI), which is derived through the measured viscosities within two different temperatures. This change in viscosity with temperature must be kept to a minimum for a lubricant to be effective. Thus, the performance of the lubricant is improved by a greater VI. Viscosity Index Improvers (VIIs)

additives were incorporated into lubricating oils to regulate the rate at which viscosity changes in response to temperature fluctuations. The behavior of the polymer molecules in the oil affects how well VIIs work. The most crucial characteristics of these VIIs are their molecular weight, durability to strain breakdown and polymer solubility. The lubricant causes the polymer molecule in solution, which is a randomized coil, to enlarge. As the polymer molecules shift from a tightly wound shape to an exposed framework, which has a larger volume, polymer solubility often rises with rising temperature. This addition of volume makes the oil more viscous, counteracting the natural decline in viscosity with rising temperature. The polymer capacity in an oil solution rises along with the polymer molecular weight. As a result, a polymer with a greater molecular weight will have a greater viscosity index than one with reduced molecular weight of similar kind. Acrylate - based polymers have been proved to be very good VIIs.

Some additives are antioxidants in nature. They can enhance the life span of a lubricant through the raising of oxidative constrains of base oils. This is known as anti – wear (AW) property of lubricant, with which they can lower the extent of friction in between the movable portions of those oils, by absorbing shock, reducing noise and minimization of the corrosion towards the portions. With decreasing the friction, decreases the extent of heat generation and thus reduction of most of the wear and tear portions occurs.Such additives are known as the anti – wear additives. They are known as extensive pressure additive and able to make a film or barrier or a protective layer on the wear surfaces.

Castor oil is one of the most popular vegetable oils, obtained from the seeds of the castor bean. It has a wide range of industrial prospects and can be used medicinally as a purgative and an adhesive. Because of their low virulence, bio-absorbability, and outstanding wrangling qualities, such as excellent lubricity, minimal effervescence, great viscosity index [1] and cost effectiveness, this is one of the most commonly used recycled assets for the manufacturing of chemicals and polymers. Automotive technology [2, 3], medicine, the coatings industry [4], cosmetics, surface-active agents, nutrition, the food and beverage industry, inks [5], pesticides, and plasticizers [6] are just a few industries that use bio-dependent compositions extensively. This oil is basically made up of triglycerides entity of fatty acids with long chain. These fatty acids consist of various triglyceride kinds, most of which are unsaturated. The fatty acid (FA) chain of this oil has a significant extent of unsaturation (-C=C-), which results in low thermal and oxidative stability and restricts such significance like lubricants into a moderate temperature [7]. To enhance the

convenient rigidness and technical features, the synthetic modification of triglyceride entity is necessary before its application to the field. For this accomplishment, polymerization of the oil is mandatory to enhance its molecular weight and extent of cross linking. Once more, copolymerization of this substance with the proper monomers can provide further benefits, such as ecological phenomenon of the currently prepared copolymer.

Polyacrylates and methacrylates are popular effective execution additives for lube oil. Methacrylates are frequently used as pour point depressant (PPD) and viscosity modifier (VM) of lube oil [8, 9]. However, in modern trend, the use of greener lubricants has brought some limitations to their vast application in automobile industries. In last few decades, to maintain the environmental sustainability and greener approach, the researchers are very much focused to initiate production of environmentally benign lubricants or greener additives for inventing better fuel wealth, multi utilitarian skill development and remove chemical threats [10, 11]. Castor oil was taken as a prospective element of copolymerization as it is promotionally accessible for trading, cost effective and contains satisfactory unsaturation. The current research performs an intense scanning onto the additive efficiency of produced polymericones with styrene and castor oil. Four varieties of copolymers of castor oil - styrene were constructed by different styrene concentrations in the mass (8%, 6%, 4% and 2%). The paper performs synthesis of the polymers followed by their characterization, performance evaluation and ecological explanation of all polymers.

With this framework, present study is governed to the production of copolymer of castor oil – styrene succeed by characterization of them (by thermogravimetric analysis to measure thermal stability of polymers, gel permeation chromatographic analysis [GPC] to determine their molecular weight and spectroscopic analysis [IR, NMR] for structural analysis) and estimation of their additive performance (as PPDs, AW and VMs) in lubricating oil. Moreover, the extent of biodegradability was also determined by GPC [12].

The outcomes of biodegradability experiment for polymers that was conducted are quite promising. Their performance comparisons have also been assessed and reported. The castor oil and styrene copolymer **(Figure II.A.1.)** demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives. This study represents a challenging approach for constructing a novel lubricant composition with enhanced flexible additive

properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD).

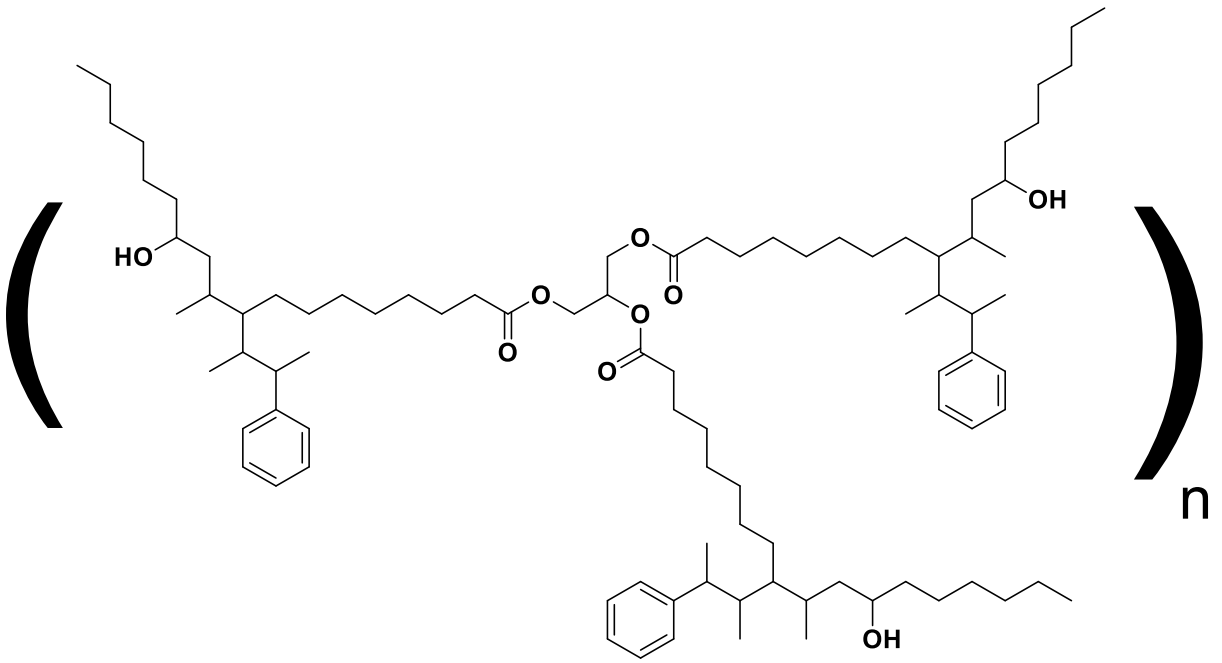


Figure II.A.1.: Structure of Castor oil – Styrene co – polymer

II.A.2. Experimental section:

II.A.2.1. Materials:

Sigma-Aldrich, an Indian company, supplied the hydroquinone (> 99%) whereas, Conc. H_2SO_4 (98%) and Toluene (GC 99.5%) was supplied by Merck Specialties Pvt. Ltd. The Castor oil (CO) (see Table II.A.1. for its fatty acid composition) was obtained from local suppliers, whereas, Styrene (GC 99.8%)) and Methanol (GC 99.8%) was received from Thomas Baker Chemicals Pvt., Ltd., India. Azobisisobutyronitrile (AIBN, GC 98%,) was obtained from Spectrochem Pvt. Ltd. in Mumbai, India, and was recrystallized from $CHCl_3$-MeOH. All other chemicals were utilized in its original form as received from the supplier without any additional purification. The fungal samples were cultured and obtained from the Microbiology Department of the affiliated organization and the Mineral base oils (BO1 and BO2) (see Table II.A.2 for properties) used in the present study was provided by Indian Oil Corporation Ltd. (IOCL), India.

II.A.2.2. Preparation of Castor Oil homo polymer:

Following the same process outlined in the literature [13], homopolymer of castor oil was created at 90 ^{o}C by polymerization reaction in a three necked circularbase flask **(Figure II.A.2.)** for 6 h.



Figure II.A.2. : Three necked round bottomed flask for polymerization

II.A.2.3. Preparation of copolymers:

The castor oil – styrene copolymer was constructed by utilizing various concentrations of styrene with castor oil. Four varieties of copolymers of castor oil – styrene were constructed with different castor oil concentrations in the mass (8%, 6%, 4% and 2%). The radical polymerization was performed using the technique that has been previously reported [14].

II.A.3. Measurements, Result and discussion:

II.A.3.1. Spectroscopic measurements:

FT - IR and NMR techniques were used to characterize the polymers' and composites' spectrum properties. IR spectra in the 400 – 4000 cm^{-1} wave number region were captured using 0.1 mm KBr cells at room temperature on a Shimadzu FT-IR 8300 spectrometer. Using a 5 mm BBO probe and $CDCl_3$ solvent, NMR spectra were captured utilizing a Bruker Advance NEO 400 MHz FT-NMR spectrometer. TMS was employed as a source of standard information.

II.A.3.1.1. Analysis of the Spectroscopic Data:

The analysis of spectroscopic data for the prepared polymers confirmed the predicted structure of the additives. For copolymers, the presence of the ester carbonyl group of castor oil was verified by the characteristic IR absorption peak at 1743 cm^{-1}. Additionally, peaks in the range of 2857-2931 cm^{-1} indicated the presence of other components. The peaks at 695 cm^{-1},724 cm^{-1}, 756 cm^{-1}, and 810 cm^{-1}were indicative of the aromatic part of styrene **(Figure II.A.3.).**

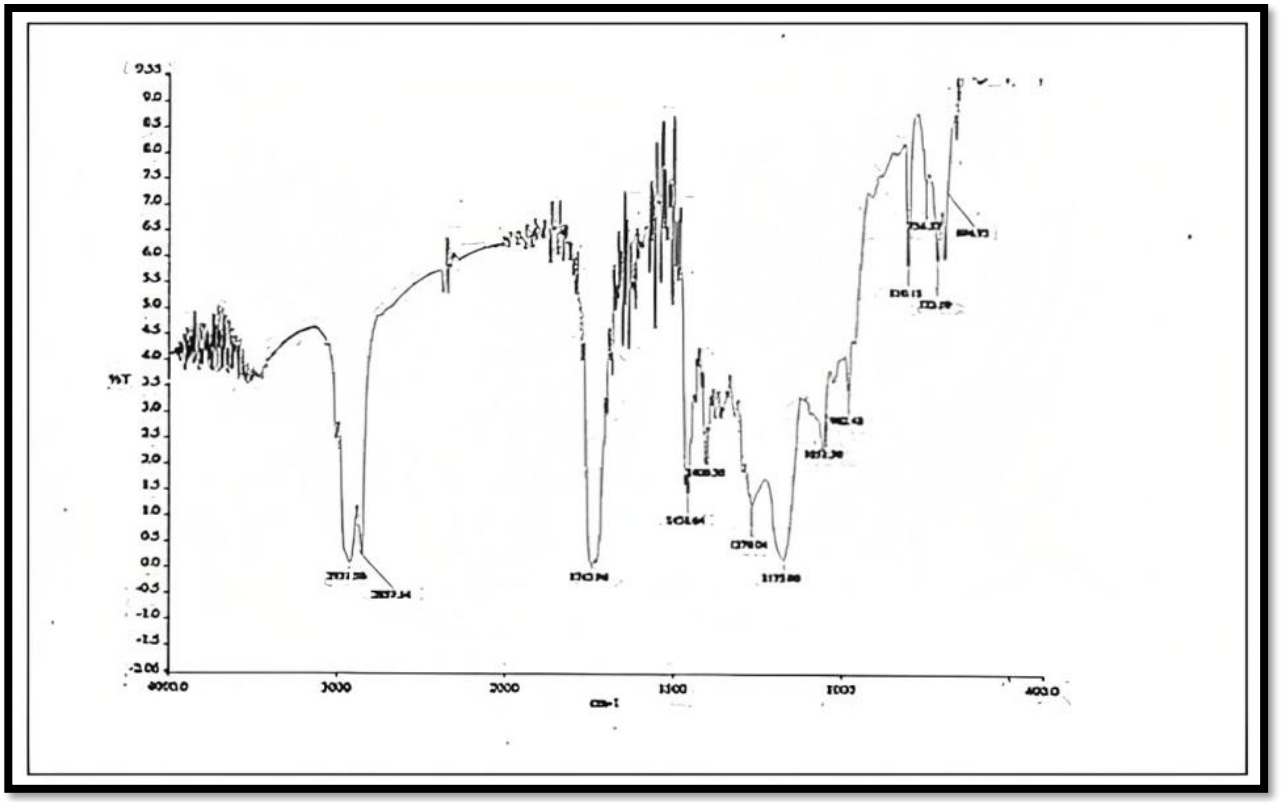


Figure II.A.3. : FT-IR spectroscopic image for the copolymer of Styrene-Castor oil

The ^{1}H NMR spectra analysis revealed specific chemical shift ranges corresponding to different proton groups in the polymers. Protons in the methyl group were observed between 0.88 - 0.90 ppm. Protons in the methylene group were assigned peaks ranging from 1.28 - 1.63 ppm. The methine protons were observed within 2.04 - 2.30 ppm. The proton associated with $-OCH_2$ group appeared at 4.08 ppm. Protons from the $-COOCH_2$ group of castor oil peaks are represented by the peaks in the range of 4.10 - 4.15 ppm. The aromatic ring protons of styrene exhibited a broad peak spanning from 6.80 - 7.64 ppm **(Figure II.A.4.).**

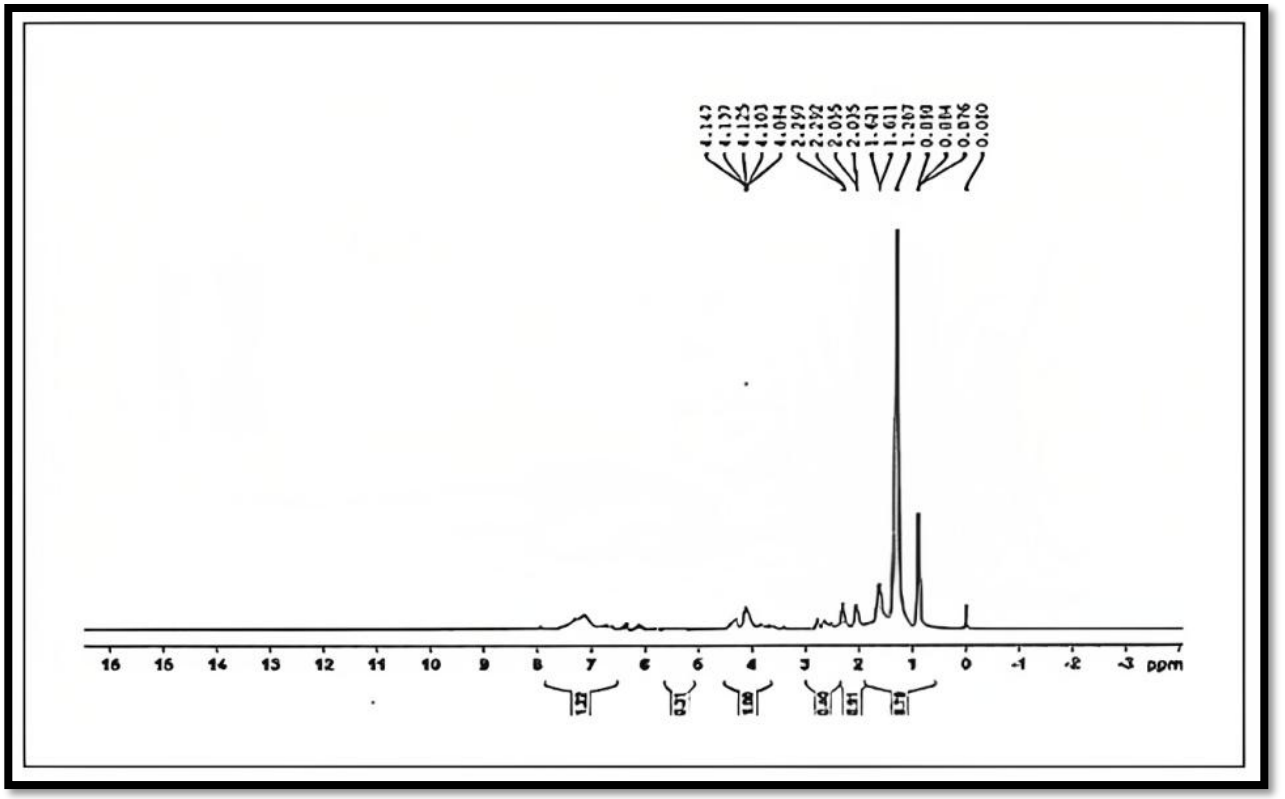


Figure II.A.4. : ^{1}H NMR spectroscopic image for the copolymer of Styrene - Castor oil

In the ^{13}C NMR spectra, different carbon groups in the copolymer exhibited specific chemical shift ranges, allowing for their identification. Carbon atoms in the CH_3 and CH_2 groups appeared within the range of 14.1 - 41.0 ppm. Peaks at 58.1 ppm testify the existence of methine carbons in the -CH- of the -COCH group. Peaks ranging from 60.0 to 62.1 ppm and 64.6 - 68.9 ppm represents carbon atoms in the $-OCH_2$ groups and $-CH_2$ carbons in the $-OCOCH_2-$ group respectively. The peaks in the range of 127.9 - 130.8 ppm and 165.6 - 173.0 ppm represent the aromatic carbons and ester carbonyl carbon **(Figure II.A.5.).**

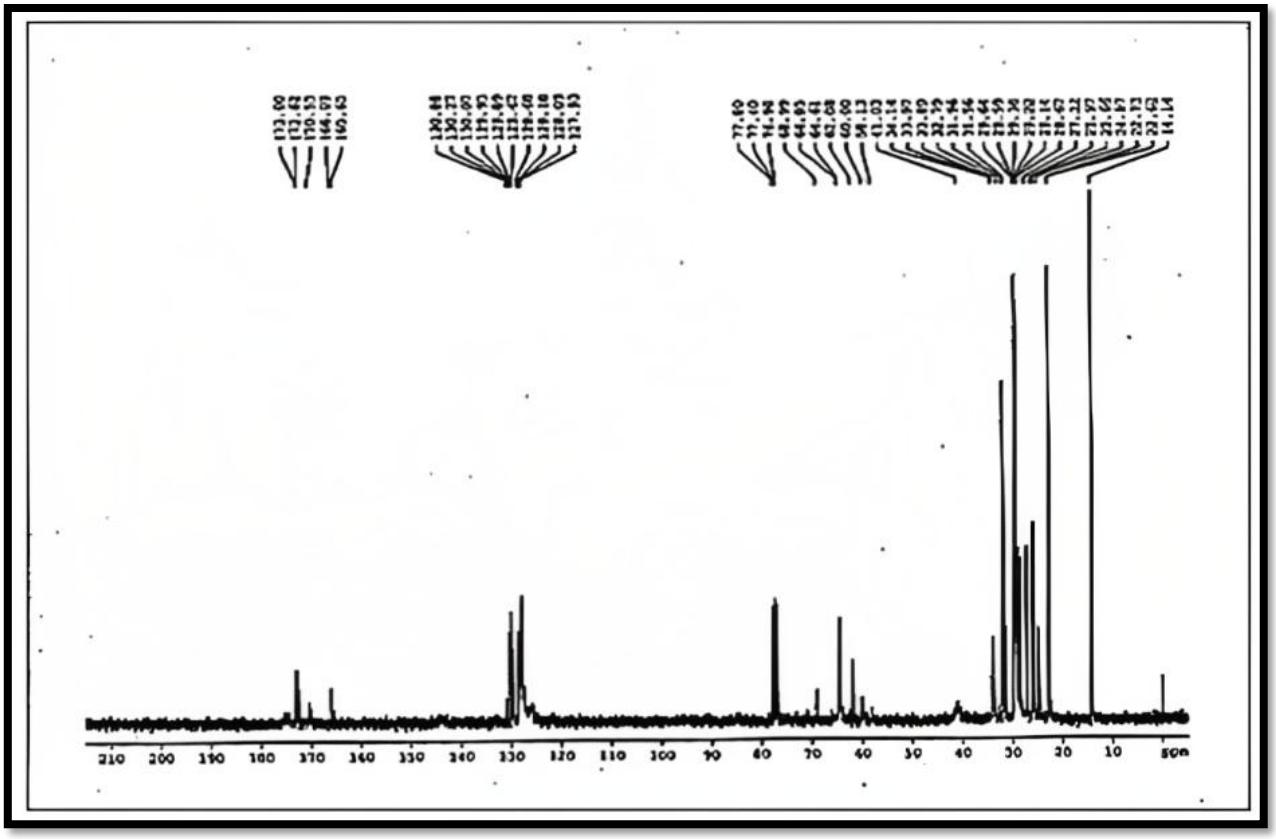


Figure II.A.5. : ^{13}C NMR spectroscopic image for the copolymer of Styrene - Castor oil

The homopolymer of castor oil, showed IR absorption band at 1741 cm^{-1} (**Figure II.A.6.**).

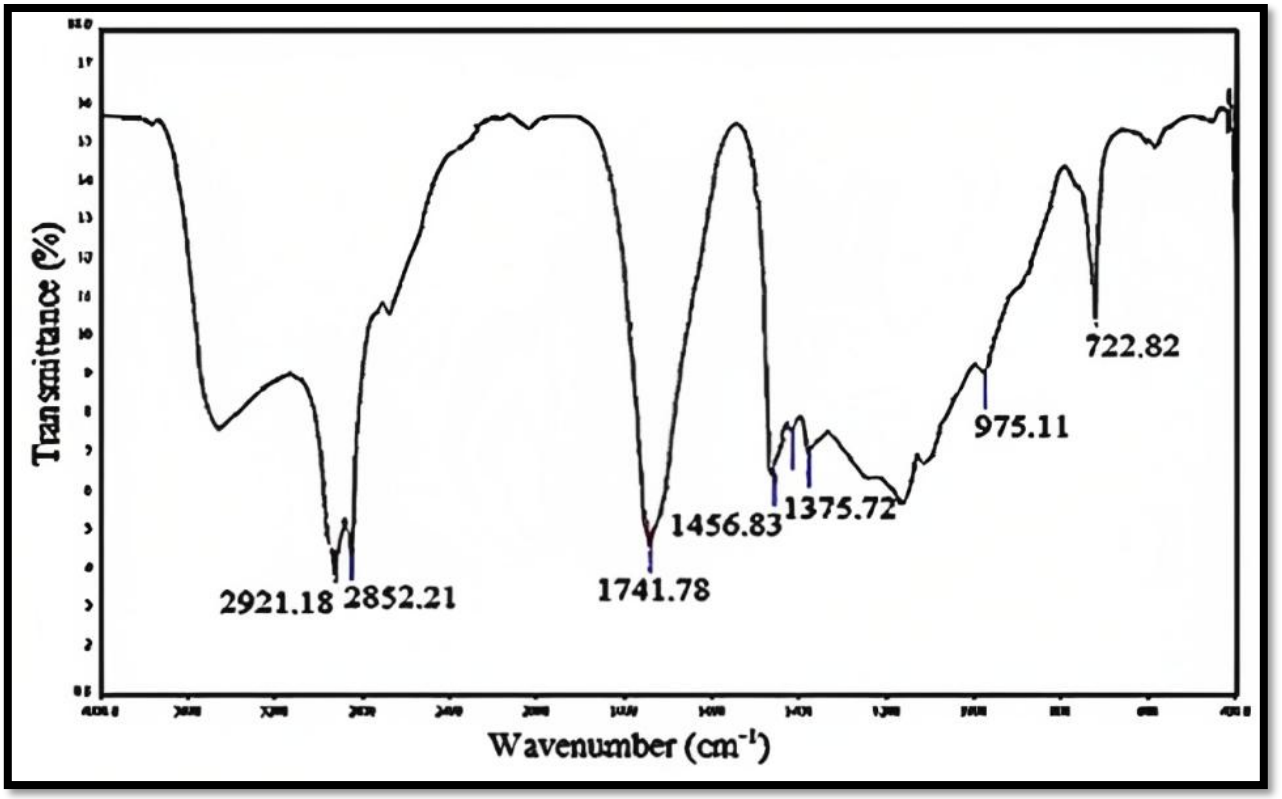


Figure II.A.6. : FT-IR spectroscopic image of the homopolymer of Castor oil

The ^{1}H NMR spectra of castor oil is presented in **Figure II.A.7.**. The peaks observed within 4.1 - 4.3 ppm, 0.8 - 0.9 ppm, 1.2 - 1.6 ppm and 2.2 - 2.3 ppm. **Figure II.A.8.** indicated the presence of protons from the -$COOCH_2$ group in castor oil, methyl protons, the methylene protons and methine protons specific to the alkyl chains.

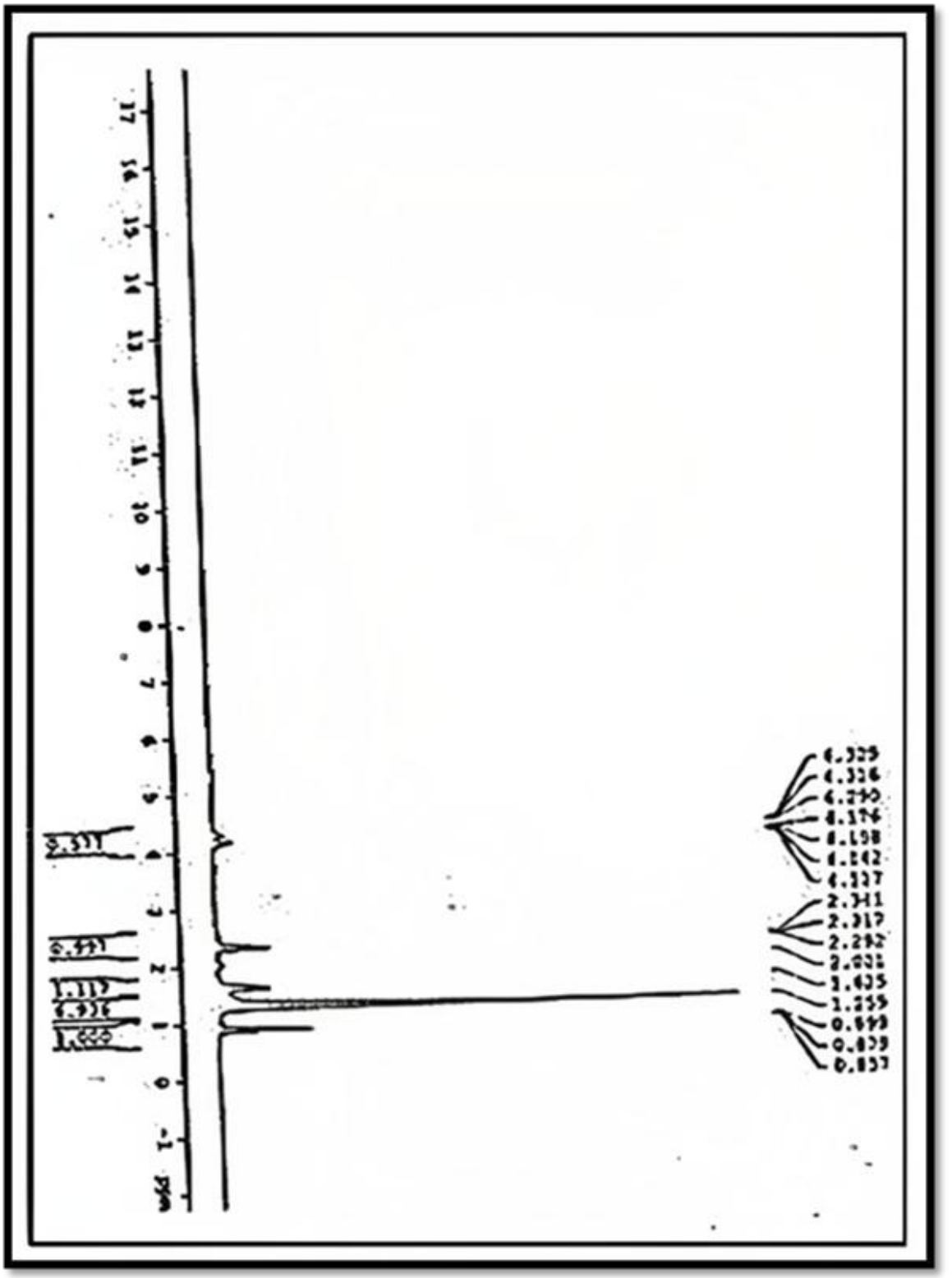


Figure II.A.7. : ^{1}H NMR spectroscopic image of homo polymer of Castor oil

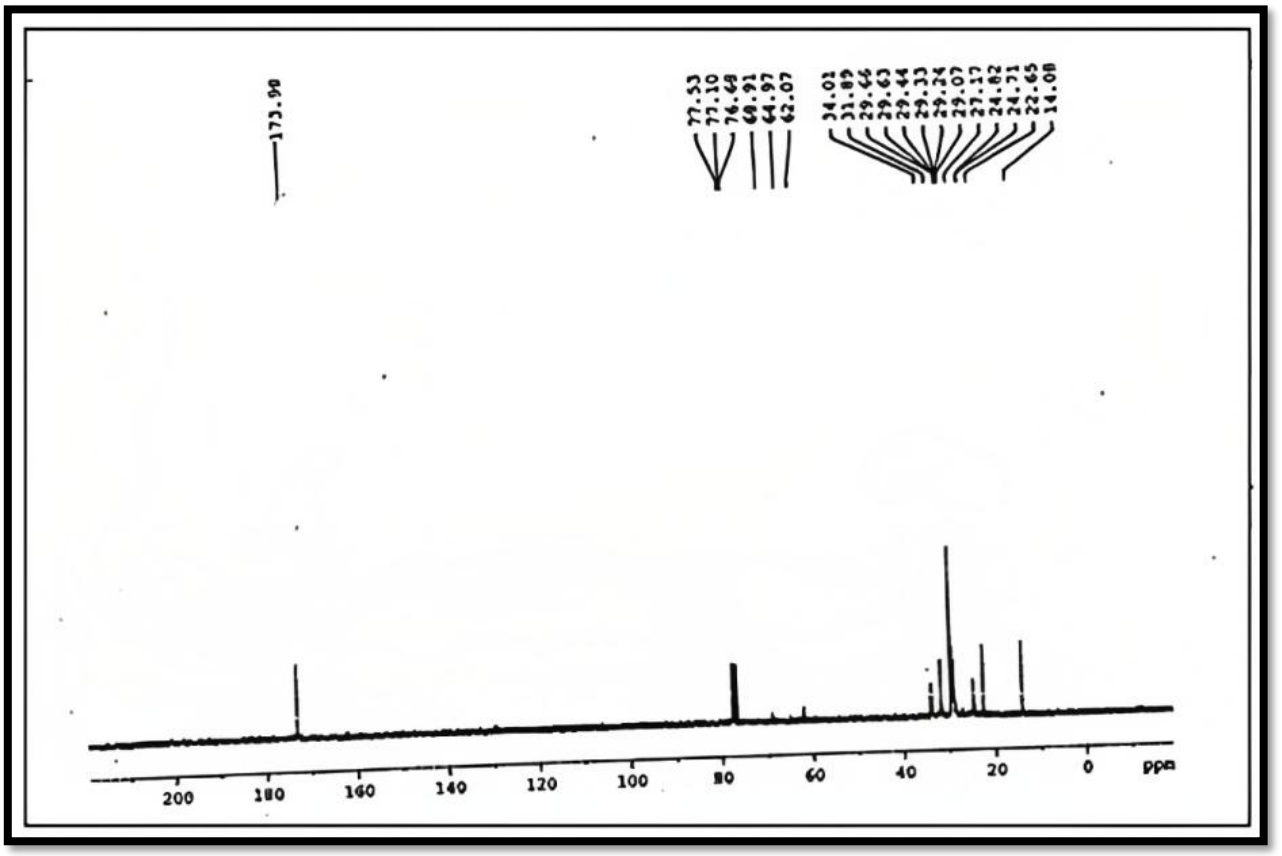


Figure II.A.8. : ^{13}C spectroscopic image of homo polymer of Castor oil

The **Figure II.A.8.** represents the ^{13}C NMR spectra for the homopolymer of castor oil, where peak at 173.9 ppm represents ester carbonyl group and the peaks in the range 62.1 - 68.9 ppm represent the carbons of $–OOCH_2$ group. **Figure II.A.9.** is representing the FT-IR spectroscopic image of the copolymer post biodegradability study.

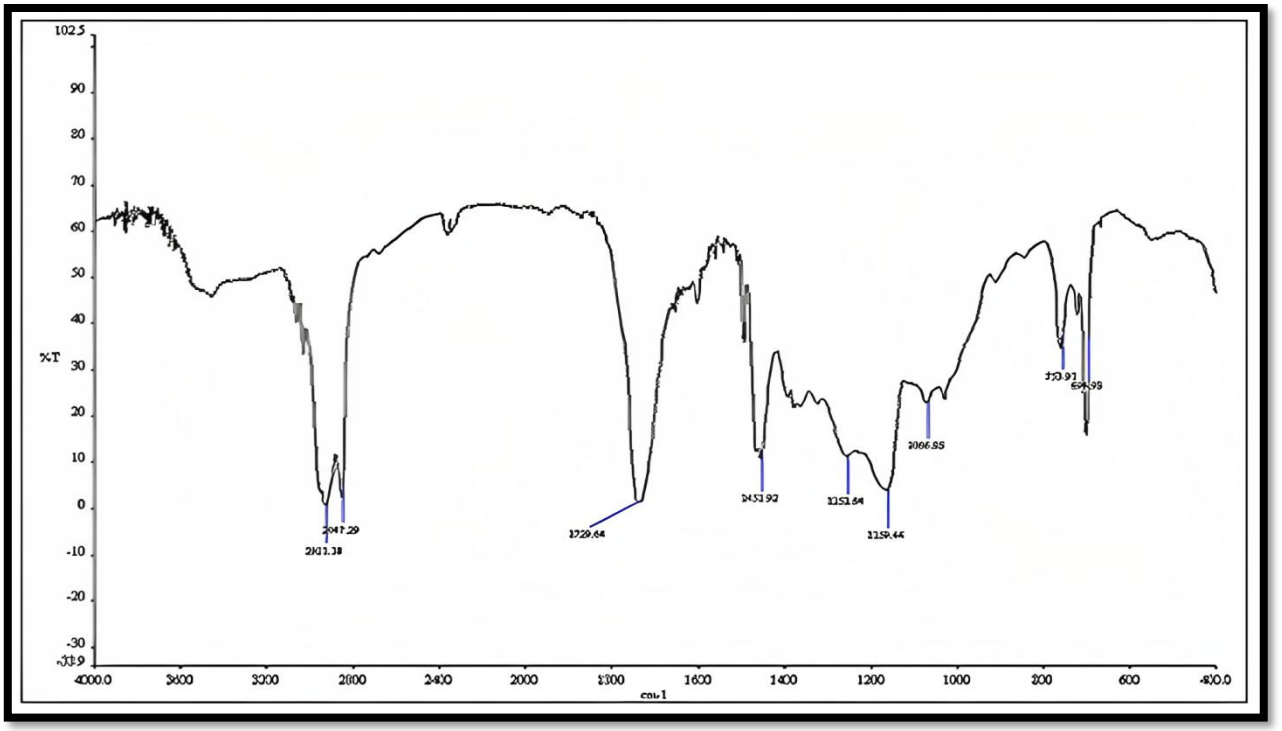


Figure II.A.9. : FT-IR spectroscopic image of the copolymer post biodegradability study

II.A.3.2. Thermo gravimetric analysis (TGA):

Alumina crucible in air was used to measure the thermal stabilities of the synthesized co-polymer and homo polymer using a thermo gravimetric evaluator (Shimadzu TGA-50). A 10 °C/min heating rate was used to operate the system. Calculations were made to determine the samples' percentage weight loss (PWL) as the temperature rose.

Table II.A.1. : Fatty acid components present in castor oil

Fatty acid	Percent composition in castor oil
	Castor Oil
Palmitic(16:0)	3
Stearic(18:0)	3
Oleic acid(18:1)	9
Ricinoleic acid(18:1)	75
Linoleic acid(18:2)	10

Table II.A.2. : Physical properties of base oils

Properties	Method	BO1	BO2
Viscosity at 40 °C in cSt	ASTM D445	7.229	23.472
Viscosity at 100 °C in cSt	ASTM D445	1.874	3.938
Viscosity Index	ASTM D2270	81	86
Pour Point, °C	ASTM D97	-3	-6
Density ($g.cm^{-3}$) at 40 °C	ASTM D4052	0.83689	0.85514

*BO collected from IOCL, Dhakuria, West Bengal

Thermo gravimetric analysis (TGA) study:

The TGA (Thermo gravimetric Analysis) values of the five polymers have been presented in **Table II.A.3.** and **Figure II.A.10.** is representing the Plausible Schematic diagram of Thermo Gravimetric Analysis (TGA) with a number of TGA values. Based on the information provided, several conclusions can be drawn. Polymer P-1 exhibits higher thermal degradation compared to the other polymers, indicating that it is less thermally stable. It begins significant decomposition at 180°C, resulting in approximately 28% weight loss.

For Polymer P-2, major decomposition starting at around 220°C, leading to approximately 25% weight loss. On the other hand, the thermal decomposition of polymers P-5, P-4, and P-3 is nearly similar, with major decomposition initiating at approximately 255°C. Therefore, it can be concluded that the copolymerization process has enhanced the thermal stability of the castor oil-based polymers.

Table II.A.3. Percentage composition and TGA values of the prepared polymers

Polymer code	*% Composition of monomer (w/w) in the feed*		*TGA values*	
	Castor oil	**Styrene**	Decom. Temp	**PWL**
P1	**100**	**0**	180/350	**28/85**
P2	**98**	**2**	220/360	**25/90**
P3	**96**	**4**	245/385	**20/82**
P4	**94**	**6**	260/396	**17/79**
P5	**92**	**8**	270/402	**16/75**

Decom. Temp.= Decomposition temperature, PWL=Percentage Weight Loss

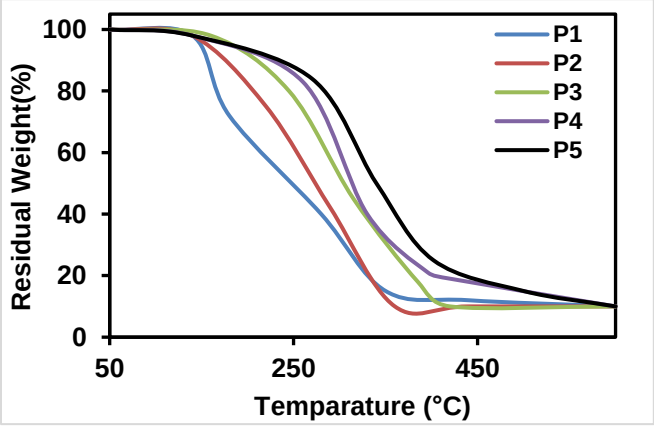


Figure II.A.10. : Plausible Schematic diagram of Thermo Gravimetric Analysis (TGA) values

II.A.3.3. Determination of average molecular weights of the copolymer:

The number average molecular weight (Mn) and weight average molecular weight (Mw) of the polymers were determined using the Gel Permeation Chromatography (GPC) method. The GPC system used was Water 2414, and polystyrene calibration was employed. The measurements were conducted in HPLC grade THF (Tetrahydrofuran) at room temperature, with a flow rate of 1 mL/min.

The experimental data in **Table II.A.4.** presents the weight average molecular weights (Mw) and number average molecular weights (Mn) of the prepared polymers (P-1 to P-5). Among all the polymers, P-5 exhibits the highest molecular weight, indicating a larger average molecular size. Enhancing styrene percentage of the castor oil skeleton, correlates with an increase in molecular weight. This suggests that the proportion of styrene significantly influences the polymerization process. The observed trend highlights the significance of the styrene percentage in determining the resulting molecular weight of the polymers. Therefore, it can be concluded that, the presence and proportion of styrene in the polymer backbone has a crucial impact on the molecular weight characteristics of prepared polymers.

Table II.A.4. Molecular weight of the prepared polymers

Polymer code	Average Molecular weight (before biodegradation)			Average Molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P1	**7911**	**10663**	**1.21**	**4561**	**5023**	**1.11**
P2	**16723**	**24792**	**1.11**	**13221**	**21325**	**1.63**
P3	**18563**	**30768**	**1.26**	**15342**	**26756**	**1.77**
P4	**20279**	**34908**	**1.35**	**16765**	**30289**	**1.79**
P5	**27068**	**40346**	**1.41**	**22390**	**33435**	**1.51**

II.A.3.4. Determination of viscosity index:

To assess the effectiveness of the manufactured polymeric additives as viscosity modifiers, the viscosity index (VI) of the additives in paraffinic base oil (VM) was determined. The VI calculations were performed using the formulae provided by Tanveer and Prasad, following the ASTM D2270 method. VI values were calculated for various concentrations of additives in the base oil, ranging from 1% to 5% (w/w). The experimental VI values are presented in **Table II.A.5.**VI values enhance as the concentration of polymers in the base oil increases. This suggests that higher polymer concentrations have a positive impact on viscosity index. The viscosity of lubricating oil typically represents an inversely proportional relationship with temperature. However, with increasing temperature, polymer molecules expand, resulting in the enlargement of micelles. The increased micelle size hinders the viscosity reduction of the lubricant. When the concentration of polymer in lubricating oil is increased, it results in an augmentation of the

volume of polymer micelles. Consequently, this enhances the viscosity index (VI) property of the lubricating oil. Incorporating styrene in the skeleton of the homopolymer of castor oil leads to an increase in VI values which results in higher crosslink density of the copolymers. Among the copolymers, P-5 demonstrates the maximum impact on VI enhancement, followed by P-4, P-3, P-2, and P-1. Grater VI values observed in P-5 can be attributed to its larger solvated additive molecule (micelle) volume. This characteristic can be linked with greater average molecular weight and lower PDI (Polydispersity Index) value.

Table II.A.5. Viscosity index (VI) values of polymer blended base oil

Polymer code	VI of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

II.A.3.5. Determination of pour point:

The pour points of the lubricants used in the present study was determined (in accordance with ASTM D97 standard) using a Cloud and Pour Point Tester model WIL-471 (India). The instrument can also be used for the measurement of pour point depressant characteristic of base oils with polymeric additives. Additionally, five distinct additive concentrations were applied for every sample in this instance.

Table II.A.6. displays the pour point values of the lubricants obtained by blending the polymers at different concentration levels ranging from 1% to 5% (w/w). All the polymers exhibit effectiveness as pour point depressants (PPD). This means that they are capable of reducing the pour point temperature of the lubricants.The efficiency of the polymers as pour point depressants increases with an increase in the concentration of polymers, up to limit 4% concentration. Beyond this concentration, further increases do not significantly enhance the pour point performance. The effective interaction between the polymer and the paraffinic wax present in the base oil is believed to be responsible for the improved pour point performance. At the optimal concentration (4%), the

polymer effectively interacts with the paraffinic wax, leading to a reduction in the crystal size of the wax [17]. P-4 demonstrates the best efficiency as a pour point depressant. It exhibits superior efficiency in lowering the pour point temperature compared to the other polymers. In summary, the experimental data suggests that all the polymers can be utilized as pour point depressants, till a certain threshold level. Additionally, among the prepared polymers, P-4 stands out as the most effective pour point depressant.

Table II.A.6. Pour point (PPt) values of polymer blended base oil

Polymer code	PPt of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

II.A.3.6. Analysis of Anti Wear Properties:

Table II.A.7. presents the values of wear scar diameter (WSD) obtained through the FBWT (Four Ball Wear Test) apparatus, using a 392 N load, for the lubricant compositions. Blending the polymers with the lubricant leads to a significant improvement in the antiwear performance, as represented by the lower WSD values of the lubricant compositions. This indicates that the addition of polymers enhances the ability of the lubricant to reduce wear between moving metal surfaces.The copolymers exhibit better antiwear performance compared to the homopolymer. This suggests that the presence of multiple monomers in the copolymers contributes to their improved tribological properties. Among the polymers, P-5 at a concentration of 5% demonstrates the highest reduction in WSD values. The lubricant composition with P-5 forms a strong film amid the two moving metal surfaces; effectively reducing wear.The observed improvement in antiwear performance is due to several factors. Firstly, the higher molecular weight of the polymers, especially in the case of P-5, contributes to a greater number of polar side chains from ester carbonyl groups and hydroxyl groups present in rapeseed oil. These polar groups enhance the lubricant's film-forming properties. Additionally, the higher percentage of styrene in the polymer

feed, with its aromatic ring structure, likely plays a substantialpart in enhancing the tribological properties of the lubricant composition.

Table II.A.7. Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition

Polymer code	Anti-wear property in terms of wear scar diameter (WSD in mm) of polymer blended base oil at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P1	1.107	1.045	1.025	1.016	1.009	1.001
P2	1.107	1.039	1.017	1.008	1.005	0.995
P3	1.107	1.034	1.011	1.002	0.994	0.983
P4	1.107	1.028	1.004	0.995	0.988	0.978
P5	1.107	1.022	O.998	0.986	0.981	0.969

II.A.3.7. Photo micrograph and wax modification:

To investigate the impact of an additive on wax crystallization, the wax modification of the base fluid was examined using a Banbros polarizing microscope (BPL-400B, India) equipped with a cooling thermostat. The microscope provided a magnification of 200X, enabling detailed observation of the base fluid. The temperature was controlled at 0°C during the study to ensure consistent conditions for the examination of wax crystallization. By capturing photo micrographic images of the base fluid under these controlled settings, the effectiveness of the additive in controlling wax crystallization could be evaluated.

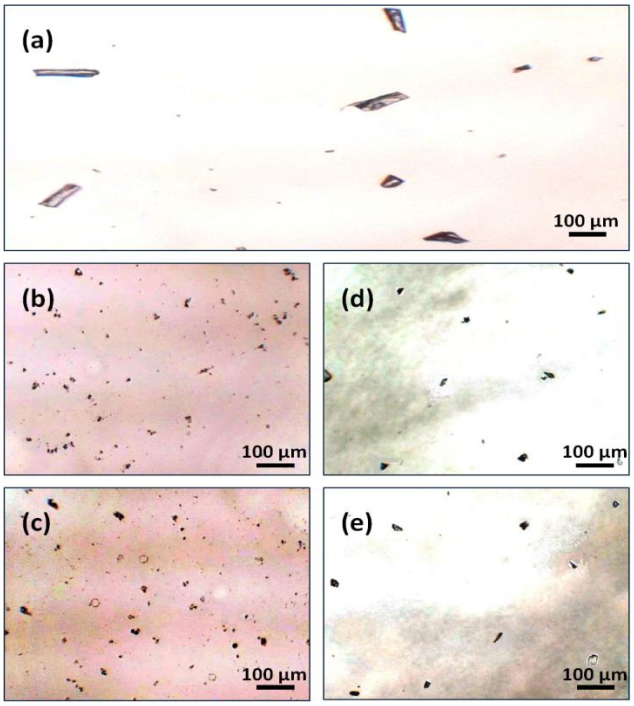


Figure II.A.11. : Photomicrograph of: (a) pure base fluid (b) base fluid + additive P-1 (4%, w/w) (c) base fluid + additive P-3 (4%, w/w) (d) base fluid + additive P-4 (4%, w/w) (e) base fluid + additive P-5 (4%, w/w)

II.A.3.7.1. Analysis of the photo micrographic image:

The photomicrographs of the pure base fluid and the pure base fluid with added additives are presented in **Figure II.A.11.** The photo micrograph **(Figure II.A.11.a)** of the original base fluid (pour point = −6°C, Fig. 8a) reveals the presence of large rod-shaped wax crystals. These crystals contribute to the high pour point of the base fluid. Upon adding additive P-2 (pour point = −24°C, **Figure II.A.11.b) (Figure II.A.11.b)** and additive P-3 (pour point = −25°C, **Figure II.A.11.c) (Figure II.A.11.c)** to the base fluid at a concentration of 4% (w/w), a significant decrease in the volume and shape of the wax crystals is observed. The obtained crystals appear to be more dispersed compared to the original base fluid. Similarly, additive P-4 **(Figure II.A.11.d)** (pour point = −28°C, **(Figure II.A.11.d)**) and additive P-5 (pour point = − 30°C, **Figure II.A.11.e**) **(Figure II.A.11.e)** also result in a substantiallessening in the size of the wax crystals. The crystals appear highly dispersed in the base fluid.

II.A.3.8. Biodegradability analysis:

The extent of biodegradability was assessed using the ISO 846:1997 method for soil burial testing and the disc diffusion method against fungi. After the experiments, weight loss in the polymer samples was evaluated, and IR spectra were collected to look for any noticeable shifts in IR frequencies [18, 19]. With the recovered polymers, further GPC examination was underwent in expectation of changes in Mn and Mw following biodegradation [12].

II.A.3.8.1. Disc diffusion method:

In Petri dishes, culture media for fungi strains were made using the necessary quantity of agar, dextrose and potato extract mixture. Before usage, all the glass equipments underwent autoclaving. The test involved the use of five different fungal pathogens: Curvulariaeragrostidis (CE), Colletotrichum gloeosporioides (CG), Alternaria alternata (AA), Fusarium equiseti (FE) and Colletotrichumcamelliae (CC). The culture media's transformation from yellow to black confirmed the growth of the fungus. One gram of specific polymer samples was placed to Petri dishes, where they were then cultured at 310 K for 30 days. After 30 days, rescued polymer samples were purified, chloroformed - cleaned, and dried in an open tank [18]. Dry sample masses were determined, and then FT-IR and GPC analyses were performed.

II.A.3.8.2. Soil burial degradation test:

The ISO 846:1997 method was used to conduct the soil burial test. We buried polymer films in soil that was dug up from the university campus. In a humidity chamber, a thermostat was used to maintain a temperature of 303 K while adjusting the soil's humidity to between 50% and 60% prior to usage. After 60 days, the films that had been buried were found. Polymer samples were purified, dried, and chloroform washed [20]. After the dried samples were examined, FT-IR and GPC analyses were performed.

II.A.3.8.3. Analysis of Biodegradability Test:

The results of the biodegradability tests, as presented in **Table II.A.8**, indicate significant biodegradability for both the homopolymer (P-1) and copolymers (P-2 to P-5) when exposed to fungal pathogens, specifically Calletotricheme camellia and Alternaria alternata. As expected, the homopolymer of castor oil (P-1) exhibited better biodegradability compared to the copolymers.

Detailed analysis of the experimental data revealed noticeable biodegradation for all the samples.The results obtained from the Sequential Biodegradation (SBD) study indicates a progressively increasing trend for the for the degradation of the polymeric additives with test duration. Moreover, both the homopolymer and copolymers exhibited substantial weight losses when exposed to the fungal pathogens, particularly Alternaria alternata, in the Direct Degradation (DD) test.

As anticipated, the homopolymer (P-1) with zero styrene content and the presence of natural monomer units displayed the highest level of biodegradability among all the additives, as observed in both tests. In the Fourier Transform Infrared (FT-IR) analysis, the peaks corresponding to the polymer P-1 exhibited shifts in their positions and a significant reduction in the height of peak and its intensity after DD test. This confirms biodegradable nature of prepared polymers, as indicated by the changes in the IR peak positions, peak intensities, and the Polymer Weight Loss (PWL) values before and after the biodegradation tests.

Table II.A.8. Result of biodegradability test by the disc diffusion method and soil burial degradation

Sample	Weight loss in disc diffusion method in gm					Weight loss in soil burial degradation method in gm
	Pathogens used					
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.56	0	0.59	0	0	0.55
P-2	0.44	0	0.51	0	0	0.48
P-3	0.35	0	0.46	0	0	0.39
P-4	0.31	0	0.34	0	0	0.33
P-5	0.27	0	0.26	0	0	0.28

CC=Calletotricheme camellia, FE= Fussariumequisitae, AA=Alterneria alternate CG=Colletrichumgleosproides, CE=Curvulariaeragrostidies

II.A.4. Conclusions:

i. Copolymers of castor oil and styrene have higher thermal stability than castor oil alone. Again, when styrene concentration in the copolymers rises, so does thermal stability. However, the shear stability of castor oil homopolymer is higher than that of their styrene copolymers, and shear stability declines as styrene concentrations in the copolymers rises.

ii. The castor oil – styrene copolymer functions as a much better PPD and viscosity modifier than the castor oil homopolymer, according to performance assessment of the additives.

iii. Additionally, research shows that while castor oil homopolymer is significantly biodegradable, but very poor solubility in lube oil and showed low thermal stability and middling performances as a PPD and VM. Contrarily, the castor oil and styrene copolymer demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives.

Indeed, the study mentioned above presents a promising approach for formulating a novel lubricant composition with enhanced flexible additive properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD). This approach can contribute to the development of environmentally friendly lubricants that offer enhanced performance and functional capabilities, making them an attractive option for various applications.

II.A.5. References:

References are displayed in **BIBLIOGRAPHY** under **Chapter II, Section A,** that is, **"Synthesis and Performance Evaluation of Castor oil – Styrene Co - polymer: an Outstanding Multipurpose Directional Lubricant Additive"** (pp. 235-237**).**

Section – B

Evaluation and Synthesis of Environmentally Benign multifunctional additives for lube oil

II.B.1. Introduction:

Lubricants consist of a combination of a base fluid and additives designed to enhance performance. The additive content typically ranges from 1% to 30% or even higher. While mineral oils of petroleum origin are commonly used as base fluids, vegetable and synthetic oils also find application. Polymeric additives are introduced to the base fluid to improve the operational efficiency of engine oil and extend the engine's lifespan.

Additives typically serve various functions, such as ameliorating the pour point (PP) [1] of base oils through the dissolution of wax crystal deposits [2] at lower temperatures, boosting the viscosity index (VI) [3] to maintain viscosity stability amidst temperature fluctuations, minimizing wear, and effectively transporting contaminants away. These components are commonly labeled as viscosity index improvers (VII) [5], pour point depressants (PPD) [4], detergent-dispersants [7] and antiwear agents [6].

Commercially available synthetic acrylate-based additives, although effective, are non-biodegradable, prompting environmental concerns. The increasing desire for environmentally friendly technology has spurred researchers to create lubricant additives that are ecologically benign.Vegetable oils [8-11], recognized for their natural occurrence, biodegradability, non-toxicity, and high viscosity index, present a promising alternative [12]. They exhibit excellent tribological properties, acting as antiwear and friction modifiers in lubricant formulations [13, 14].

Modified vegetable oils have been utilized as additives in lubricating oils in numerous cases, with patents describing their application as extreme pressure additives, friction modifiers, and viscosity index improvers [15-17]. In line with these considerations and as part of our ongoing efforts to develop chemical additives for lubricating oil, our present investigation focuses on synthesizing copolymers of acrylate ester based citral through copolymerization. The aim is achieving an optimal balance between performance and environmentally friendly chemistry. The study encompasses the synthesis and characterization of behenyl acrylate (BA) homopolymer and BA copolymer with citral, followed by biodegradability testing and evaluation of their effectiveness as pour point depressants, viscosity modifiers, and antiwear additives.

II.B.2. Material and methods:

1. Materials:

Hydroquinone, sulfuric acid and Toluene, were sourced from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilized with 0.02% Hydroquinone monomethylether), Behenyl alcohol and n-Hexane were procured from SRL Pvt. Ltd. Methanol and Benzoyl Peroxide (BZP) were obtained from Thomas Baker (Chemicals) Pvt. Ltd. and LOBA chemicals respectively. They underwent recrystallization using a $CHCl_3$-MeOH mixture before application. Citral was sourced from a nearby grocery store, and the base oils were acquired from IOCL (Indian Oil Corporation Ltd.), Kolkata, India. Remaining substances were utilized in their pristine condition without extra purification. All specimens were subjected to testing before reaching their designated expiration dates.

2. Methods:

The thermal radical polymerization of behenyl acrylate and its subsequent copolymerization with citral at varying concentrations (5%, 10%, and 15% w/w) were carried out employing benzoyl peroxide (BZP) as the initiator. The resulting additives were subjected to thorough characterization using spectral analysis techniques, including Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The determination of the average molecular weight of the polymeric additives, both number average (Mn) and weight average (Mw), was accomplished using gel permeation chromatography (GPC). Tetrahydrofuran (THF) of high-performance liquid chromatography (HPLC) grade served as the mobile phase in the water GPC system, calibrated with polystyrene, and the analysis was conducted at 40°C.

The thermal stability of the additives was evaluated using the Mettler TA-3000 system, employing a heating rate of 10 K min^{-1}. The multifunctional performance of the base oil treated with additives, encompassing improvements in viscosity index, pour point depression, and antiwear properties, was assessed in accordance with ASTM methods. The antiwear (AW) characteristics were determined utilizing a Four-ball wear test apparatus, following the ASTM D 4172-94 method [18], with a weld load of 392 N at 75°C for 30 minutes and a rotational speed of 1200 rpm.

The biodegradability of the polymeric additives underwent testing through the disc diffusion method [19], evaluating their effectiveness against fungal pathogens, and the soil burial test as per

ISO 846:1997 [20, 21]. Microbial degradation was confirmed by measuring the shift in the infrared (IR) frequency of the ester carbonyl after the biodegradability test.

II.B.3. Results and discussion:

1. Spectroscopic description:

In FT-IR spectrum, homopolymer of behenyl acrylate (P-1) **(Figure II.B.1.)** demonstrated an absorption peak at 1732 cm^{-1}, corresponding to ester carbonyl, attached with distinctive peaks at 1467, 1271, 1190, and 1060 cm^{-1}. The ^{1}H NMR spectra of homopolymer of behenyl acrylate **(Figure II.B.2.)**, revealed a broad singlet centered at 4.02 ppm, associated with the $–OCH_2$ protons. Methyl protons from the behenyl chain were evident between 0.81 ppm and 0.86 ppm, and the lack of a singlet in the 5-6 ppm range indicated the absence of vinylic protons in the polymer. The ^{13}C NMR spectrum of P-1 **(Figure II.B.3.)**, disclosed the carbonyl carbon at 174.4 ppm, along with other SP^3 carbons ranging from 65.03 to 10.66 ppm.

In FT-IR spectrum of the copolymers **(Figure I.B.4.)**, the ester carbonyl peak appeared at 1731 cm^{-1}, containing a peak at 1738 cm^{-1} corresponding to the citral's aldehydic group. The ^{1}H NMR of copolymers **(Figure I.B.5.)** exhibited a multiplet in the span of 4.119-4.402 ppm, indicating $–OCH_2$ protons. SP^3 protons were observed within 1.259-1.989 ppm, while peaks at 5.343 ppm and 5.360 ppm were attributed to ethylenic unsaturation from citral portion of copolymer. One peak around 10 ppm indicated presence of the aldehydic hydrogen of citral in that copolymer. In ^{13}C NMR of the copolymer **(Figure I.B.6.)**, peaks within 167.70 - 173.36 ppm indicated the ester carbonyl carbon. Peaks at 190.81 ppm were due to the aldehydic carbonyl group of citral. The $–OCH_2$ carbon peak appeared at 68.93 ppm. Peaks within 14.09-34.05 ppm represented all SP^3 carbons of the copolymer.

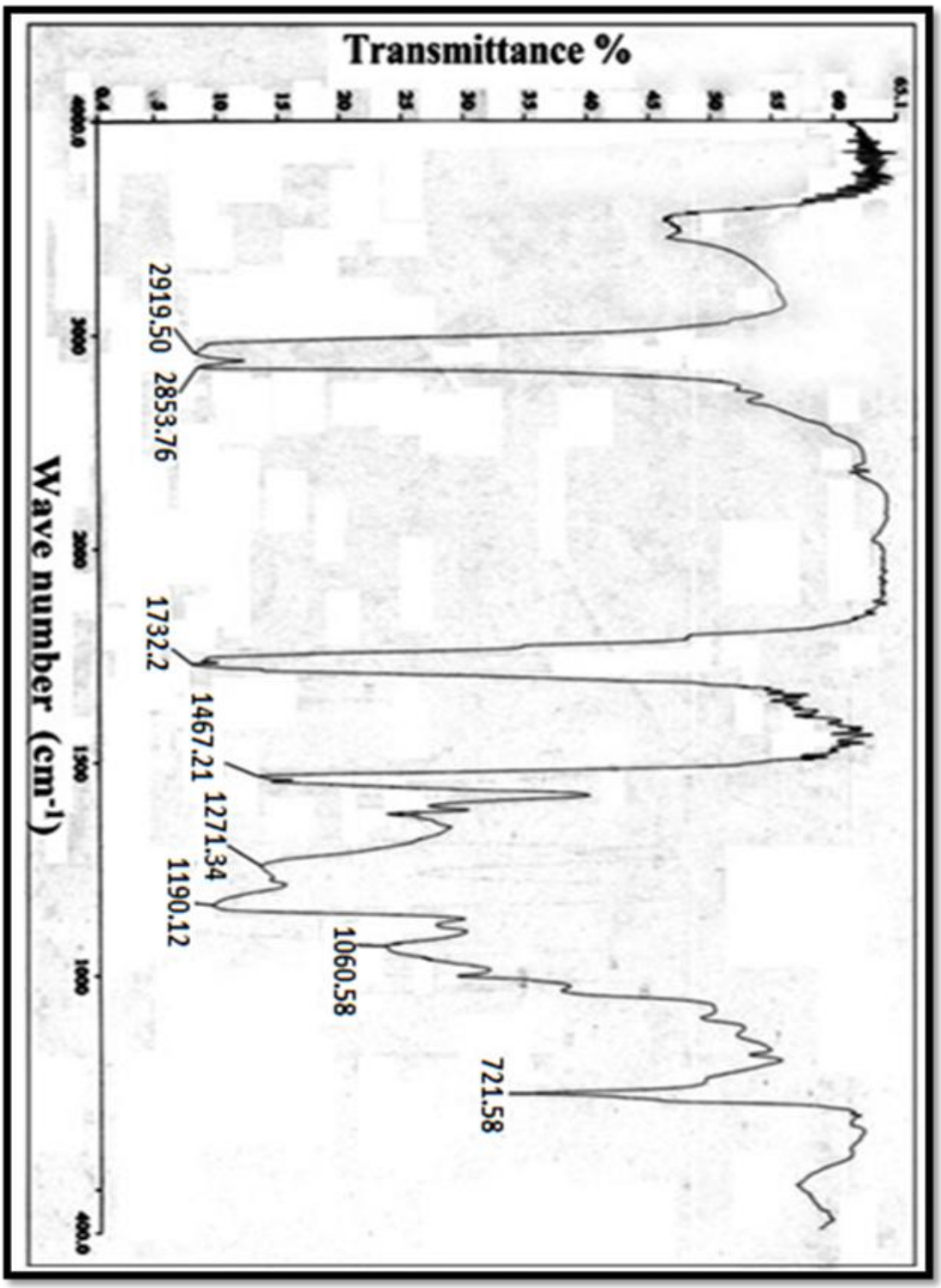


Figure II.B.1. : FT-IR spectra of homo poly Behenyl Acrylate

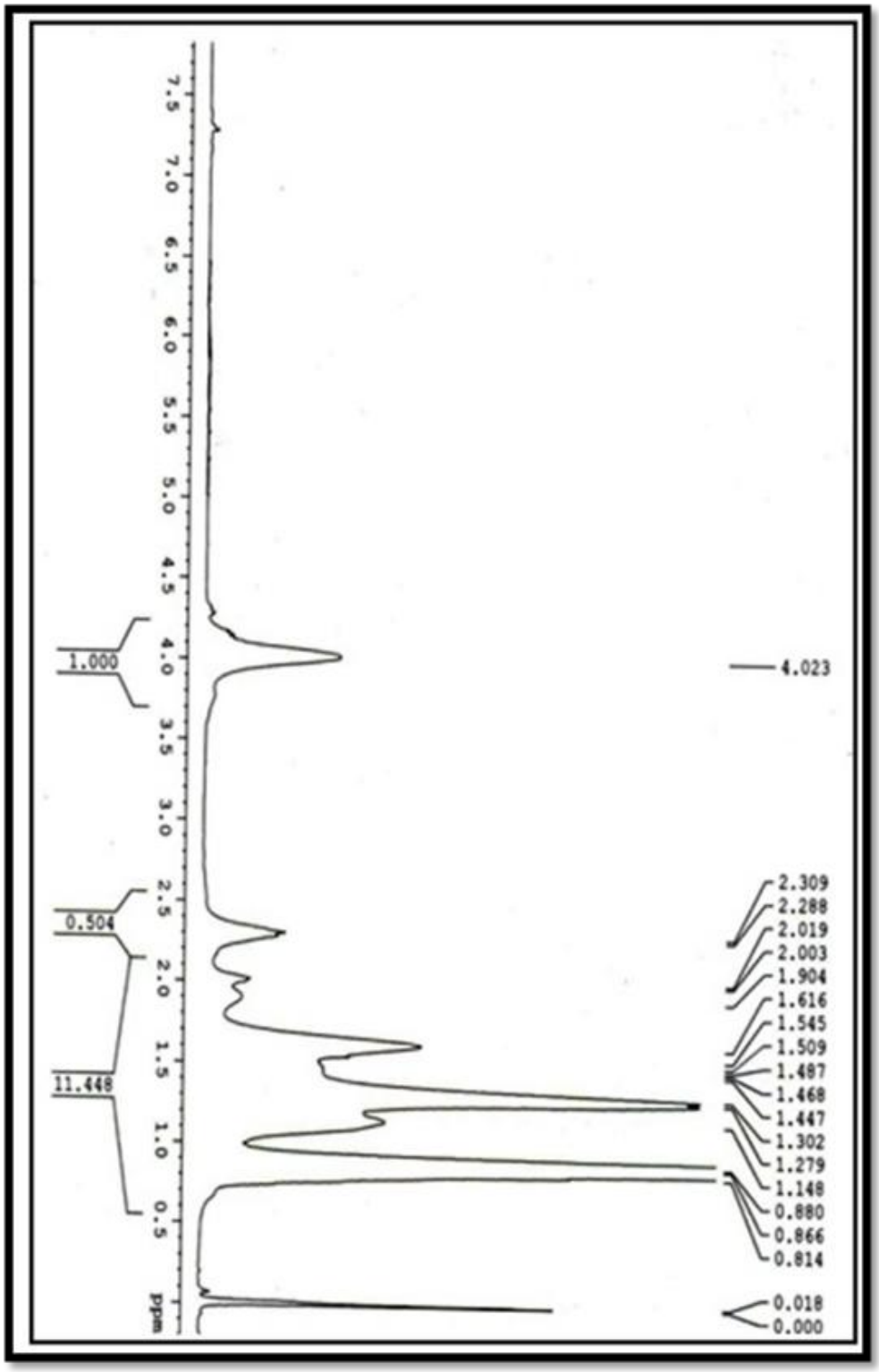


Figure II.B.2. : ^{1}H NMR spectra of homo poly Behenyl Acrylate

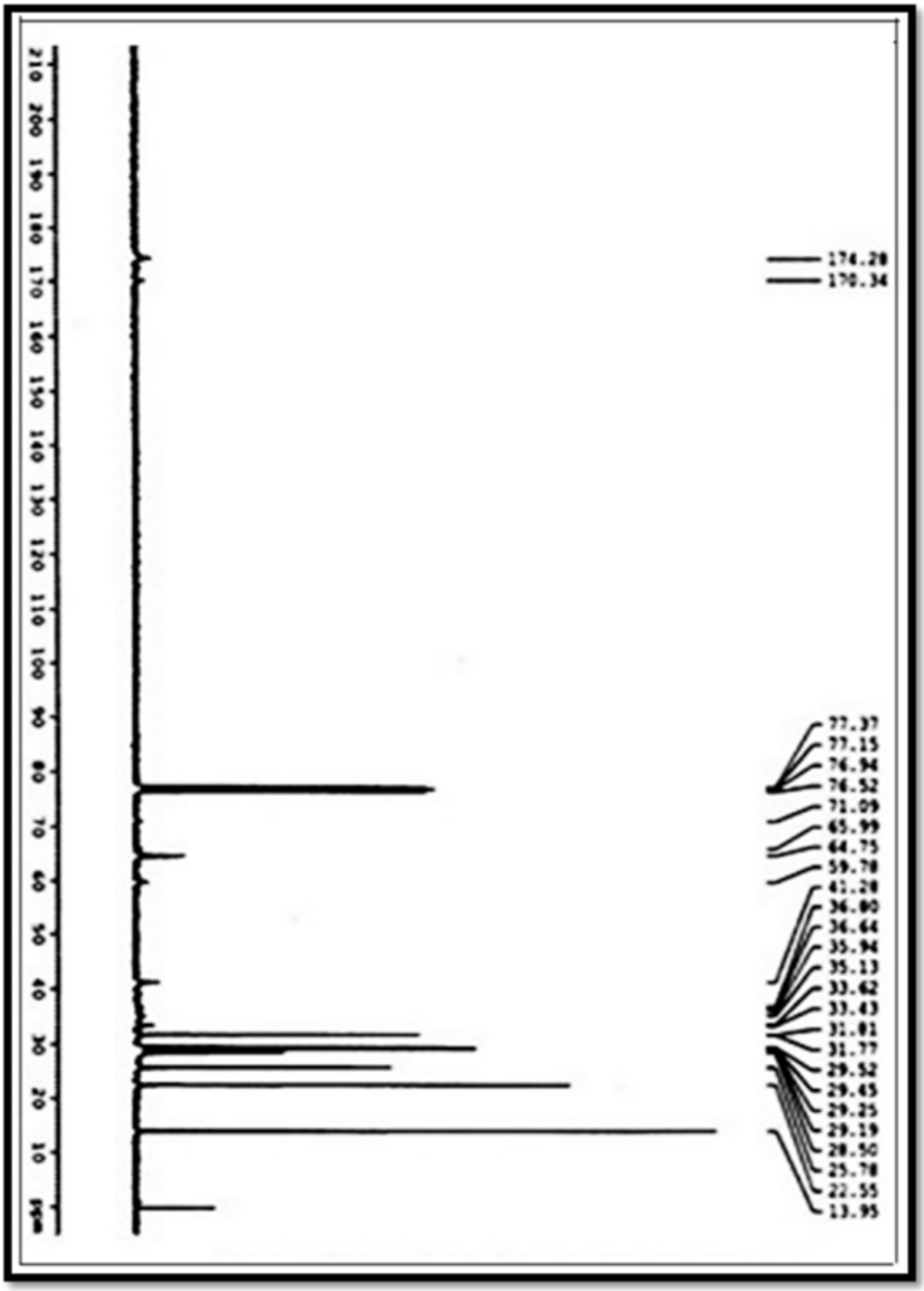


Figure II.B.3. : ^{13}C NMR spectra of homo poly Behenyl Acrylate

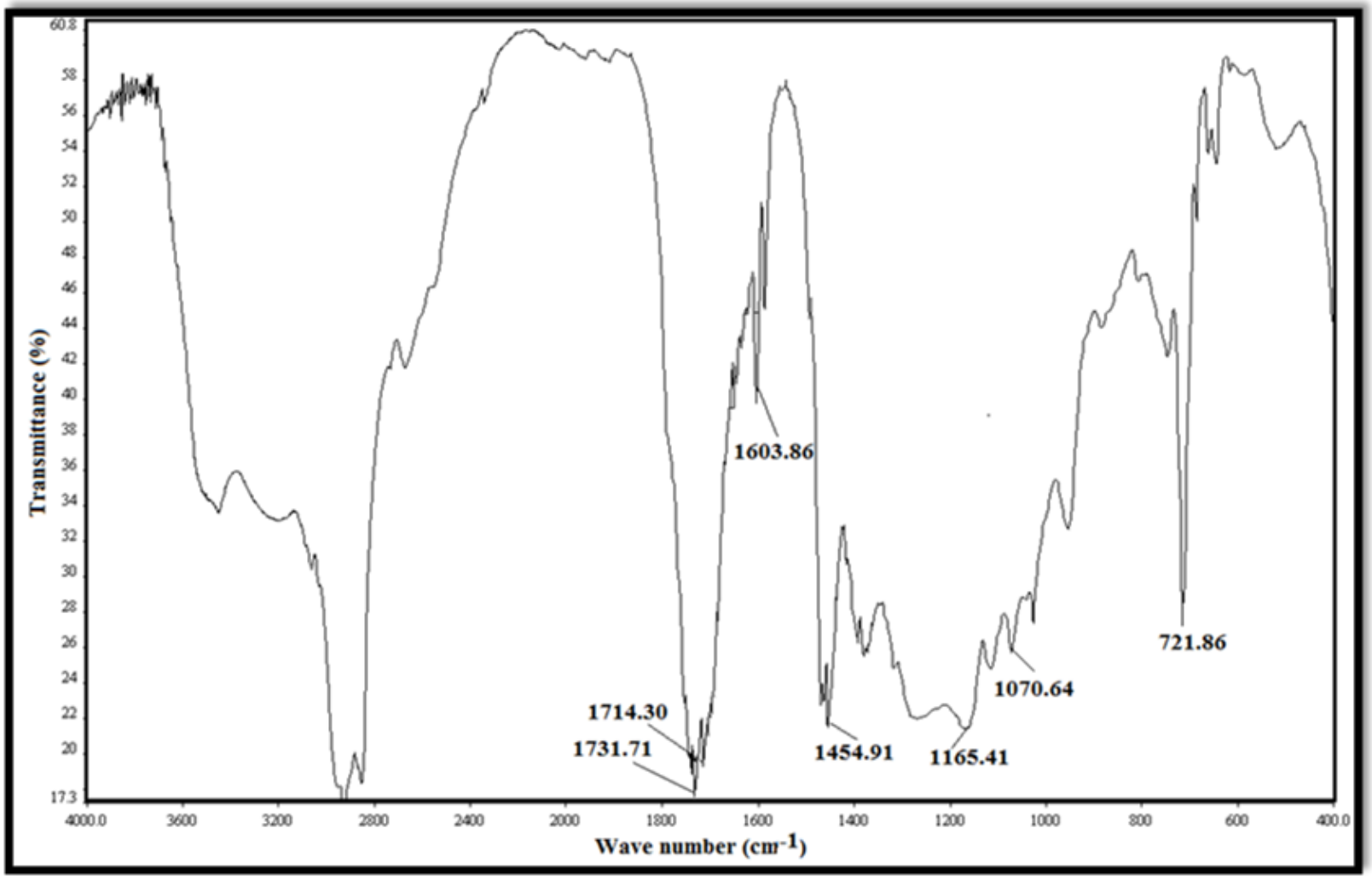


Figure II.B.4. : FT-IR spectra of copolymer of Behenyl Acrylate with citral

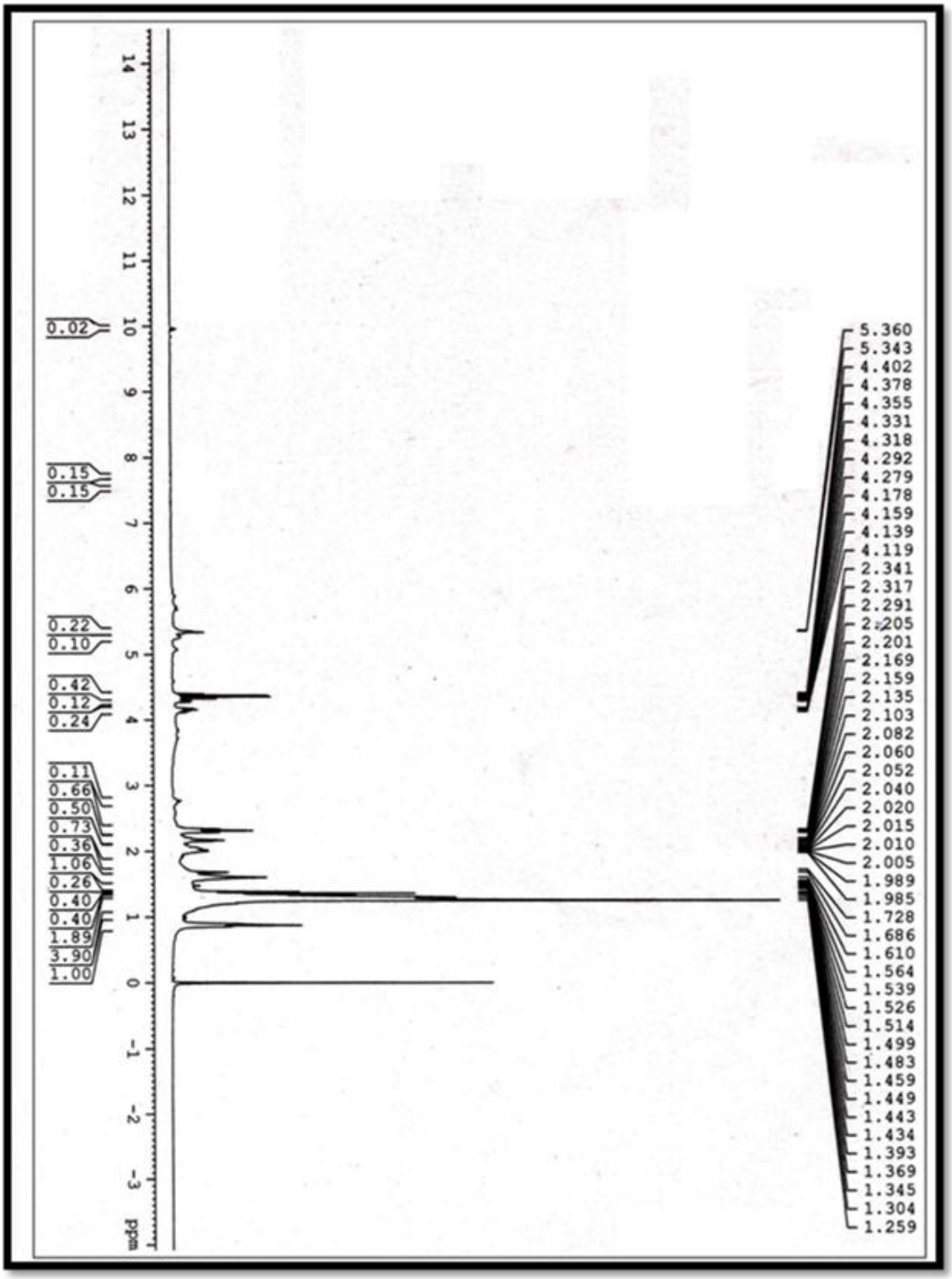


Figure II.B.5. : ^{1}H NMR spectra of copolymer of Behenyl Acrylate with citral

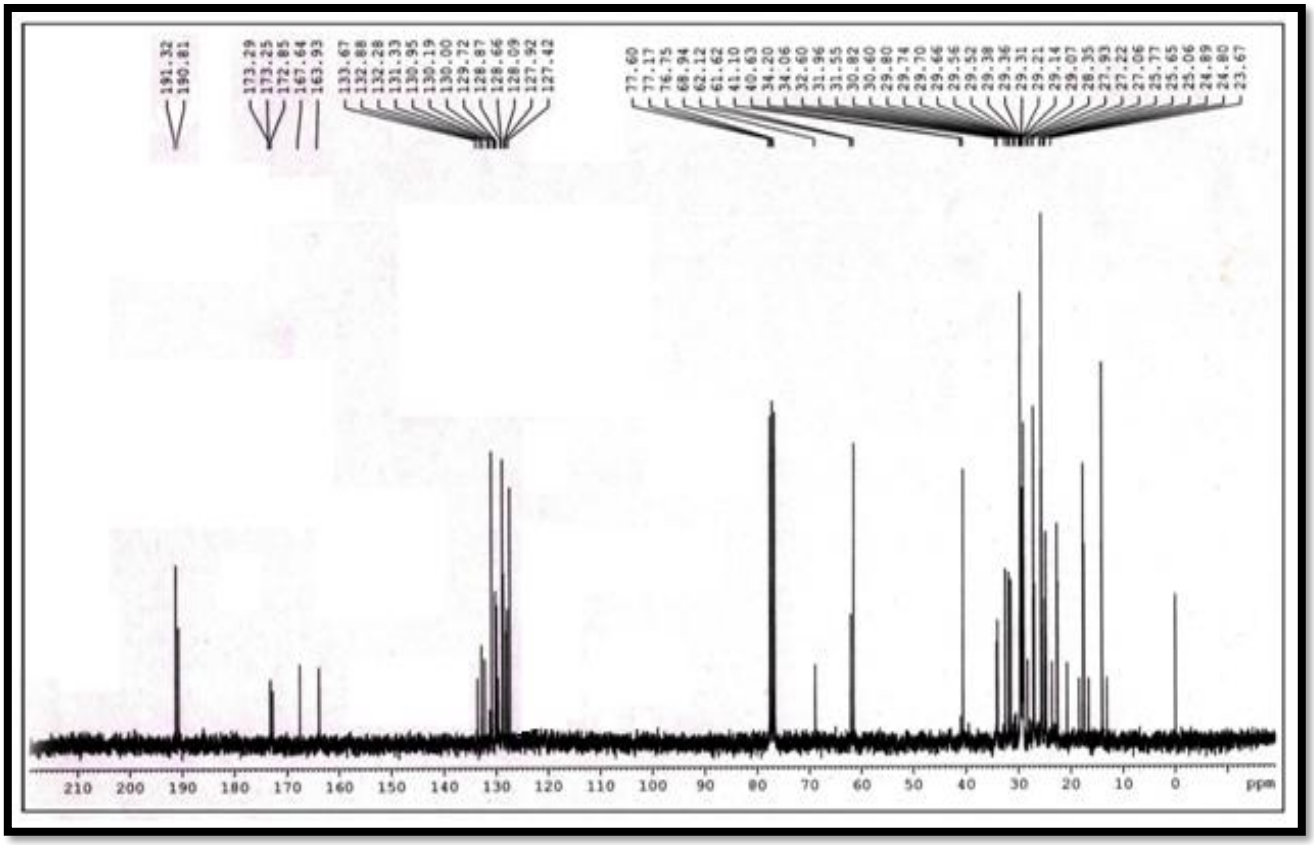


Figure II.B.6. : ^{13}C NMR spectra of copolymer of Behenyl Acrylate with citral

II.B.4. Performance of the prepared additives in the form of pour point depressant:

The results of samples' pour point depressants (PPDs), covering a range of additive concentrations within 1 wt% to 5 wt%, are outlined in **Table II.B.1.** The data vividly demonstrates the efficacy of the prepared additives as pour point depressants, showcasing a consistent reduction in pour point with increasing additive concentration. Notably, the pour point magnitudes of copolymers (P-2, P-3, and P-4) exhibit a remarkable similarity and consistently register lower values compared to the homopolymer (P-1). Consequently, all copolymers demonstrate exceptional pour point depressant properties.

Table II.B.1: Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

PPD in BO1 Concentration of additives, % in w/w								PPD in BO2 Concentration of additives, % in w/w					
Sample	0	1	2	3	4	5		0	1	2	3	4	5
P-1	-3	-12	-15	-15	-15	-13		-6	-12	-15	-16	-16	-14
P-2	-3	-12	-18	-21	-24	-28		-6	-15	-17	-25	-28	-28
P-3	-3	-12	-17	-24	-27	-30		-6	-18	-21	-27	-30	-32
P-4	-3	-11	-15	-22	-26	-28		-6	-16	-21	-27	-29	-30

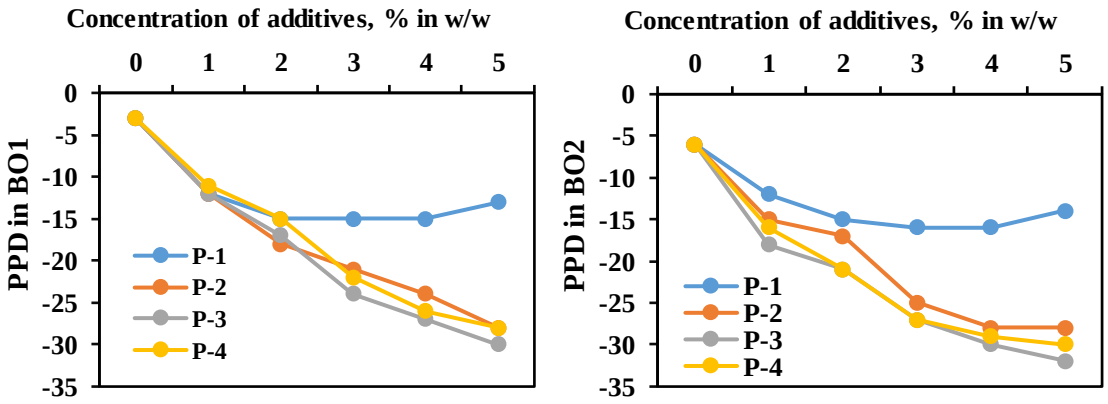


Figure II.B.7. : Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

The efficacy of the polymers as potent pour point depressants was evaluated through photomicrographic experimentation. The wax crystal size exhibited a notable reduction, transitioning from a large crystal structure in the base oil to very small dots dispersed in the oil phase of the lubricating oil [22]. **Figure II.B.7.** is representing diagrammatically, the Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration.

Figure II.B.8. represents Photomicrographic images of more crystallized base oil at the left side and multifunctinal additive (P-1, P-2, P-3 and P-4) Doped base oil at the right side.

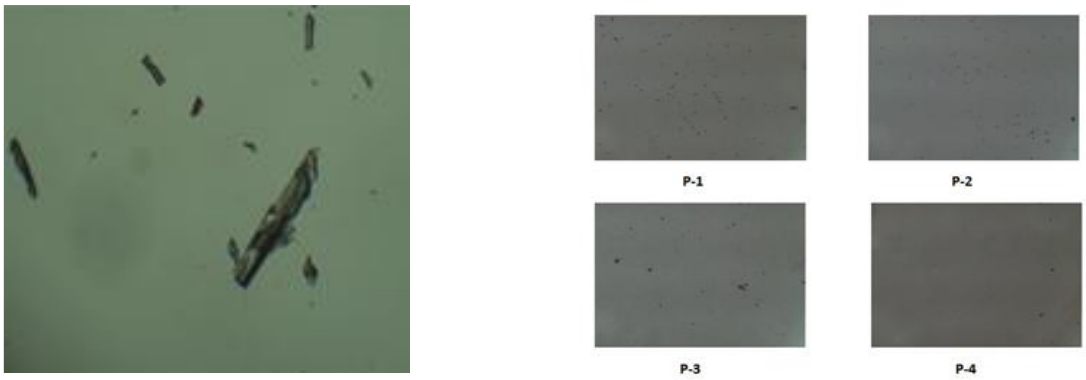


Figure II.B.8. : Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) Doped base oil (right side)

II.B.5. Performance of the prepared additives as viscosity index improver (VII):

Table II.B.2. presents the viscosity indexes for base oils treated with additives derived from polymers (P-1, P-2, P-3, and P-4). The data reveals a steady increase in VI magnitudes as the polymer concentration rises in both base oil types (BO1 and BO2), reaching a peak at 4%. The elevated polymer concentration corresponds to an increased volume of polymer micelles within the oil solutions. Consequently, a higher concentration of the polymer contributes to a higher VI, in contrast to a lower concentration of the same polymer. The VIs corresponding to additive-doped base oils are summarized in **Table II.B.2.** and diagrammatically represented in **Figure II.B.9.**

Table II.B.2. VIs corresponding to additive-doped base oils

	VI in BO1 Concentration of additives, % in w/w							**VI in BO2 Concentration of additives, % in w/w**					
Sample	0	1	2	3	4	5		0	1	2	3	4	5
P-1	80	110	112	114	118	121		89	109	112	119	121	122
P-2	80	113	116	119	119	127		89	114	118	121	122	122
P-3	80	121	126	131	135	141		89	115	126	129	133	137
P-4	80	119	121	123	127	134		89	116	122	122	124	128

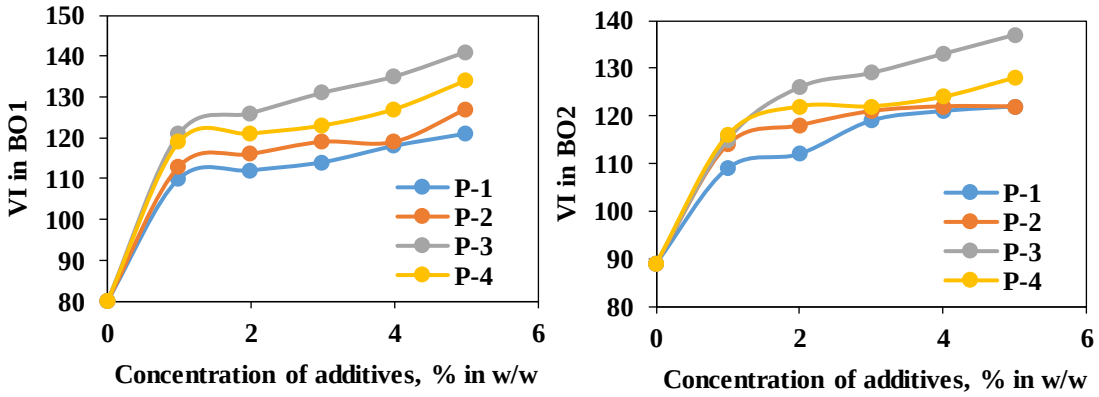


Figure II.B.9. : The VIs corresponding to additive-doped base oils

II.B.6. Performance of the prepared additives as antiwear additive:

A reduction in wear scar diameter (WSD in mm) was observed with increasing additive concentration in the case of studied base stocks with varying load conditions. The most distinct drop was observed at 20 kg load condition, as illustrated in **Figures II.B.10.** This suggests that the additives exhibited comparatively lesser effectiveness at higher load conditions. However, there was no noteworthy enhancement in the performance beyond a 5% additive concentration.

It was observed that the studied copolymers exhibited superior antiwear properties compared to the homopolymer (P-1). The presence of aldehydic functionality and ester functionality can be attributed to such observation [23, 24]. As a result, copolymer (P-4), with larger fraction of citral units, demonstrated enhanced antiwear performance **(Table II.B.3.)**.

Table II.B.3. : Antiwear values in terms of WSD in mm, of polymers P-1, P-2, P-3 and P-4 in the base oils (BO1 and BO2) at 40 kg load

	WSD in mm in BO1 Concentration of the additives, % in w/w						**WSD in mm in BO2 Concentration of the additives, % in w/w**					
Sample	0	1	2	3	4	5	0	1	2	3	4	5
P-1	1.067	0.991	0.887	0.718	0.713	0.665	1.110	0.984	0.907	0.865	0.844	0.823
P-2	1.067	0.954	0.861	0.711	0.688	0.645	1.110	0.971	0.891	0.843	0.821	0.812
P-3	1.067	0.901	0.813	0.703	0.641	0.633	1.110	0.898	0.822	0.804	0.791	0.776
P-4	1.067	0.903	0.811	0.710	0.632	0.635	1.110	0.846	0.798	0.806	0.793	0.781

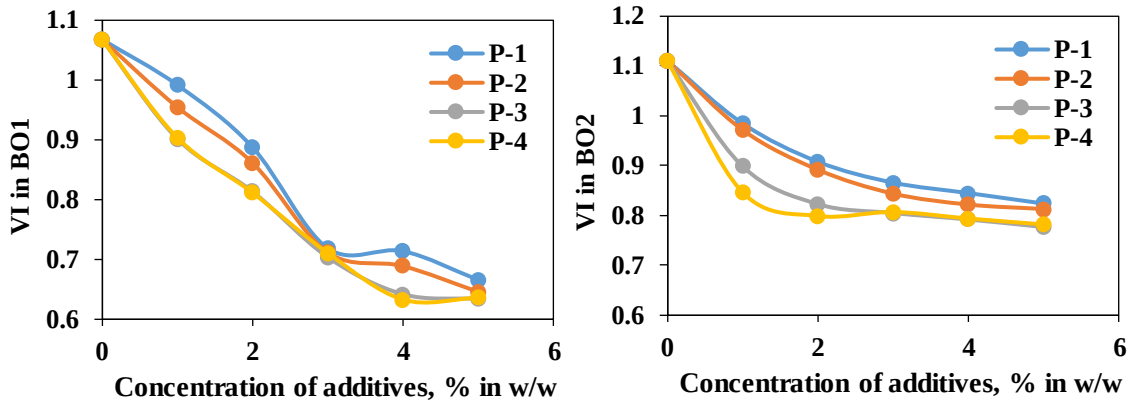


Figure II.B.10. : Antiwear values of polymers P-1, P-2, P-3 and P-4 in the base oils (BO1 and BO2) at 20 to 40 kg load

II.B.7. Analysis of biodegradability test result:

The biodegradability test results obtained from disc diffusion method and soil burial test **(Table II.B.4)** indicates notable biodegradability for fungal pathogen Alternaria alternata, compared to the homopolymers. This observation was substantiated by the shift in the IR frequency of the ester carbonyl. As anticipated, the copolymer exhibited superior biodegradability in comparison to the homopolymer. **(Figure II.B.11.).**

Table II.B.4 Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives:

	Disc diffusion method	***Soil burial test***
Polymers	***Alternaria alternata*** **Wt. loss(%)**	**Microorganism** **Wt. loss(%)**
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

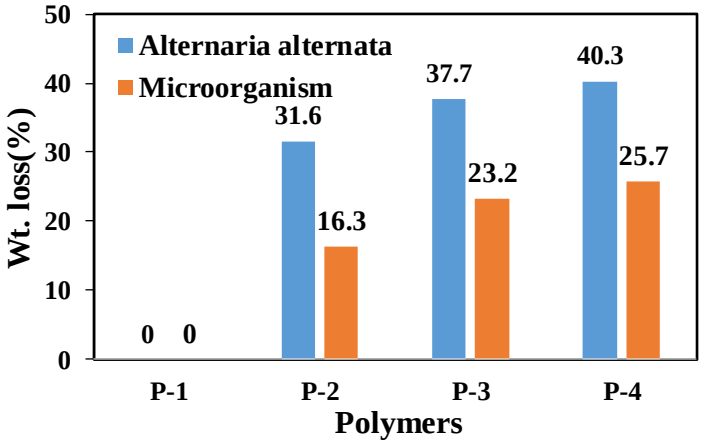


Figure II.B.11. : Biodegradability test by disc diffusion method and soil burial test for polymeric additives

II.B.8. Determination of Molecular weight of the polymers:

Table II.B.5. represents the number average and weight average molecular weight values along with their poly dispersity index (PDI) values. **Figure II.B.12.** depicts the diagrammatic representation of overall PDI values.

Table II.B.5: Molecular weight characteristics of the polymers

Polymer sample	M_W	M_n	*PDI*
P-1	33789	38412	1.14
P-2	31854	37407	1.17
P-3	25118	30574	1.22
P-4	24272	29872	1.23

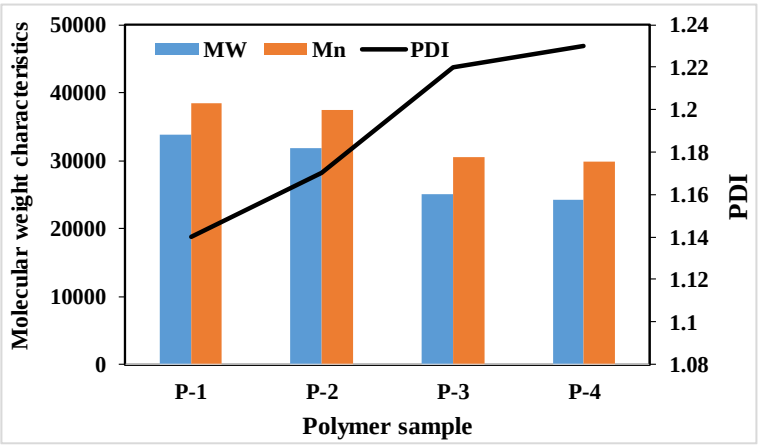


Figure II.B.12. : Molecular weight characteristics of the polymers

II.B.9.TGA data of all the polymer samples:

Table II.B.6. displays the Thermogravimetric Analysis (TGA) data for both the homopolymer and copolymer of dodecyl acrylate. The data reveals that the copolymers (P-2, P-3, and P-4) exhibit greater thermal stability compared to the homopolymer (P-1). Furthermore, there is a discernible trend indicating that as the concentration of citral in the feed increases, the thermal stability of the copolymers also increases. **Figure II.B.13.** represents the diagrammatic representation of TGA data.

Table II.B.6: TGA data for homo and copolymer of behenylacrylate

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
P-1	513	84
	541	77
	562	16
	589	4
P-2	523	86
	551	80
	577	21
	611	5
P-3	561	85
	584	79
	605	23
	627	8
P-4	566	85
	589	80
	617	7
	640	5

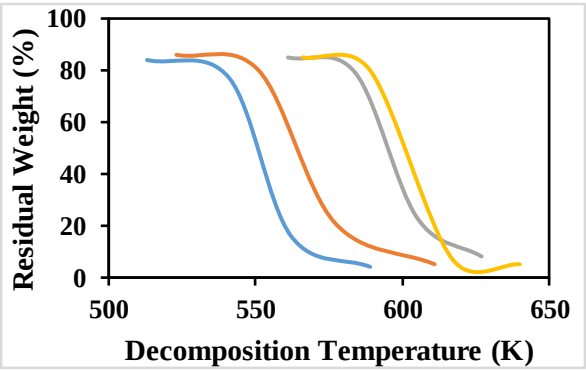


Figure II.B.13. : TGA data for homo and copolymer of behenylacrylate

II.B.10.Physical properties of Base oils:

The physical properties of two base oils were determined first before the progression of whole procedure. This **Table II.B.7.** consists of all the values related to it.

Table II.B.7. Physical Properties of Base Oils

Properties	***BO1***	***BO2***
Density(kg.m^{-3}) at 313K	839.98	918.68
Viscosity at 313K	5.97×10^{-6}	20.31×10^{-6}
Viscosity at 373K	1.48×10^{-6}	3.25×10^{-6}
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

II.B.11.Conclusions:

All the copolymers (P-2, P-3, and P-4) along with the homopolymer (P-1) demonstrated exceptional pour point depressant (PPD) and antiwear (AW) properties. Additionally, the copolymer exhibited outstanding biodegradability. Therefore, the copolymer, derived from castor oil and behenyl acrylate, holds promise as a potential environmentally friendly multifunctional additive for lubricating oil.

II.B.12.References:

References are displayed in **BIBLIOGRAPHY** under **Chapter II, Section B,** that is, "**Evaluation and Synthesis of Environmentally Benign multifunctional additives for lube oil"** (pp. 237-239**).**

Section – C

Synthesis of octadecyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives

II.C.1. Introduction:

Modern lubricants consist of the base oil as a major constituent along with some additives required for providing some specific characteristics or sometimes enhancing the existing properties [1]. Antioxidants, detergents, dispersants, corrosion inhibitors, viscosity index improvers (VIIs), pour point depressants (PPDs), antiwear and antifriction additives are some of the important types of these additives. Out of these, VIIs and PPDs are added in the large quantities because the viscosity and fluidity variation with temperature determines the applicability of a lubricant formulation in low and high temperature operational conditions with effective and efficient performance [2]. Utilization of polymeric additives as chemical treatment is considered as the most valuable and economic method to inhibit the wax precipitation at low temperature. Usually polymeric additives contain non polar long hydrocarbon chain of 14 to 25 carbon atoms along with a polar segment typically acrylates or acetatesn [3,4]. It is the polar head group which is responsible for the modification of wax crystals morphology whereas the non–polar long hydrocarbon chain is responsible for the interaction between the additives and paraffin.

Several polymeric additives have been created and utilized as PPDs, especially linear polymers of alkyl acrylate or methacrylate having a pendent alkyl side chain of specific length has been extensively used as flow improvers (FIs) or pour point depressants (PPDs) [5-11]. The function of PPDs has already been discussed in our previous works where it is clearly mentioned that PPDs co–crystallize along with the wax species present in the oil at lower temperature and modify the growing pattern of wax crystal structures [3]. Recently a considerable number of studies have been reported on the structure–reactivity relationship for the polymers of higher alkyl acrylates and methacrylates [12, 13]. These studies invoked the research towards modified processes for the polymerization of *n*–alkyl acrylates with narrow molecular weight distribution (MWD) [14].

Various polymeric additives are available commercially such as poly (ethylene–co–vinyl acetate) (EVA) [15], poly(ethylene-butene) (PEB) [16], polymethacrylates [17] and modified maleic anhydride copolymers [4]. Number of studies have been reported on versatile application of these additives including polyacrylate polymers with polar building blocks as wax modifier [18], linear polymer or copolymer having pendant hydrocarbon chains as flow improvers [19] and again some studies also investigated the effect of molecular weight (MW) and molecular weight distribution (MWD) on the performance of these additives [20].

Homopolymers of alkyl acrylates and methacrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour point depressants and flow improvers in high waxy crude oils, lubricating oils and fuel oils. The alkyl chain length in these polymers is usually more than 14 carbons. Octadecyl acrylate (OA) consists of a mixture of C_{22}, C_{20} and C_{l8} acrylates and is used extensively in the preparation of these additives [13]. Recently development of the novel additives based on copolymers containing n–alkyl acrylates has gained huge attention due to their multifunctional nature and the fact that the comb shaped polymeric additives can be more effective as PPD in lube oil by providing different nucleation sites for the precipitation of wax [21]. Dao in 2017 has reported that copolymers formed by stearyl methacrylate and behenyl acrylate with vinyl acetate using AIBN as initiator give high efficiency to reduce pour point temperature [22]. R. K. Singh et al. have reported the successful synthesis, characterization, and performance evaluation of two homopolymers of C_{18} alkyl acrylate and N,N–dimethyl acryl amide and their three copolymers as synthesized by using 1:1, 1:2, and 2:1 monomer ratios as VII and PPDs in polyol base oil taking the homopolymers as reference [2]. B. Subrahmanyam et al. had presented a thorough study on the effect of initiator concentration and monomer concentration on the molecular weight and molecular weight distribution in octadecyl acrylate polymerization. They found that at higher concentration of initiator and monomer, the branching reactions led to gel formation in octadecyl acrylate polymerization. They reported that viscosity of the polymerizing medium also influenced the high conversion polymerization in alkyl acrylate polymerization [13].

Thus growing demand for requirement of high performance characteristics and increasing environment related concerns have forced the researchers to develop new multifunctional polymeric additives so that maximum activity can be achieved with minimum dosage. Citral (3,7-dimethyl-2,6-octadienal) is basically a monoterpenoid. It is a yellow coloured flavonoid found in lemongrass oil having characteristic lemon like odor. It has been explored for plenty of biological activities especially as antifungal agent [23]. It contains huge percentage of active unsaturation with polar functional groups and thus is very much prone towards effective polymerization and also efficient for enhancement of lubricant performances (pour point, antiwear). Hence we have these for our present context. Here we have prepared homopolymers of octadecyl acrylate and further its copolymers with Citral at variable percentages. All the prepared polymers have been characterized by FT–IR and NMR spectroscopy. Their thermal stability and molecular weight

were determined and then they were evaluated as VII and PPD in lube oil. Further their Thermo gravimetric analysis and biodegradability test were also performed.

II.C.2. Materials and Methods:

1. Materials:

Octadecyl alcohol (Merck Specialties Pvt. Ltd.), acrylic acid (Merck Specialties Pvt. Ltd.) was used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. The properties of the used base oils are tabulated in **Table II.C.1.**Citral (95% pure) was bought from SRL Pvt. Ltd.

Table II.C.1. : Base Oil (BO) Properties

Physical Property	BO1	BO2
Density (gcm^{-3} at 40 ^oC)	0.837	0.868
Viscosity at 40 ^oC in cSt	7.136	23.392
Viscosity at 100 ^oC in cSt	1.856	3.915
Pour Point (PP in ^oC)	–3	–6
Cloud Point (^oC)	–10	–8

BO1, BO2 collected from IOCL, Dhakuria, West Bengal

2. Preparation of esters:

The ester (Octadecyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of Octadecyl alcohol. The reactants were mixed with toluene along with few drops of concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor in a resin kettle and heated gradually from room temperature to 403K using a well–controlled thermostat under a slow stream of deoxygenated nitrogen. The whole

process was carried out in reflux condition. The extent of esterification was monitored by the amount of liberated water.

3. Purification of prepared esters:

The prepared ester was refluxed for 3 hours with suitable amount of charcoal and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separatory funnel several times to ensure complete removal of untreated acid. The ester was then washed repeatedly with distilled water to remove any traces of sodium hydroxide. The purified ester was then left overnight on calcium chloride. It was then removed by distillation under reduced pressure. Then the ester was ready to be used in the polymerization process.

4. Preparation and purification of the polymers:

The polymers (homo and copolymers) were prepared by free radical polymerization at different percentage composition of monomers (**Table II.C.2**) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The polymerization process was were carried out in a four-necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of deoxygenated nitrogen at 90^{o}C for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol to terminate the polymerization process and precipitate the polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40^{o}C.

II.C.3. Measurements:

II.C.3.1. Molecular weight determination:

With the help of Gel Permeation Chromatography (GPC, Water 2414, polystyrene calibration), the number average molecular weight (M_n) and weight average molecular weight (M_w) of the prepared polymers were measured in HPLC grade THF (0.4%, w/v) at 308 K temperature at a flow rate of 1mL/min. The values are given in **Table II.C.2.**

II.C.3.2. Spectroscopic Measurements:

IR spectra were recorded on a Shimadzu FT–IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range (400 to 4000 cm^{-1}). NMR spectra were recorded in Bruker Avance 300 MHz FT–NMR spectrometer using a 5 mm BBO probe. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as reference material.

II.C.4. Performance evaluation as pour point depressants in base oil:

The effect of additive concentration on pour point of two base oils (BO1 and BO2) was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for each of the prepared polymers. According to the ASTM D 97–09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL–471 (India) given in **Table II.C.3.** & **II.C.4.**

II.C.5. Performance evaluation as viscosity index improver (VII):

Viscometric parameters were determined according to ASTM D 2270–10. The kinematic viscosity of the base oils containing the polymers determined at 313 and 373 K. Different concentrations of the polymers in the base oil (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive–doped lube oil. All of the experimental data given in **Table II.C.5 & II.C.6.** were noted by taking an average of three experimental results under identical conditions in each case.

II.C.6. Determination of thermo gravimetric analysis (TGA) data:

TGA data **(Table II.C.7.)** was measured on Mettler TA–3000 system, at a heating rate of 10K min^{-1}. The variation of temperature within the range was ±10K during the experiment. The uncertainty in determining percent weight loss (PWL) within the range was ±1.5%.

II.C.7. Biodegradability test:

To evaluate biodegradability of the prepared polymers, Soil Burial Test (SBT) method was utilized as per ISO 846:1997 standard [24] using the soil sample collected from North Bengal University campus with pH 7.2and 25% moisture. Percentage weight loss (PWL) of the polymer samples after a definite interval of times was calculated to determine the extent of degradation.

The results were verified by IR spectroscopy and molecular weight determination by GPC method. For Soil Burial Test (SBT), separate films containing about 2.0 g of different samples were buried in the soil which were then incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30^{o} C with relative humidity of 60% for 3 months and thus subjected to the action of microorganisms present in the soil. After each regular interval of 15 days, the soil sample is taken out and the polymer sample was recovered from it by dissolving in chloroform, filtered, dried and percentage of decomposition was measured. The detailed experimental procedure followed is mentioned in our previous work [25].

II.C.8. Results and discussion:

II.C.8.1. Molecular Weight Analysis:

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity index data (PDI) of the prepared polymers are given in **Table II.C.2.** Analysing the experimental data, it was found that the homopolymer of octadecyl acrylate (P_1) had higher number average and weight average molecular weight than the others. Since it is a homopoymer of C_{25} monomer, it is obvious that its molecular weight is higher compared to the copolymers where Citral was incorporated. Again in terms of polydispersity index (PDI) P_4 polymer is least poly-dispersed which indicates better uniformity. With increasing concentration of Citral, the polymers (P_2, P_3 & P_4) exhibited higher molecular weight and lesser polydispersity index.

Table II.C.2.: Weight percentage (%) composition, M_n, M_w and PDI values of polymers (P_1 to P_8)

Polymer	% of OA	% of Citral	M_n	M_w	PDI
P_1	100	–	38563	53217	1.38
P_2	98	2	28832	38347	1.33
P_3	96	4	28510	35067	1.23
P_4	94	6	29567	33115	1.12

OA = Octadecyl acrylate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

II.C.8.2. Spectroscopic analysis:

In FT–IR spectroscopy almost all the polymers being acrylate produced similar spectra. Peaks around 1732–1735 cm^{-1} clearly indicated the presence of ester carbonyl group in each case. Strong peak at around 1695 cm^{-1} corresponding to conjugated aldehydic C=O group accounted for successful incorporation of citral while copolymerization. In general any alkenyl C–H stretching produces IR peak at about 3100 cm^{-1}, but here in the homopolymerno corresponding peak has been obtained. This observation supported complete and successful homopolymerisation. But in case of the copolymers medium peak around 1610 cm^{-1} accounted for the conjugated C=C group.

In ^{1}H NMR spectra peaks appeared in the range of 3.94–4.12 ppm clearly indicated the presence of $–OCH_2–$ protons. The absence of peaks around 6 ppm indicated absence of C=C unsaturation and hence supported total polymerisation in case of the homopolymer. Again peaks around 9.68 ppm indicated presence of aldehydic C–H group in the copolymers which further accounted for successful incorporation of citral while copolymerization. In ^{13}C NMR spectra, peaks at 176–178 ppm indicated the presence of ester carbonyl carbon. The peaks at 64.67–66.06 ppm corresponded to the $–OCH_2–$ carbons, peaks ranging from 13.09–44.66 ppm for all other sp^3 carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization in the homopolymer. In the copolymers peaks around 190 ppm accounted for the aldehyde group of citral.

II.C.9. Performance evaluation as pour point depressant:

The pour point data given in **Table II.C.3. & II.C.4.** clearly prove that the prepared polymers are good pour point depressants for both the base oils. In case of the homopolymer (P_1), with increasing concentration its effectiveness as PPD decreases. Very high molecular weight of this polymer might be the reason for its low solubility at higher concentration in both the base oils. But the copolymers have been proved to be better PPDs in both the base oils. Comparing all the pour point data, it can be said that the copolymer of 94% Octadecyl acrylate and 6% citral (P_4) gave the best result. Almost in all the cases the pour point depression curves get flattened above 4% concentration since at higher concentration the polymers suffer lower solubility and hence their effectiveness as PPD also diminishes.

Table II.C.3.: Pour point (°C) data with respect to the different concentrations of the additives in BO1

Additive	1%	2%	3%	4%	5%	6%
P_1	–13.3	–13.6	–12.9	–12.7	–12.3	–11.8
P_2	–16.0	–16.5	–17.2	–17.8	–18.1	–18.0
P_3	–18.1	–18.6	–19.2	–19.4	–19.4	–19.1
P_4	–20.9	–21.2	–21.6	–22.1	–22.0	–22.0

Conc^n represents concentration in % w/w

Table II.C.4.: Pour point (°C) data with respect to the different concentrations of the additives in BO2

Additive	1%	2%	3%	4%	5%	6%
P_1	–20.4	–20.3	–19.4	–18.8	–18.1	–17.6
P_2	–25.5	–25.8	–26.1	–26.4	–26.2	–26.2
P_3	–26.4	–26.9	–27.2	–27.6	–27.6	–27.3
P_4	–28.6	–29.1	–29.4	–29.8	–30.2	–30.2

Conc^n represents concentration in % w/w

II.C.10. Performance evaluation as viscosity index improver:

Solubility of the polymer, its molecular weight and composition play important role on its performance as viscosity index improver [26]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases solubility of the polymer increases and it unfolds itself to an open configuration of higher volume and hence overall higher viscosity is exhibited at higher temperature by polymer–doped base oil. This activity offsets the normal trend of decrease in viscosity with increase in temperature [27].

It is seen from the **Table II.C.5. & II.C.6.** that all the prepared polymers are effective viscosity index improvers for both the base oils. Here again due to very high molecular weight and hence lower solubility, the homopolymer of octadecyl acrylate (P_1) is least effective as VII among all.

On the other hand, the copolymer of octadecyl acrylate and 6% citral (P_4) has been proved to be the best viscosity index improver in both the base oils. The rests are almost comparable VIIs. With increasing concentration of the polymer in the base oil, total volume of the polymer micelle increases and hence the viscosity index data also increases [28].

Table II.C.5.:Viscosity Index (VI) data with respect to the different concentrations of the additives in BO1

Additive	0%	1%	2%	3%	4%	5%	6%
P_1	85	97	98	100	101	103	102
P_2	85	98	99	101	104	114	118
P_3	85	100	102	103	106	117	120
P_4	85	110	112	113	115	120	122

Conc^n represents concentration in % w/w

Table II.C.6.:Viscosity Index (VI) data with respect to the different concentrations of the additives in BO2

Additive	0%	1%	2%	3%	4%	5%	6%
P_1	80	102	104	107	109	115	119
P_2	80	104	105	106	109	116	119
P_3	80	105	106	108	110	118	120
P_4	80	120	121	123	125	130	132

Conc^n represents concentration in % w/w

II.C.11. Analysis of TGA data:

The thermal studies confirmed that all the prepared polymers are thermally stable **(Table II.C.7).** Lower the percent weight loss (PWL) higher will be the thermal stability. Therefore, among the prepared polymers, the copolymer of octadecyl acrylate and 2% citral (P_2) is thermally most stable while the homopolymer of octadecyl acrylate (P_1) is thermally least stable. Higher thermal stability of the additives indicated their suitability as lubricant additives.

Table II.C.7: TGA data of the polymers

Polymer	Decomposition temperature	Percent weight loss (PWL)
P_1	250/340	23/86
P_2	250/360	12/82
P_3	260/380	14/85
P_4	250/380	13/80

II.C.12. Analysis of biodegradability test results:

From the results obtained from biodegradable test **(Table II.C.8)** it was found that the degradation of the recovered samples taken every 15 days interval increases with increasing time. The copolymer of octadecyl acrylate and 6% citral (P_4) showed highest degradation and after 90 days' span the recovered sample showed over 40% weight loss followed by P_3 (over 37% weight loss) and P_2. Among the four polymers, the homopolymer P_1 showed least biodegradation and after 90 days' span the recovered sample showed no weight loss at all. Therefore, the lube oil additives prepared from citral exhibited significant biodegradation.

Table II.C.8.: Results of biodegradability test by soil burial test for polymeric additives

Soil burial test	
Polymers	**Microorganism Wt. loss (%)**
P-1	00
P-2	31.60
P-3	37.70
P-4	40.30

II.C.13. Conclusions:

The above study may be summarized as follows. All the prepared polymers have been evaluated as effective multifunctional and thermally stable additives for lube oil. In terms of molecular weight the homopolymer of octadecyl acrylate exhibited highest number average and weight average molecular weight. Again the PDI value accounts for better uniformity in the copolymers. But the homopolymer is very much less effective as PPD as well as VII which may be attributed to its solubility problem. All the other polymers have been proved to be good flow improvers in

both the base oils. Especially the copolymer of octadecyl acrylate and 6% citral resulted highest depression in pour point in both cases. This polymer was also proved to be the best VII among all the prepared ones. All the prepared polymers were thermally stable as well. Furthermore the citral based polymers were proved to be biodegradable also which accounted for their eco–friendly nature.

II.C.14. References:

References are displayed in **BIBLIOGRAPHY** under **Chapter II, Section C,** that is, "**Synthesis of octadecyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives"** (pp. 240 -242**).**

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Chapter I

A concise explanation about the perspective towards some production of biologically significant compounds with heterocyclic moiety

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Chapter I

Section A

(Humic Acid: A Rarely Explored, Robust, Green Catalyst for Solvent-Free Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and Benzo[*d*]thiazole)

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Chapter I

Section B

(Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent–Free Synthesis of 3,3'–(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol))

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Chapter II

General Introductory part

(Wide-ranging analysis of polymeric exploration, synthesis and evaluation)

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Chapter II

Background of the Present Study

(Wide-ranging analysis of polymeric exploration, synthesis and evaluation)

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Chapter II

Section A

(Synthesis and Performance Evaluation of Castor oil – Styrene Co - polymer: an Outstanding Multipurpose Directional Lubricant Additive)

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Chapter II

Section B

(Evaluation and Synthesis of Environmentally Benign multifunctional additives for lube oil)

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Chapter II

Section C

(Synthesis of behenyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives)

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REPRINT OF SOME PUBLISHED PAPERS

Research on Chemical Intermediates
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Humic acid: a rarely explored, robust, green catalyst for solvent-free synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate and benzo[*d*]thiazole

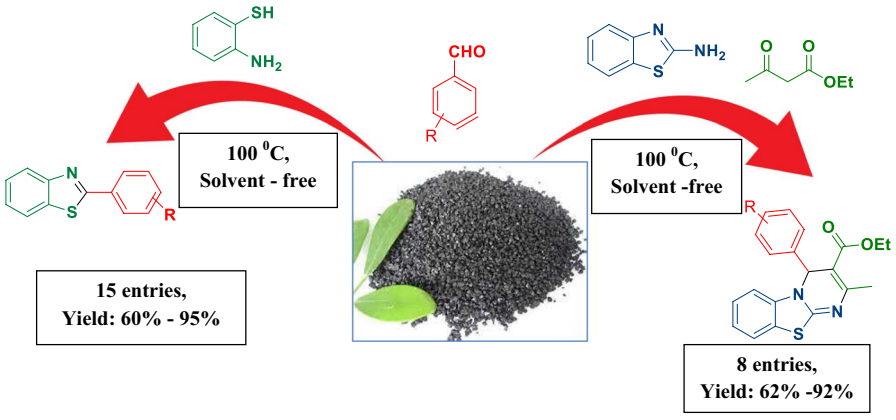
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Abstract

Humic acid, a rarely used non virulent, easily accessible, inexpensive, environmentally benign, high molecular weight polymer, because of its extraordinary catalytic activity has been explored for the synthesis of functionalised 4*H*-benzo[4,5] thiazolo[3,2-*a*]pyrimidine-3-carboxylate and its derivatives along with functionalised benzo[*d*]thiazole. Environmental friendliness, low catalyst loading, outstanding yield, magnificent functional group forbearance and renewability up to fifth run without any noteworthy loss of its activity at the finishing point of reaction, are the cue significances of these methods.

Graphical abstract



Keywords Aldehydes · Benzo[*d*]thiazole · Heterocycles · Humic acid and Thiazolo[3,2-*a*]pyrimidine

Extended author information available on the last page of the article

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Introduction

In the past several decades, research practices in chemistry are constantly evolving through overcoming the rigidities such as, fixed reaction patterns, systematic approaches inside the confines of a laboratory. In order to make any system sustainable, attempts should be made to keep the laboratory experimental conditions in accordance with the environment, surrounding us. Therefore, any alteration, innovation or discovery, made in the system must be handled with great care and consideration to ensure its suitability to the surroundings. The continuous environmental degradations and it is already visible devastating impacts have made the researchers and scientists to be focused on to the suitability of their research like never before. As a consequence, like any other procedures, organic synthesis must look at the sustainability aspect through the application of innovative and greener protocols that avoid the use of hazardous solvents, toxic chemicals, poisonous catalysts, and harsh reaction conditions. Use of such substances can result in massive environmental pollution and damage to the nature, during the synthesis of chemical components, particularly organic molecules. For that reason, organic synthetic methodologies must attempt to replace the traditional solvents and catalysts (wherever possible) with appropriate alternatives. The need to keep the drug industry flourishing through maintaining the sustainable protocols makes it worthwhile to pursue chemical synthesis.

Solvent-free protocols are greener and one of the best solutions to these environmental issues, since they can eliminate most of the flaws like pyrophoric property of harmful and hazardous solvents with high volatility and poor recovery. There are ample scopes in future, for further more detailed inspection of the solvent-free pathway, basically, as a part for synthesizing of organic molecules through greener methodology. Due to such factors, solvent-free pathways of organic synthesis have become very much popular in recent years. The aim of this initiative is to enhance earthly consciousness above a number of hazardous chemicals and substitution of harmful solvents and substituting those using greener products to progress towards green chemistry [1–14].

Generally, high molecular weight materials are very much useful for organic synthesis because of their low toxicity, ease of separation, easy recovery and reusability. Among them humic acid is very rarely used, nontoxic, easily accessible, inexpensive, environmentally benign, high molecular weight polymer with extraordinary catalytic activity. Humic acid is derived primarily from biodegradation of dead and decreased organic materials and obtained mostly in peat, soil, coal, upland streams, dejected lakes and well water. It is interesting and essential catalytic activity is exhibited owing to the presence of wide range of most ample functional groups, e.g. carboxyl (–COOH) and phenolic hydroxyl (=CH–OH) group in its structure. However, a careful review of the literature reveals that, only a few articles have reported the application of catalyst. Therefore, there is an enormous scope of further detailed exploration of its catalytic venture in multidirectional protocols of biosynthesis. Low catalyst loading, outstanding yield and significant functional group toleration are some of the extraordinary

characteristics of humic acid in its catalytic approach. Another important convenience about humic acid is its renewability. Structure of humic acid is shown below (Fig. 1) [6, 15, and 16].

The previously reported humic acid mediated solvent-free production of multiple collection of functionalised bis(indolyl)methanes, bis(pyrazolyl)methanes, biscoumarins and bis-lawsones by the reaction of vast range of aldehydes with Indole, 3-methyl-1-phenyl pyrazolone, 4-hydroxy coumarin and 2-hydroxy naphthalene-1,4-dione respectively [6]. Another previously reported humic acid catalysed reaction was one pot, three components, water mediated preparation of 5-substituted 1*H*-tetrazoles, from a number of aldehydes, hydroxylamine hydrochloride in presence of sodium azide [15]. Again, humic acid was used as a support of Pd/Ni bimetallic catalyst for Heck coupling reaction, in one of the previous studies [16].

4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine is a very essential compound under the highly important branch of fused heterocycles, with a vast pharmacological [17], pharmaceutical [18] and industrial [18] properties. It consists of a large number of biological activities, such as, antibacterial [18], anti-tumour [18], anti-inflammatory [18], antiviral [18], anticonvulsant [18], anticancer [18], antifungal [18] or fungicidal [19], antiallergic [19], antimicrobial [19], antimycobacterial [19], antiproliferative [19], anticoagulant [20], antiherbicidal [20], antituberculosis [21] . It can be used as a salient synthon to design various modern medicinal drugs [22] for synthesizing a number of biologically active compounds [23] and natural products [10]. It is a remarkable optical liquid [13] with electronic properties [13] and used as dyes[24] and fluorescent [16] materials. This compound is so much useful for constructing medicines, associated with human and cattle contagious disorder such as, AIDS, hepatitis B and C, tuberculosis and bovine viral diarrhoea, drug resistant cancers i.e. leukaemia, carcinoma, melanoma and multi drug resistant tumours, which has no definite remedy or effective availability of vaccines till date [15].

It is very well known fact, that, heterocyclic and polycyclic compounds, containing nitrogen, sulphur and oxygen (N, S, and O respectively) are very much flexible and necessary framework for designing a variety of drugs [25]. Some basic skeletal structures of such bioactive drugs are shown below (Fig. 2). Benzothiazole and its derivatives, the important part of heterocyclic [17] and polycyclic compounds [17], represent a number of biological [26], medicinal [27], pharmacological [18],

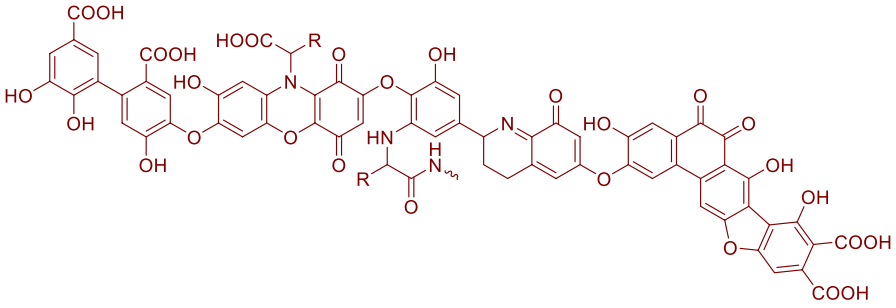


Fig. 1 Structure of humic acid

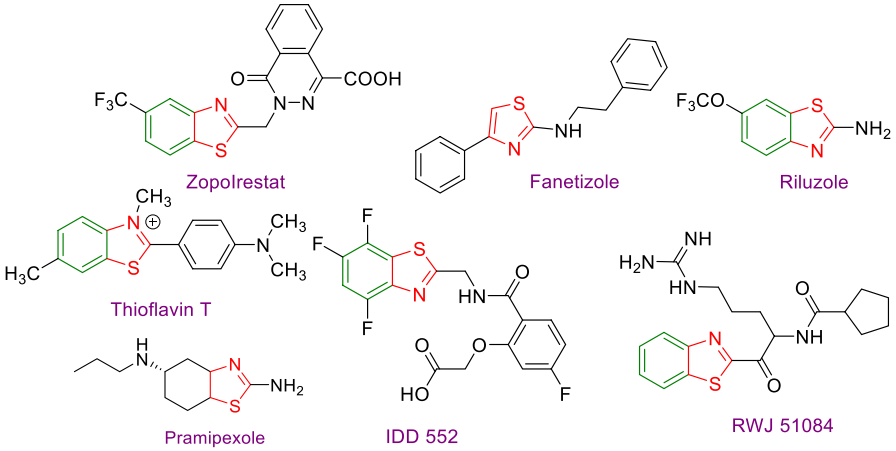


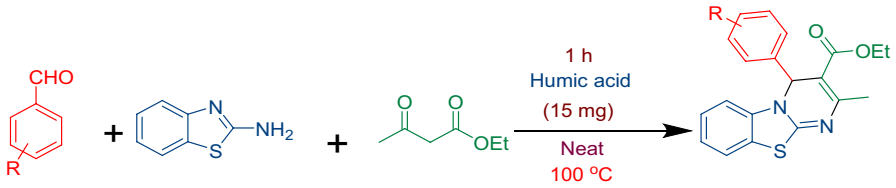
Fig. 2 Some examples of biologically active drugs

pharmaceutical [28] significances like analgesic [19], antiepilepsy [29], antilateral sclerosis [21], antihypertensive [19], anti HIV [19], antiulcer [19], anti diabetic [30], anti Parkinson [31], antithrombotic [19], antihistamine [32], antiemetic [24], antianxiety [33], antistress [34], antiglutamate [23], antiparasitic [22], antihelminthic [35]—etc. They are used in autoimmune diseases [21]. Benzothiazoles are extensive important class of pervasive heterocyclic moieties [36] and exist as molecules or molecular framework in many bioactive natural products [28], e.g. vitamin B_{12} [16]. They have huge applications in material sciences [28] or material chemistry [28] as the primary components of materials with optical or electronic belongings [37] and also used as ligands of transition metals and intermediates of organic reactions [38]. They play an important role as ligands in asymmetric transformations [30]. It has great application prospect in synthesis of variety of agrochemical compounds [30]. They are pharmacophores and applied in variety of modern drug discovery and development like omeprazole (proton-pump deterrence), candesartan and telmisartan (AT1 receptor nemesis), mebendazole (drug to prevent parasitic worm infection), dabigatran (direct thrombin inhibitor), flunoxaprofen (NSAID) and riluzole (sodium channel barricade and drug to fend off amyotrophic lateral sclerosis)—etc. [31]. Benzothiazole derivatives are also present in Fanetizole (anti-inflammatory agent), UDP-galacto-pyranose mutase inhibitor, κ and μ narcotic receptor and small molecular somatostatic receptor subtype 5 (SST5R) antagonists –etc. [39]. It can act as efficient enzyme inhibitor, e.g. it is very popular inhibitor of Chemokin receptor ($CXCR_3$) [30], Lymphocyte tyrosine kinase (LCK) [32], Glycinamide ribonucleotide transformylase (GARTfase) [41], Topo isomerase-1 [19], Aldol reductase [42], HIV reverse transcriptase [19]—etc. Some derivatives of benzothiazole behave as plant growth regulators [43], photosensitizes, LTD_4 receptors [22], potent cationic Trypsin receptor [34] and chemosensor [44] for a range of analytes. They are actively used in corrosion science [45]. These compounds are especially found in the moieties, which can conduct the life cycles in various cells [32]. They act a very significant role in metabolic process, taking place in living organisms [24]. They

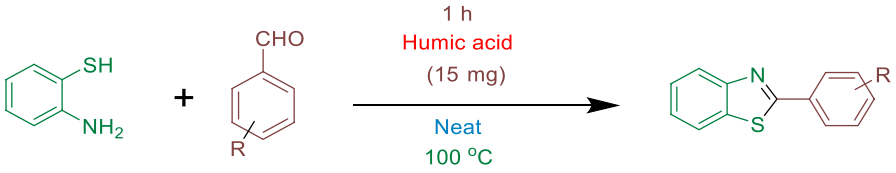
have vast industrial significances [11]. In industry, they are used as antioxidants [17], vulcanization accelerators [22], dopants in light emitting organic electroluminescent devices, i.e. nonlinear optical luminescent [17]. They can exhibit florescent properties [17] and so, they are used in designing sensor molecules of specific categories [17]. They can form the compounds with cytotoxic activities [19] and imaging agent for Ca^{2+} channel antagonist [17].

4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate was synthesized previously by using the catalysts like; magnetic nano catalyst (nano—kaoline or hydrated aluminium silicate Al_2O_3, $2SiO_2$, $2H_2O$)/Ti^{4+}/Fe_3O_4 [18], nano-Co-[4-chlorophenyl-salsylaldimine-pyranopyridine dione]Cl_2 or nano-Schiff base complex [46], DBU and CPB (cetyl pyridinium bromide) [19], phosphorus containing ionic liquids [17], Fe_3O_4@nano-cellulose/Cu(II) [47], Fe_3O_4@SiO_2-$TiCl_3$ nano particles [48], nano cellulose/BF_3/Fe_3O_4 [21], nano-$TiCl_2$/cellulose [20], L-proline [49], Lewis acid, covalently grafted over sulfonic acid functionalised carbon@titania composites [50], ager [51], ammonium chloride [23], microwave over *p*-TSA clay [52], MgO or 12-tungstophosphoric acid [53], chitosan [54], phosphoric acid supported on alumina (H_3PO_4-Al_2O_3) [55], Mg–Al–CO_3 and Ca–Al–CO_3 hydrotalcite [56], TBAHS [57] – etc.

Benzo[*d*]thiazole was synthesized previously by using the catalysts like; amino quinolone B,B-diphenyl complex as the photocatalyst [58], enzyme like Trypsin, Lipase, Bovin—etc. [26], H_2SO_4, HCl, H_3PO_4, HF—etc. traditional acid catalysts [27], Bronsted acid surfactant combined ionic liquids [36], I_2 in TBHP (Tert butyl hydroperoxide) [59], Cu(II)-Glycerol/MCM-41 (nanocatalyst) [24, 88], mesoporous titania—alumina mixed oxide [60], magnetic Co-doped $NiFe_2O_4$ [40], nano composite, mesoporous silica supported samarium [61], Ag_2O (in microwave) [62], epichlorohydrin cross linked *β*-cyclodextrin (*β*-CD polymer) [63], YCl_3 [64], UIO-66-NH_2 derived Bronsted acid catalyst [65], nanosealed UIO-66-NH-RSO_3H catalyst [57], ZnO nanoparticles [66], iron catalyst [41], ruthenium silicate zeolite [25], vanadium and molybdenum Schiff base complexes [32], fluorescein (photocatalyst i.e. visible light in presence of O_2) [37], fluorinated phosphoric acid [38], camphor sulfonic acid [33], hydrotalcite, visible LED light in photosensitizer [67], laccase/DDQ [68], NH_2-MIL-125(Ti) metal–organic framework [69], tin modified mono ammonium phosphate fertilizer ($SnCl_2$ in MAP) or SnP_2O_7 in EtOH [70], hybrid crystal $H_3N(CH_2)_4NH_3SiF_6$ (monoalkyl ammonium hexafluorosilicate) [35], $NiFe_{2-x}Eu_XO$ nanostructured catalyst [71], TiO_2 nanoparticle in H_2O_2(in P_{25} nanoparticles) [31], mesoporous poly(melamine–formaldehyde) [42], water(H_2O) [72], magnetic nanoparticles supported tungsto silicic acid [73], iron phthalocyanine [39], NaY zeolite functionalised by sulfamic acid/$Cu(OAC)_2$ or NaY zeolite-$NHSO_3H$/$Cu(OAC)_2$ as hybrid catalyst [29], oxalic acid: L-proline [44], solid acid supported on magnetic nanoparticles (solid acid catalyst [Fe_3O_4@SiO_2@$(CH_2)_3$NPC-SO_3H]Cl) [74], MIL-101(Fe)hexagonal microspindle [22], functionalised magnetic core shell nanoparticles, containing I_3^-, i.e. [Fe_3O_4@SiO_2@$(CH_2)_3NMe_3^+$]I_3^- [75], chitosan-SO_3H [76], $H_3N(CH_2)_5NH_3BiCl_5$ [77], copper containing nano silica thioalated dendritic material [45, 89], two dimensional Bi_2WO_6 nanosheets as a sturdy catalyst (towards photocatalyzation) [43], phosphoric acid supported on alumina



Scheme 1 Humic acid mediated synthesis of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine



Scheme 2 Humic acid mediated synthesis of functionalised benzo[*d*]thiazole

(H_3PO_4/Al_2O_3) [55], CuI [78], $VOSO_4$ catalyst in ethanol [79], calcinized egg shell [30], copper(II)-diaminosarcophagine functionalised SBA-15 [34], proline-based ionic liquid catalyst [80], nano-titania-supported sulfonic acid catalyst (n-TSA) [81], tBuONa [82], visible light photo catalyst [83], i.e. CdSe nanocomposites, made by monmorillonitrile (MMT) [75], SiO_2-HNO_3 [84], Ag_2O_3/Celite [85], $Fe_3O_4/SiO_2/(CH_2)_3NMe_3^+ Br^-$ core shell nanoparticles [86], $CuFe_2O_4$ nanoparticle catalyst [87]—etc.

Metal catalysts are very much expensive, hazardous, dangerous, poisonous, fatal, toxic, and huge time consuming to be prepared. Ionic liquids are also very much expensive, auto toxic, especially for human and aquatic organisms. Moreover, ionic liquids have their limited solubility and they cannot be removed by distillation. Therefore, we have chosen humic acid since; it is much superior in its catalytic approach with respect to the other mentioned catalysts. This makes the overall methodology of those reactions is superior in greener and environmentally more sustainable approach with respect to their previous studies.

The discussion, presented in the previous paragraphs, indicates the points of interests to synthesize compounds, containing benzothiazole moieties with a large no. of conveniences. The target compounds in this experiment, were functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine along with its derivatives in addition to functionalised benzo[*d*]thiazole and its derivatives. The present study utilized humic acid as significant greener catalyst and used some greener pathway like, solvent-free methodology (Schemes 1, 2). Scheme 1 shown here, the reaction of benzaldehyde, 2-aminobenzothiazole andethyl acetoacetate; along with the formation of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine; on the other hand, Scheme 2 shown below, the reaction of benzaldehyde and 2-aminothiophenol; along with the formation of functionalised benzo[*d*]thiazole; in presence of humic acid catalyst, under absolute solvent—free condition.

Experimental

General information

All the compounds were acquired from commercial suppliers and used without further purification. All the products were purified by column chromatography on silica gels (60 – 120 Mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were utilized. ^{1}H NMR,^{19} F and ^{13}C NMR were recorded using 400 MHz, 376 MHz and 100 MHz, respectively, on Bruker AV 400 NMR spectrometer using TMS as internal standard. Splitting manners of protons were explained as s (singlet), d (doublet), t (triplet) and m (multiplet).

General procedure for the synthesis of 4H-benzo[4,5]thiazolo[3,2-a]pyrimidine

A mixture of 2-aminobenzothiazol (1 mmol), benzaldehyde (1 mmol),ethyl acetoacetate (1 mmol) and humic acid (15 mg) was blended at 100 °C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept track of using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by easy filtration and was extracted with ethyl acetate twice (2 × 20 ml). Amalgamated extracts were cleaned with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate−petroleum ether). The products obtained were known compounds and were recognized by their colour, melting point and NMR spectroscopy.

General procedure for the synthesis of benzo[d]thiazole

A mixture of 2-aminothiophenol (1 mmol) benzaldehyde (1 mmol) and humic acid (15 mg) was blended at 100 °C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept an eye on using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by smooth filtration technique and was extracted with ethyl acetate twice (2 × 20 ml). Amalgamated extracts were washed with purified water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate−petroleum ether). The products obtained were known compounds and were recognized by their colour, melting point and NMR spectroscopy.

Spectral data of some compounds

The NMR data of Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate, the desired product of the model reaction, is given below:

^{1}H NMR (400 MHz, DMSO-*d6*) δ (ppm): 1.085 (t, $J=7$ Hz, 3H), 2.419 (s, 3H), 4.026 (q, $J=6.8$ Hz, 2H), 6.662 (s, 1H), 7.175 (t, $J=7.6$ Hz, 1H), 7.282 (t, $J=7.6$ Hz, 1H), 7.511 (d, $J=8$ Hz, 1H), 7.576 (t, $J=8$ Hz, 1H), 7.737 (d, $J=7.6$ Hz, 1H), 7.827 (d, $J=7.6$ Hz, 1H), 8.058 (d, $J=8$ Hz, 1H), 8.315 (s, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ (ppm): 14.448, 23.774, 56.338, 60.227, 102.428, 112.873, 122.225, 123.246, 123.478, 123.809, 124.861, 127.510, 130.956, 133.875, 137.646, 143.997, 148.160, 155.598, 163.556, and 165.707.

The NMR data of 2-(3-Nitrophenyl)benzo[*d*]thiazole, the desired product of the model reaction, is given below:

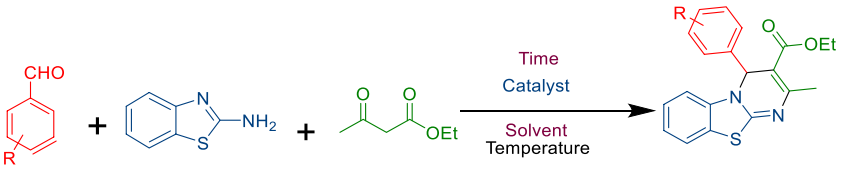
^{1}H NMR (400 MHz, CDCl3) δ (ppm): 7.456 -7.476 (m, 1H), 7.551 (d, $J=0.8$ Hz, 1H), 7.694 (t, $J=8$ Hz, 1H), 7.954 (d, $J=8$ Hz, 1H), 8.120 (d, $J=8$ Hz, 1H), 8.325 (s, 1H), 8.424 (d, $J=8$ Hz, 1H), 8.935 (m, 1H).

^{13}C NMR (100 MHz, CDCl3) δ (ppm): 121.840, 122.348, 123.761, 125.189, 126.041, 126.842, 130.113, 133.004, 135.187, 135.309, 148.773, 153.954, and 164.899.

Result and discussion

Catalyst, solvent and temperature are important driving components of any chemical reactions. So, it is necessary to maintain properly, the extent of catalyst, solvent and temperature throughout the target synthetic procedure. 1 mmol of benzaldehyde, 1 mmol of 2-aminobenzothiazole and 1 mmol ofethyl acetoacetate were taken as reactants to undergo model reaction (Scheme 1). We started our optimization technique (Optimization procedure of Scheme 1, has been shown in Table 1, below, in details), at first, with solvent, in presence of 30 mg of catalyst and next, it was observed that, refluxing with water, methanol and ethanol, the yield of the product was extensively low (Table 1, entry 1, 2, and 3). After that, by refluxing for 6 h continuously, the yield of the product was 50% with DMF (Table 1, and entry 4). When we carried out the same reaction, under neat condition, at 100 °C, with same amount of catalyst, then the yield of the product was enhanced up to 95% (Table 1, entry 5). Then we started the optimization of catalyst by lowering the quantity as, 25 mg, 15 mg, 10 mg and 5 mg (Table 1, entry 6, 7, 8, and 9). As a result, we observed that, 15 mg of catalyst was enough to carry out this pathway and the yield of the product was 92% (Table 1, and entry 7). On the other hand, the reaction could never be undergone in devoid of catalyst (Table 1, and entry 10). After that, by lowering the temperature up to room temperature, the yield of the product was reduced gradually (Table 1, entry 11, 12 and 13). Next, we kept track of the required time, for proceeding of the reaction and we found that, 1 h is sufficient for obtaining the maximum amount of product, under the indistinguishable reaction condition (Table 1, entry 15).

Table 1 Optimization of reaction condition (Scheme 1)



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield (%)[a]
1	Water	30	reflux	6	trace
2	Methanol	30	reflux	6	30
3	Ethanol	30	reflux	6	42
4	DMF	30	reflux	6	50
5	Neat	30	100	6	95
6	Neat	25	100	6	94
7	Neat	15	100	6	92
8	Neat	10	100	6	49
9	Neat	5	100	6	43
10	Neat	Nil	100	6	–
11	Neat	15	70	6	77
12	Neat	15	50	6	65
13	Neat	15	rt	6	trace
14	Neat	15	100	3	92
15	**Neat**	**15**	**100**	**1**	**92**

The bold part signifies the optimized conditions

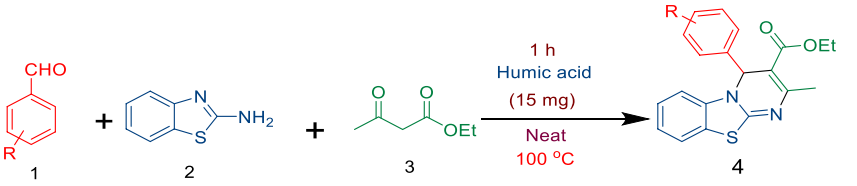
Reaction of benzaldehyde (1 mmol), 2-aminobenzothiazole (1 mmol) andethyl acetoacetate (1 mmol)

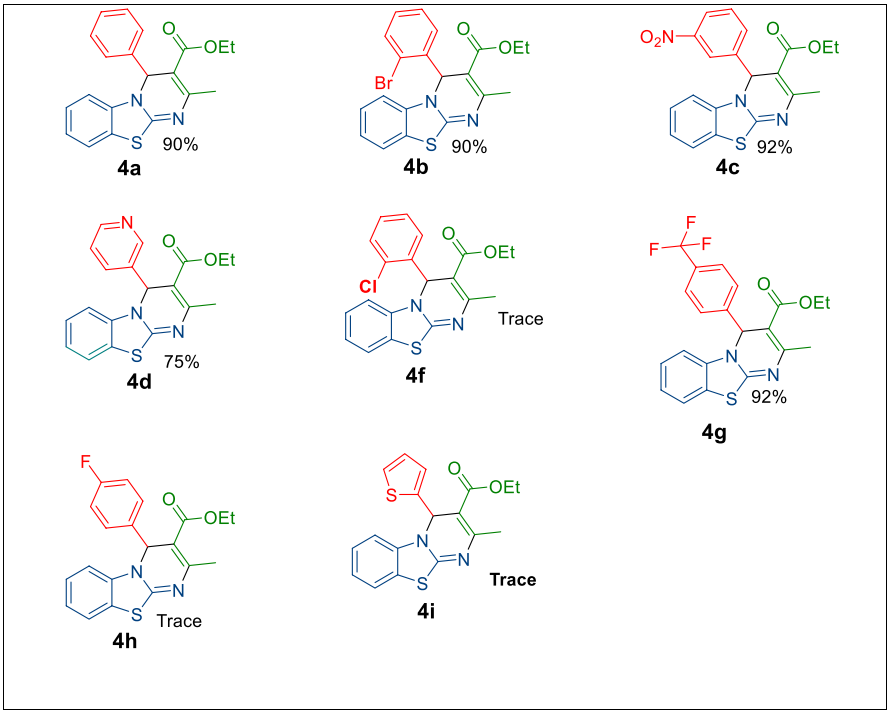
[a]Isolated yield was extracted through column chromatography

To perform in detailed study of our schemes, functionalised aldehydes were treated with 2-aminobenzothiazole andethyl acetoacetate (Scheme 1), under optimized condition and a variety of a number of 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate derivatives were constructed. The resulted compounds have been tabulated in Table 2.

It was observed that, when electron withdrawing groups, especially nitro and trifluoromethyl were present in aldehyde, the product yield was very good (Table 2, entry 4c, g, respectively). But it was observed that, when aldehyde contained heterocyclic moiety, like thiophene, the product yield was not good (Table 2, entry 4i). However, aldehyde with heterocyclic moiety, like pyridine, produced the products with medium yield (Table 2, entry 4d). On the other hand, electron withdrawing groups like bromo, at ortho position, gave good yield (Table 2, entry 4b). On the contrary, electron withdrawing group chloro at ortho position and that of fluoro at para position, gave poor yield of the product (Table 2, entry 4f, h, respectively).

Table 2 Synthesis of functionalised thiazolo[3,2-*a*]pyrimidine derivatives (Scheme 1)

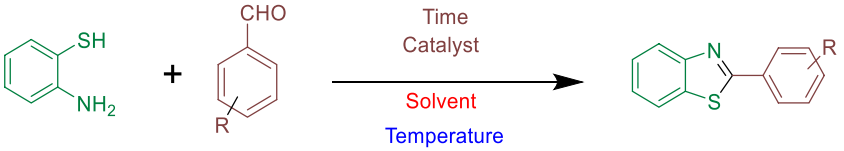




Reaction of aldehydes (1 mmol), 2-aminobenzothiazole (1 mmol), ethylacetoacetate (1 mmol) and humic acid (15 mg), under solvent-free condition for 1 h

In Scheme 2, we took 1 mmol of 2-aminothiophenol and 1 mmol of benzaldehyde as reactants to undergo model reaction (Scheme 2). In the screening method of this reaction, (Optimization procedure of Scheme 2, has been shown in Table 3, below, in details), at first we choose solvent, in presence of 30 mg of catalyst, refluxing with water, DMF, methanol and ethanol the yield of the product was very low (Table 3, entry 1, 2, 3, 4). By maintaining of 100 °C temperature continuously for 4 h, the yields of the product were 50% and 32% with PEG-200 and DMSO, respectively (Table 3, entry 5, and 6).When we underwent the same reaction in neat condition, at 100 °C, with same amount of catalyst, then the yield of the product was enhanced up to 98% (Table 3, entry 7). Then we initiated the optimization of catalyst, by reducing the amount of catalyst (Table 3, entry 8, 9, 10, 11). Thus, it was observed that, 15 mg of catalyst was enough to carry out this procedure and the yield of the product was 97% (Table 3, entry 9). On the other hand, the reaction could never be

Table 3 Optimization of reaction condition (Scheme 2)



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield (%)[a]
1	Water	30	reflux	4	–
2	DMF	30	reflux	4	42
3	Methanol	30	reflux	4	trace
4	Ethanol	30	reflux	4	30
5	PEG-200	30	100	4	50
6	DMSO	30	reflux	4	32
7	Neat	30	100	4	98
8	Neat	25	100	4	98
9	Neat	15	100	4	97
10	Neat	10	100	4	88
11	Neat	5	100	4	82
12	Neat	Nil	100	4	–
13	Neat	15	70	4	87
14	Neat	15	50	4	81
15	Neat	15	rt	4	Trace
16	Neat	15	100	2	97
17	**Neat**	**15**	**100**	**1**	**97**

The bold part signifies the optimized conditions

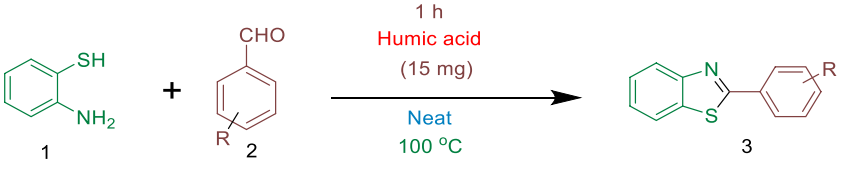
Reaction of benzaldehyde (1 mmol) and 2-aminothiophenol (1 mmol)

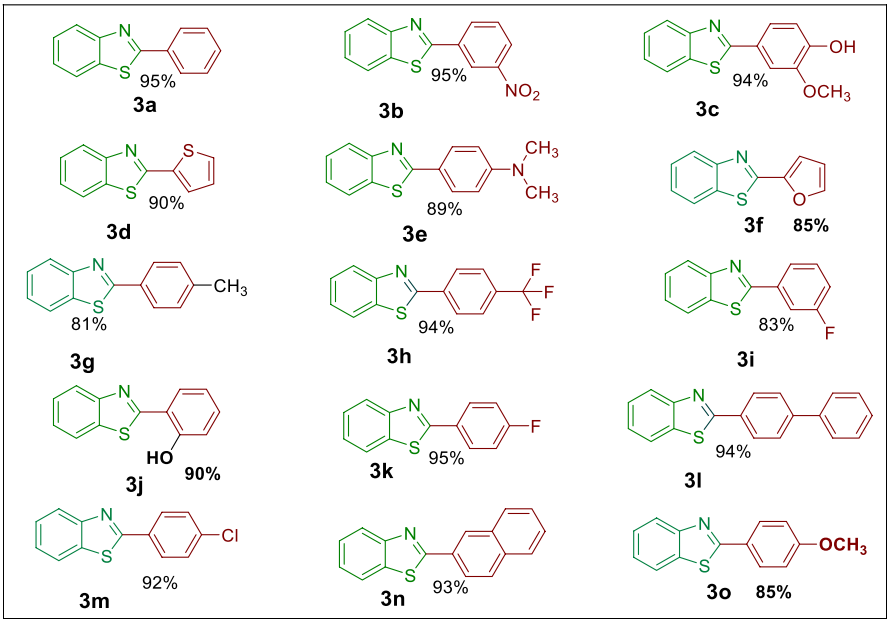
[a]Isolated yield was extracted through column chromatography

feasible to perform in devoid of catalyst (Table 3, entry 12). After that, by lowering the temperature, the yield of the product was reduced frequently (Table 3, entry 13, 14, 15). Next, we kept an eye on the required time for proceeding of the reaction and we discovered that, 1 h is sufficient for gaining the maximum amount of product, under exactly the same reaction condition (Table 3, entry 17).

To go through the detailed study of scheme 2, functionalised aldehydes were treated with 2-aminothiophenol (Scheme 2) under optimized condition and a variety of a number of benzo[*d*]thiazole derivatives were prepared. The resulted compounds have been tabulated in Table 4. From this table, it was observed that, when electron withdrawing groups i.e. nitro at meta position, fluoro, chloro, trifluoromethyl and biphenyl at para position, were present in aldehyde, the product yield was excellent (Table 4, entry 3b, k, m, h, l respectively). But it was also observed that, when an aldehyde contained electron withdrawing group i.e. fluoro at meta position, the yield was medium (Table 4, entry 3i). When an aldehyde contained heterocyclic moieties

Table 4 Synthesis of functionalised benzo[*d*]thiazole derivatives (Scheme 2)





Reaction of aldehydes (1 mmol), 2-amino-thiophenol (1 mmol) and humic acid (15 mg) under solvent-free condition for 1 h

like thiophene and furan, the product yield was medium to good (Table 4, entry 3d, f, respectively). Aldehyde, containing electron donating N, N dimethyl and methoxy groups, at para position, produced medium to good yield (Table 4, entry 3e, o, respectively). Vaniline and Salicylaldehyde gave very good yield (Table 4, entry 3c, j, respectively). Also, 2 naphthaldehyde produced a very good yield (Table 4, entry 3n).

Reusability experiment

Renewability of humic acid was confirmed through a model reaction, with benzaldehyde (5 mmol) and 2-aminothiophenol (5 mmol) in presence of 75 mg humic acid, under optimized reaction condition. After finishing of the first run, ethyl acetate (4 ml) was added to the reaction mixture. Catalyst was taken back smoothly from the reaction mixture by easy filtration procedure. Then, the

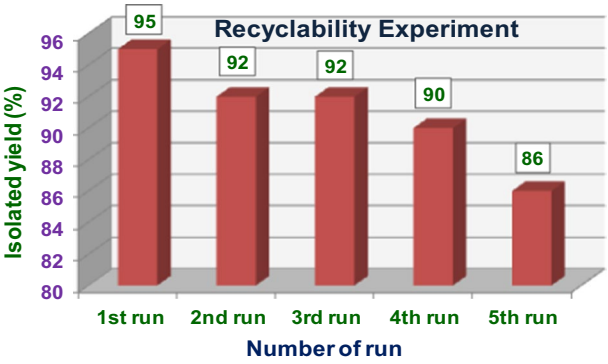


Fig. 3 Reusability of humic acid catalyst

recovered catalyst was washed with ethyl acetate (3 × 4 ml) and next it was dried before being handed down for the next run. The filtrate of reaction mixture was shifted to another container and this method was done for two times repetitively. The catalyst was then washed with ethyl acetate again and after that, it was dried for affording the black coloured humic acid, which was used in the next run, with its dryness. Recuperation of humic acid was slightly lower than the amount used in the first run. However, the recuperated catalyst was used continuously for four runs with almost similar affinity and there was no noteworthy degradation in the transformation. This recyclability test of humic acid catalyst has been shown in Fig. 3, below, through bar diagram. It signifies that, humic acid can expose its catalytic activity up to five successive runs without any considerable reduction in it and in lowering of the yield of the product.

Gram—scale reaction

The application of this methodology was examined in large scale, through carrying out the reactions in **gram-scale** (10 mmol scale) procedure. These also produced good yield, like the yield obtained in small scale reaction techniques. This Gram – Scale Reaction technique has been shown below, schematically, through Fig. 4.

Scale-up experiments

See Fig. 4**.**

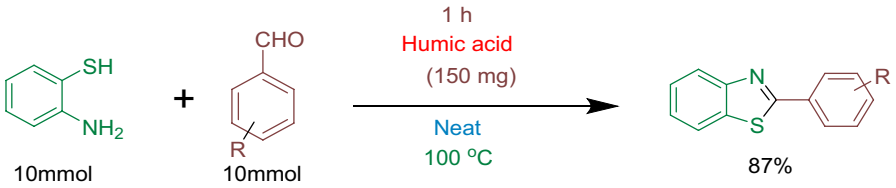
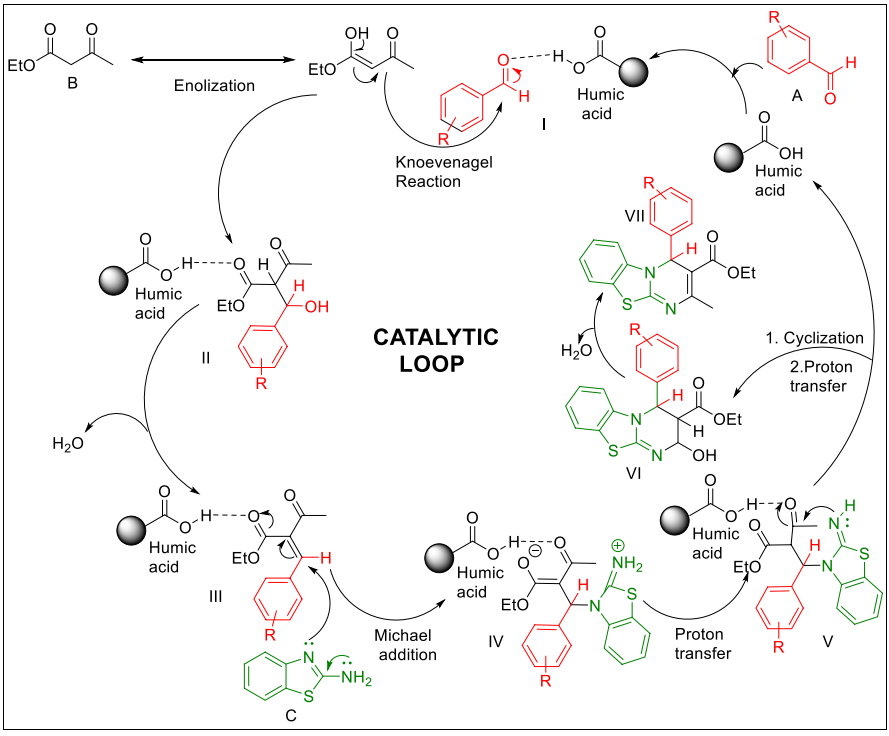


Fig. 4 Gram—scale reaction

Plausible mechanism for the synthesis of 4H-benzo[4,5] thiazolo[3,2-a]pyridine-3-carboxylate and benzo[d]thiazole

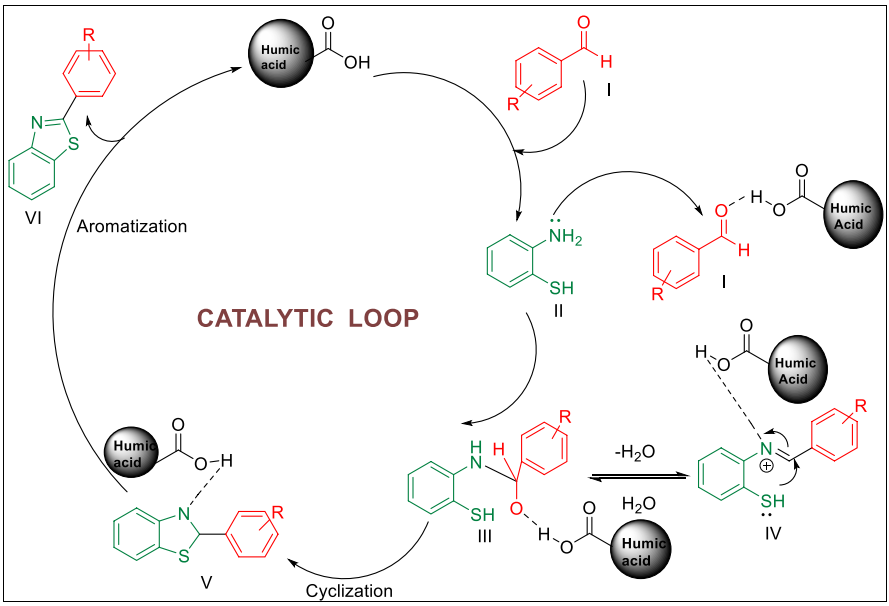
From the literature survey we have prepared the plausible mechanism for the synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate, which is shown in scheme 3. At first, the catalyst activates the aldehyde (A), through its acidic part (–COOH) to enhance the electrophilicity of the carbonyl group so that it can help the nucleophilic attack by enolised form ofethyl acetoacetate (B), by simple nucleophilic addition pathway and the intermediate (II) is formed. Humic acid activates further, the carbonyl carbon of –COOEt in intermediate (II). Then, after water elimination we



Scheme 3 Plausible mechanistic pathway for synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

get the intermediate (III), into which, the nucleophilic centre of 2-aminobenzohiazole (C) attacks through Michael addition pathway i.e. at the four position. Thus we get the intermediate (IV) in which carbonyl carbon is activated again by humic acid catalyst. After that, through proton transfer, we get the intermediate (V), which then undergoes cyclization, followed by proton transfer process. Thus, we get the compound (VI), which forms the final product 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (VII), by elimination of water and after that, the humic acid catalyst is restored. This reaction mechanism and pathway have been diagrammatically shown through the following Scheme 3.

From the surveying of literature, we have designed the plausible mechanism for the synthesis of benzo[*d*]thiazole, which is shown in scheme 4. At first, the catalyst activates the aldehyde (I) through its acidic part (–COOH), to increase the electrophilic nature of carbonyl group and so, it helps the nucleophilic attack by $–NH_2$ group of 2-aminothiophenol (II) by simple nucleophilic addition pathway and intermediate (III) is formed. This is transformed into intermediate (IV), by the loss of a water molecule. The enamine intermediate (IV) is activated again by the catalyst. Then, nucleophilic attack occurs by –SH group of the same compound, followed by cyclization and aromatization. Through the formation of intermediate (V), the expected product benzo[*d*]thiazole (VI) is formed. After that the humic acid catalyst is restored. This reaction mechanism and pathway have been diagrammatically shown through the following Scheme 4.



Scheme 4 Plausible mechanistic pathway for synthesis of benzo[*d*]thiazole

Conclusion

In conclusion, we have represented an environment friendly and feasible technique for synthesizing a number of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate and benzo[*d*]thiazole derivatives under the absence of any solvent, taking humic acid as catalyst to activate carbonyl oxygen of respective aldehydes and ester for enhancing the electrophilicity of carbonyl carbon, followed by nucleophilic addition onto that position. The overall mechanism proceeds through Cascade reaction, involving a well known Knoevenagel and Michael Addition pathway. Since, no metal was used here, so, the overall method was maintained as greener synthetic one. Again, the solvent-free condition, contributes a huge environmental sustainability to the protocol. Humic acid catalyst can be regained through easy filtration procedure and its recovery factor can proceed up to fifth run in devoid of any characteristic deviation of its extent of activity. So, the basic uniqueness and creativity manifestation of this methodology, is, the utilization of environmentally benign, easily accessible and low priced humic acid catalyst, instead of any toxic, fatal, dangerous, exhaustive, hazardous and expensive metal catalyst. This methodology proposed in the present study can be considered as a part of the consistent effort of the scientists and researchers by creating a significant evolution within the chemical world of medicines, synthetic pathways of natural products and drug industries, in future endeavours.

Supporting information summary

Supporting Information contains the experimental analysis, spectroscopy data and scanned copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of some of the synthesized compounds.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11164-024-05237-1.

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Authors contribution MN has completed the whole experimental work, preparation of manuscript and contributed equally to these methodologies. BM helped her in the generation of idea of work, reviewing and editing of the whole procedure, under the supervision of PG.

Declarations

Conflict of interests The authors declare no competing interests.

Ethical approval Hereby, I consciously assure that, for this manuscript, entitled here, the following items are fulfilled. At present, this paper is not being contemplated for publication, elsewhere. All authors have been involved, actively and personally, in all the considerable work, leading to the paper and will take public accountability for this content.

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Synthesis and Performance Evaluation of Castor Oil-Styrene Co-Polymer: An Outstanding Multipurpose Directional Lubricant Additive

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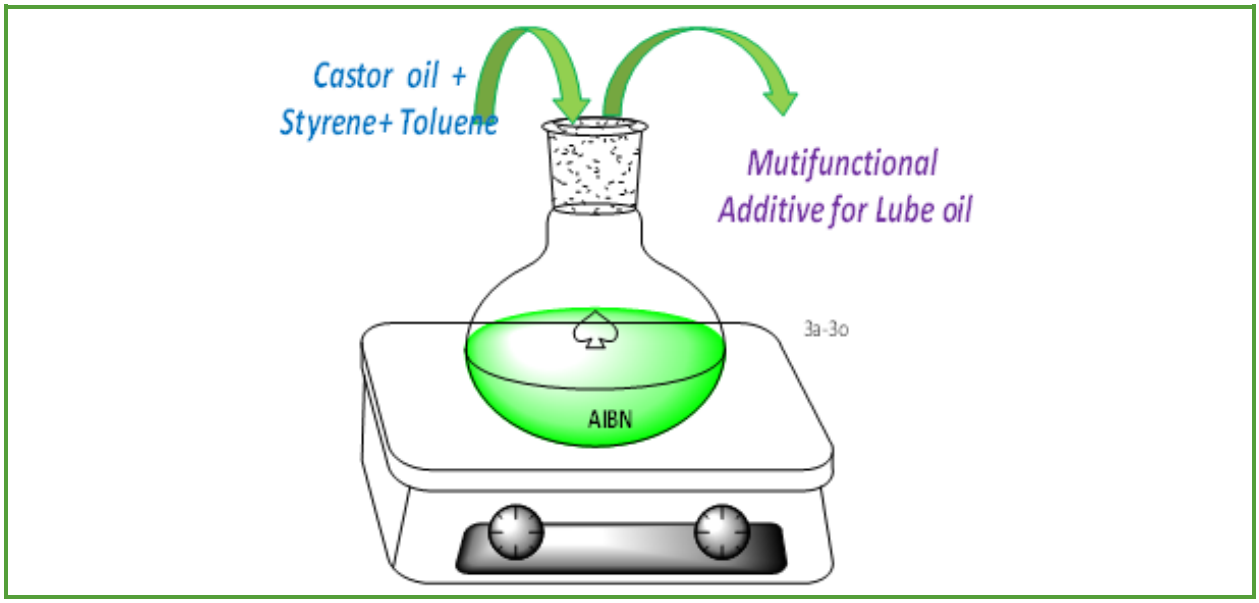
Additives
Pour Point Depressant
Viscosity Modifier
Castor oil
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ABSTRACT

Polymer and chemical industries are actively concentrating on the discovery and application of vegetable oils for polymer composites. In this work, castor oil homopolymers and their copolymers with styrene were made, as well as their assessment was done by spectroscopic methodology, thermo gravimetric analysis (TGA), and gel permeation chromatographic (GPC) strategy. The ASTM standard approach was employed to determine these polymers' efficiency in base oil. Photo-micrographic imaging was utilized to assess the efficacy of additives as pour point depressants by examining their impact on the microstructure. The biodegradability experiment for polymers was also conducted and outcomes are quite promising. Their performance comparisons have been further assessed and reported.
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Graphical Abstract



Introduction

There are many different base fluids and chemical additives used in the formulation of sophisticated lubricants.

The moving surfaces are kept separated from one another by the basal liquid, which creates a fluid zone between them to reduce friction. It reduces the amount of heat generated during operating condition and gets rid of the wear particles. Without sophisticated lubrication, additive chemistry and lubricant conceptualization, it would have been difficult to develop advanced engine and gearbox technologies. Contemporary engine oils are made up of various additives combined with base oils to create a comprehensive product that can meet even the most rigorous performance standards.The compounds, known as additives, satisfy the desired properties of lubricating and repelling the same.

In most cases, they are chemical compounds with a non-polar hydrocarbon chain and a polar head group. Numerous lubricating oil additives are employed, including detergent-dispersants, corrosion inhibitors and substances for usage under extremely high pressures, viscosity index improvers (VIIs), antioxidants (AOs), and pour point depressants (PPDs).

The least temperature at which lubricating oil flows without interruption when refrigerated within defined parameters is known as the pour point. Paraffinic wax, a component of petroleum oils, crystallizes into stiff lattice-like frameworks at lower temperatures, obstructing flow. Hindering the production of wax crystal formations that would block passage of oil at low temperatures is how some high molecular weight polymers work. These chemical additives are also known as pour point depressants, flow improvers, paraffin antagonists, or wax moderators. Pour point depressants have no impact on the temperature or quantity of developed crystals.

The adsorption, co-crystallization, aggregation, and enhanced wax dissolution rate of these compounds are among their most generally acknowledged modes of action. Pour point depressants allow flowing at

temperatures underneath the pour point of unaltered lubricant, because they co-crystallize along with paraffinic wax; alter the development of the lattice-like organization.

Chlorinated polymers, wax alkylated phenol polymers, wax alkylated naphthalene polymers and polymethacrylates are examples of popular pour point depressants.

Another crucial lubricant property, viscosity is assessed using the arbitrary Viscosity Index (VI), which is derived through the measured viscosities within two different temperatures. This change in viscosity with temperature should be kept to a minimum for a lubricant to be effective. Thus, the lubricant performance is improved by a greater VI. Viscosity Index Improvers (VIIs) additives were incorporated into lubricating oils to regulate the rate at which viscosity changes in response to temperature fluctuations.

The behavior of polymer molecules in the oil affects how well VIIs work. The most crucial characteristics of these VIIs are their molecular weight, durability to strain breakdown, and polymer solubility. The lubricant causes the polymer molecule in solution, which is a randomized coil, to enlarge. As the polymer molecules shift from a tightly wound shape to an exposed framework, which has a larger volume, polymer solubility often rises with rising temperature. This volume addition makes the oil more viscous, counteracting the natural decline in viscosity with rising temperature.

The polymer capacity in an oil solution rises along with the polymer molecular weight. As a result, a polymer with a greater molecular weight will have a greater viscosity index than one with reduced molecular weight of similar kind. Acrylate-based polymers have been proved to be very good VIIs.

Some additives are antioxidants in nature. They can enhance the life span of a lubricant through the raising of oxidative constrains of base oils. This is known as anti-wear (AW) property of lubricant, with which they can lower the friction extent in between the movable portions of those oils, by absorbing shock, reducing noise and minimization of the corrosion towards the portions. With decreasing the friction, decreases the extent of heat generation and thus reduction of most of the wear and tear portions occurs. Such additives are known as the anti-wear additives. They are known as extensive pressure additive and able to make a film or barrier or a protective layer on the wear surfaces.

Castor oil is one of the most popular vegetable oils, obtained from the seeds of the castor bean (Figure 1).

It has a wide range of industrial prospects and can be used medicinally as a purgative and an adhesive. Because of their low virulence, bio-absorbability, and outstanding wrangling qualities, such as excellent lubricity, minimal effervescence, great viscosity index [1], and cost effectiveness, this is one of the most commonly used recycled assets for manufacturing chemicals and polymers. Automotive technology [2, 3], medicine, the coatings industry [4], cosmetics, surface-active agents, nutrition, the food and beverage industry, inks [5], pesticides, and plasticizers [6] are just a few industries that use bio-dependent compositions extensively.

This oil is basically made up of triglycerides entity of fatty acids with long chain. These fatty acids consist of various triglyceride kinds, most of which are unsaturated. The fatty acid (FA) chain of this oil has a significant extent of unsaturation (-C=C-), which results in low thermal and oxidative stability and restricts such significance like lubricants into a moderate temperature [7].

To enhance the convenient rigidness and technical features, the synthetic modification of

triglyceride entity is necessary before its application to the field. For this accomplishment, polymerization of the oil is mandatory to enhance its molecular weight and extent of cross linking. Once more, copolymerization of this substance with the proper monomers can provide further benefits, such as ecological phenomenon of the currently prepared copolymer.

Polyacrylates and methacrylates are popular effective execution additives for lube oil. Methacrylates are frequently used as pour point depressant (PPD) and viscosity modifier (VM) of lube oil [8, 9].

However, in modern trend, the use of greener lubricants has brought some limitations to their vast application in automobile industries. In last few decades, to maintain the environmental sustainability and greener approach, the researchers have mainly focused to initiate production of environmentally benign lubricants or greener additives for inventing better fuel wealth, multi utilitarian skill development, and remove chemical threats [10, 11].

Castor oil was taken as a prospective element of copolymerization as it is promotionally accessible for trading, cost effective, and contains satisfactory unsaturation. The current research performs an intense scanning onto the additive efficiency of produced polymeric ones with styrene and castor oil. Four varieties of copolymers of castor oil-styrene were constructed by different styrene concentrations in the mass (8%, 6%, 4%, and 2%).

The paper performs the polymers synthesis followed by their characterization, performance evaluation, and ecological explanation of all polymers.

With this framework, present study is governed to the copolymer production of castor oil-styrene succeed by their characterization (by thermogravimetric analysis to measure thermal stability of polymer and gel permeation chromatographic analysis [GPC] to determine their molecular weight and spectroscopic analysis [IR and NMR] for structural analysis) and estimation of their additive performance (as PPDs, AW, and VMs) in lubricating oil. Moreover, the extent of biodegradability was determined by GPC [12].

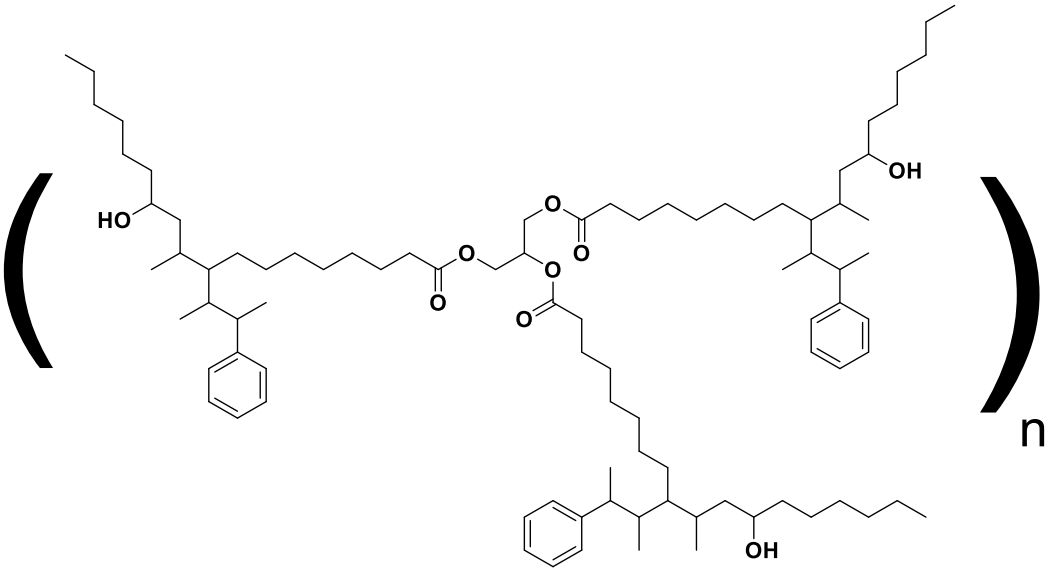


Figure 1. Structure of castor oil-styrene co-polymer

The outcomes of conducted biodegradability experiment for polymers are quite promising. Their performance comparisons have been also assessed and reported. The castor oil and styrene co-polymer demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives.

This study represents a challenging approach for constructing a novel lubricant composition with enhanced flexible additive properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD).

Experimental

Materials and Methods

Sigma-Aldrich, an Indian company, supplied the hydroquinone (> 99%) whereas Conc. H_2SO_4 (98%) and Toluene (GC 99.5%) was supplied by Merck Specialties Pvt. Ltd. The castor oil (CO) (see Table 1 for its fatty acid composition) was obtained from local suppliers whereas Styrene (GC 99.8%)) and Methanol (GC 99.8%) was received from Thomas Baker Chemicals Pvt., Ltd., India. Azobisisobutyronitrile (AIBN, GC 98%,) was obtained from Spectrochem Pvt. Ltd. in Mumbai, India, and was recrystallized from $CHCl_3$-MeOH. All other chemicals were utilized in its original form as received from the supplier without any additional purification. The fungal samples were cultured and obtained from the Microbiology Department of the affiliated organization and the Mineral base oils (BO_1 and BO_2) (see Table 2 for properties) used in the present study was provided by Indian Oil Corporation Ltd. (IOCL), India.

Table 1. Fatty acid components present in castor oil

Fatty acid	Percent composition in castor oil
	Castor oil
Palmitic(16:0)	3
Stearic(18:0)	3
Oleic acid(18:1)	9
Ricinoleic acid(18:1)	75
Linoleic acid(18:2)	10

Table 2. Physical properties of base oils

Properties	Method	BO_1	BO_2
Viscosity at 40 °C in cSt	ASTM D445	7.229	23.472
Viscosity at 100 °C in cSt	ASTM D445	1.874	3.938
Viscosity Index	ASTM D2270	81	86
Pour Point, °C	ASTM D97	-3	-6
Density ($g.cm^{-3}$) at 40 °C	ASTM D4052	0.83689	0.85514

**BO collected from IOCL, Dhakuria, West Bengal.*

Preparation of castor oil homo polymer

Following the same process outlined in the literature [13], homopolymer of castor oil was created at 90 ^{o}C by polymerization reaction in a three necked circularbase flask for 6 h.

Preparation of copolymers

The castor oil- styrene copolymer was constructed using various concentrations of styrene with castor oil. Four varieties of copolymers of castor oil-styrene were constructed with different castor oil concentrations in the mass (8%, 6%, 4%, and 2%). The radical polymerization was performed using the technique that has been previously reported [14].

Results and Discussion

Spectroscopic measurements

FT-IR and NMR techniques were used to characterize the polymers' and composites' spectrum properties. IR spectra in the 400-4000 cm^{-1} wave number region were captured using 0.1 mm KBr cells at room temperature on a Shimadzu FT-IR 8300 spectrometer. Using a 5 mm BBO probe and $CDCl_3$ solvent, NMR spectra were captured through a Bruker Advance NEO 400 MHz FT-NMR spectrometer. TMS was employed as a source of standard information.

Analysis of the spectroscopic data

The analysis of spectroscopic data for the prepared polymers confirmed the predicted structure of the additives.

For copolymers, the presence of ester carbonyl group of castor oil was verified by the characteristic IR absorption peak at 1743 cm^{-1}. In addition, peaks in the range of 2857-2931 cm^{-1} indicated the presence of other components. The peaks at 695 cm^{-1},724 cm^{-1}, 756 cm^{-1}, and 810 cm^{-1}were indicative of the aromatic part of styrene (Figure S1, supporting information).

The ^{1}H-NMR spectra analysis revealed specific chemical shift ranges corresponding to different proton groups in the polymers. Protons in the methyl group were observed between 0.88-0.90 ppm. Protons in the methylene group were assigned peaks ranging from 1.28-1.63 ppm. The methine protons were observed within 2.04-2.30 ppm. The proton associated with -OCH_2 group appeared at 4.08 ppm. Protons from the -$COOCH_2$ group of castor oil peaks are represented by the peaks in the range of 4.10-4.15 ppm. The aromatic ring protons of styrene exhibited a broad peak spanning from 6.80-7.64 ppm (Figure S2, supporting information).

In ^{13}C-NMR spectra, different carbon groups in the copolymer exhibited specific chemical shift ranges, allowing for their identification. Carbon atoms in the CH_3 and CH_2 groups appeared within the range of 14.1-41.0 ppm. Peaks at 58.1 ppm testify the existence of methine carbons in the -CH- of the -COCH group. Peaks ranging from 60.0 to 62.1 ppm and 64.6-68.9 ppm represents carbon atoms in the -OCH_2 groups and -CH_2 carbons in the -$OCOCH_2$- group respectively. The peaks in the range of 127.9-130.8 ppm and 165.6-173.0 ppm represent the aromatic carbons and ester carbonyl carbon (Figure S3, supporting information). The homopolymer of castor oil, showed IR absorption band at 1741 cm^{-1} (Figure S4, supporting information file).

The ^{1}H-NMR spectra of castor oil is presented in Figure S5 (supporting information). The peaks observed within 4.12-4.33 ppm, 0.86-0.90 ppm, 1.26-1.62 ppm and 2.29-2.34 ppm.

Figure S6 (supporting information), indicated the presence of protons from the -

COOCH2 group in castor oil, methyl protons, the methylene protons, and methine protons specific to the alkyl chains.

The Figure S7 of supporting data represents the ^{13}C-NMR spectra for the homopolymer of castor oil, where peak at 173.9 ppm represents ester carbonyl group and the peaks in the range 62.1-68.9 ppm represent the carbons of –OOCH$_2$ group.

Thermo gravimetric analysis (TGA)

Alumina crucible in air was used to measure the thermal stabilities of the synthesized co-polymer and homo polymer using a thermo gravimetric evaluator (Shimadzu TGA-50). A 10 °C/min heating rate was used to operate the system. Calculations were made to determine the samples' percentage weight loss (PWL) as the temperature rose.

Thermo gravimetric analysis (TGA) study

The TGA (Thermo gravimetric Analysis) values of the five polymers are presented in Table 3 and Figure 2. Based on the provided information, several conclusions can be drawn. Polymer P-1 exhibits higher thermal degradation compared to the other polymers, indicating that it is less thermally stable. It begins significant decomposition at 180 °C, resulting in approximately 28% weight loss. For Polymer P-2, major decomposition starting at around 220 °C, leading to approximately 25% weight loss. On the other hand, the thermal decomposition of polymers P-5, P-4, and P-3 is nearly similar, with major decomposition initiating at approximately 255 °C. Therefore, it can be concluded that the copolymerization process has enhanced the thermal stability of the castor oil-based polymers.

Determination of average molecular weights of the copolymer

The number average molecular weight (Mn) and weight average molecular weight (Mw) of the polymers were determined using the Gel Permeation Chromatography (GPC) method. The GPC system used was Water 2414 and polystyrene calibration was employed. The measurements were conducted in HPLC grade THF (Tetrahydrofuran) at room temperature, with a flow rate of 1 mL/min.

The experimental data in Table 4 presents the weight average molecular weights (Mw) and number average molecular weights (Mn) of the prepared polymers (P-1 to P-5). Among all the polymers, P-5 exhibits the highest molecular weight, indicating a larger average molecular size. Enhancing styrene percentage of the castor oil skeleton, correlates with an increase in molecular weight.

Table 3. Percentage composition and TGA values of the prepared polymers

Polymer code	% Composition of monomer (w/w) in the feed		TGA values	
	Castor oil	Styrene	Decom. Temp	PWL
P1	100	0	180/350	28/85
P2	98	2	220/360	25/90
P3	96	4	245/385	20/82
P4	94	6	260/396	17/79
P5	92	8	270/402	16/75

**Decom. Temp.= Decomposition temperature and PWL=Percentage Weight Loss*

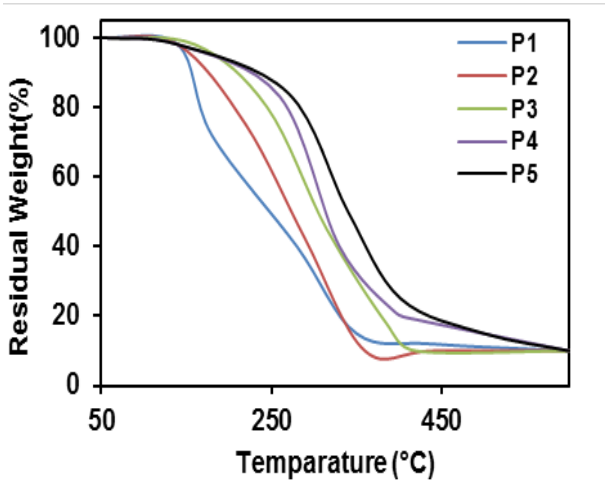


Figure 2. Plausible Schematic diagram of Thermo Gravimetric Analysis (TGA) values

Table 4. Molecular weight of the prepared polymers

Polymer code	Average Molecular weight (before biodegradation)			Average Molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P1	7911	10663	1.21	4561	5023	1.11
P2	16723	24792	1.11	13221	21325	1.63
P3	18563	30768	1.26	15342	26756	1.77
P4	20279	34908	1.35	16765	30289	1.79
P5	27068	40346	1.41	22390	33435	1.51

This suggests that the styrene proportion significantly influences the polymerization process. The observed trend highlights the significance of styrene percentage in determining the resulting molecular weight of the polymers.

Therefore, it can be concluded that the presence and proportion of styrene in the polymer backbone has a crucial impact on the molecular weight characteristics of prepared polymers.

Determination of viscosity index

To assess the effectiveness of the manufactured polymeric additives as viscosity modifiers, the viscosity index (VI) of the additives in a paraffinic base oil (VM) was determined (Table 5). The VI calculations were performed using the formulae provided by Tanveer and Prasad, following the ASTM D2270 method. VI values were calculated for various concentrations of additives in the base oil, ranging from 1% to 5% (w/w). The experimental VI values are presented in Table 5. VI values enhance as the polymers concentration in the base oil increases.

This suggests that higher polymer concentrations have a positive impact on viscosity index. The viscosity of lubricating oil typically represents an inversely proportional relationship with temperature. However, with increasing temperature, polymer molecules expand, resulting in the enlargement of micelles. The increased micelle size hinders the viscosity reduction of the lubricant.

When the polymer concentration in lubricating oil is increased, it results in an augmentation of the volume of polymer

micelles. Consequently, this enhances the viscosity index (VI) property of the lubricating oil. Incorporating styrene in the homo-polymer skeleton of castor oil, leads to an increase in VI values which results in higher crosslink density of the copolymers. Among the copolymers, P-5 demonstrates the maximum impact on VI enhancement, followed by P-4, P-3, P-2, and P-1. Grater VI values observed in P-5 can be attributed to its larger solvated additive molecule (micelle) volume. This characteristic can be linked with greater average molecular weight and lower PDI (Polydispersity Index) value.

Determination of pour point

The pour points of the lubricants used in the present study was determined (in accordance with ASTM D97 standard) using a Cloud and Pour Point Tester model WIL-471 (India). The instrument can also be used for the measurement of pour point depressant characteristic of base oils with polymeric additives. In addition, five distinct additive concentrations were applied for every sample in this instance.

Table 6 displays the pour point values of the lubricants obtained by blending the polymers at different concentration levels ranging from 1% to 5% (w/w). All the polymers exhibit effectiveness as pour point depressants (PPD). This means that they are capable of reducing the pour point temperature of the lubricants. The efficiency of the polymers as pour point depressants increases with an increase in the concentration of polymers, up to limit 4% concentration.

Beyond this concentration, further increases do not significantly enhance the pour point performance. The effective interaction between the polymer and the paraffinic wax present in the base oil is believed to be responsible for the improved pour point performance. At the optimal concentration (4%), the polymer effectively interacts with the paraffinic wax, leading to a reduction in the crystal size of the wax [17].

P-4 demonstrates the best efficiency as a pour point depressant. It exhibits superior efficiency in lowering the pour point temperature compared to the other polymers. To sum up, the experimental data suggests that all the polymers can be utilized as pour point depressants, till a certain threshold level. Furthermore, among the prepared polymers, P-4 stands out as the most effective pour point depressant.

Analysis of anti-wear properties

Table 7 lists the values of wear scar diameter (WSD) obtained through the FBWT (Four Ball Wear Test) apparatus, using a 392 N load, for the lubricant compositions. Blending the polymers with the lubricant leads to a significant improvement in the anti-wear performance, as represented by the lower WSD values of the lubricant compositions.

Table 5. Viscosity index (VI) values of polymer blended base oil

Polymer code	VI of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

Table 6. Pour point (PPt) values of polymer blended base oil

Polymer code	PPt of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

Table 7. Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition

Polymer code	Anti-wear property in terms of wear scar diameter (WSD in mm) of polymer blended base oil at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P1	1.107	1.045	1.025	1.016	1.009	1.001
P2	1.107	1.039	1.017	1.008	1.005	0.995
P3	1.107	1.034	1.011	1.002	0.994	0.983
P4	1.107	1.028	1.004	0.995	0.988	0.978
P5	1.107	1.022	0.998	0.986	0.981	0.969

This indicates that the addition of polymers enhances the lubricant's capability to reduce wear between moving metal surfaces.The copolymers exhibit better anti-wear performance compared to the homopolymer. This suggests that the presence of multiple monomers in the copolymers contributes to their improved tribological properties.

Among the polymers, P-5 at a concentration of 5% demonstrates the highest reduction in WSD values. The lubricant composition with P-5 forms a strong film amid the two moving metal surfaces; effectively reducing wear. The observed improvement in anti-wear performance is due to several factors. Initially, the higher molecular weight of the polymers, especially in the case of P-5, contributes to a greater number of polar side chains from ester carbonyl groups and hydroxyl groups present in rapeseed oil.

These polar groups enhance the lubricant's film-forming properties. Moreover, the higher percentage of styrene in the polymer feed, with its aromatic ring structure, likely plays a substantialpart in enhancing the tribological properties of lubricant composition.

Photo micrograph and wax modification

To investigate the impact of an additive on wax crystallization, the wax modification of the base fluid was examined using a Banbros polarizing microscope (BPL-400B, India) equipped with a cooling thermostat (Figure 3). The microscope provided a magnification of 200X, enabling detailed observation of the base fluid.

The temperature was controlled at 0 °C during the study to ensure consistent conditions for the examination of wax crystallization.

By capturing photo micrographic images of the base fluid under these controlled settings, the effectiveness of the additive in controlling wax crystallization could be evaluated.

Analysis of the photo micrographic image

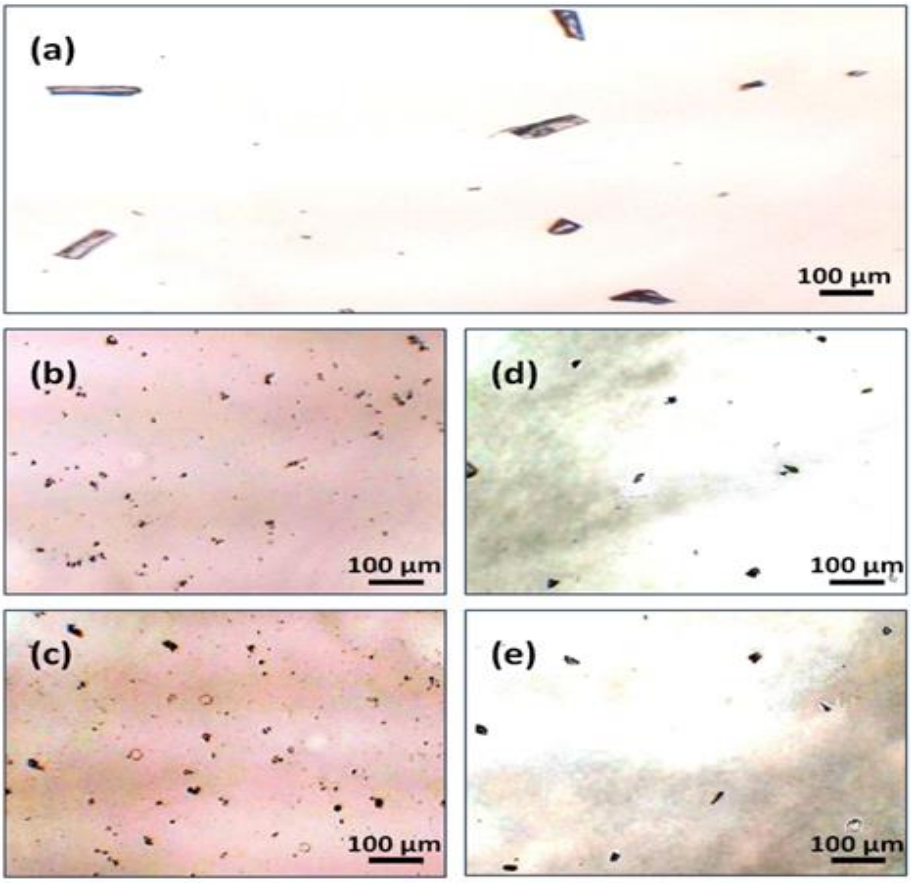


Figure 3. Photomicrograph of: (a) pure base fluid, (b) base fluid + additive P-1 (4%, w/w), (c) base fluid + additive P-3 (4%, w/w), (d) base fluid + additive P-4 (4%, w/w), and (e) base fluid + additive P-5 (4%, w/w)

Table 8. Result of biodegradability test by disc diffusion method and soil burial degradation

Sample	Weight loss in disc diffusion method in gm					Weight loss in soil burial degradation method in gm
	Pathogens used					
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.56	0	0.59	0	0	0.55
P-2	0.44	0	0.51	0	0	0.48
P-3	0.35	0	0.46	0	0	0.39
P-4	0.31	0	0.34	0	0	0.33
P-5	0.27	0	0.26	0	0	0.28

**CC=Calletotricheme camellia, FE= Fussariumequisitae, AA=Alterneria alternate*
**CG=Colletrichumgleosproides, and CE=Curvulariaeragrostidies.*

The photomicrographs of the pure base fluid and the pure base fluid with added additives are presented in Figure 3. The photo micrograph (Figure 3a) of the original base fluid (pour point =-6 °C) reveals the presence of large rod-shaped wax crystals. These crystals contribute to the high pour point of the base fluid. Upon adding additive P-2 (pour point = -24 °C, Figure 3b) and additive P-3 (pour point = -25 °C) (Figure 3c) to the base fluid at a concentration of 4% (w/w), a significant decrease in the volume and shape of the wax crystals is observed. The obtained crystals appear to be more dispersed

compared to the original base fluid. Similarly, additive P-4 (Figure 3d) (pour point = -28 °C) and additive P-5 (pour point = -30 °C, Figure 3e) also result in a substantiallessening in the size of the wax crystals. The crystals appear highly dispersed in the base fluid.

Biodegradability analysis

The extent of biodegradability was assessed using the ISO 846:1997 method for soil burial testing and the disc diffusion method against fungi. After the experiments, weight loss in the polymer samples was evaluated, and IR spectra were collected to look for any noticeable shifts in IR frequencies [18, 19]. With the recovered polymers, further GPC examination was underwent in expectation of changes in Mn and Mw following biodegradation [12].

Disc diffusion method

In Petri dishes, culture media for fungi strains were made using the necessary quantity of agar, dextrose and potato extract mixture. Before usage, all the glass equipments underwent autoclaving. The test involved the use of five different fungal pathogens: Curvulariaeragrostidis (CE), Colletotrichum gloeosporioides (CG), Alternaria alternata (AA), Fusarium equiseti (FE), and Colletotrichumcamelliae (CC). The culture media's transformation from yellow to black confirmed the fungus growth. One gram of specific polymer samples was placed to Petri dishes, where they were then cultured at 310 K for 30 days. After 30 days, rescued polymer samples were purified, chloroformed-cleaned, and dried in an open tank [18]. Dry sample masses were determined, and then FT-IR and GPC analyses were performed.

Soil burial degradation test

The ISO 846:1997 method was used to conduct the soil burial test. We buried polymer films in soil that was dug up from the university campus. In a humidity chamber, a thermostat was used to maintain a temperature of 303 K while adjusting the soil's humidity to between 50% and 60% prior to usage. After 60 days, the films that had been buried were found. Polymer samples were purified, dried, and chloroform washed [20]. After the dried samples were examined, FT-IR and GPC analyses were performed.

Analysis of biodegradability test

The results of the biodegradability tests, as presented in Table 8, indicate significant biodegradability for both the homopolymer (P-1) and copolymers (P-2 to P-5) when exposed to fungal pathogens, specifically Calletotricheme camellia and Alternaria alternata. As expected, the homopolymer of castor oil (P-1) exhibited better biodegradability compared to the copolymers. Detailed analysis of the experimental data revealed noticeable biodegradation for all the samples. The results obtained from the Sequential Biodegradation (SBD) study indicate a progressively increasing trend for the degradation of polymeric additives with test duration. Moreover, both the homopolymer and copolymers exhibited substantial weight losses when exposed to the fungal pathogens, particularly Alternaria alternata, in the Direct Degradation (DD) test.

As anticipated, the homopolymer (P-1) with zero styrene content and the presence of natural monomer units displayed the highest level of biodegradability among all the additives, as observed in both tests. In the Fourier Transform Infrared (FT-IR) analysis, the peaks corresponding to the polymer P-1 exhibited shifts in their positions and a significant reduction in the height of peak and

its intensity after DD test. This confirms biodegradable nature of prepared polymers, as indicated by the changes in the IR peak positions, peak intensities, and the Polymer Weight Loss (PWL) values before and after the biodegradation tests.

Conclusion

Copolymers of castor oil and styrene have higher thermal stability than castor oil alone. Again, when styrene concentration in the copolymers rises, so does thermal stability. However, the shear stability of castor oil homopolymer is higher than that of their styrene copolymers, and shear stability declines as styrene concentrations in the copolymers rises. The castor oil-styrene copolymer functions as a much better PPD and viscosity modifier than the castor oil homopolymer, according to performance assessment of the additives. In addition, research shows that while castor oil homopolymer is significantly biodegradable, but very poor solubility in lube oil and showed low thermal stability and middling performances as a PPD and VM. In contrast, the castor oil and styrene copolymer demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives. Indeed, the study mentioned above presents a promising approach for formulating a novel lubricant composition with enhanced flexible additive properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD). This approach can contribute to the development of environmentally friendly lubricants that offer enhanced performance and functional capabilities, making them an attractive option for various applications.

Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Supporting Information

Supporting information contains the experimental analysis, spectroscopic data, and scanned copies of ^{1}H-, ^{13}C-NMR and FT-IR spectra of some synthesized homopolymers and co-polymers.

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Evaluation and Synthesis of Environmentally Benign Multifunctional Additives for Lube Oil

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Behenyl acrylate (BA) homo-polymer and its copolymers with citral were synthesized with varying percentage compositions (w/w) and subjected to thorough characterization through GPC (gel permeation chromatography) analysis and spectroscopic techniques (FT-IR, NMR). The polymers' capability was assessed through viscosity index improvers/viscosity modifiers (VII or VM), anti wear (AW) additives and pour point depressants (PPD) for base oils (lubricating oil). The action mechanism of the PPD properties was investigated through photomicrographic analysis. Additionally, the thermal stability of the polymers was measured using TGA or thermo gravimetric analysis. Biodegradability tests on copolymers were conducted using soil burial test (SBT) and the Disc Diffusion (DD) method. The copolymers exhibited exceptional PPD, VII, and AW performance when incorporated into lubricating oil.

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Keywords: Citral; copolymer; biodegradable; lube oil; viscosity index improver; pour point depressant; anti wear; photo micrographic analysis.

1. INTRODUCTION

Lubricants consist of a combination of a base fluid and additives designed to enhance performance. The additive content typically ranges from 1% to 30% or even higher. While mineral oils of petroleum origin are commonly used as base fluids, vegetable and synthetic oils also find application. Polymeric additives are introduced to the base fluid to improve the operational efficiency of engine oil and extend the engine's lifespan.

Additives typically serve various functions, such as ameliorating the pour point (PP) [1] of base oils through the dissolution of wax crystal deposits [2] at lower temperatures, boosting the viscosity index (VI) [3] to maintain viscosity stability amidst temperature fluctuations, minimizing wear, and effectively transporting contaminants away. These components are commonly labeled as viscosity index improvers (VII) [4], pour point depressants (PPD) [5], detergent-dispersants [6] and antiwear agents [7].

Commercially available synthetic acrylate-based additives, although effective, are non-biodegradable, prompting environmental concerns. The increasing desire for environmentally friendly technology has spurred researchers to create lubricant additives that are ecologically benign. Vegetable oils [8-11], recognized for their natural occurrence, biodegradability, non-toxicity, and high viscosity index, present a promising alternative [12]. They exhibit excellent tribological properties, acting as antiwear and friction modifiers in lubricant formulations [13,14].

Modified vegetable oils have been utilized as additives in lubricating oils in numerous cases, with patents describing their application as extreme pressure additives, friction modifiers, and viscosity index improvers [15-17]. In line with these considerations and as part of our ongoing efforts to develop chemical additives for lubricating oil, our present investigation focuses on synthesizing copolymers of acrylate ester based citral through copolymerization. The aim is achieving an optimal balance between performance and environmentally friendly chemistry. The study encompasses the synthesis and characterization of behenyl acrylate (BA) homopolymer and BA copolymer with citral, followed by biodegradability testing and evaluation of their effectiveness as pour point depressants, viscosity modifiers, and antiwear additives.

2. MATERIALS AND METHODS

2.1 Materials

Hydroquinone, sulfuric acid and Toluene, were sourced from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilized with 0.02% Hydroquinone monomethylether), Behenyl alcohol and n-Hexane were procured from SRL Pvt. Ltd. Methanol and Benzoyl Peroxide (BZP) wereobtained from Thomas Baker (Chemicals) Pvt. Ltd. andLOBA chemicals respectively.They underwent recrystallization using a $CHCl_3$-MeOH mixture before application. Citral was sourced from a nearby grocery store, and the base oils were acquired from IOCL (Indian Oil Corporation Ltd.), Kolkata, India. Remaining substances were utilized in their pristine condition without extra purification. All specimens were subjected to testing before reaching their designated expiration dates.

2.2 Methods

The thermal radical polymerization of behenyl acrylate and its subsequent copolymerization with citral at varying concentrations (5%, 10%, and 15% w/w) were carried out employing benzoyl peroxide (BZP) as the initiator following the method as reported elsewhere [16]. The resulting additives were subjected to thorough characterization using spectral analysis techniques, including Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The determination of the average molecular weight of the polymeric additives, both number average (Mn) and weight average (Mw), was accomplished using gel permeation chroma-tography (GPC). Tetrahydrofuran (THF) of high-performance liquid chromatography (HPLC) grade served as the mobile phase in the water GPC system, calibrated with polystyrene, and the analysis was conducted at room temperature.

The thermal stability of the additives was evaluated using the Mettler TA-3000 system,

employing a heating rate of 10 K min^{-1}. The multifunctional performance of the base oil treated with additives, encompassing improvements in viscosity index, pour point depression, and antiwear properties, was assessed in accordance with ASTM methods. The antiwear (AW) characteristics were determined utilizing a Four-ball wear test apparatus, following the ASTM D 4172-94 method [18], with a weld load of 392 N at 75°C for 30 minutes and a rotational speed of 1200 rpm.

The biodegradability of the polymeric additives underwent testing through the disc diffusion method [19], evaluating their effectiveness against fungal pathogens, and the soil burial test as per ISO 846:1997 [20,21]. Microbial degradation was confirmed by measuring the shift in the infrared (IR) frequency of the ester carbonyl after the biodegradability test.

3. RESULTS AND DISCUSSION

3.1 Spectroscopic Description

In FT-IR spectrum, homopolymer of behenyl acrylate (P-1) demonstrated an absorption peak at 1732 cm^{-1}, corresponding to ester carbonyl, attached with distinctive peaks at 1467, 1271, 1190, and 1060 cm^{-1}. The ^{1}H NMR spectra of P-1 revealed a broad singlet centered at 4.02 ppm, associated with the $–OCH_2$ protons. Methyl protons from the behenyl chain were evident between 0.81 ppm and 0.86 ppm, and the lack of a singlet in the 5-6 ppm range indicated the absence of vinylic protons in the polymer. The ^{13}C NMR spectrum of P-1 disclosed the carbonyl carbon at 174.4 ppm, along with other SP^3 carbons ranging from 65.03 to 10.66 ppm.

In FT-IR spectrum of the copolymers, the ester carbonyl peak appeared at 1731 cm^{-1}, containing a peak at 1714 cm^{-1} corresponding to the citral's aldehydic group. The ^{1}H NMR of copolymers exhibited a multiplet in the span of 4.119-4.402 ppm, indicating $–OCH_2$ protons. SP^3 protons were observed within 1.259-1.989 ppm, while peaks at 5.343 ppm and 5.360 ppm were attributed to ethylenic unsatura-tionfrom-citralportion of copolymer. One peak around 10 ppm indicated presence of the aldehydic hydrogen of citral in that copolymer. In^{13}C NMR of the copolymer, peaks within 167.70-173.36 ppm indicated the ester carbonyl carbon. Peaks at 190.81 ppm were due to the aldehydic carbonyl group of citral. The $–OCH_2$ carbon peak appeared at 68.93 ppm. Peaks within 14.09-34.05 ppm represented all SP^3 carbons of the copolymer.

3.2 Performance of the Prepared Additives in the Form of Pour Point Depressant

The results of pour point depressant (PPD) properties of the prepared samples, covering a range of additive concentrations within 1 wt% to 5 wt%, are outlined in Fig. 1. The figure vividly demonstrates the efficacy of the prepared additives as pour point depressants, showcasing a consistent reduction in pour point with increasing additive concentration. Notably, the pour point magnitudes of copolymers (P-2, P-3, and P-4) exhibit a remarkable similarity and consistently register lower values compared to the homopolymer (P-1). Consequently, all copolymers demonstrate significant pour point depressant properties.

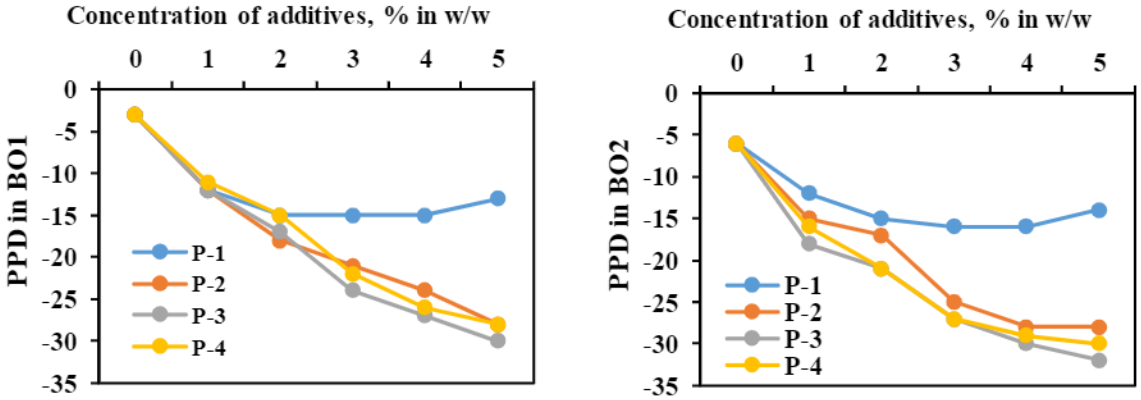


Fig. 1. Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

The efficacy of the polymers as potent pour point depressants was evaluated through photomicrographic experimentation. The wax crystal size exhibited a notable reduction, transitioning from a large crystal structure in the base oil to very small dots dispersed in the oil phase of the lubricating oil [22].

3.3 Performance of the prepared additives as viscosity index improver (VII)

Fig. 3 presents the viscosity indexes for base oils treated with additives derived from polymers (P-1, P-2, P-3, and P-4). The data reveals a steady increase in VI magnitudes as the polymer concentration rises in both base oil types (BO1 and BO2), reaching a peak at 4%. The elevated polymer concentration corresponds to an increased volume of polymer micelles within the oil solutions. Consequently, a higher concentration of the polymer contributes to a higher VI, in contrast to a lower concentration of the same polymer.

3.4 Performance of the Prepared Additives as Anti Wear Additive

A reduction in wear scar diameter (WSD in mm) was observed with increasing additive concentration in the case of studied base stocks with varying load conditions (Table 1). The most distinct drop was observed at 20 kg load condition, as illustrated in Figs. 2 and 3. This suggests that the additives exhibited comparatively lesser effectiveness at higher load conditions. However, there was no noteworthy enhancement in the performance beyond a 5% additive concentration.

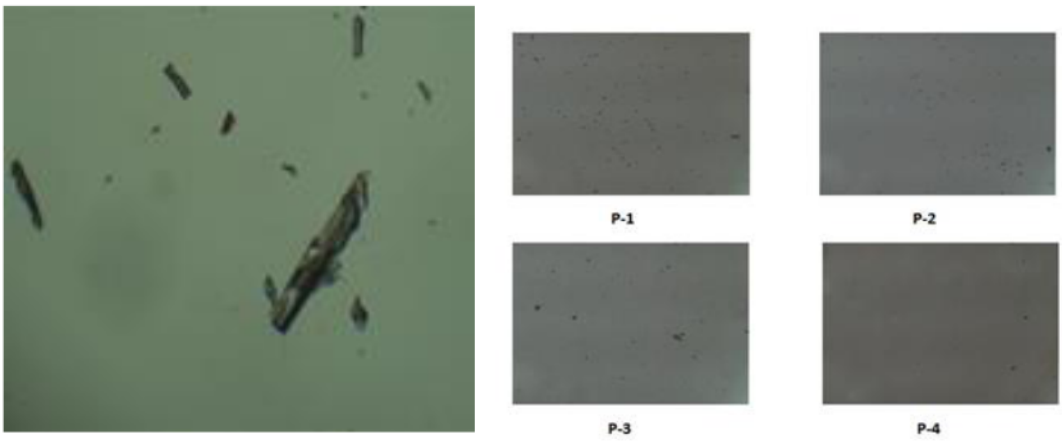


Fig. 2. Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) Doped base oil (right side)

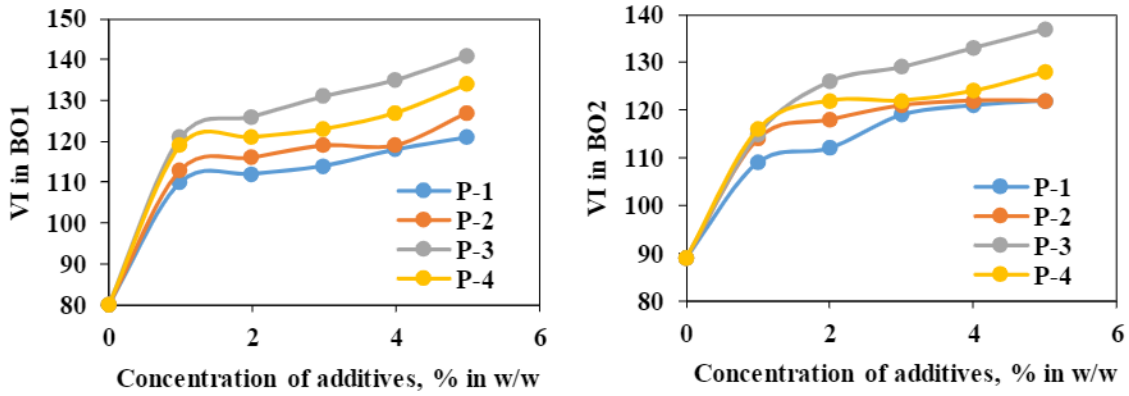


Fig. 3. The VIs corresponding to additive-doped base oils

Table 1. Anti wear values in terms of WSD in mm of polymers P-1, P-2, P-3 and P-4 in the base oils (BO1 and BO2) at 40 kg load

	WSD in mm. in BO1 Concentration of the additives, % in w/w						WSD in mm. in BO2 Concentration of the additives, % in w/w					
Sample	0	1	2	3	4	5	0	1	2	3	4	5
P-1	1.067	0.991	0.887	0.718	0.713	0.665	1.110	0.984	0.907	0.865	0.844	0.823
P-2	1.067	0.954	0.861	0.711	0.688	0.645	1.110	0.971	0.891	0.843	0.821	0.812
P-3	1.067	0.901	0.813	0.703	0.641	0.633	1.110	0.898	0.822	0.804	0.791	0.776
P-4	1.067	0.903	0.811	0.710	0.632	0.635	1.110	0.846	0.798	0.806	0.793	0.781

It was observed that the studied copolymers exhibited superior antiwear properties compared to the homopolymer (P-1). The presence of aldehydic functionality and ester functionality can be attributed to such observation [23,24]. As a result, copolymer (P-4), with larger fraction of citral units, demonstrated enhanced antiwear performance.

3.5 Analysis of Biodegradability Test Result

The biodegradability test results obtained from disc diffusion method and soil burial test (Table 2) indicates notable biodegradability for fungal pathogen Alternaria alternata, compared to the homopolymers. This observation was subst-antiated by the shift in the IR frequency of the ester carbonyl. As anticipated, the copolymer exhibited superior biodegradability in comparison to the homopolymer.

Table 2. Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives

Disc diffusion method		*Soil burial test*
Polymers	***Alternariaalternata* Wt. loss(%)**	**Microorganism Wt. loss(%)**
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

3.6 Determination of Molecular Weight of the Polymers

The molecular weight data obtained from the GPC analysis method (Fig. 4) indicates the drop in molecular weight, both Mw and Mn compared to the homopolymers. The GPC data also suggested that the gradual increase in citral concentration in the feed of polymerization resulted in a gradual decrease in the Mol wt and the drop is directly related to the increase in performance of the additive doped base oil upto a certain limit. The poly dispersity index values indicated the linear nature of the polymer chain which is a very significant parameter to yield the best performance of the polymeric additives.

3.7 TGA Data of all the Polymer Samples

Table-3 displays the Thermogravimetric Analysis (TGA) data for both the homopolymer and copolymer of dodecyl acrylate. The data reveals that the copolymers (P-2, P-3, and P-4) exhibit greater thermal stability compared to the homopolymer (P-1). Furthermore, there is a discernible trend indicating that as the concentration of citral in the feed increases, the thermal stability of the copolymers also increases.

Table 3. TGA data for homo and copolymer of behenylacrylate

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
P-1	513	84
	541	77
	562	16
	589	4
P-2	523	86
	551	80
	577	21
	611	5
P-3	561	85
	584	79

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
	605	23
	627	8
P-4	566	85
	589	80
	617	7
	640	5

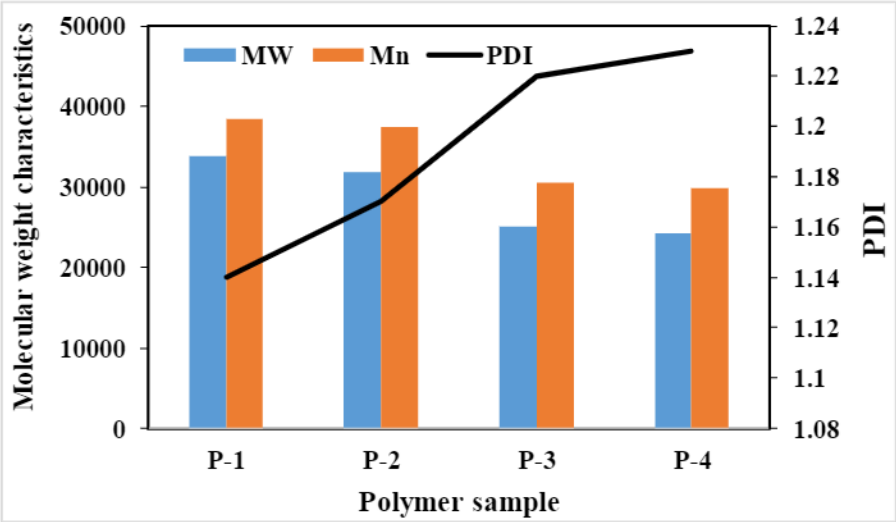


Fig. 4. Molecular weight characteristics of the polymers

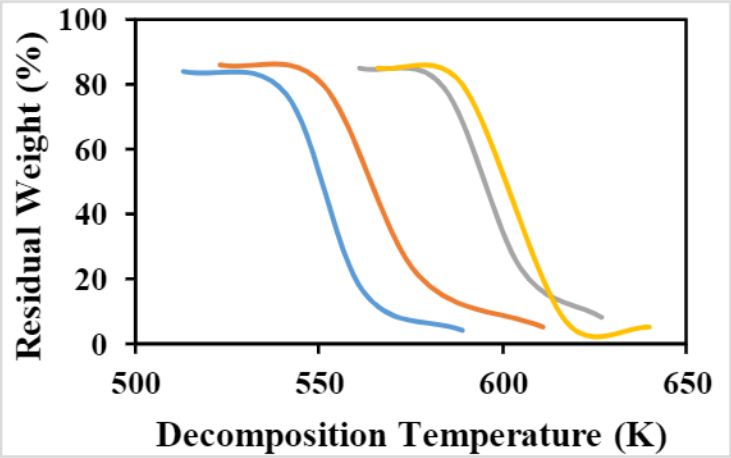


Fig. 5. TGA data for homo and copolymer of behenylacrylate

3.8 Physical Properties of Base Oils

Table 4. Physical properties of Base oils

Properties	*BO1*	*BO2*
Density(kg.m^{-3}) at 313K	839.98	918.68
Viscosity at 313K	5.97×10^{-6}	20.31×10^{-6}
Viscosity at 373K	1.48×10^{-6}	3.25×10^{-6}
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

4. CONCLUSIONS

All the copolymers (P-2, P-3, and P-4) along with the homopolymer (P-1) demonstrated excellent viscosity index improver (VII), pour point depressant (PPD) and antiwear (AW) properties. Additionally, the copolymer also exhibited significant biodegradability. Therefore, the copolymer, derived from castor oil and behenyl acrylate, holds promise as a potential environmentally friendly multifunctional additive for lubricating oil.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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