

A Catalyst Design for Preparation of Ultrahigh Molecular Weight Polyethylene

by

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Under the supervision of
Dr. Samir H. Chikkali (Supervisor),
Dr. H. V. Pol (Co-Supervisor)



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Dedicated to



Late Tarabai V. Bodkhe

You will always be remembered.....

Special Thanks

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Father



Brother



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Sister



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Abstract

List of Publications and Patents

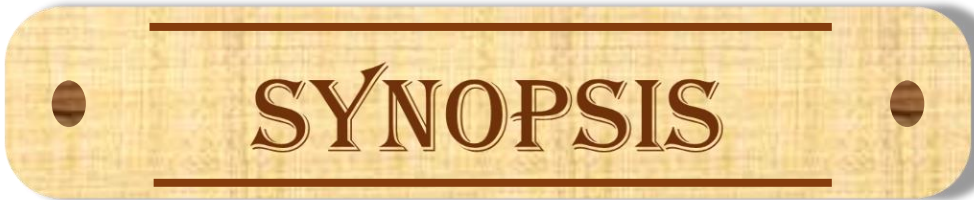
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ABBREVIATIONS

aq	Aqueous
Benz.	Benzoxazinone
Mv	Viscosity average molecular weight
Mn	Number average molecular weight
Mw	weight average molecular weight
PDI	Polydispersity index
Tm	Melting temperature
χ	Crystallinity
Ti (NMe ₂) ₄	Tetrakis(dimethylamino)titanium (IV)
CCDC	Cambridge Crystallographic Data Centre
CDCl ₃	Deuterated chloroform
cm	Centimeter
conv	Conversion
CSD	Cambridge Structural Database
d	Doublet
Da	Dalton
DCM	Dichloromethane
DEPT	Distortionless enhancement by polarization transfer
HSQC	Heteronuclear Single Quantum Coherence
HMBC	Heteronuclear Multiple Bond Correlation
DFT	Density functional theory
DMF	Dimethylformamide
DSC	Differential scanning calorimeter
Equiv	Equivalent
ESI-MS	Electro-Spray Ionization Mass-Spectroscopic
EtOH	Ethanol
EtOAc	Ethyl acetate
etc	et cetera
Fig.	Figure
FTIR	Fourier-transform infrared spectroscopy
gm	Grams

HCl	Hydrochloric acid
hr	Hour
Hz	Hertz
LN ₂	Liquid nitrogen
m	Multiplet
M ⁺	Molecular ion
MeOH	Methanol
mg	Milligrams
MgSO ₄	Magnesium sulfate
MHz	Megahertz
min	Minutes
mL	Milliliter
mmol	Millimole
n-BuLi	n-Butyllithium
Na ₂ SO ₄	Sodium sulfate
NEt ₃	Triethyl amine
NMR	Nuclear Magnetic Resonance
q	Quartet
RT(rt)	Room temperature
Rt	Retention time
Rf	Retention factor
br	Broad
s	Singlet
t	Triplet
Tol.	Toluene
TLC	Thin layer chromatography
WAXD	Wide-angle X-ray diffraction
TOF	Turnover frequency
MAO	Methylaluminoxane
HT-GPC	High Temperature Gel Permeation Chromatography
TDMAT	Tetrakis dimethyl amido titanium precursor
TiCl ₄	Titanium tetrachloride
d-entangled PE	Disentangled Polyethylene
UHMWPE	Ultrahigh Molecular Weight Polyethylene



SYNOPSIS

A Catalyst Design for Preparation of Ultrahigh Molecular Weight Polyethylene

		Synopsis of the Thesis to be submitted to the Academy of Scientific and Innovative Research for Award of the Degree of Doctor of Philosophy in Sciences/ Engineering	
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Co-supervisor		Dr. H. V. Pol	

1. Introduction:

The thesis, titled “*A Catalyst Design for Preparation of Ultrahigh Molecular Weight Polyethylene*” is organized into five chapters. **Chapter-1** provides a literature review on significant advancements in the area of catalyst development for the production of UHMWPE and highlights the challenges in achieving ultrahigh molecular weight polymer (UHMWPE) synthesis. The chapter also explores methods to specifically produce disentangled UHMWPE rather than its entangled counterpart.^{1,2} **Chapter-2** presents a surprise encountered during the synthesis of imine carboxylate ligand backbone, leading to detailed investigations into the formation of benzoxazinone.³ **Chapter-3** details the synthesis of a neutral titanium (**Cat.1**) complex, [bis-dimethylamido-Ti-(bis-iminocarboxylate)]. **Cat. 1** was synthesized by treating [Ti (NMe₂)₄] with 2-((4-methoxybenzylidene) amino) benzoic acid, yielding the desired complex [bis-dimethylamido-Ti-(bis-iminocarboxylate)]. The identity of **Cat.1** was confirmed through a combination of 1D and 2D NMR spectroscopy and mass spectrometry. Various cocatalysts were tested for activation, among which MMAO (modified methylaluminoxane) was found to be the most effective.⁴ **Chapter- 4** presents sterically tuned three different cyclohexylphenoxyimine



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ligands and their corresponding titanium complexes. These complexes were characterized using multiple spectroscopic techniques, The steric bulk was calculated using DFT, and its effects on ethylene polymerization were studied for the production of disentangled UHMWPE. **Chapter-5** summarizes the findings and outlines potential directions for future research.

2. Methodology and Results

Chapter 2: *Inverting the Reactivity of an Aldehyde and Amine to Benzoxazinones: Mechanistic Understanding*

Schiff-base reactions have long been pivotal in synthetic chemistry, enabling the construction of a wide range of functional molecules. However, the inherent reversibility of these reactions poses significant challenges, including low yields and poor selectivity, particularly when synthesizing complex molecules such as benzoxazinones. Benzoxazinones are a valuable class of compounds with applications as a prodrug in pharmaceuticals and fine chemical manufacturing. Traditional synthetic approaches for these compounds often require harsh conditions or exhibit limited scope, restricting their practical and industrial utility. The key challenge lies in achieving selective suppression of Schiff-base formation while promoting alternative pathways for benzoxazinone synthesis.

In response to these challenges, a groundbreaking synthetic strategy has been developed, leveraging secondary interactions to regulate the reactivity of amines and aldehydes. Specifically, the strategic placement of an ortho-substituent suppresses Schiff-base formation and enhances benzoxazinone production. This innovative approach introduces hydrogen-bonding motifs at the hemiaminal intermediate stage, effectively directing the condensation reaction.

Experimental evidence demonstrates the efficacy of our strategy, with reactions such as 2-amino-6-methylbenzoic acid and benzaldehyde achieving 86% selectivity for the desired benzoxazinone. Impressively, the reaction with pentafluoro benzaldehyde resulted in quantitative benzoxazinone formation. The robustness of the strategy was highlighted by the synthesis of a 30-compound library and successful gram-scale production. Remarkably, the reaction remained insensitive to



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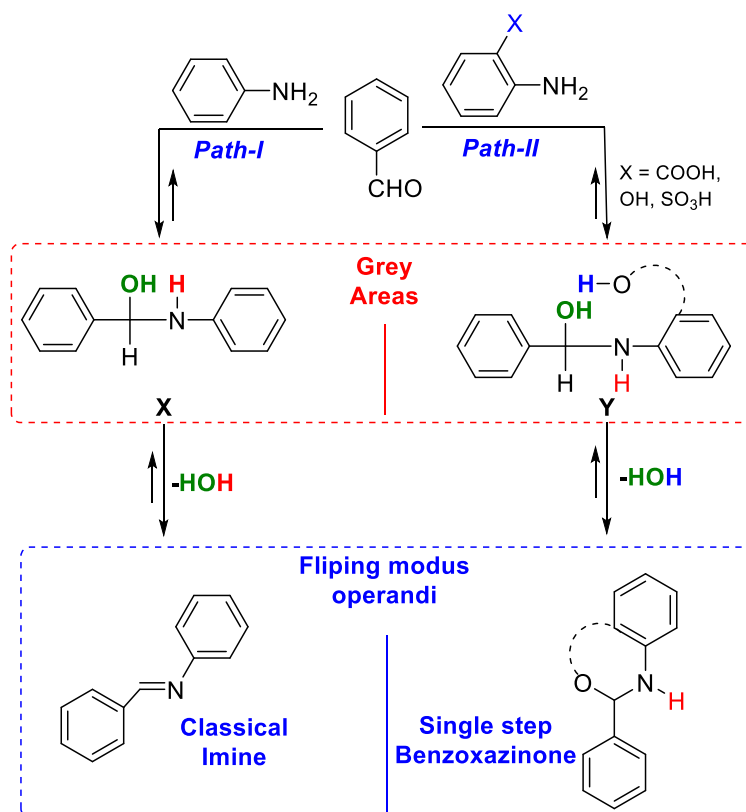


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electronic substituent effects, delivering high yields across a range of electron-donating and electron-withdrawing substituents. Even aliphatic aldehydes like cyclohexane carboxaldehyde achieved near-quantitative benzoxazinone yields. (Scheme 1)



Scheme 1: Benzoxazinone synthesis by Schiff base reaction and reactivity modulation.

The mechanistic investigations, supported by low-temperature NMR, UV–Vis spectroscopy, and isotopic labeling, confirmed the predominance of Pathway B, with DFT calculations showing it as the lowest energy route (20 kcal/mol lower than Pathway A and 35 kcal/mol lower than Pathway C). These findings underscore the critical role of weak secondary interactions in enabling precise control over reaction outcomes.

This work addresses the limitations of conventional methods by offering a scalable, selective, and versatile approach to benzoxazinone synthesis. It sets the stage for broader applications of this

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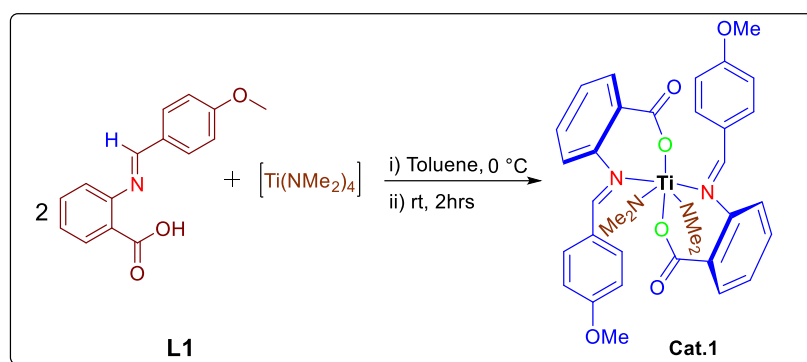
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strategy in pharmaceutical and fine chemical industries, transforming how Schiff-base chemistry is applied to complex molecular architectures.

Chapter 3: Ti-iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene

Disentangled ultrahigh molecular weight polyethylene (d-UHMWPE) is a niche, highly sought-after, and emerging class of engineering polyethylene. However, the synthesis of d-UHMWPE is uncommon and is equally challenging. Here, we report a Ti-iminocarboxylate complex that produces d-UHMWPE under ambient polymerization conditions.



Scheme 2: Synthesis of amido Ti-iminocarboxylate complex **Cat.1**.

Treatment of tetrakis(dimethylamido-titanium) $[Ti(NMe_2)_4]$ with 2-((4-methoxybenzylidene)amino) benzoic acid produced a novel titanium complex (**Cat.1**) [bis-dimethylamido-Ti-(bis-iminocarboxylate)] (Scheme 2). The identity of **Cat.1** was unambiguously ascertained using a combination of 1-2D NMR spectroscopy and mass analysis. **Cat.1** was activated using various co-catalysts, and MMAO (modified methylaluminoxane) outperformed the others. Screening of polymerization parameters suggested an Al/Ti ratio of 1000, 4 bar ethylene pressure, 35 °C temperature, and a polymerization time of 30 minutes as the optimal condition. Under the optimized polymerization conditions, **Cat.1** polymerizes ethylene to ultrahigh molecular weight polyethylene with a weight average molecular weight (M_w) of 2.5×10^6 g/mol. The thermal behavior of the prepared material disclosed a highly crystalline [crystallinity χ (DSC) 96%],

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strictly linear polyethylene. Detailed thermal analysis of the nascent polyethylene using a specifically designed DSC method revealed the existence of a high melting peak at 139-140 °C, which is a hallmark of disentangled UHMWPE. Thus, a homogeneous, single-site ethylene polymerization catalyst has been developed, which upon activation with MMAO produced highly crystalline d-UHMWPE.

Chapter 4: Sterically Tailored Phenoxy-imine Titanium Complexes as a Catalyst for the Preparation of Ultrahigh Molecular Weight Polyethylene

Ultrahigh molecular weight polyethylene (UHMWPE) is a highly desirable material due to its exceptional properties, including high molecular weight, excellent mechanical strength, and chemical resistance. These attributes make it invaluable for applications in industries ranging from medical devices to engineering materials. However, the synthesis of UHMWPE demands precise control over the polymerization process to achieve the desired molecular weight and polymer architecture. Despite advances in catalyst design, significant challenges remain in controlling key mechanistic aspects of ethylene polymerization.

One critical challenge is β -hydride transfer, a process that prematurely terminates polymer chain growth by transferring a β -hydrogen from the polymer chain back to the metal center. This undesirable reaction pathway limits the molecular weight of the polymer, making it difficult to achieve UHMWPE. Addressing β -hydride transfer requires catalysts that not only exhibit high activity and stability but also effectively suppress this transfer mechanism while maintaining efficient chain propagation.

In this study, a series of phenyl cyclohexylimine titanium complexes (Scheme 3) were synthesized and evaluated for their ability to polymerize ethylene into UHMWPE. By strategically introducing steric bulk around the active site, the complexes aimed to modulate catalytic activity and molecular weight minimized β -hydride elimination. However, excessive steric congestion, as observed in the case of catalyst C3, hindered monomer access and reduced activity, emphasizing the delicate balance required for optimal catalyst design.



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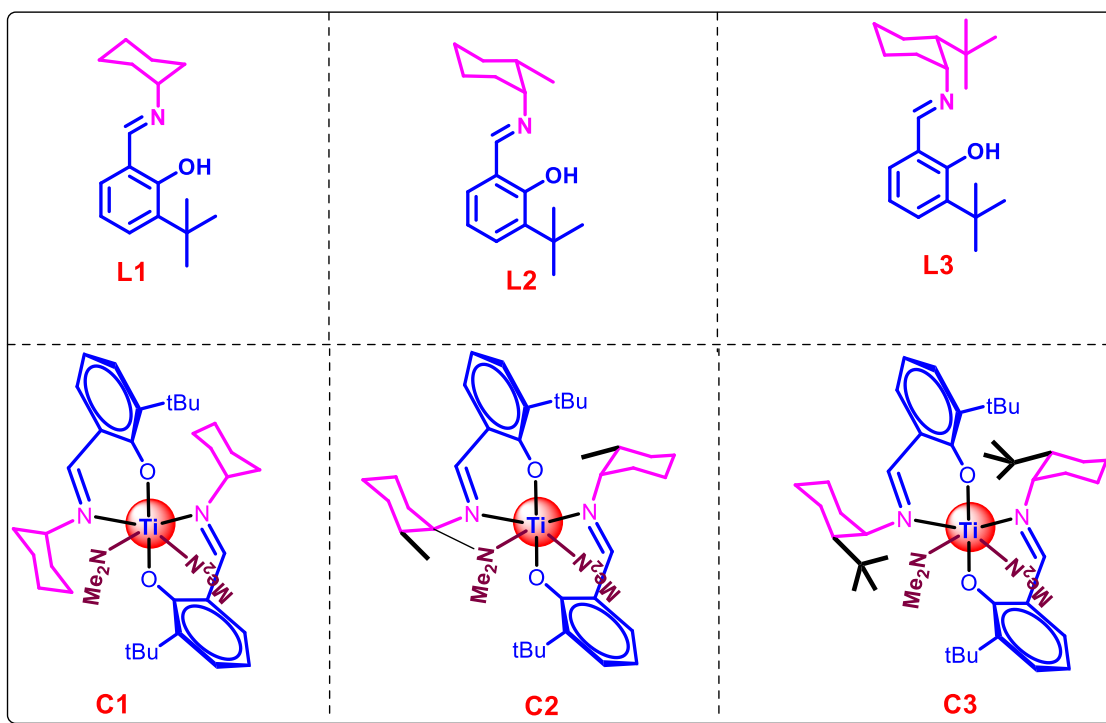


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Using methyl aluminoxane (MMAO) as the cocatalyst, reaction parameters were optimized polymerization conditions, including an Al/Ti ratio of 2000, 2 bar ethylene pressure, 40 °C temperature, and a polymerization period of 10 minutes. Under these conditions, C2 (catalyst 2) demonstrated exceptional performance, producing disentangled UHMWPE with a weight average molecular weight (M_w) of 2.75×10^6 g/mol. The resultant polymer exhibited high crystallinity (95%) and a melting peak at 140–143 °C, reflecting the suppression of β -hydride transfer and successful chain propagation.



Scheme 3: Structure of phenoxy imine ligands and their Ti-phenoxy cycloalkylimine complexes C1-C3.

3. Conclusions and outlook

This study presents a dual approach to the synthesis of benzoxazinones and UHMWPE using novel synthetic strategies and catalysts. The first part of the research focuses on regulating the reactivity of amines and aldehydes through secondary interactions by introducing ortho-substituents. This

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strategy effectively suppresses Schiff base formation while enhancing the production of benzoxazinones, a class of prodrugs. Mechanistic insights, supported by computational modeling, show that the ortho-substituent facilitates hydrogen bonding during the hemiaminal stage, guiding the reaction along a low-energy pathway. This method demonstrated broad substrate scope, high selectivity, and scalability, with reactions showing insensitivity to electronic effects. The approach offers a sustainable and scalable method for synthesizing benzoxazinones, with significant potential in pharmaceutical and fine chemical applications. In the second part, a titanium-based catalyst, [bis-dimethylamido-Ti-(bis-iminocarboxylate)] complex (**Cat.1**), was synthesized and evaluated for ethylene polymerization, producing Ultra High Molecular Weight Polyethylene (UHMWPE). Under optimized conditions and MMAO activation, **Cat.1** produced UHMWPE with a molecular weight of 2.5 million g/mol and 96% crystallinity. Advanced DSC analysis showed the formation of disentangled UHMWPE (d-UHMWPE), confirming the catalyst's effectiveness. Furthermore, the study explored the role of steric bulk in enhancing catalytic performance, achieving high activity and UHMWPE production with a molecular weight of 2.75×10^6 g/mol, high crystallinity (95%), and a melting peak at 140–143 °C. These findings contribute to efficient catalyst design and offer a scalable route for UHMWPE synthesis.

Further modifications to the titanium catalyst could lead to improved catalytic activity, high polymerization rates with potentially lower operational costs. The results presented in this Thesis suggest that there is enough room for rational catalyst design and UHMWPE production using these catalysts. Additionally, scaling up the process for industrial applications remains a key focus, with efforts aimed at maximizing polymer quality and consistency while minimizing environmental impact. The focus of this Thesis was only titanium, Zr and Hf could be equally effective in producing d-UHMWPE. Therefore, a future direction could be replacing titanium in Cat.1, C1-C3 with Zr and Hf, and examining the performance of the resultant zirconium and hafnium in the production of d-UHMWPE. The findings offer a solid foundation for the development of highly efficient, scalable methods for UHMWPE production, with applications in diverse industrial fields.⁵



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4. Publications

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4. Patel, K.[§]; Deshmukh, S.[§]; **Bodkhe, D. V.[§]**; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanan, P. R.; Nandi, S.; Vaidhyanath, R.; Chikkali, S. H. Secondary Interactions Arrest the Hemiaminal Intermediate to Invert the Modus Operandi of Schiff Base Reaction: A Route to Benzoxazinones. *J. Org. Chem.* **2017**, *82*, 4342–4351. DOI: 10.1021/acs.joc.7b00352 ([§] = **Equal author contribution**).
5. **Bodkhe, D. V.;** Patel, K. P.; Shaikh, M. H.; Shivaram, S.; Chikkali, S. H. Sterically Tailored Phenoxy-imine Titanium Complexes as a Catalysts for the Preparation of Ultra-High Molecular Weight Polyethylene. ([Manuscript under preparation](#)).

5. Patent

1. Chikkali, S. H.; Patel, K.; Deshmukh, S.; **Bodkhe, D. V.** Metal-Free Single-Step Synthesis of Substituted Benzoxazinones. *Indian Patent* IN201611002384, 2016.



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- (2) Patel, K.; Chikkali, S. H.; Sivaram, S. Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications. *Prog. Polym. Sci.* **2020**, *109*, 101290.
- (3) Patel, K.; Deshmukh, S.; Bodkhe, D. V.; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanan, P. R.; Nandi, S.; Vaidhyanath, R.; Chikkali, S. H. Secondary interactions arrest the hemiaminal intermediate to invert the modus operandi of schiff base reaction: A route to Benzoxazinones. *J. Org. Chem.* **2017**, *82*, 4342–4351.
- (4) Bodkhe, D. V.; Chikkali, S. H. Ti-Iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene. *Eur. Polym. J.* **2023**, *182*, 111725.
- (5) Antonov, A. A.; Bryliakov, K. P. Post-metallocene catalysts for the synthesis of ultrahigh molecular weight polyethylene: Recent advances. *Eur. Polym. J.* **2021**, *142*, 110162.

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Chapter 1



Introduction

1.1. Introduction

1.1.1. Early years in olefin polymerization

Olefin polymerization is known for several decades. The different types of polymers, polyethylene (PE) and polypropylene (PP) are two of the most commonly used ones worldwide.¹ These versatile materials have revolutionized various industrial sectors, including packaging, automotive, construction, and textiles. Polyethylene and polypropylene offer exceptional properties and therefore are widely used.² These polymers possess a unique combination of strength, flexibility, chemical resistance, and thermal stability, making them ideal for a wide range of applications. Their low cost, lightweight, and ease of processing further contribute to their popularity. Polyethylene is widely used for packaging materials, including plastic bags, films, and bottles. It is also employed in the manufacturing of pipes, wire insulation, and automotive components. Polypropylene, on the other hand, finds applications in food packaging, textiles, medical devices, and automotive parts. The demand for these polymers continues to grow as industries seek lightweight, durable, and

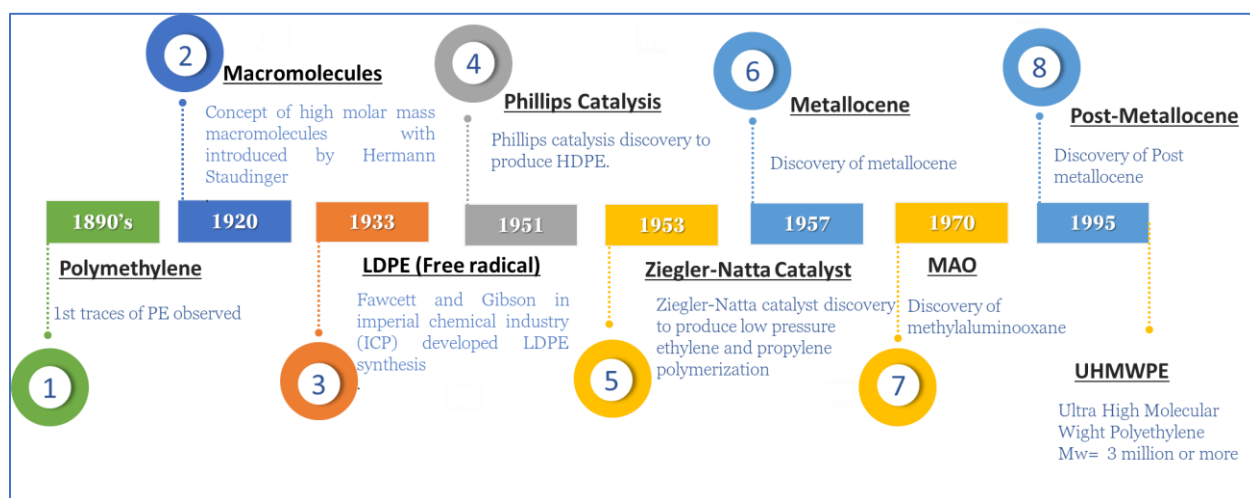


Figure 1.1: Significant advancements in the development of polyolefins.

sustainable materials. The global production of polyolefins is close to 200 million tons per annum and it is bound to increase in the near future.⁴

Moving back in time, we may follow the history of the synthesis of polyethylene and polypropylene, which has an intriguing tale before we take the stock of the most recent

advancements in olefin polymerization. Around the end of the 19th century, for the first time, traces of polyethylene were observed during a thermal decomposition reaction of diazomethane, which was named “polymethylene”. During that period, the field of polymer science was underdeveloped and was not accepted by the community. German chemist Hermann Staudinger proposed that polymers consist of long chains, connected through covalent bonds. This theory was initially met with skepticism, but it was eventually widely accepted and laid the foundation of rational polymer science. In 1933, Fawcett and Gibson at the Imperial Chemical Industry (ICI) found a white powdery material on the reactor wall while performing a high-pressure condensation reaction of ethylene and benzaldehyde (Figure 1.1). When they were repeating the experiment without benzaldehyde, the reactor exploded and the project was halted. It took a couple of years to understand this and develop radical polymerization of ethylene to polyethylene. The ICI process operates at high pressure (1000-4000 bars) and high temperature (200-300 °C). After this discovery, several academic groups-initiated research programs on ethylene polymerization to make polyethylene.

The major breakthroughs were reported in the early 1950s. The first one was by Hogan and Banks at the Phillips Petroleum Company who reported low molecular weight oligomer from gaseous olefin using nickel oxide supported by alumina or silica.³ In 1951, when researching how supported nickel and chromium oxides affect silica or alumina, they found solid HDPE in their reactor.¹ In the 1950s, Ziegler, at the Max Planck Institute in Mülheim, Germany, made a significant breakthrough in ethylene polymerization. Before embarking on the journey of polyethylene, he was investigating the reactivity of alkyl lithium/alkyl aluminum compounds with ethylene. These organometallic reagents formed the foundation for his development of the "Aufbaureaktion," a process enabling the synthesis of 1-olefins, aliphatic alcohols (known as alfol synthesis), and high-purity alumina through the oxidation of alkyl aluminum compounds. By a stroke of luck, Ziegler discovered that the presence of nickel had a profound effect on the "Aufbaureaktion" by favoring chain termination, resulting in 1-butene production. This Unexpected occurrence, known as "the nickel effect," was attributed due to the autoclave's nickel content resulting from before hydrogenation reactions. In the 1950s, Professor Karl Ziegler's pioneering work laid the foundation for the revolutionary field of metal-catalyzed olefin polymerization. Ziegler's students embarked on extensive metal screening experiments,

investigating the interplay of different metal precursors with alkyl aluminum compounds. By 1953, Ziegler's team explored combinations of triethyl aluminum with diverse transition metal compounds such as chromium, vanadium, manganese, and platinum. A breakthrough emerged when zirconium acetylacetonate paired with triethyl aluminum yielded an impressive conversion rate of over 90% for introduced ethylene. This success led to the birth of the patented "Mülheim Atmospheric Process," renowned for its operation at lower temperatures and ethylene pressures below 55 bars. The collaborative efforts of Ziegler and the Italian chemist Professor Giulio Natta reached a pinnacle in March 1954 with propylene's stereospecific polymerization. Employing a catalyst of Ziegler comprising titanium trichloride and triethyl aluminum, their groundbreaking achievement earned them the Nobel Prize in Chemistry in 1963. The impact of Ziegler and Natta's discovery reverberated across olefin polymerization, ushering in subsequent catalyst developments like metallocene's, methylaluminoxane (MAO), and post-metallocene's. Despite the longevity and extensive use of the Ziegler-Natta catalytic process, its ability to create specialty materials through parameter manipulation continues to inspire both academic and industrial research. Generations of Ziegler-Natta catalysts have evolved, initially focusing on hypercognizing the process, resulting in supported Ziegler-Natta catalysts. Overcoming the limitations of heterogeneity, the shift towards homogeneous catalysts was catalyzed by Cossee and Arlman's monometallic mechanism proposal in 1964, which is now widely accepted. The advent of MAO marked a turning point in homogeneous olefin polymerization catalysts, introducing novel polyolefin materials. This breakthrough set the stage for homogenous catalysis in stereoregular olefin polymerization, with subsequent developments including metallocene's, post-metallocene's, and other catalysts finding niche markets for specialty applications.⁴

Ultimately, the manipulation of ethylene, propylene, and higher α -olefins within polyolefin chains empowers the tailoring of diverse physical and chemical properties, resulting in a vast array of polymers. Seven decades after its inception, the field of olefin polymerization remains dynamic, with the demand for polyolefins continuing to influence and shape our daily lives. One of the most popular synthetic polymers among the different classes of polyolefins is polyethylene (PE), which has the simplest repeating unit of methylene ($-\text{CH}_2-$). PE's long-term demand (high density, Linear low-density and low-density polyethylenes (LLDPE and LDPE) were projected to reach a production volume of 99.6 million metric tons by 2018, valued at \$164 billion.⁵ A small portion

of this requirement will be met by the high-pressure radical polymerization method but majority of it will be produced by metal catalyzed coordination polymerization route. In 1950s, Karl Ziegler discovered catalytic pathway to produce PE at low pressure and temperature. In this process, catalyst determines how monomer will be inserted in a polymer chain and thus effectively defines micro-structural properties of formed polymer. Based on density, branching content, cross linking and molecular weight, PE can be classified into several categories.⁶

1.2 Types of polyethylene

Table 1. There are three types of polyethene

Polyethylene	Density (g/cm ³)
PE with a low density (LDPE)	0.910-0.940
Linear low-density PE (LLDPE)	0.910-0.920
High density PE (HDPE)	0.941-0.967

1.2.1 Types of high-density PE

A polymer whose density 0.941-0.967 is known as high density polyethylene, or HDPE. An extremely high strength to density ratio characterizes this thermoplastic. With a wide range of uses, including storage bottles and pipes, HDPE is a particularly adaptable plastic. High density polyethylene has an elevated melting point when compared to other polymers.

Table 2. The classification of linear PE Classification based on density, molecular weight, and melt flow index (MFI) is outlined as follows:

Polyethylene	Density (g/cm ³)	MFI (g/10 min) (190 °C/2.16 kg ASTM D1238)	Molecular Weight (Mw) (× 10 ⁶ g/mol)	Melting Temperature (T _m) (°C)
HDPE	0.94–0.97	0.1–100	0.1–0.5	125–135
HMW HDPE	0.94–0.97	0.01–0.1; 2–14 (HLMI) ¹	0.2–1.0	130–135
UHMW PE	0.94–0.97	Lack of Flow	> 3 ²	135–148

Notes:

¹ HLMI: High Load Melt Index. ² Molecular weight exceeds 3×10^6 g/mol.

The linear polymer known as high molecular weight high-density polyethylene (HMW HDPE)

has an average molecular weight between 0.2 and 1.0 million g/mol, either as a homopolymer or copolymer. To improve processability during melting, these polymers are often engineered with a broad or bimodal molecular weight distribution. HMW HDPE is known for its excellent mechanical properties, including high rigidity, outstanding abrasion resistance, and strong chemical durability. It is commonly processed through methods such as injection molding, blow molding, film extrusion, and pipe extrusion.⁷

1.2.2. Ultrahigh molecular weight polyethylene (UHMW-PE)

1.2.2.1 Definition

A linear polyethylene with an average molecular weight (M_v) greater than 3 million g/mol is referred to as ultra-high molecular weight polyethylene (UHMWPE) in accordance with ASTM specifications.⁸ In contrast to ordinary HDPE, which is several orders of magnitude longer at 700 to 1800 monomer units, PE chains are usually 100,000 to 250,000 units long. At temperatures about 130 °C, they are soluble in solvents with a high boiling point. As a result, techniques for high temperature polymer characterization must be used, such as high temperature GPC and diluted solution viscosity. Due to the UHMWPE's exceptionally high melt viscosity, measuring the melt flow is challenging. Additionally, UHMWPE cannot be processed using traditional methods that are utilized for HDPE.

Ultrahigh molecular weight polymers are often chosen for demanding applications due to the unique properties imparted by their high molecular weight, including high resistance to corrosive chemicals, good impact strength, and biocompatibility. In addition to heart valves, bulletproof armor, gear, UHMWPE fibers are utilized to make advanced medical devices such as implants for the hip, knee, and spine. Demand for some resources has increased recently.⁹

Other classes of PE typically display branched and linear chain architectures and serve wide array of uses in rigid food containers, hoses and tubing, Industrial packaging films, food packaging films, garbage bags, plastic bags, pipes, wire and cable coatings and coverings, storage containers, and several other consumer goods. However, these classes fail to deliver properties where high impact strength, high abrasion resistivity, low coefficient of friction is required. To meet these demands ultrahigh molecular weight polyethylene (UHMW-PE) was introduced, which attracted significant attention due to its unmatched physical and mechanical properties. Notably,

UHMWPE has higher ultimate strength, impact strength, greater abrasion and wear resistance than any other known PE grades.¹⁰

1.2.2.2 Characteristic features

With a molecular mass typically ranging from 1 to 6 million g/mol, UHMWPE is made up of incredibly long chains that strengthen intermolecular connections through Van der Waals bonds, also known as "entanglement," to better transfer load to the polymer backbone. As a result, the material becomes extremely durable and outperforms all other thermoplastics in terms of impact strength. UHMW-PE is harmless, tasteless, and odorless. It is very resistant to corrosive chemicals, except for oxidizing acids. It absorbs very little moisture & its coefficient of friction is quite low. It is highly resistant to abrasion. and is self-lubricating; in certain forms, it is 15 times more resistant than carbon steel. The unique feature such as light weight, chemical inertness, impact resistance, biocompatibility associated with UHMWPE makes it a special polymer that can serve demanding applications.

1.2.2.3 Applications

UHMW-PE fibres are utilised in armour, specifically in vehicle armour and personal armour. It is being used in the manufacturing of high-performance sails, climbing gear, cut-resistant gloves, bow strings and suspension lines on



Figure 1.2: Applications of UHMWPE.

sport parachutes and gliders, clothing in yachting, aircraft to name a few.

In ice rinks where typical ice creation and maintenance are impractical due to ambient temperatures or energy expenditures, UHMWPE sheet is also utilized as synthetic ice. The material is ideal for this use because of its resilience to abrasion and cutting. Since the 1980s, UHMW-PE has been used as a biomaterial for hip joint, knee joint, and implants of spine. Additionally, UHMW-PE is utilized in the manufacturing of fluid seals and bearings. For medium-sized machinery tasks, it performs well in unlubricated, lube, water, and pneumatic approach. Although it is more appropriate for soft mating surfaces, it has good abrasion resistance.

With ever growing applications, UHMW-PE is finding more takers and the market is bound to grow.² This has been evident from a patent search that revealed More than 300 patents have been granted to various businesses in the recent past.¹¹

1.2.3 Challenges to achieve UHMWPE

The synthesis of UHMWPE is not straightforward and requires careful catalyst design. The equilibrium of three essential rates determines the polymer's molecular weight: The propagation rate (k_p), the rate of transfer (k_{tr}), and the rate of termination (k_t). The synthesis of UHMWPE requires that the propagation rate is much higher than the termination and transfer rates.

To achieve this balance, a suitable catalyst must be designed that consists of an appropriate metal cation and ligand framework. The metal center should be highly acidic or oxophilic, allowing the chain to grow faster. At the same time, the ligand should force the β -H out of the metal-plan and suppress the rates of transfer and termination.

The synthesis of UHMWPE requires a carefully designed catalyst that balances the rate of propagation, transfer, and termination. The catalyst should have an acidic metal center and a ligand that suppresses the latter two rates. The correct choice of reaction parameters also plays a crucial role in synthesizing UHMWPE with the desired molecular weight and physical properties.¹²

1.3 New developments in UHMWPE catalyst family

1.3.1 Principles for choosing a catalyst

It is quite difficult and definitely not simple to repeatedly insert ethylene into a polyethylene molecule to produce one with such a large molecular weight. Simply expressed, in order to generate extraordinarily large molecular weight, either the rate of propagation (k_p) must be

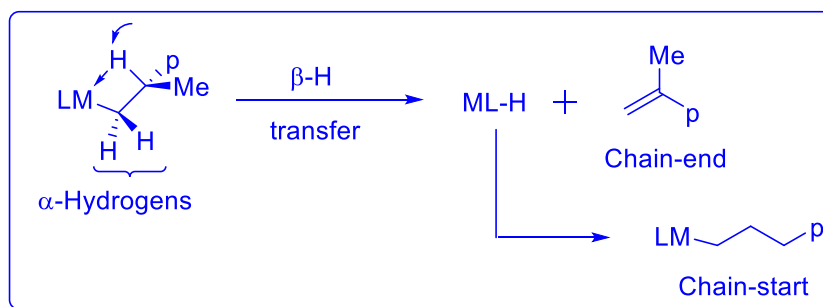
increased, transfer rate (k_{tr}) must be decreased, or both must occur. To achieve this, one or more of the following concepts should be used in the design of catalysts; a) high electrophilicity should be present in the metal center, b) The division of the slowest possible pace should be used for the transfer to an activator or β -hydride, aluminum, or comonomer. c) The proper ratio of steric and electronic effects at the catalytic centre must be provided by the ligands around the metal in order to maximize the insertion rate and decrease the transfer rate. d) The maximum Mw that can be reached with a particular catalyst depend on several factors, including the catalyst, the activator, and reaction parameters like temperature and monomer concentration. Therefore, when aiming for UHMWPE synthesis, reaction conditions should be considered.

1.3.2 Kinetics and chain growth mechanisms

The efficiency of an ethylene insertion reaction to produce ultrahigh molecular weight polyethylene depends on the relative rates of chain propagation and chain transfer. The following are the main chain scission processes that are typically seen in ethylene insertion reactions.

1.3.3 β -H transfer to metal center

When the metal centre abstracts an H-atom from the growing polymer chain's β -C to create an M-H bond (M-transition metal), a polymer that has a vinyl terminated chain end is created (Scheme 1.1). Testing examination revealed that metal hydrides and olefins are produced by the efficient β -hydride transfer facilitated by post-metallocene-based catalysts, cationic group 4 metallocene alkyl, and group 3 metallocene alkyl. The method by which β -H is transferred to metal is unimolecular.

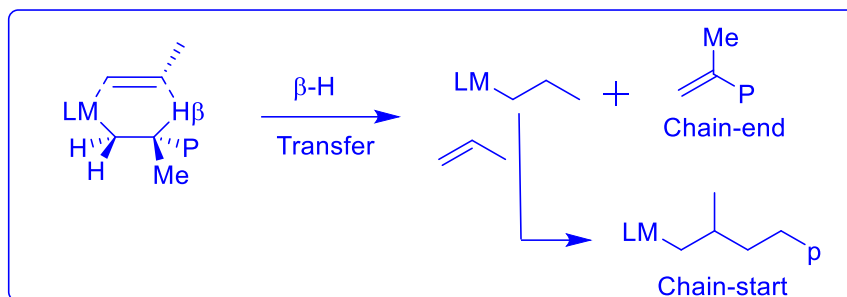


Scheme 1.1: β -H transfer to the metal center.

1.3.4. β -H transfer to incoming monomer

This bimolecular reaction follows the insertion of the olefin. And the primary chain termination method for olefin polymerization supported by group 4 metal catalysts is β -Hydrogen transfer

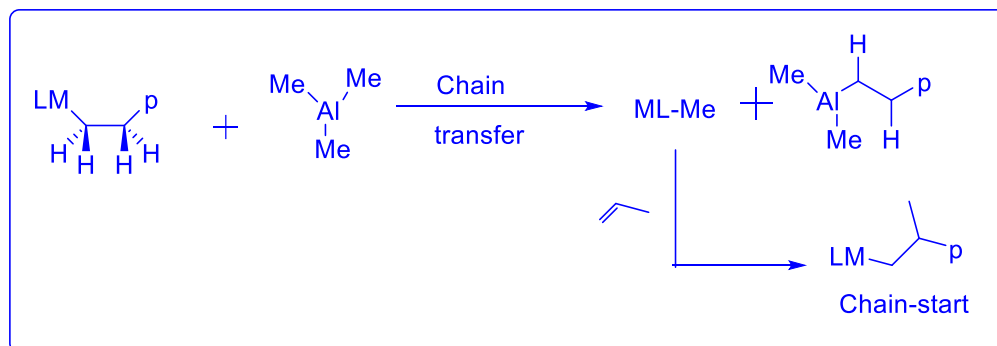
(BHT) to monomer (Scheme 1.2). Regarding the monomer concentration, this process adheres to first-order kinetics.



Scheme 1.2: β -H transfer to the monomer.

1.3.5. Mechanisms of chain transfer to main group metal alkyls

Homogenous olefin polymerization depends heavily on chain transfer between alkyls in the main group and transition element complexes (Scheme 1.3). Cocatalysts like TMA or MAO are good examples of how to adjust Mw and end groups of polymers. More crucially, transfer of chain presents the opportunity to enhance the chains number formed by each catalytic site in live coordination polymerization. This is used in the quick and reversible chain transfer to chain transfer agent (CTCTA) process used in coordinative chain transfer polymerization (CCTP), which involves main group metal alkyls such as AlR_3 , ZnR_2 , and MgR_2 . Extremely narrow molecular weight distributions result from the requirement that CTCTA be performed considerably more quickly than monomer insertion under CCTP circumstances.



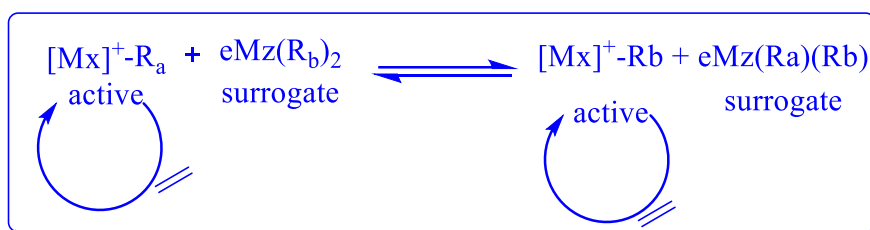
Scheme 1.3: Chain transfer to the aluminum in polymerization.

1.3.6. Transfer free polymerization (living polymer)

When there is little to no transfer reaction during an ethylene insertion reaction, it is referred as transfer free polymerization. In theory, this technique can produce large molecular weight polymers because the polymer chain continues to develop until the monomer is exhausted. "Living

Polymerization" is another name for this kind of transfer-free polymerization. One metal complex is bonded to one polymer chain end during live polymerization, making the reaction stoichiometric with regard to the metal. The literature has sufficiently covered this subject.

A novel mechanism of coordinated catalytic chain transfer polymerization (CCTP) has been presented in order to get beyond the restriction of stoichiometric catalyst need while still allowing transfer free polymerization, an ordinary live coordination chain transfer polymerization process. Reversible trans-metalation between an active transition metal alkyl species (M_x) that drives chain growth and a stand-in main group metal alkyl species (M_z) is known as CCTP. By allowing for the synthesis of more polymer chains per active center, the technique overcomes the crucial constraint of living polymerization, "one polymer chain per active center." Although the basic idea seems very simple, large molecular weight polymers require careful balancing of the transition metal precatalyst, activator, and main group metal alkyl species.⁵



Scheme 1.4: Coordinative chain transfer polymerization mechanism (M_x: Active transition metal propagating center; M_z: Inactive main group metal alkyl (polymeryl) species; R_a and R_b: polymeric groups of chain lengths a and b).

1.3.7. Reaction conditions

The rate of ethylene insertion and competing transfer processes are strongly influenced by the reaction circumstances. The amount of ethylene that dissolves in a diluent depends on the reaction temperature. The solubility of ethylene drops above a specific temperature, resulting in a reduced k_p . In general, chain transfer reactions have larger activation energies than insertion reactions, and as the temperature rises, the proportional rate of propagation to transfer decreases.¹³ The pace of the transfer process slows down and the molecular weight grows. At longer reaction times, a noticeable broadening of the molecular weight distribution has been seen. Increasing ethylene pressure is generally reported to increase the rate of insertion due to higher monomer concentration. The type of diluent has a variety of effects on the polymerization reaction. Metal

catalyst and monomer solubility depend on the kind of solution. Increasing ethylene pressure is generally reported to increase the rate of insertion due to higher monomer concentration. The type of diluent has a variety of effects on the polymerization reaction. Metal catalyst and monomer solubility depend on the kind of solution. The active center of metallocene complexes is cationic in nature. Therefore, solvation and ion-pair separation will be significantly impacted by the solvent's polarity. One of the important aspects that has a significant impact on both k_p and k_{tr} is the nature of the co-catalyst or activator. For the production of high molecular weight polyethylene, organo aluminums are frequently utilized as an activator with Mg-Ti type catalysts. Methyl aluminoxane is used as an activator with complexes of the metallocene class. During the ethylene insertion and polymerization processes, both types of organoaluminium activators take part in chain transfer reactions. It is also possible to use non-nucleophilic activators with metallocene type complexes. The most popular activators are from tris-pentafluoro phenyl boranes. Chain transfer reactions to the activator are reduced, which is a benefit of boron activators.¹⁴

1.4. Families of catalysts

Three different groups of catalysts are primarily used in gas phase or slurry procedures to make UHMWPE.

- 1) Mg-Ti heterogeneous catalysts.
- 2) Supported or homogeneous metallocene complexes.
- 3) Phenoxy-imine (FI) or other post metallocene that are homogeneous or heterogeneous.

In this class the typical composition of catalyst is $TiCl_4$ epitaxially adsorbed on anhydrous $MgCl_2$ supports and activated with aluminum alkyls. The Chain transfer to aluminum and monomer happens when the polymerization temperature is over 60 °C. However, with the right modifications, a Mg-Ti catalyst system can produce UHMWPE with a molecular weight (Mw) that is nearly 10 million g/mol. Because of the closeness of the active sites in the supported Mg-Ti catalysts, the polymer chains grow close to one another. Furthermore, heterogeneous catalysts have many active sites with various reactivities that result in the production of polymers with a wide range of molecular weights. The closeness of developing chains in these systems enhances the likelihood of chain entanglement, and the high polymerization temperature used in them decreases the crystallization rate. Using standard melt processing methods, it is challenging to process an entangled UHMWPE. Furthermore, flaws at the grain boundary are produced during processing of entangled UHMWPE. In items like knee-joint prostheses, the presence of such grain boundaries

between particles of several nanometer size creates weak areas that cannot bear mechanical force. Homogeneous catalytic systems have received a great deal of attention for olefin polymerization during the past 25 years. They include catalysts from group 4 metallocene di-Cp and early transition metals with bidentate ligands, primarily bis (phenoxy imine).¹⁵ Due to advantageous β -agnostic interactions, Group 4 zirconium based metallocene complexes have a greater tendency to β -hydrogen transfer reaction. Therefore, it is challenging to produce PE utilizing such catalyst complexes with a weight average molecular weight $>10^6$ g/mol. However, there are known exceptions, and under certain polymerization conditions, a few metallocene complexes are known to form PE with a Mw $> 10^6$ g/mol. Due to the more open ligand framework of group 4 transition metal catalysts, mono-cyclopentadienyl complexes of these metals favors β -hydrogen transfer reactions and typically do not result in high molecular weight PE. Under particular reaction circumstances, bis-phenoxy imine group 4 metal complexes show the traits of transfer free polymerization. As a result, these catalysts may produce PEs with unusually high molecular weight.^{16,17}

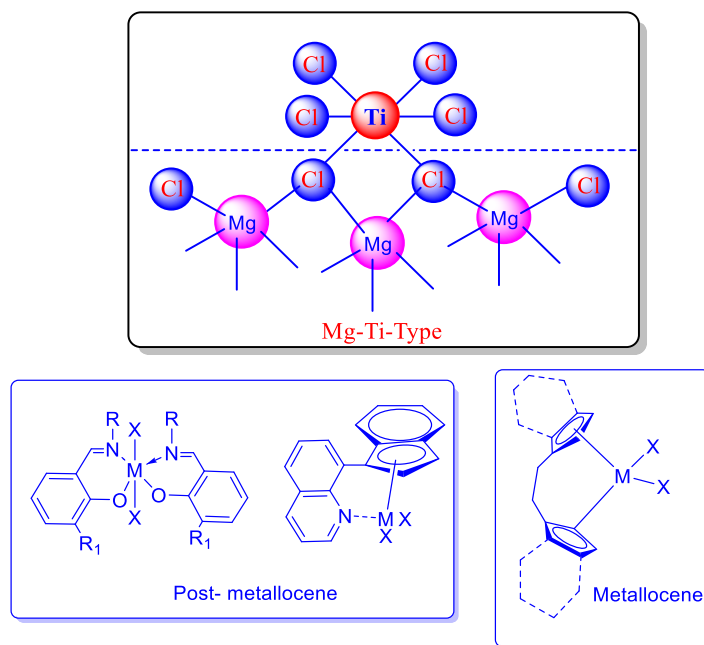


Figure 1.3: Types of homogeneous and heterogeneous catalysts often used in UHMWPE production.

1.5. Catalyst families and their performance

Based on the nature of catalysts used in coordination polymerization, catalysts have been divided into two groups: (i) heterogeneous, (ii) homogeneous. In the heterogeneous systems the

catalyst is supported on various supports such as silica or magnesium dichloride which makes it insoluble in the polymerization medium, while for homogeneous systems, the catalyst is soluble in the polymerization medium.

1.5.1. Mg-Ti catalysts

Heterogeneous catalyst family is mostly based on titanium complexes supported on suitable support (SiO_2 , MgCl_2). Back in 1960's, development of MgCl_2 -supported titanium catalysts showed high efficiency towards ethylene polymerization and generated significant interest in polyolefin industry. Despite of its high activity for ethylene polymerization at commercial level, rational design of a well-defined catalyst for polyolefin was largely missing. Kinetic experiment indicate that MgCl_2 acts as a support, it could increase concentration of active species and function as an activator, and thus enhancing propagation rate.¹⁸ These catalytic systems operate at polymerization temperature in between 60-100 °C, which leads to increased k_p . However, at this temperature, rates associated with transfer reaction become more accessible and thus reduce selectivity towards chain growth mechanism. Only in handful articles high selectivity towards k_p over k_{tr} , and PE with molecular weight in the order of 1-10 million g/mol has been reported. Careful selection of concentration of catalyst, choice of co-catalyst, mole ratio of catalyst/co-catalyst components, additives (internal and external donors) coupled with controlled reaction parameter (reaction temperature and monomer pressure) is crucial to produce UHMWPE.

Striking features of such catalytic systems are, the Mg-Ti systems produce PE particles with controlled morphology, high bulk density, show less reactor fouling and reveal uniform particle size distribution. Major drawbacks associated with these systems are; 1) Multiple active sites that leads to a broad molecular weight distribution (MWD), 2) presence of vinyl end groups in polymer chain, and 3) increased chain entanglement density (imposes difficulty in processing). Therefore, nature of the catalytic system greatly influences polymer morphology, final structure, processibility properties of the polymer.¹⁹ Recent advances in catalyst design have significantly improved the control over ethylene polymerization, enabling the synthesis of ultrahigh molecular weight polyethylene with tailored properties.^{20, 21, 22}

Unlike heterogeneous catalyst, homogeneous catalyst can offer an opportunity to tailor catalytic sites at molecular level. In this regard, a family of single site catalyst called metallocene and post-metallocene were introduced. These systems possess well defined catalytic

sites homogenized in reaction media, and are capable of producing polyolefin with narrow molecular weight distribution.

1.5.2. Metallocene

Metallocene's are organometallic coordination compounds in which a transition metal is sandwiched to and only to the face of two cyclopentadienyl ligands. These were discovered in 1952 by Fischer, which were soluble in organic solvent and were initially used to investigate the mechanism of Ziegler polymerization in presence of co-catalyst. Discovery of methyl aluminoxane (MAO) in 1980's by Sinn and Kaminsky revolutionized the field of metallocene catalyzed olefin polymerization. This catalytic system displayed outstanding catalytic activity which was found to be about 10000 times more active than the classical Mg-Ti system. This initial discovery paved the way for subsequent developments and performance of metallocene catalyst in olefin polymerization was reported. Structurally, metallocene consists of two five membered aromatic ring that can be connected by a bridging unit (*ansa* metallocene complexes) or without bridging group. The two aromatic ligands can be of the same type or different, i.e., cyclopentadienyl, indenyl, or fluorenyl. By now, the effect of substitution on certain positions of the two aromatic ligands and/or the bridge on polymerization rate and stereo- and regio- selectivity of α -olefins is well established. Though, these catalysts family are known to undergo frequent transfer reaction (making them inaccessible for achieving molecular weight $>10^6$ g mol⁻¹), few metallocene catalysts are capable of producing polyethylene with a molecular mass $>10^6$ g mol⁻¹.

It is most likely that structures with large steric bulk, effectively block the transfer or/and termination through β -H elimination reaction and thus, yield high molecular weight polymers. Another crucial parameter was found to be temperature. Temperature played an important role in slowing down the possible reaction pathway responsible for transfer or/and termination. It is believed that polymerization at higher temperature leads to increased transfer or/and termination reactions and reduces ethylene selectivity towards insertion.²³ Through strategic modifications in the ligand framework, metallocene catalysts can achieve ultrahigh molecular weight polyethylene synthesis with precise control over molecular architecture and properties.^{24, 25}

In fact, metallocene catalyst provided an opportunity to systematically investigate the relationship between metallocene structure, polymerization mechanism and polymer properties. This rational understanding led to the development of *ansa*-metallocenes for stereo-selective polymerization of propylene. The unique features of metallocene's led to widespread patenting

and consequent patent infringements and litigations, which actually slowed down the pace of commercialization of metallocene grade polyolefins. At present metallocene technology is being practiced on industrial scale and the contribution of metallocene grade polyolefins is limited to only 5-8 % of the total polyolefin market.

1.5.3. Post-metallocene

Progressive research in olefin polymerization continued past metallocene's and gave rise to new family of catalyst called as post-metallocene. These newly designed catalytic families generated substantial interest as they offered an excellent opportunity, to improve and control resultant polymer properties, to explore new monomer combinations which were inaccessible by metallocene catalyst. Post-metallocene's comprise of many metal complexes with early as well as late transition metals with diversified ligand frameworks. However, for present study, we considered early transition metal olefin polymerization catalysts as they furnish linear high molecular weight PE, whereas late metal catalysts based on nickel or palladium typically give rise to low molecular weight polymers with branched structures due to chain walking mechanism.

In early transition metal complexes, family of catalysts developed by Fujita and his group at Mitsui chemicals Japan, created significant interest, as these metal complexes provide better control over propagation and transfer/termination rates. This catalyst family consists of non-symmetric bidentate ligand framework and they are phenoxy-imine, pyrrolide-imine, indolide-imine, phenoxy-pyridine, phenoxy-ether, or imine-pyridine chelate ligands.^{26, 27, 28, 29}

1.5.4. Bis(imino)phenoxy group 4 complexes

Based on the concept of "ligand-oriented catalyst design", Fujita and co-workers introduced a family of catalysts called phenoxy-imine systems (Figure 1.4). A systematic investigation was under taken to pin point the effect of structural changes in the phenoxy-imine catalyst on the polymer properties and elaborate literature is now available. Rational understanding followed and structural tuning led to the development of a versatile class for olefin polymerization catalysts.³⁰

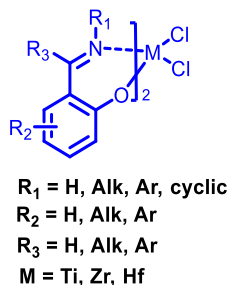


Figure 1.4: Bis(phenoxy) imine group 4 metal complexes.

1.6. Structural features

Bis (phenoxy– imine) group 4 metal complexes adopt a distorted *Octahedral* geometry around the metal centre with two chelating ligands having two imine nitrogen's, two phenolic oxygens, and two non-spectator ligands. Notably, this type of catalyst is reported to exhibit five possible structural isomers (Figure 1.5) that are in dynamic equilibrium, which are distinguishable based on the nature of bonding in the axial and equatorial position.

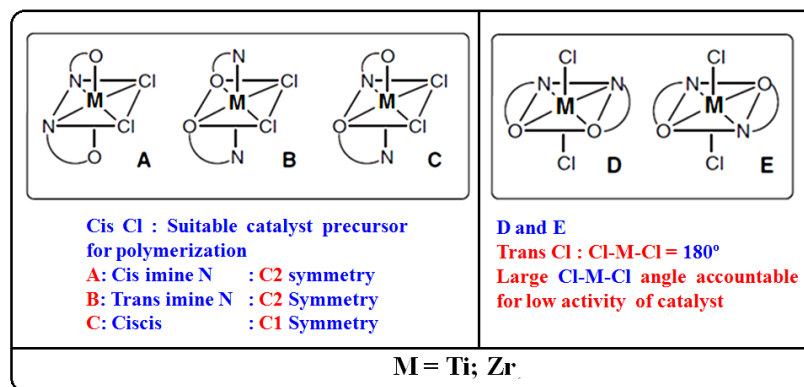


Figure 1.5: Five possible isomers for bis(phenoxy-imine) group 4 metal complexes.

All five isomers are in dynamic equilibrium in solution state hence, it is difficult to identify a specific isomer responsible for ethylene polymerization. Out of these five isomers three isomers (A-C) are considered to be active in olefin polymerization because of *cis* arrangement of two chloride atoms (Figure 1.4) (Considered as potential site for polymerization). Out of these three isomers, isomer A and B is defined by their arrangement of imine nitrogen and phenolic oxygen atoms either in *cis*- or *trans*- position. Whereas, isomer C is characterized by its *cis*- arrangement with regards to imine nitrogen, phenolic oxygen atoms and non-spectator ligands. All these

isomers are in dynamic equilibrium with each other and their presence in the solution has been verified by spectroscopy and X-ray analysis. Thus, presence of these isomers in phenoxy-imine catalysts becomes an important feature in understanding their performance in polymerization. It is suggested that isomerization (fluxional behavior) occurs via metal imine nitrogen bond dissociation because of labile nature of the imine-nitrogen. Hence, substitution pattern on imine nitrogen and reaction temperature greatly influences liability of imine nitrogen. At time of isomerisation, catalyst conformation changes where one of the metal nitrogen coordinate bonds is released after which rotation of the ligand occurs. This free rotation can generate a situation where all nitrogen's, oxygens and non-spectator ligands are arranged in *cis* isomer with respect to each other (Figure 1.6). Existence of such fluxionality in solution renders the possibility of differential kinetics of polymerization and creates ambiguity regarding the nature of active site in chain growth polymerization.

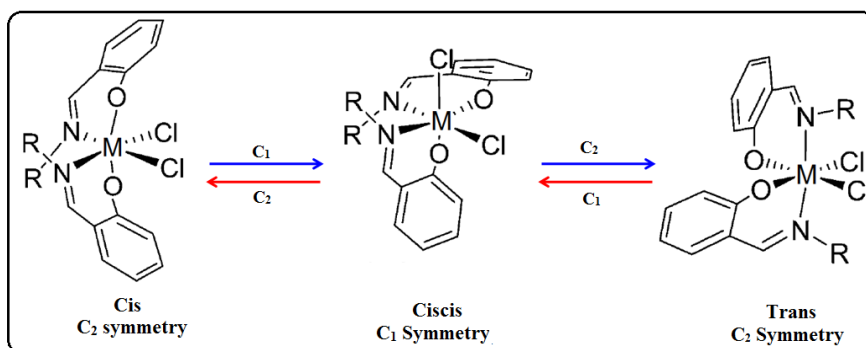


Figure 1.6: The three isomers of phenoxy-imine system in olefin polymerization.

The bis(phenoxy)imine group 4 metal complexes with specific substitution have shown immense potential to yield ultrahigh molecular weight polyethylene under suitable reaction conditions. Thus, a comprehensive picture of how substitution in metal complexes and reaction parameters influence chain growth mechanism will be presented in the following sections.³¹

1.7. Type of metal complexes

The mechanism by which ethylene is polymerized will ultimately determine the microstructure and therefore the properties of the resultant PE. An early transition metal complex (due to higher Lewis's acidity) has higher propensity towards C-C bond formation as compared to late transition metal complexes.

1.7.1. Effect of transition metal cation

Because of higher Lewis's acidity, early transition metal complexes show higher activity in chain growth polymerization. In addition to this, size of metal cations has significant impact on the generated polymer's molecular weight. From first row to second row, ionic radii increase of (Ti^{4+} (0.68 Å) & 0.86 Å for Zr^{4+}). Although the two complexes have the same structures, a larger zirconium congener has less shielding and more sterically exposed space than a titanium congener. As a result, β -hydride transfer is easily experienced by zirconium. It is believed to be one of the primary causes of the decline in molecular weight.³ According to previous research, altering the transition metal causes a polyethylene's molecular weight to rise in the following order: $\text{Ti} > \text{Zr}$.³ ⁴ Because of the thermodynamically stronger Hf-C bonds, the majority of hafnium complexes produce polymers with larger molecular weights than their comparable zirconium complexes.³²

1.7.2. Effect of ligand environment

Suitable ligand backbone with the proper ratio of steric and electronic characteristics is extremely crucial and can greatly influence k_p/k_{tr} ratio. It was found that the phenoxy group raised the MW of generated PE in ortho to an increase in steric bulk. Even in the instance of zirconium, increasing the steric crowding on the imine phenyl ring further was beneficial. The interaction between β -hydrogen and the metal centre is probably significantly inhibited by steric crowding surrounding the metal centre, leading to an increase in MW. The electronic environment around the metal can either reduce the electrophilic character of the metal or increase the electrophilicity. It has been noted that higher MW is the result of greater metal centre electrophilicity. However, substituting electron withdrawing group in either R_1 and R_5 or R_1 - R_5 (position) has significantly suppressed the k_{tr}/k_t rate and under defined reaction conditions the catalysts start behaving like a living polymerization catalyst.³³

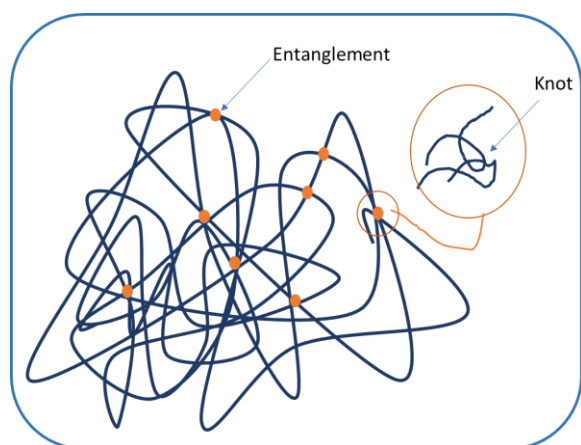
1.7.3. Early transition metal complexes active in producing UHMWPE

Many other research groups contributed in producing UHMWPE based on early transition metal complexes. Mainly these families are of group 4 metal complexes of calix [4] arene, bulky monoanionic bidentate guanidine and anilido-imine tetra-azane, that enabled ultra-high selectivity towards ethylene polymerization to produce UHMWPE. Further, few half-sandwich chromium complexes reported by Mu, Ender and Jin are found to be active in producing molecular mass of polyethylene in the range of 10^6g/mol^{-1} .³⁴

1.8. Concept of entanglement and disentanglement

The entanglements are intermolecular topological interactions and are physically crossed linked (Van der Waals forces) between the long chains. With their interconnected hooks, these entanglements resembled cooked spaghetti. Figure 1.7(a) shows a schematic illustration of entanglement.

a) Entanglement of UHMWPE



b) Disentanglement of UHMWPE

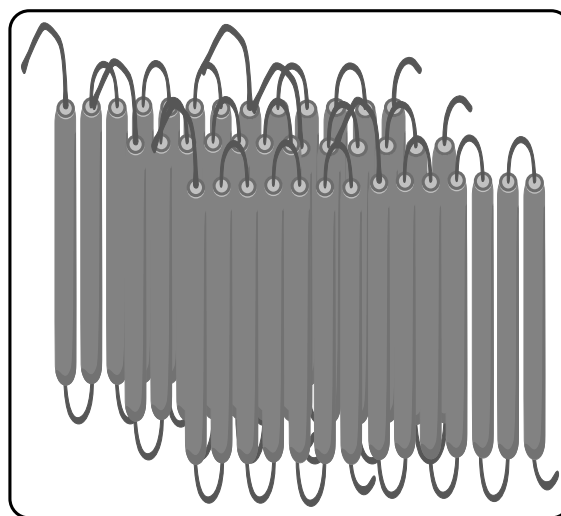


Figure 1.7: A model depicting pictorial form of chain a) entanglement and b) dis-entanglement. Ultra-High Molecular Weight Polyethylene (UHMWPE) Below its melt temperature, it may be conventional compression-mold into semi-transparent, mechanically coherent films and displays solid-state flow behavior (figure 1.7(b)). The scattered UHMWPE increases the blend's tensile strength when combined with HDPE. This improvement is credited to the effective dissolution of UHMWPE into the HDPE matrix, showcasing its potential for reinforcing polymer blends.

1.9. Characterization tools for UHMWPE

The fundamental challenge in the field of UHMWPE is a characterization of formed polymer. In case of UHMWPE, the important characteristic features are MW, MWD, the presence of branches, and melting temperature. Structure-activity relationship can be established if comprehensive

picture for the microstructural property of synthesized polymer can be obtained. Light scattering, melt rheometric (for M_w), solution viscosity (for M_v), and Gel permeation chromatography, or GPC, is another name for size exclusion chromatography (SEC), for M_z and M_n) are the analytical methods used to quantify molecular mass and MWD of UHMWPE. However, in case of UHMWPE above 2-4 million g/mol, HT-GPC measurements usually fail to give consistent results as the polymer sample is difficult to dissolve in the typical solvents used in GPC studies due to extremely high molecular masses. Rastogi and colleagues (2008) demonstrated that the melt rheology approach is a suitable determining method for the molecular mass and molecular weight distribution of UHMWPE (between 2 and 10 million g/mol) with a higher degree of accuracy than GPC. Furthermore, it was discovered that this method was more suitable for detecting the existence of chain branching, providing a more comprehensive and trustworthy image of the microstructural characteristics of a polymer that was formed.

With DSC, heating rate of 10 °C per minute, there is a noticeable melting peak at 140 °C when UHMWPE nascent sample is present. The entangled versus disentangled nature of UHMWPE was probed using two techniques, namely, DSC and rheology. Rastogi and co-workers have developed a DSC method that allows access to the two states of UHMWPE.³⁵ This method was employed and the melting temperature was recorded at a time interval of 5, 15, 30, and 60 minutes (Figure 1.7). The 5-minute DSC thermogram disclosed two melting temperatures, one at 134 and another at 139.5 °C. These two curves indicate the T_m of the entangled and the disentangled domain respectively. As the hold time (Figure 1.8, center, step B-C) increases, the disentangled domain starts to convert to an entangled domain, which is a thermally stable state. Consistent with the DSC's conclusions, the rheological analysis revealed that an equilibrium storage modulus of 1.82 MPa is attained after 37 hours.

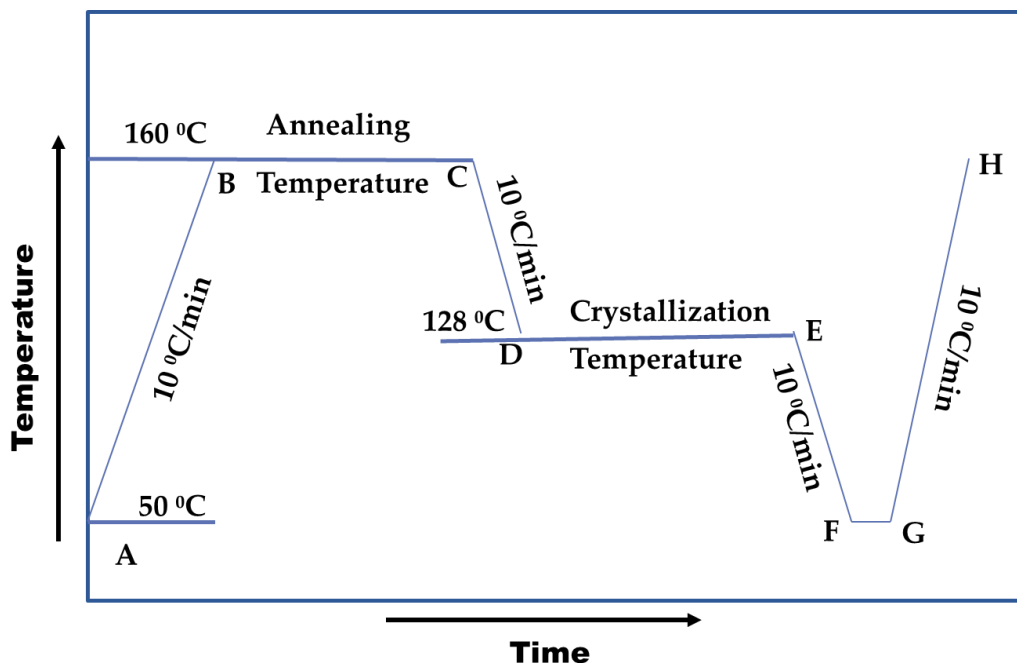


Figure 1.8: Thermal protocol developed to demonstrate disentangled nature of UHMWPE. Thermal protocol: Ramp 1: 50 °C to 160 °C (A-B) @ 10 °C/min. hold @160C for 5 min. (B-C). Ramp 2: Cooling to 128 °C @ 10 °C/min. (C-D) and hold at 128 °C for 180 min. (D-E). Ramp 3: Cooling to 50 °C at 10 °C/min. (E-F) and hold at 50 °C for 1 min. (F-G). Ramp 4: Heating from 50 to 160 °C at 10 °C/min. (G-H).

1.10. Summary

More efficient load transfer to the polymer backbone is possible with UHMW-PE. Consequently, it has the highest impact strength of any thermoplastic currently produced, making it an extremely durable material. UHMW-PE can become a demanding substance with a broad variety of uses. However, processing of UHMW-PE in melt state makes them intractable via conventional processing routes because of presence of high degree of entanglement (high melt viscosity), which leads to in-homogeneity or fusion defects, a common problem in all the products prepared from UHMW-PE so far.

It has been clearly defined how nature of catalyst combined with reaction parameters significantly influenced MW, MWD and entanglement density in UHMW-PE. Homogeneous catalysts as compared to heterogeneous ones provides well defined single catalytically active center, effectively producing disentangled nascent UHMW-PE with very narrow molecular weight distribution directly from reactor by controlled polymerization conditions, and showed improved

processability as compared with commercially fully entangled UHMW-PE (Heterogeneous Ziegler-Natta catalyst). However, the direct synthesis of highly disentangled UHMW-PE via solvent free route using well-defined single site catalyst provides substantial benefits for polymer processing because it does not have the disadvantages of gel spinning. where huge amount of solvent needs to be processed at high temperature. Whereas, catalytic route for polymer production provides economic and environmental advantages over the existing gel spun process. Thus, catalytic route has enhanced the processability of the material. Thus, processed materials show improved mechanical performance which are free from grain boundaries.

1.11. Aim of thesis

The main objective of the thesis is to develop a stable and easily accessible synthesized alternative catalytic system for olefin polymerization, addressing the limitations of existing systems. This involves exploring new ligand designs that offer improved stability and simpler synthetic protocols compared to traditional imine-based ligands. Specifically, the research focus is on nonsymmetric imine backbones as potential candidates for ligand design, aiming to create complexes suitable for olefin polymerization. The envisioned ligand design and complexes are expected to maintain the essential components necessary for effective polymerization while offering enhanced stability and simplified synthesis procedures. In our pursuit of developing group 4 metal polymerization catalysts that can generate UHMW-PE, or ultra-high molecular weight polyethylene, we will prepare selected a bidentate monoanionic imine based [N, COO⁻, O⁻] ligand motif (Figure 1.9)

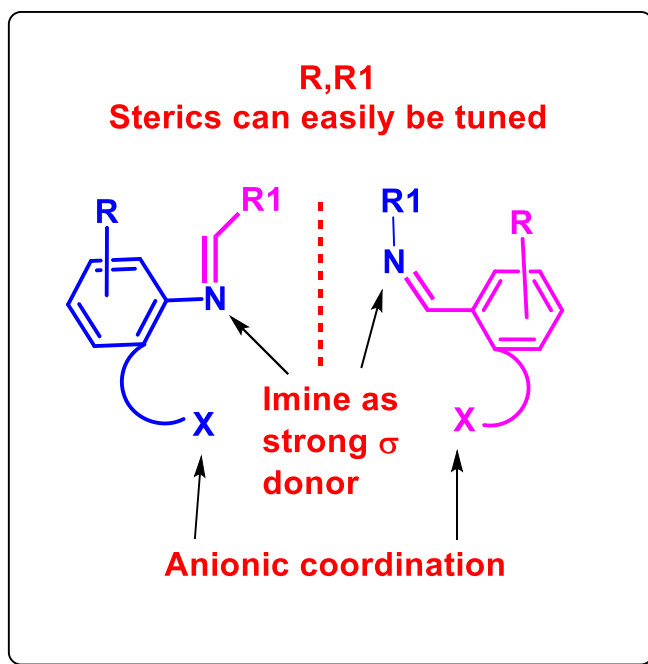


Figure 1.9: Imine based ligands framework.

This ligand framework offers the potential for forming complexes with enhanced metal-nitrogen bond strength in octahedral geometry. The imine ligand framework possesses a lower HOMO-LUMO gap, providing electronic flexibility essential for maintaining the electrophilicity of group 4 metal complexes. Through careful selection of amine and aldehyde components, steric and electronic parameters of the ligand is readily modifiable. Therefore, the development of group 4 metal polymerization catalyst systems has made remarkable progress, with significant implications in both academic and industrial realms. It has been discovered that the activity and stereo selectivity of these catalytic complexes are significantly influenced by the ligand structure. In general, catalysts with sterically encumbered substituents on the carboxylate and aldehyde rings exhibit improved performance. Higher polymerization activity results from this structural alteration, which also increases the active species' electrophilicity and frees up more space for polymerization. Therefore, our research aims to capitalize on these insights to optimize catalyst systems for the production of UHMWPE.

1.12. References

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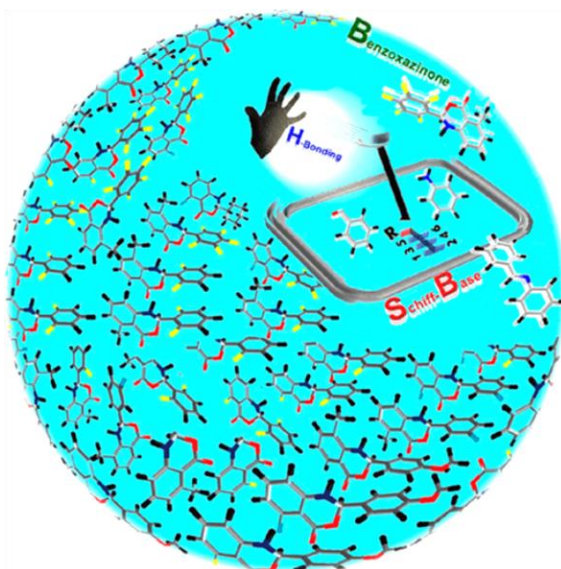
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Chapter 2



Inverting the Reactivity of an Aldehyde and Amine to Benzoxazinones: Mechanistic Understanding



This chapter is partly adapted from following publication

J. Org. Chem. **2017**, 82, 4342-4351.

2.1 Abstract:

This study introduces a strategy to control Schiff-base reactions, a fundamental step in chemistry. The approach, guided by computational models, allows for the quantitative formation of Benzoxazinones, overcoming the limitations of reversible Schiff-base reactions. The "Schiff-Benz" reaction is demonstrated to be versatile, producing various Benzoxazinones with different electronic substituents. The method's generality is confirmed through a library of Benzoxazinones, and its practical utility is highlighted by scaling up to a gram scale. Mechanistic insights reveal a hydrogen-bonding motif directing the reaction towards Benzoxazinone formation. This innovative approach provides a competitive alternative to traditional methods for Benzoxazinone synthesis in pharmaceutical and fine chemical manufacturing.

2.2 Introduction

The reversible condensation reaction between an aldehyde and an amine, resulting in the formation of a carbon-nitrogen double bond, stands as one of the most fundamental and widespread processes in the field of chemistry.^{1, 2} The foundational work of Hugo Schiff has significantly contributed to understanding this reaction, rightfully acknowledged by naming it after him.^{3, 4} Over time, substantial progress has been achieved, leading to a comprehensive understanding of the mechanistic intricacies of this reaction.⁵ Depending on the specific substitutions involved, the products of this condensation are referred to as imines, Schiff bases, or Salen's compounds. Schiff bases, in particular, play diverse roles as synthetic intermediates, ligands, and catalysts in various applications. They are extensively utilized in processes such as the cycloaddition reaction in Penicillin synthesis,^{6, 7} ligands⁸ and catalysts⁹ in molecular recognition, nano-science,¹⁰ and are influential in determining the activity of enzymes and proteins.¹¹⁻¹³ The synthetic applications of imines encompass a wide range, including but not limited to umpolung reactions,¹⁴ multicomponent reactions,¹⁵ and contributions to the development of Metal-Organic Frameworks (MOF)¹⁶ and Covalent Organic Frameworks (COF).¹⁷ This versatility underscores the importance of imines in contemporary synthetic chemistry, showcasing their applicability across diverse chemical processes and material synthesis methodologies.

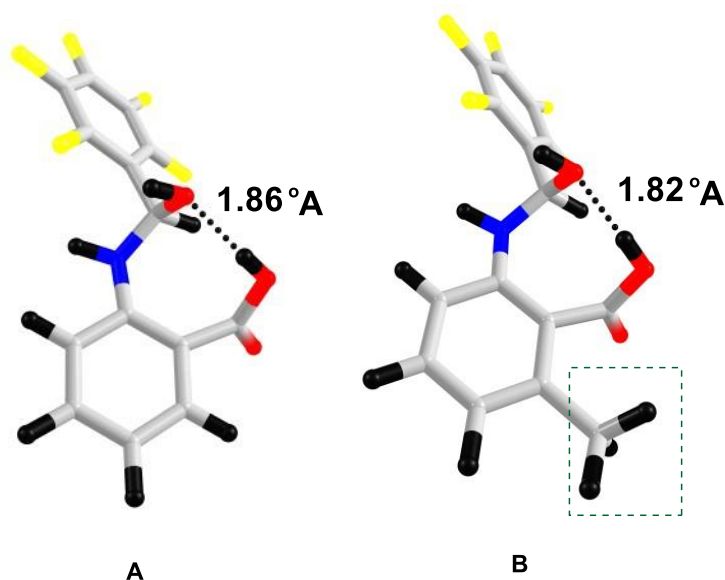
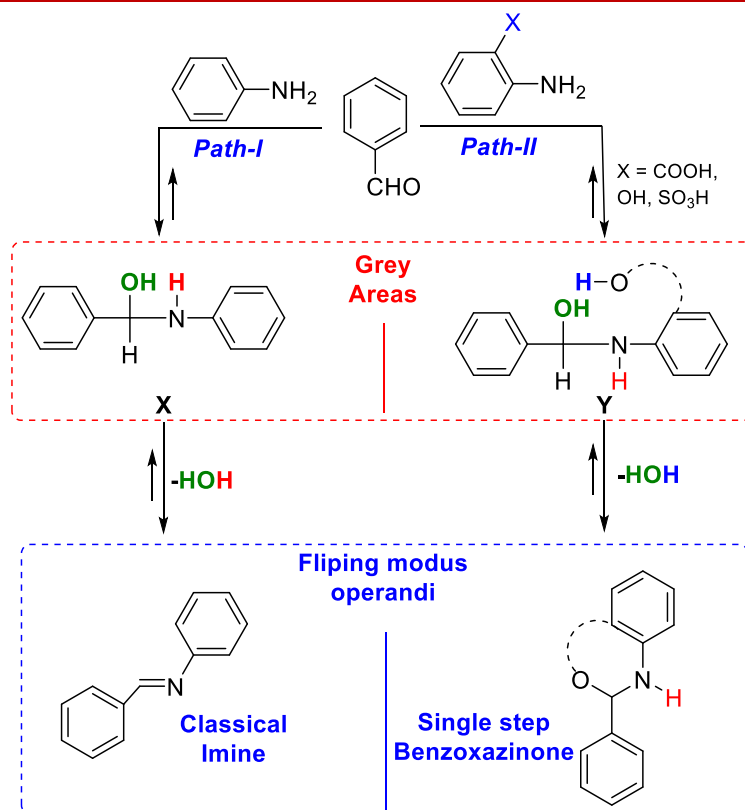


Figure 2.1: Condensation of an amine and aldehyde to imine (Schiff-base: path-I) and H-bonding assisted reversed condensation (path-II). Energy optimized structures of hemiaminal intermediates; 2-aminobenzoic acid (bottom left-A), and 2-amino-6-methylbenzoic acid (bottom right-B).

Despite the extensive range of applications for Schiff bases, establishing a clear structure-reactivity relationship between aldehydes and amines proves challenging. The intrinsic reactivity of these reaction partners results from a complex interplay of various factors, including inductive effects, conjugative effects, steric effects, and innate strains. Structural modifications, such as substitutions on the reactants, can often lead to a complete shutdown of the intended reaction, redirecting the course of reactivity in an entirely different direction. Consequently, achieving the desired alteration in the reactivity of an amine and an aldehyde in a condensation reaction requires meticulous tailoring of the reaction partners. The amine-aldehyde condensation reaction is known to progress through the formation of a hemiaminal, denoted as X in Figure 2.1, which serves as an intermediate to the subsequent formation of an imine (Im).¹⁸ The hemiaminal, however, is highly unstable, leading to the condensation of NH and H-C-OH fragments and the liberation of water, ultimately resulting in the formation of an imine with a sp^2 -carbon. Recognizing that altering the amine group or the aldehyde functionality would effectively halt the reaction, the authors propose a novel strategy. This involves introducing a competitive proton in close proximity to the hydroxy group, facilitating the construction of benzoxazinones (Bz) products with a sp^3 -carbon. This innovative approach offers a solution to selectively manipulate the reactivities of the amine and aldehyde components, steering the reaction towards the desired outcome of benzoxazinone formation.

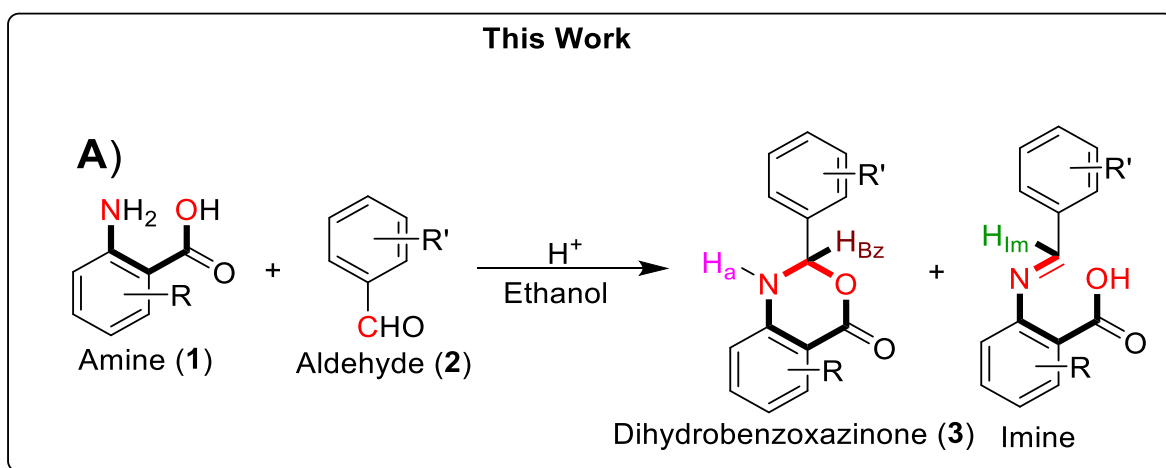
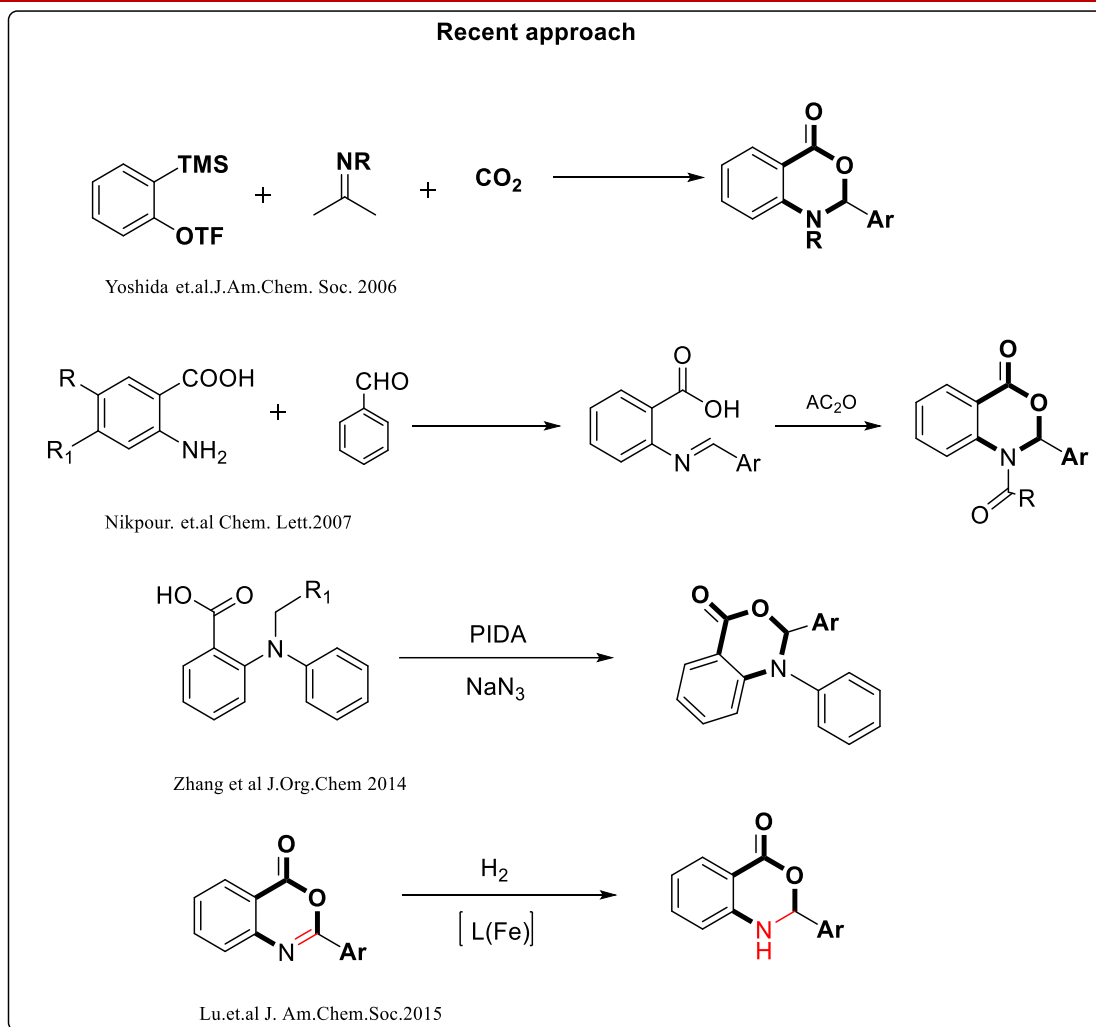


Figure 2.2: Recent synthetic methods for the synthesis of benzoxazinones (top) and this work (bottom).

Benzoxazinones, known for their extensive medical history as biologically active compounds and their current utilization as drug intermediates,^{19, 20} have traditionally been synthesized through multistep methods.²¹⁻²³ Recent advancements in the field have introduced alternative approaches to access benzoxazinones.²⁴ Yoshida et al demonstrated a direct route via aryne chemistry, while Nikpour and colleagues reported a synthesis involving the reaction between anthranilic acid and benzaldehyde, yielding dihydrobenzoxazinones under specific conditions.²⁵ Zhang et al utilized hypervalent iodine compounds for a single-step C-H activation strategy,²⁶ and Beller and co-workers employed iron-catalyzed asymmetric hydrogenation.²⁷ In this context, a new synthetic strategy is proposed, aiming to regulate the reactivity of amine and aldehyde partners in a condensation reaction through weak secondary interactions.^{28, 29} Referred to as the "flipped reaction," this method is presented as a straightforward, selective, and metal-free alternative to recent metal-catalyzed coupling reactions.^{24, 26, 27} The flipped reaction successfully establishes two new carbon-heteroatom bonds, resulting in the formation of medicinally important benzoxazinones. The versatility of the flipped reaction is demonstrated by its application in a single-step inverted condensation protocol, leading to the synthesis of a diverse library of benzoxazinones. Mechanistic investigations, coupled with density functional theory (DFT) calculations, rule out the potential of ring-closing after in-situ imine production. Rather, the proposed mechanism involves hydrogen-bond-assisted ring-closing to produce benzoxazinones. The significance of this synthetic strategy lies in its fundamental advancement in science, offering a simple, selective, and versatile approach to modulate Schiff-base reactions.

2.3 Results and discussion

2.3.1 The Schiff-Benz reaction

We envisioned that the commercially available amino acid, anthranilic acid, would be the most suitable candidate for our study due to its appropriate acidity and directional characteristics, which are conducive to facilitating the reversed condensation reaction.

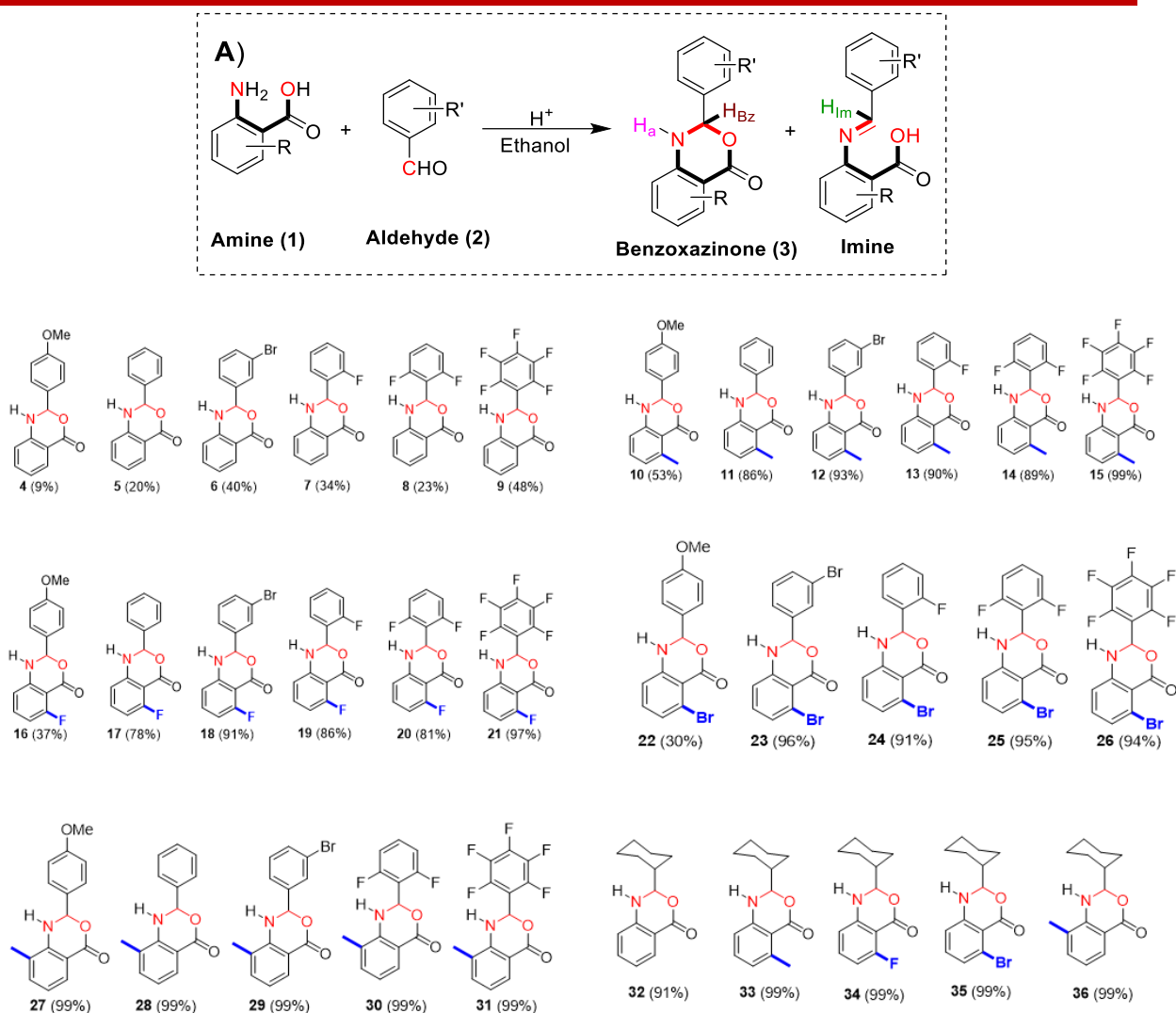


Chart 2.1: Schiff-Benz reaction and reaction scope of benzoxazinones. NMR yield is indicated by numbers in brackets.

To test our hypothesis, we opted for benzaldehyde (**2**) as the aldehyde partner alongside anthranilic acid (**1**). The condensation reactions were conducted in ethanol under reflux conditions, with the substrates activated using a catalytic amount of acetic acid. Monitoring the reaction's progress through proton NMR analysis revealed the formation of imine as the major product, constituting 80 % of the outcome. Additionally, two new resonances emerged at 6.19 and 4.84 ppm, indicating the presence of other reaction products.

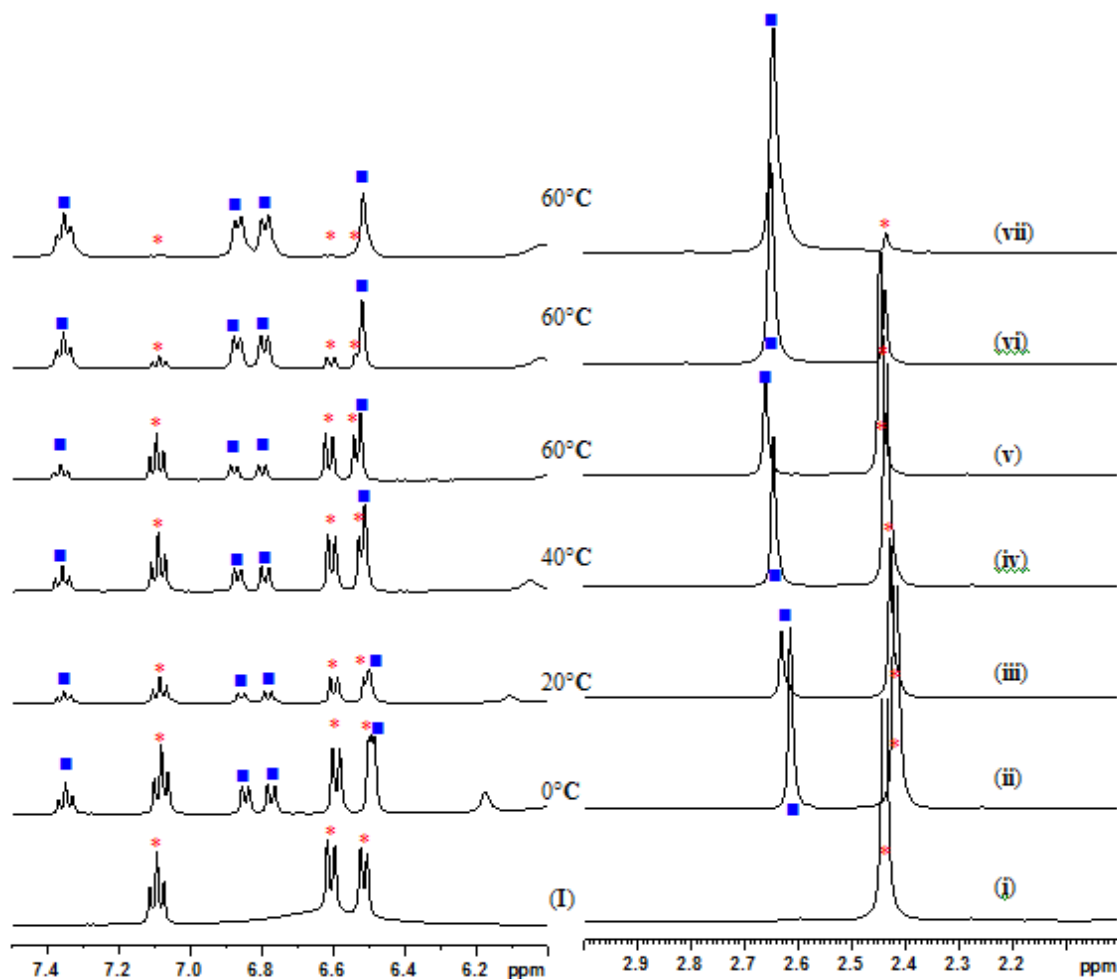


Figure 2.3: Variable temperature stacked ^1H NMR spectra of a reaction between an aldehyde(I) and amine (*) (II) in CD_3CN ; ii) addition of 0.75 equivalent of II at 0 °C; iii) NMR recorded at 20 °C; iv) NMR recorded at 40 °C; v) NMR recorded at 60 °C; vi) addition of 0.25 equivalent of (II), NMR at 60 °C; vii) addition of 0.25 equivalent of (II), NMR at 60 °C.

To our satisfaction, a detailed structural analysis of the condensation products using 2D NMR techniques, including COSY, HSQC, and HMBC, unveiled the presence of a minor fraction, approximately 20%, comprising cyclized Benzoxazinone 5 (refer to Chart 2.1). In our pursuit of entirely redirecting reactivity towards the annulation reaction, we utilized more electrophilic benzaldehydes. This strategic shift resulted in an increased formation of Benzoxazinones. Notably, the use of the highly electrophilic pentafluorobenzaldehyde led to a substantial 48% yield of 2-(per fluorophenyl)-1,2-dihydro-4H-benzo[d] [1,3] oxazin-4-one 9. Despite our efforts to enhance the Benzoxazinone yields through the exploration of various reaction parameters, our endeavors were not notably successful at this stage. The unequivocal identity of compound 14

(refer to Chart 2.1) was established through a single crystal X-ray diffraction analysis (Figure 2.4). The crystal structure of compound 14 demonstrated monoclinic unit cell arrangements within the space group $P1/c$. Notably, the molecular structure of 14 exhibited a noticeably extended C-N bond ($N2-C24 = 1.430(5)$ Å) when compared to the typical imine bond range ($C=N$ 1.26-1.30). This observation decisively excluded the presence of a $C=N$ double bond in the compound.

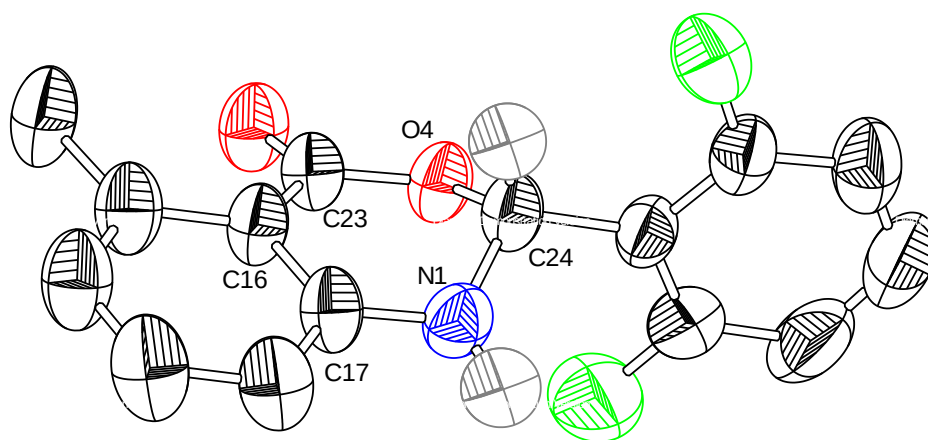


Figure 2.4: Molecular structure of compound 14 (hydrogen atoms except N-H and C-H have been deleted for clarity and thermal ellipsoids are drawn at 50% probability level); selected interatomic distance [Å] and angles [°]: C24-N1 1.428, C17-N1 1.371, C24-O4 1.447, O4-C23 1.360, C23-C16 1.465; C17-N1-C24 114.74, N1-C24-O4 108.43, C24-O4-C23 115.91, O4-C23-C16 117.34. The dihedral angle between the planes defined by C17-N1-O4 and N1-C24-O4 is 49.58°.

Remarkably, the resulting six-membered ring displays an intriguing non-planar geometry, adopting a half-boat conformation wherein one of the carbon atoms extends out of the plane. Interestingly, this is the first time that we are aware of an amine and aldehyde condensation process with 14 as the primary and effective product. To identify the requirements of the reversed condensation reaction and to understand lower selectivity towards Benzoxazinone, we turned our attention to DFT. The energy minimized structures (Figure 2.1 bottom) revealed that *ortho*-substitution on the 2-aminobenzoic acid orients the carboxylic-OH in close proximity. Intermediate **A** without any *ortho*-substitution displayed a C-HO---HOOC-Ar distance of 1.86 Å, whereas the methyl substituted analogue **B** revealed a shorter distance of 1.82 Å. Although these

distances are just indicative, the theoretical revelations paved the way for experimental design and we set out to evaluate the reactivity of 2-amino-6-methylbenzoic acid. In fact, treatment of 2-amino-6-methylbenzoic acid with benzaldehyde under identical conditions produced the annulated Benzoxazinone product **11** with excellent selectivity (86%) (Chart 2.1).

2.3.2 Mechanistic investigations

Understanding the basic procedures for reversing the condensation reaction from the textbook will be crucial to comprehending reversed reactivity and may even reveal the synthetic possibilities of this change. In a Schiff base reaction, nucleophilic attack of amine on the aldehydic carbocation leads to the generation of the crucial hemiaminal intermediate.³⁰ The underlying imine mechanism with different rates (K_1 - K_5) has been investigated in depth by Sayer^{31, 32} and others.³³ However, none of these mechanistic proposals touch upon the reactivity reversal and thus fail to explain the observed cyclization (Fig.2.3). Therefore, a sixth-rate constant (K_6) is proposed. The rate constant K_6 can follow, at least theoretically, three (**A**, **B**, **C**) different pathways to arrive at Benzoxazinone (**IV**) (Fig.2.5). First, the possibility of rearrangement of imine (**III**) to benzoxazinone (**IV**) (proposed by Nikpour,²⁵ Azarifar³⁴ although the starting compounds employed in the proposed mechanism were different) cannot be completely ignored. In our attempts to understand the *modus operandi*; we investigated this reaction using a set of NMR, UV-vis spectroscopy and DFT calculations.

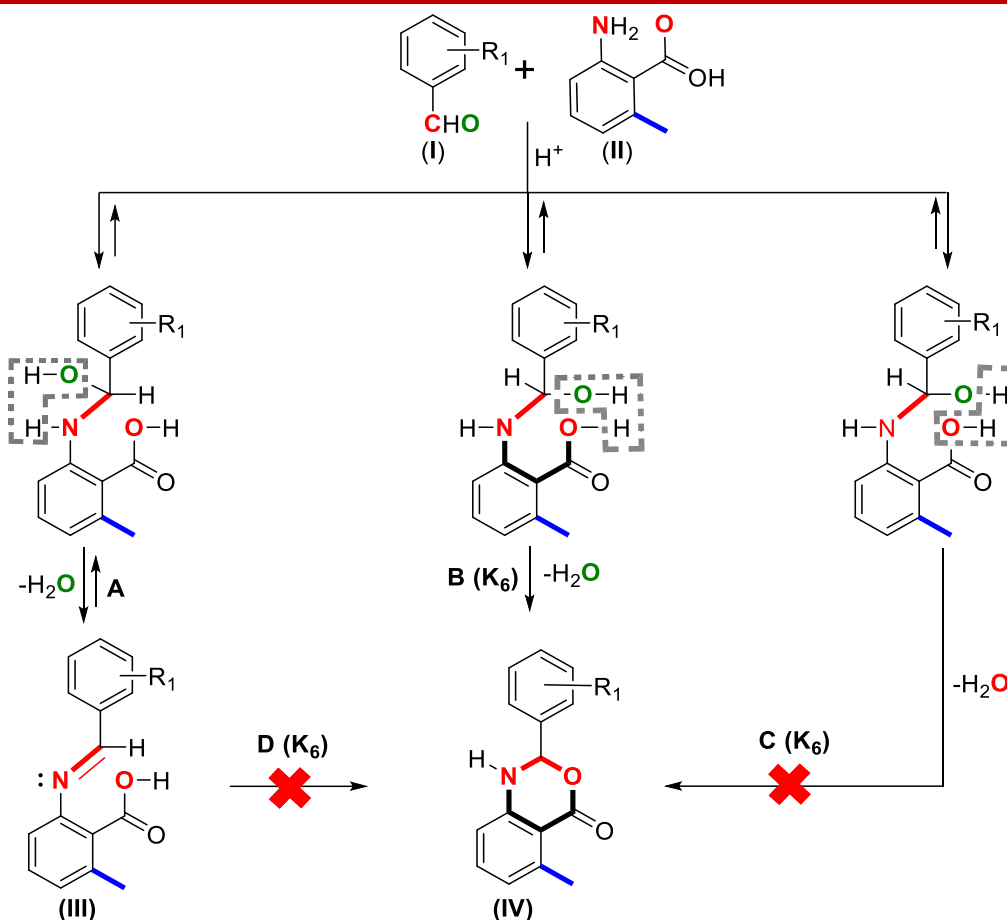


Figure 2.5: Proposed reaction pathways to Benzoxazinone (IV), ($R_1 = F_5$).

To nail down the possible intermediates, NMR tube reaction of 2-amino-6-methylbenzoic acid with pentafluoro-benzaldehyde was attempted and proton NMR spectroscopy was used to track the reaction's development. (Chart 2.1 compound 3). Even at 0°C , instantaneous formation of Benzoxazinones was observed with traces of imine (Figure 2.5). As the reaction mixture's temperature increased from 0°C to 60°C , gradual decrease in the intensity of methyl (2.41 ppm *) resonance in (II) and concomitant increase in the intensity of methyl group in (IV) at 2.60 ppm (■) was observed. Interestingly, only traces of imine (8-9 ppm) could be observed (Fig. 2.23). These findings rule out the possibility of formation of imine (route A) as the first step and subsequent conversion of (III) to (IV) [D (K_6)]. The NMR findings were corroborated by UV-vis, which revealed the absence of a C=N charge transfer band (at 319 nm) and attested to the formation of Benzoxazinone with a characteristic band at 291 nm, which was confirmed by DFT (ESI Fig. 2.29, 2.30 respectively). In order to differentiate between route B and C, we labeled the

anthranilic acid oxygen (with ^{18}O -isotope). Tracking the progress by ^{13}C NMR revealed a resonance at 77.52 ppm, which clearly indicated retention of labeled oxygen in the Benzoxazinone product (Fig 2.26). The observed isotopic (^{18}O) dependence of ^{13}C chemical shift is in agreement with literature reports (Figure 2.27).³⁵ The NMR observations were further supplemented by ESI-MS (Fig 2.28) A pseudo-molecular ion peak was found at $m/z = 332.06$ $[\text{M}+\text{H}]^+$, wherein the mass of oxygen is 18 Da. Therefore, it is very likely that route **B** is the most preferred mechanistic pathway for the reversed condensation reaction.

2.3.3 Computational insights

To obtain detailed insights in the Schiff-Benz reaction, we sought the assistance of DFT and the energies associated with potential routes A, B and C was calculated. Figure 2.5 depicts the energy barriers for hemiaminal formation and the rate determining dehydration reaction for the three routes. The initial formation of hemiaminal was identical for the three routes with a $\Delta G = 10.4$ kcal/mol. As is evident, route B proved to be the preferred pathway with the lowest barrier of 29.5 kcal/mol, as compared to 51.1 kcal/mol (uphill by +21 kcal/mol) for Pathway A and 64.9 kcal/mol (uphill by +35 kcal/mol) for Pathway C (Fig. 2.6). The lowest barrier for route B is most likely due to the secondary interaction between the acidic proton of the carboxylic acid and the hydroxyl group of the hemiaminal. The *ortho*- (to COOH) substituent likely facilitates the spatial orientation of the acidic proton and brings it to the close proximity of the hydroxyl group, leading to the favored water elimination. The above DFT results therefore complement the experimental findings and reveal the existence of secondary interactions that totally alter the course of the reaction to produce benzoxazinone *via* a mechanism that changes our perception of Schiff condensation.

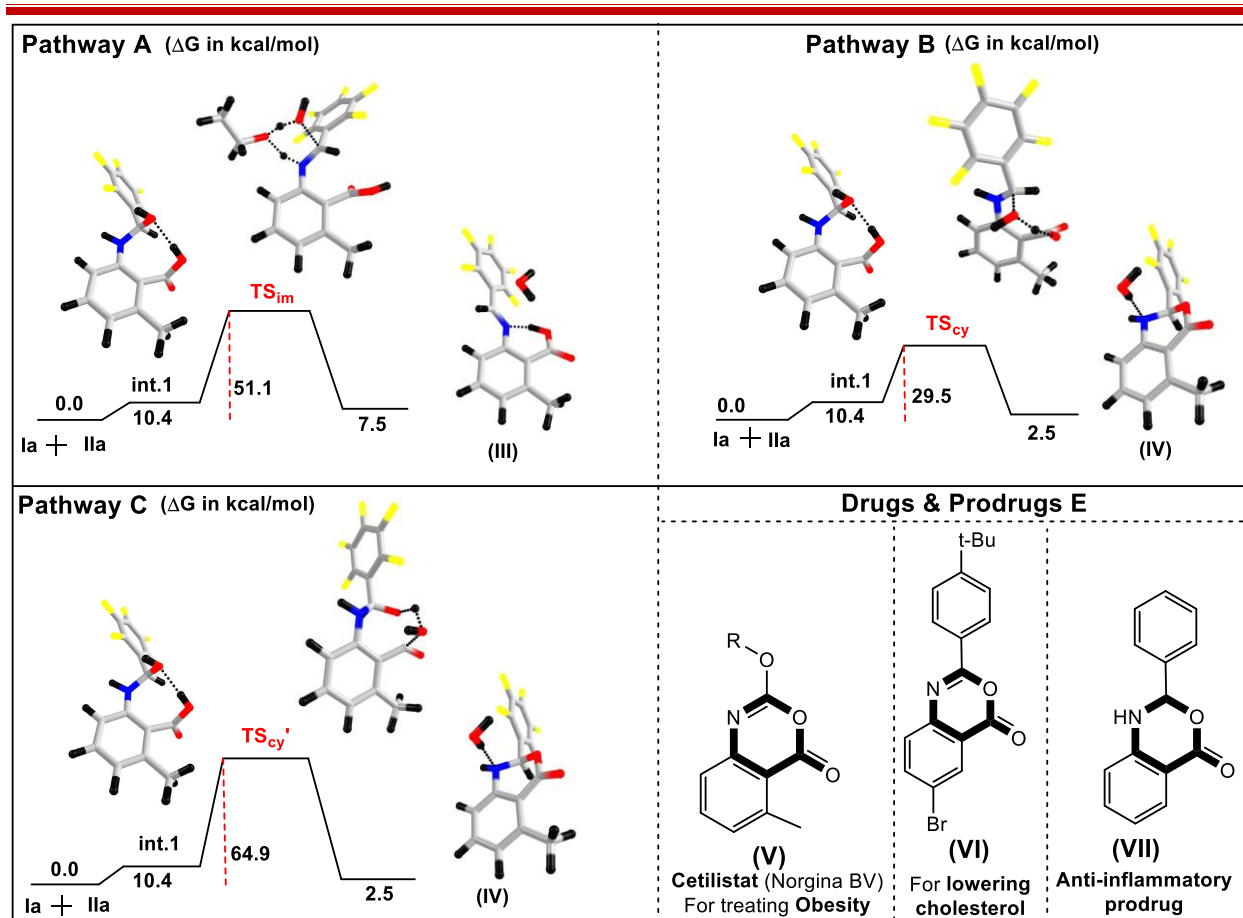


Figure 2.6: DFT calculated (A, B, C) mechanistic pathways with free energies (kcal.mol⁻¹) for various transition states and (E) Benzoxazinone as an important building block for drugs and prodrugs.

The thus produced Benzoxazinones are pharmaceutically important molecules that are commercially used to treat obesity (V),³⁶ to lower cholesterol levels (VI) and as an anti-inflammatory prodrug (VII).³⁷ We anticipate that many other reactions can be reengineered by installing a competitive source of secondary interactions to invert the *modus operandi* of these reactions.³⁸

2.4. Experimental section:

2.4.1 General methods and material:

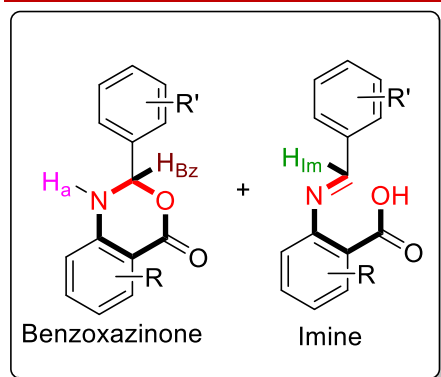
Starting materials for the experiments were purchased from commercial vendors and used without further purification processes. Unless otherwise noted, solvents were dried according to normal protocols. This method is frequently used to guarantee practicality and efficiency in synthetic chemical procedures.³⁹ Loba Chemie Pvt. Ltd. was the supplier of 2-amino benzoic acid. Benzaldehyde as well as 2-amino-6-methyl benzoic acid, 2-amino-6-fluorobenzoic acid, 2-amino-3-methylbenzoic acid, and 2-amino-6-bromobenzoic acid Sigma Aldrich provided us with 4-methoxybenzaldehyde, 3-bromobenzaldehyde, 2-fluorobenzaldehyde, 2,6-difluorobenzaldehyde, 2,3,4,5,6-pentafluorobenzaldehyde, and cyclohexane carboxaldehyde. We bought 2-Amino-6-bromobenzoic acid from Alfa Aesar. We bought CDCl₃ from Sigma Aldrich. We purchased 99.9% commercial-grade ethanol from Brampton, Canada. The remaining solvents were all acquired from nearby vendors (Avra Synthesis Pvt. Ltd.; Spectrochem Pvt. Ltd.). Bruker Avance 200, 400, and 500 MHz instruments were used to record solution NMR spectra, which were then internally referred to residual solvent signals (CDCl₃ referenced at δ 7.26 and 77.23 ppm, for example). Absolute values are provided for coupling constants. The following are multiplicities: s stands for singlet, d for doublet, t for triplet, and m for multiplet. In the NMR spectra of substances, benzoxazinone and imine are represented by the symbols Bz and Im, respectively. Using a Hypersil gold C18 column (150 x 4.6 mm diameter, 8 μ m particle size), mass spectra were captured using a Thermo Scientific Q-Exactive mass spectrometer (Quadrupole analyser). The mobile phase used was 90% methanol + 10% water + 0.1% formic acid. Using a 1 cm quartz cell, the UV-visible spectrum was captured at room temperature on a Perkin Elmer 35 LAMDA instrument. The PerkinElmer device's KBr pellet was used to record the samples' FT-IR spectra. Using the PerkinElmer 2400, C, H, and N analyses were performed. Density functional theory (DFT) and the Turbomole 7.0 software suite were used to optimise the geometry.⁴⁰ Burke, Ernzerhof, and Perdew (PBE)⁴¹ For the geometry optimisation computations, a functional was employed. For every atom, the Turbomole basis set (TZVP), which is the triple- ζ basis set enhanced by a polarisation function, was utilised. The identity resolution (RI)⁴² in addition to the multipole rapid identity resolution (marij)⁴³ The electronic Coulomb term was treated accurately and effectively by using approximations. The following factors were taken into

consideration: We have used the COSMO model to do thorough geometry optimisations of all intermediates and transition state computations.⁴⁴ using the solvent ethanol. Furthermore, these computations included used dispersion adjustments (disp-3).⁴⁵ The M06-2X functional was then used to perform single point computations,⁴⁶ on the optimized geometries. Care was made to guarantee that the transition state structures acquired throughout the research of these reactions had only one imaginary frequency that corresponded to the correct normal mode. The Gaussian 09 suite of programs was used to make calculations for compounds (III) and (IV) (HOMO-LUMO calculation).⁴⁷⁻⁴⁹ using the 6-31+G* basis set and the M062X functional. Using the time-dependent (TD-DFT) approach and the optimised ground-state structure at the M062X/6-31+G* level, the HOMO-LUMO was computed. In order to draw orbitals, the isovalue was set to 0.02.

A Bruker SMART APEX four-circle diffractometer fitted with a Cu K α radiation (1.5418 Å) and a CMOS photon 100 detector (Bruker Systems Inc.) was used to gather single-crystal data. Microfocus (IpS) was employed to focus and monochromatize the incident X-ray beam. Using Paratone-N oil, the flaky colourless crystals were affixed to nylon Cryo loops. At 100(2) K, the data was gathered. Bruker SAINT software was used to combine all of the data, and SADABS was used to adjust for absorption. The Intrinsic Phasing module of the techniques solved the structure, and the SHELXTL 97 software suite was used to enhance it. After locating every non-hydrogen atom by an iterative analysis of difference F-maps, the structure was fine-tuned using the least-squares method. Anisotropic refinement was used for all of the non-hydrogen atoms. In a riding model, hydrogen atoms were arranged geometrically.

2.4.2. General procedure for the synthesis of Benzoxazinones:

The experimental procedure involved dissolving 1 mmol of amine in 20 mL of ethanol, after which 2 mmol (2 equiv.) of aldehyde is added to the mixture. Acetic acid (0.2 equivalent) was added to the reaction mixture as a catalytic quantity. Which was then refluxed for a duration of 6 hours. Subsequently, the reaction mixture underwent vacuum concentration, resulting in a crude semi-solid residue. This residue was further treated with hexane (10 mL $\times$ 2) to obtain a free-flowing solid. The identification of both the imine and the benzoxazinone, obtained through the proposed condensation, was confirmed through various 1-2D NMR experiments. The product distribution between benzoxazinone and imine was determined using proton NMR analysis of the obtained residue. Benzoxazinones, exhibiting more than 90% selectivity, were isolated, and



their yields have been documented. In this context, the term "Benz" has been coined to describe the formation of benzoxazinones through the condensation reaction. Here, "Benz" stands for Benzoxazinone. The imine proton is referred to as HIm, while the benzoxazinone proton is denoted as HBz. Additionally, Ha represents a proton located on the nitrogen atom in benzoxazinone.

2.4.3. 2-(2,6-difluorophenyl)-5-methyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (compound 14):

General procedure as mentioned in section 2.4.2 was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv.) and 2,6-difluorobenzaldehyde (0.284 g, 2 mmol, 2 equiv.) were used as reaction partners. The ratio of the two products was determined from proton NMR. The compound was crystallized by slow evaporations from ethanol (Pure crystal, 0.231 g, 84%). Melting point (m.p.) = 94-96 °C. **¹H NMR (CDCl₃, 400 MHz, 298 K):** δ = 7.45-7.41 (m, 1H, and Ar), 7.35-7.28 (m, Ar, 1H), 6.97 (t, 2H, Ar, 2 J = 8.45), 6.88 (m, 1H, Ar, JH-H = 7.58), 6.77 (d, 1H, Ar, JH-H = 8.07), 6.49 (d, 1H, HBz, 3 JH-H = 5.38), 5.13 (br s, 1H, H), 2.70 (s, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃, 298 K):** δ = 163.7 (Ch), 162.8 (d, 3 JC-F = 6.17 Hz, C), 160.3 (d, 3 JC-F = 6.17 Hz, C), 148.3 (C), 144.5 (C), 134.1 (C), 132.2 (t, 3 JC-F = 10.63 Hz, C), 125.3 (C), 115.7 (C), 114.3 (C), 114.5 (C), 112.2 (d, 2 JC-F = 25.43 Hz, C), 78.3 (t, 3 JC-F = 3.85 Hz, 3 J = 4.62 Hz, CBz), 22.5 (CH₃). ESI-MS (+ve) m/z for C₁₅H₁₂O₂NF₂ [M+H]⁺ Calculated: 276.0831 Da, observed: 276.0826 Da; C₁₅H₁₁O₂NF₂Na [M+Na]⁺ Calculated: 298.0650 Da, Observed: 298.0644 Da

The compound was crystallized by slow evaporations from ethanol (Pure crystal, Yield = 84 %) and molecular structure is presented in figure 2.7. The selectivity of compound 14 was 89 %.

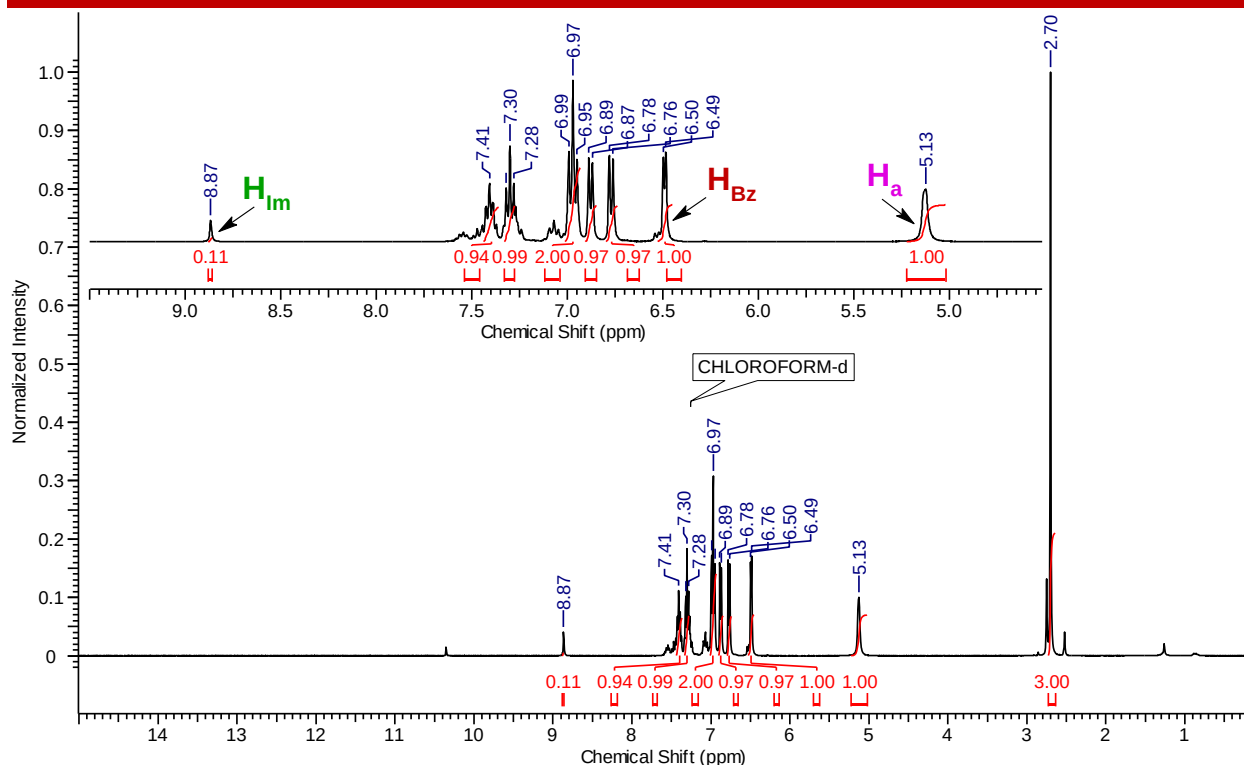


Figure 2.7: ^1H NMR spectrum of compound **14** in CDCl_3 (400 MHz) (bottom), expanded view (top).

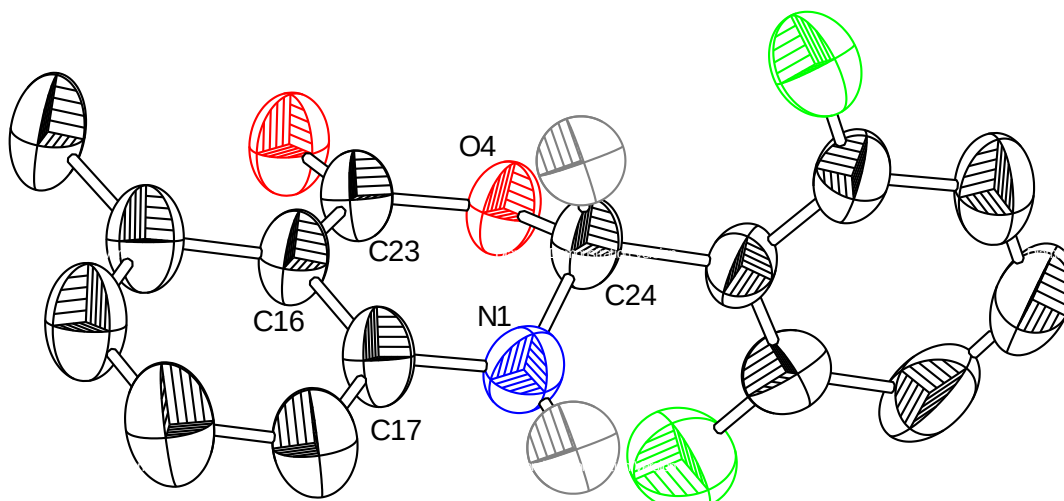


Figure 2.8: Molecular structure of compound **14** (hydrogen atoms except N-H and C-H have been deleted for clarity and thermal ellipsoids are drawn at 50 % probability level); selected interatomic distance [Å] and angles [°]: C24-N1 1.428, C17-N1 1.371, C24-O4 1.447, O4-C23 1.360, C23-C16 1.465; C17-N1-C24 114.74, N1-C24-O4 108.43, C24-O4-C23 115.91, O4-C23-C16 117.34. The dihedral angle between the planes defined by C17-N1-O4 and N1-C24-O4 is 49.58°.

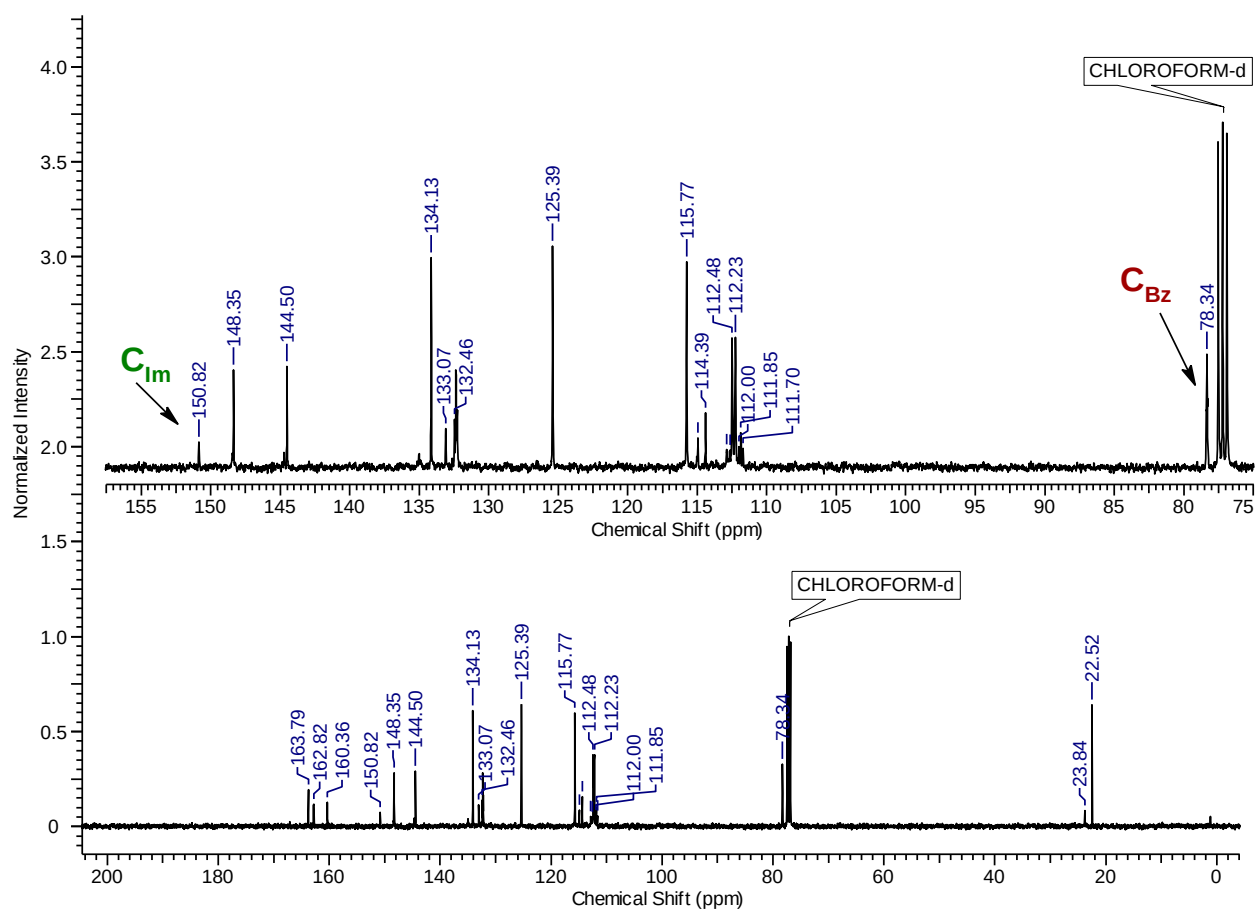


Figure 2.9: ^{13}C NMR spectrum of compound **14** in CDCl_3 (100 MHz) (bottom), expanded view (top).

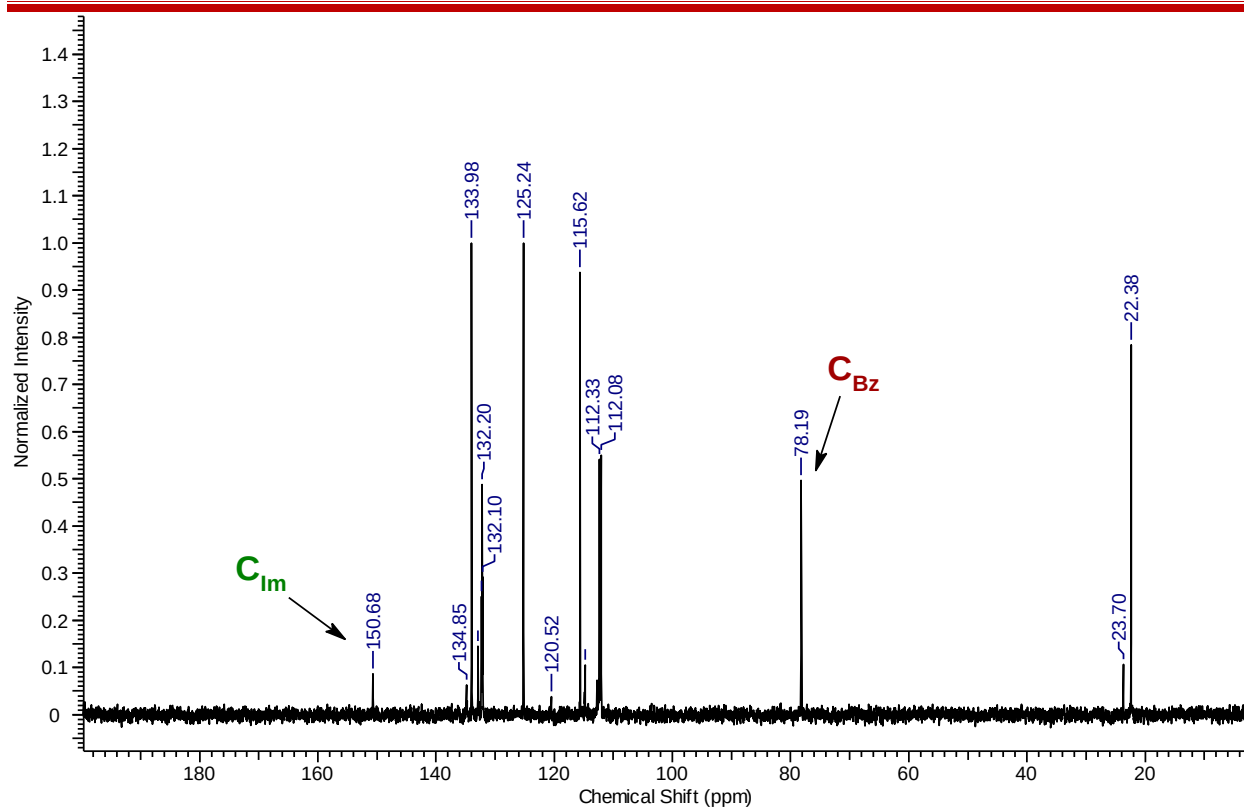


Figure 2.10: DEPT NMR spectrum of compound **14** in CDCl₃ (100 MHz) (bottom).

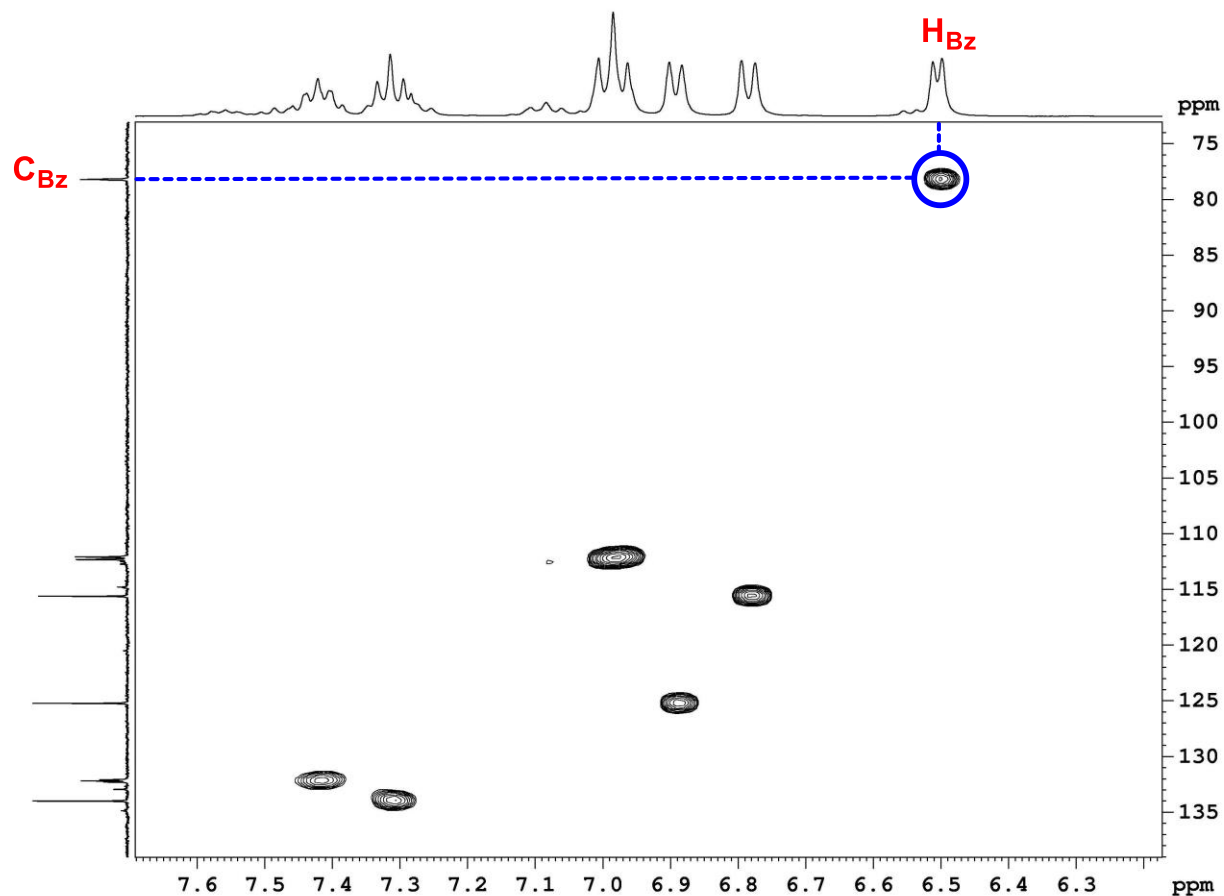


Figure 2.11: Short-range C-H correlation (HSQC) NMR spectrum of compound **14** in CDCl_3 .

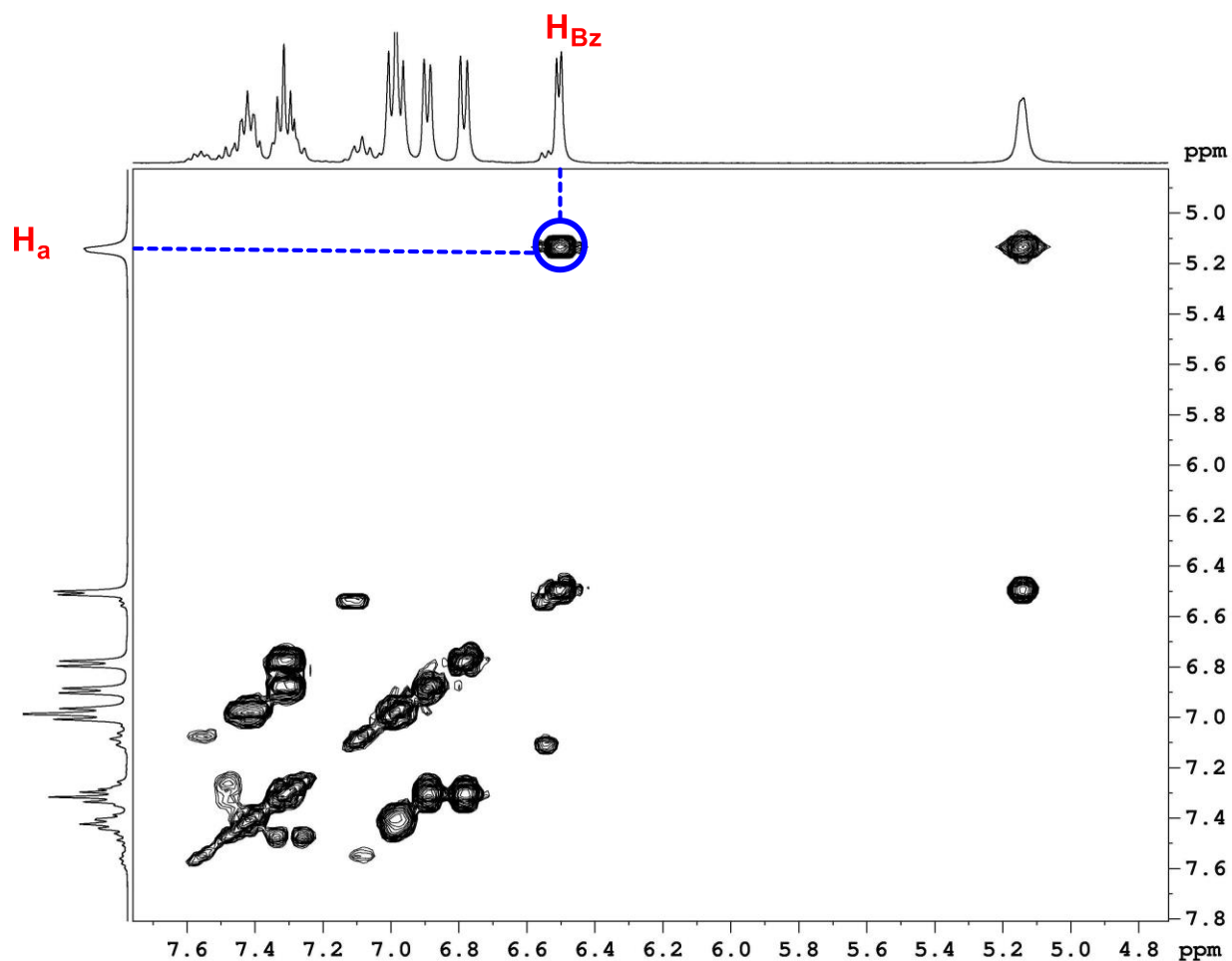


Figure 2.12: COSY (H-H correlation) NMR spectrum of compound **14** in CDCl_3 .

DVB-10 #102 RT: 0.45 AV: 1 NL: 2.90E9
T: FTMS + p ESI Full ms [100.00-1500.00]

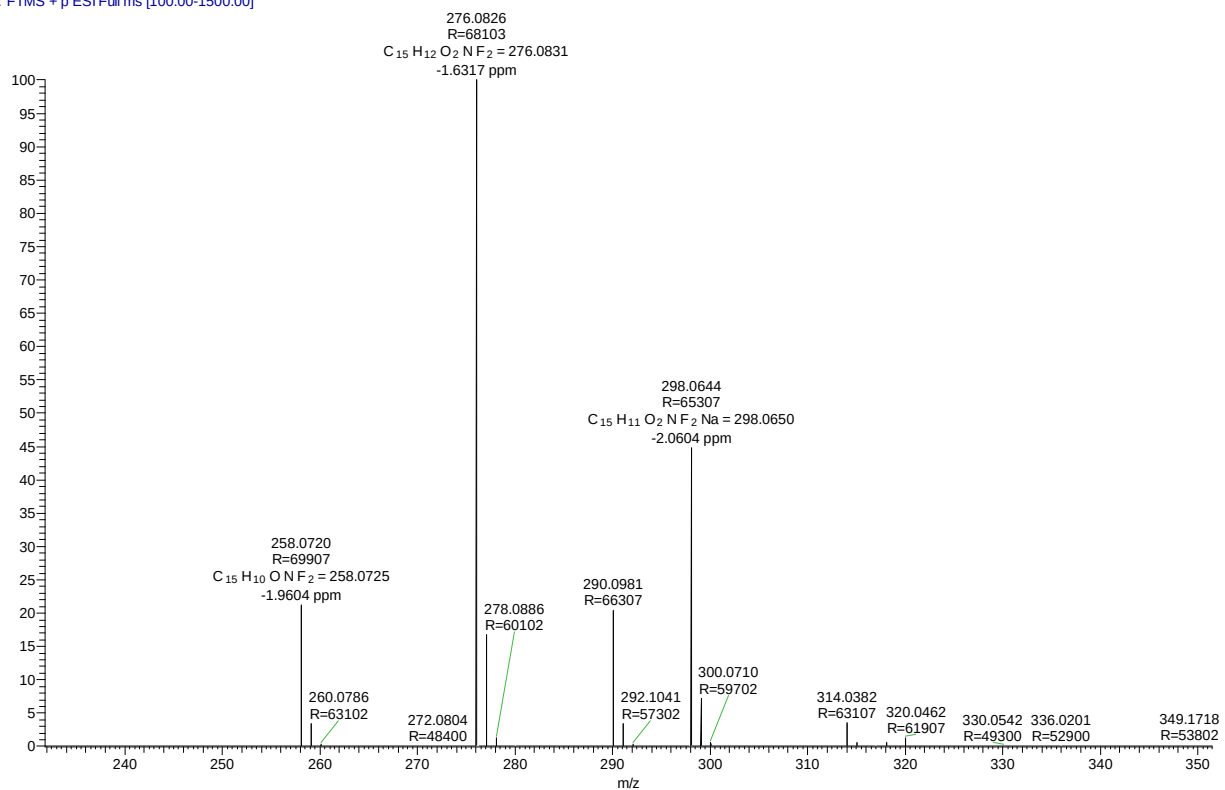
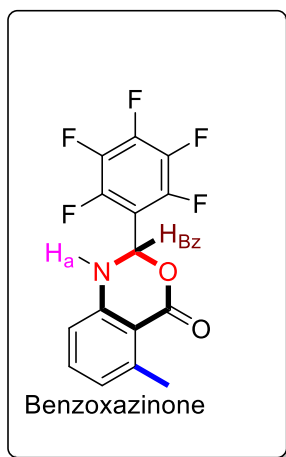


Figure 2.13: HRMS spectrum of compound 14.

2.4.4. 5-methyl-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d] [1,3] oxazin-4-one (compound 15):



General procedure as mentioned in section 2.4.2 was followed and, 2- amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv.) and 2,3,4,5,6- pentafluoro benzaldehyde (0.392 g, 2 mmol, 2 equiv.) were used as reaction partners. Compound 15 was isolated in as pale yellow solid (0.315 g, 96%) after routine hexane wash. The compound was crystalized by slow evaporations from ethanol solution and molecular structure is presented in figure 2.3. Melting point (m.p.) = 196-197 °C. **¹H NMR (CDCl₃, 400 MHz, 298 K):** δ = 7.34 (t, JH-H = 7.82, 1H, Ard), 6.92 (d, JH-H = 7.34 Hz, 1H, Arc), 6.77 (d, JH-H = 8.07 Hz, 1H, Are), 6.47 (d, 3 JH-H = 5.15 Hz, 1H, HBz), 5.03 (d, 3 JH-H = 3.42 Hz, 1H, Ha), 2.70 (s, 3H, CH₃). **¹³C NMR (CDCl₃, 100 MHz, 298 K):** δ = 162.8 (Ch), 147.9, 146.9, 144.7, 143.7, 139.1, 138.9, 136.9, 134.5, 125.8, 115.5, 115.3, 113.9, 110.7, 77.8 (CBz), 22.4 (CH₃). **¹⁹F NMR (CDCl₃, 376 MHz, 298 K):** δ = -139.87 (d, JF-F = 16.02 Hz, 2F), -149.85 (d, JF-F = 20.60 Hz, 1F), -160.16 (t, JF-F = 18.54 Hz, 2F). Elemental analysis: Calculated C 54.72, H 2.45, N 4.25 found C 54.63, H 2.38, N 4.21. FT-IR (cm⁻¹): 1705 (C=O), 1653, 1602, 1504 (N-H (br)), 1433, 1382, 1338 (C-N), 1274, 1201 (C-O), 1130 (C-O (br)), 1044, 1003. ESIMS (+ve) m/z for C₁₅H₉O₂F₅N [M+H]⁺ Calculated: 330.0548 Da, Observed: 330.0543 Da. The compound was crystalized by slow evaporations from ethanol solution and molecular structure is presented in figure 2.14 and the selectivity of compound 15 was > 99 %.

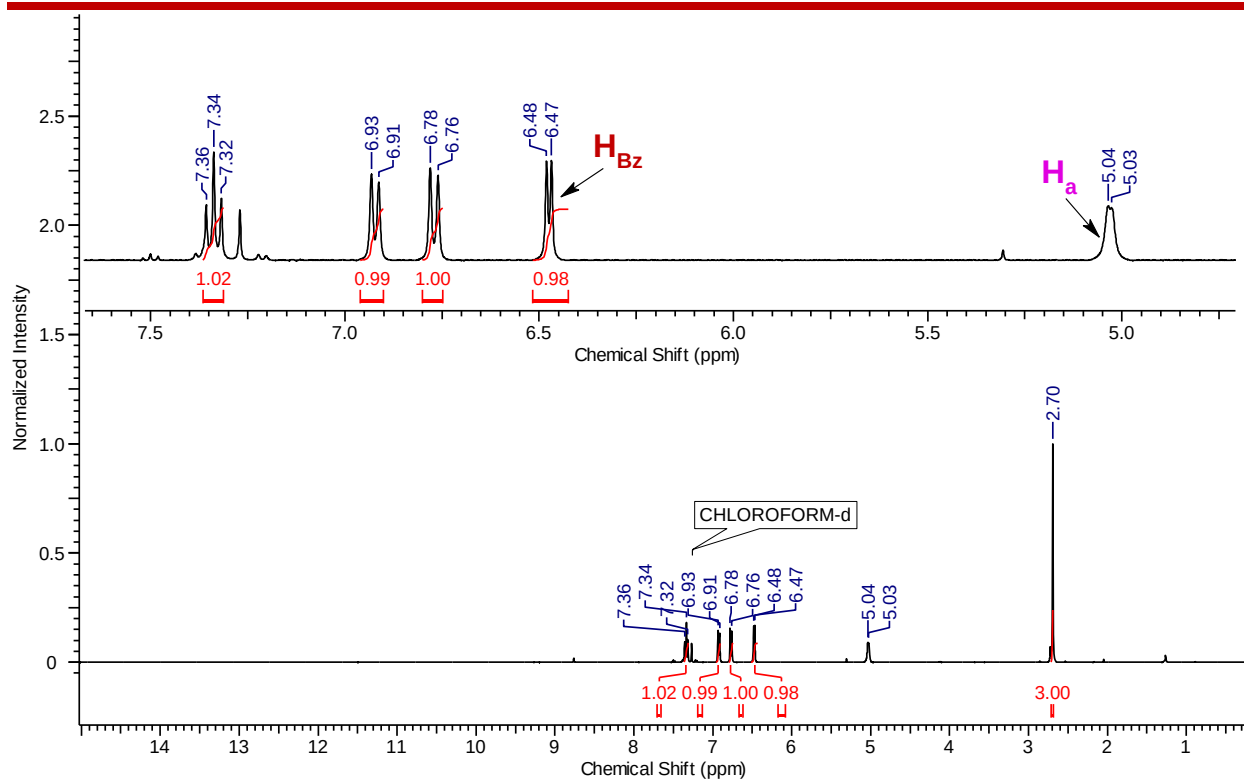


Figure 2.14: ^1H NMR spectrum of compound **15** in CDCl_3 (400 MHz) (bottom), expanded view (top).

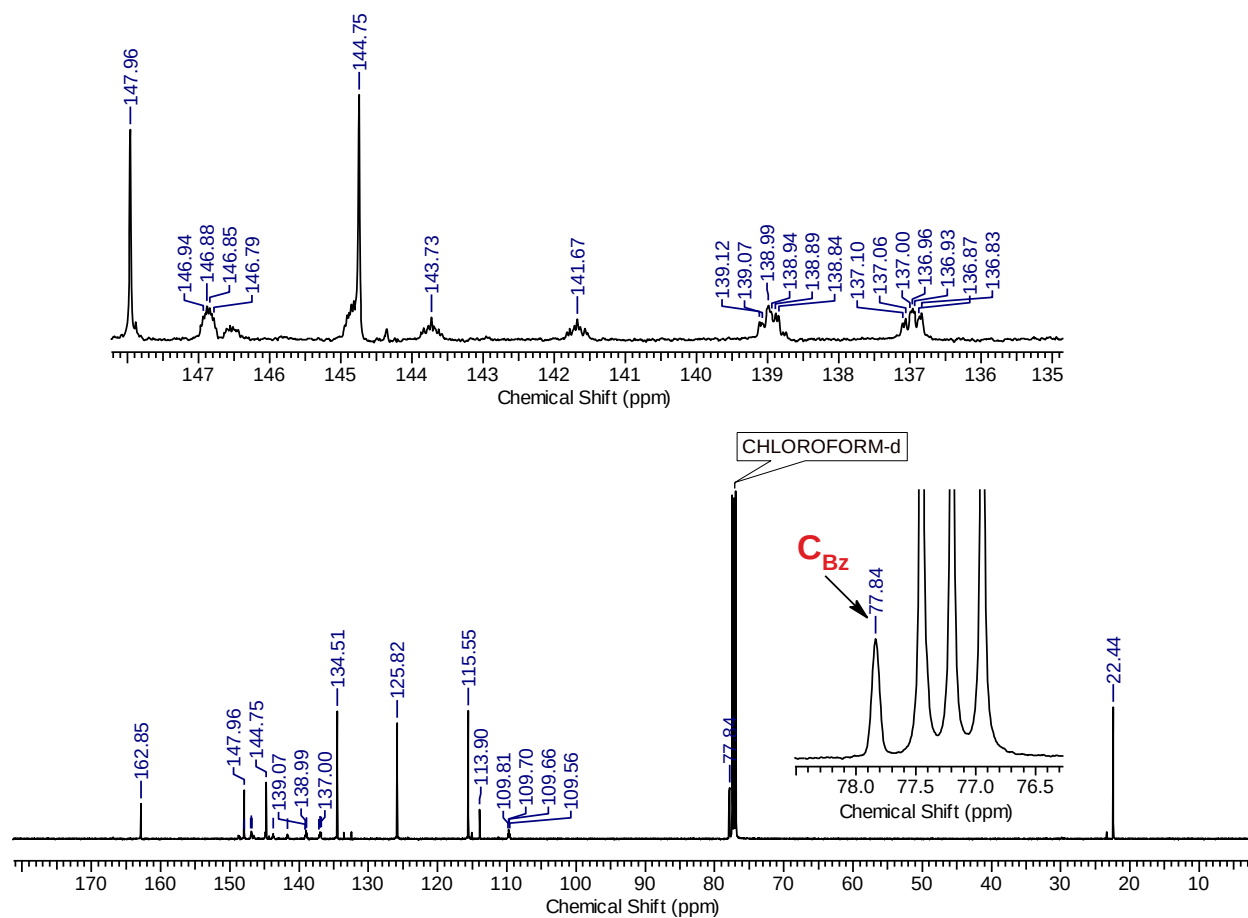


Figure 2.15: ^{13}C NMR spectrum of compound **15** in CDCl_3 (100 MHz) (bottom), expanded view (top).

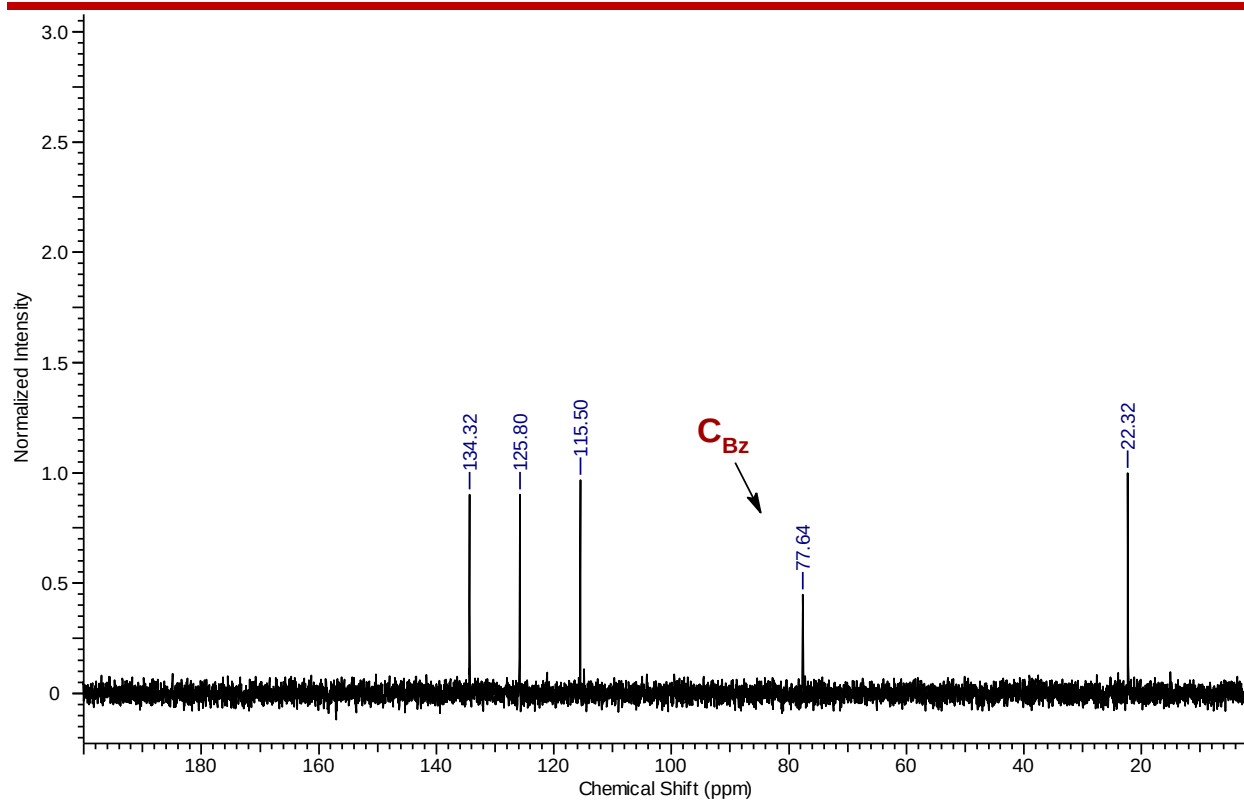


Figure 2.16: DEPT NMR spectrum of compound **15** in CDCl₃ (100 MHz).

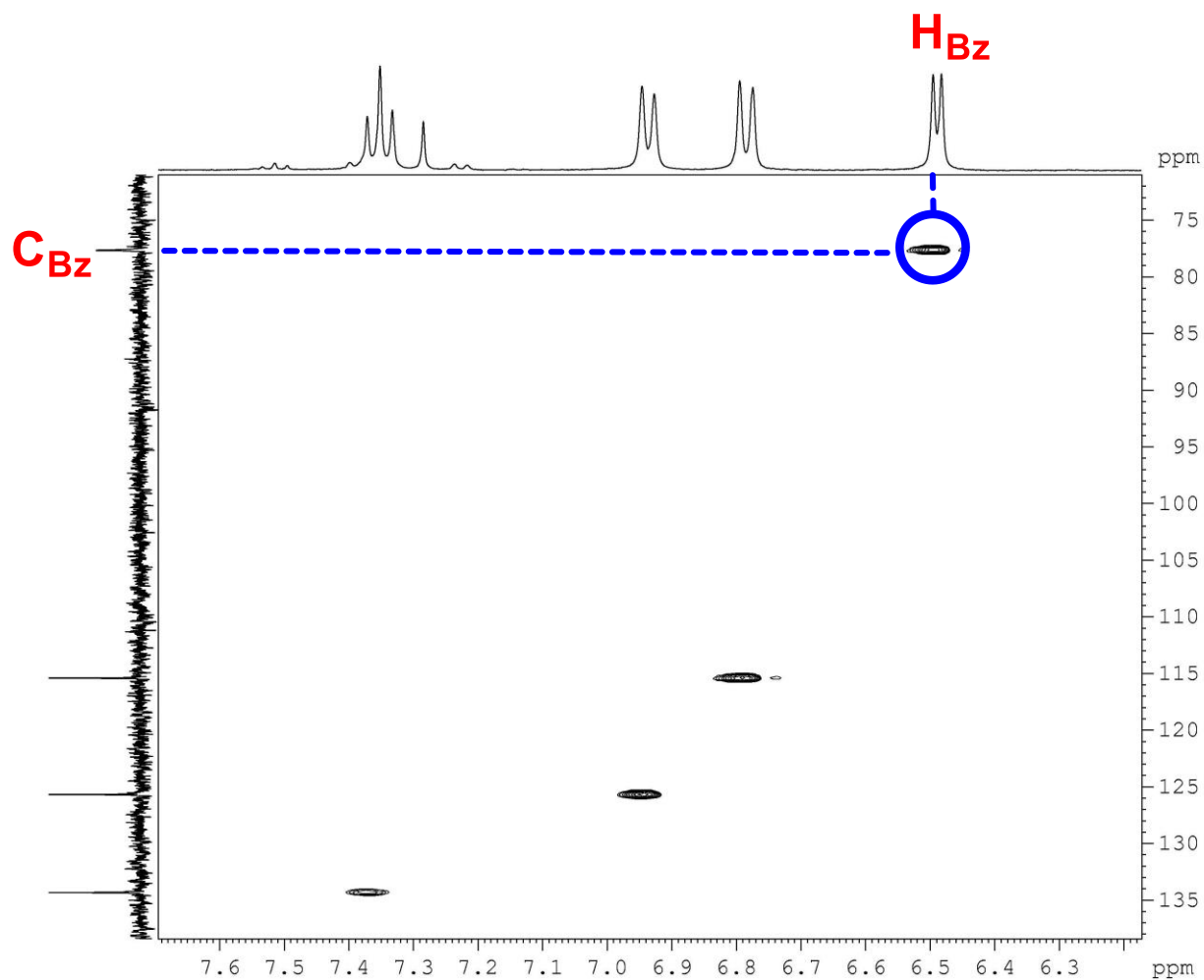


Figure 2.17: Short range C-H correlation (HSQC) NMR spectrum of compound **15** in CDCl_3 .

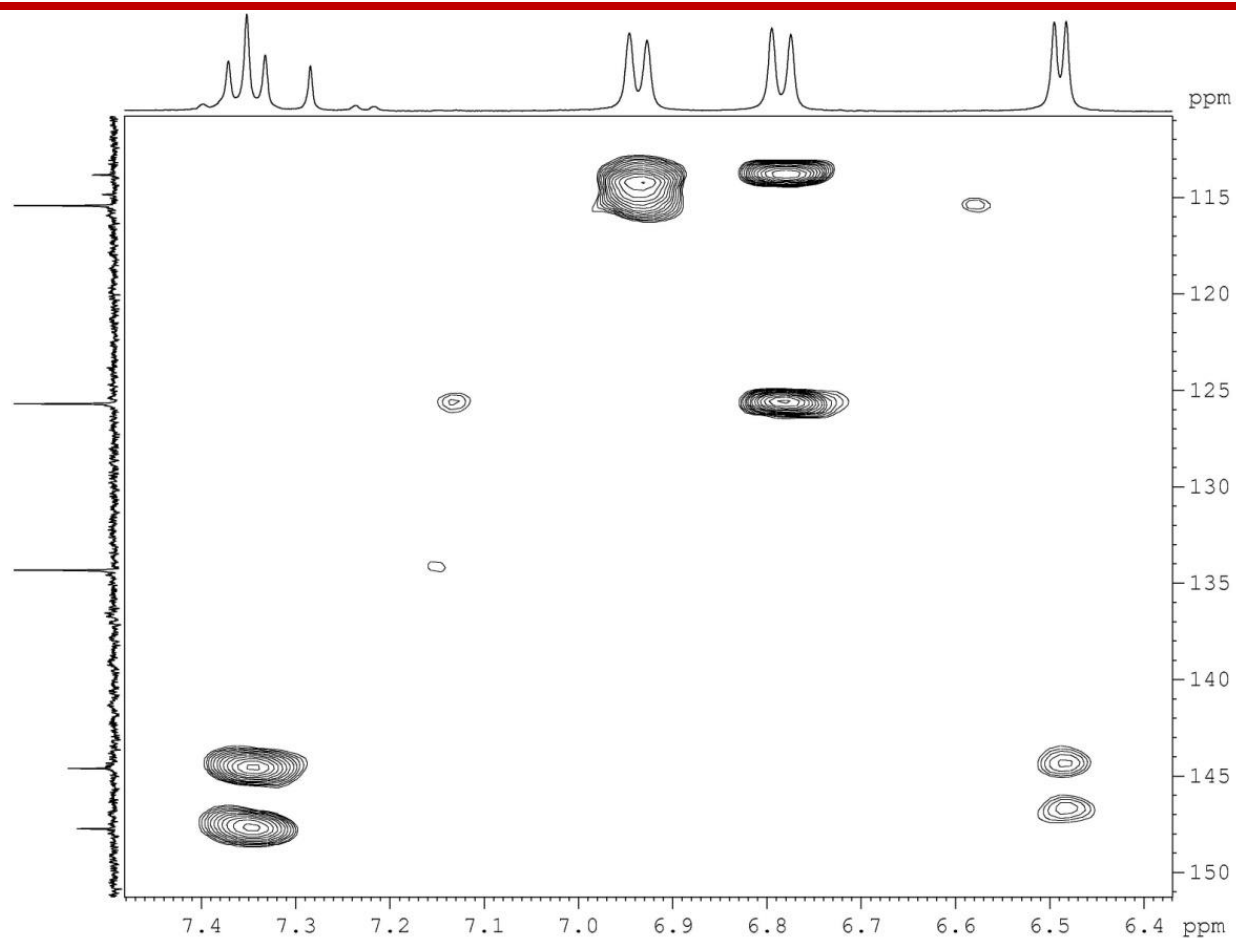


Figure 2.18: Long range C-H correlation (HMBC) NMR spectrum of compound **15** in CDCl₃.

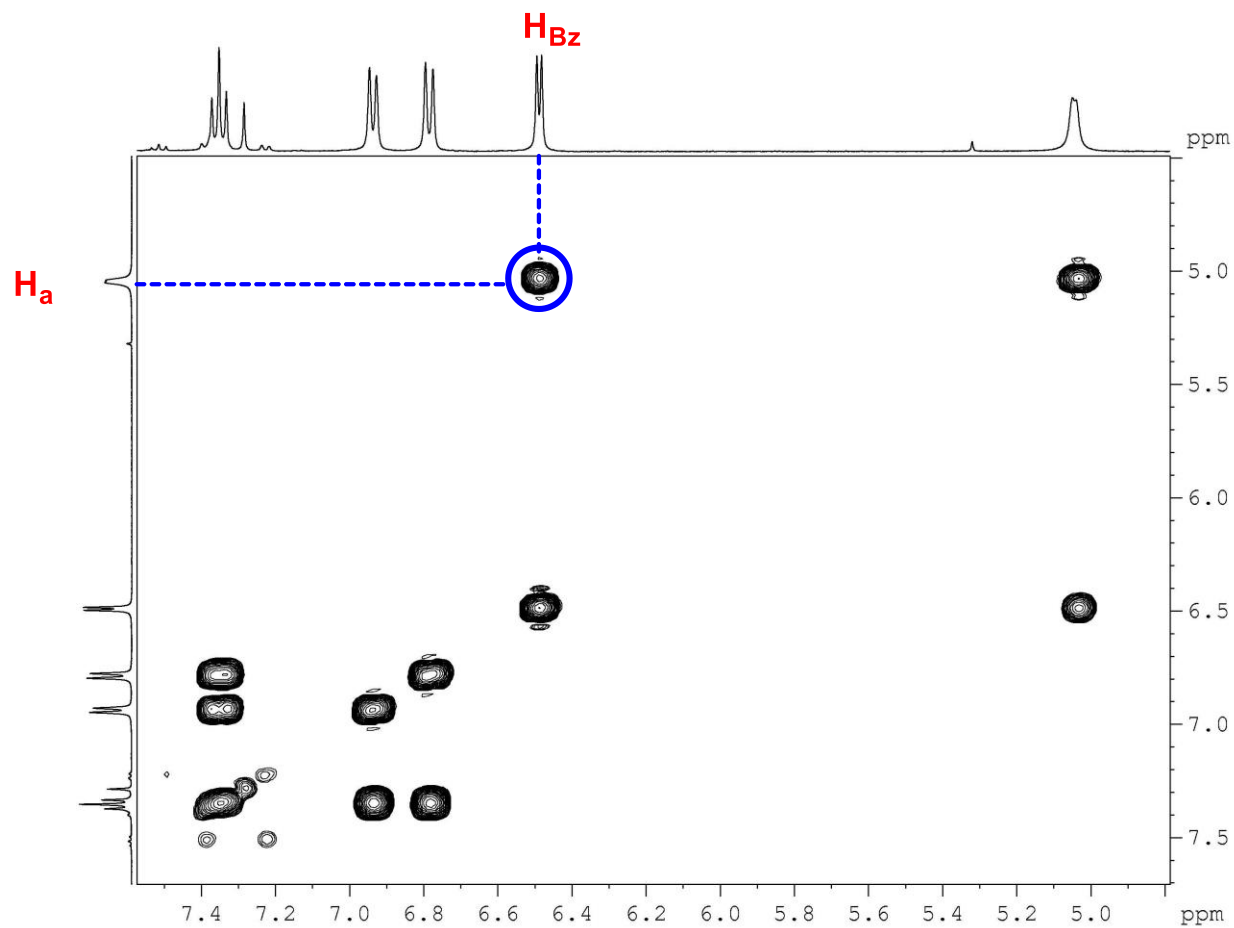


Figure 2.19: COSY (H-H) correlation NMR spectrum of compound **15** in CDCl₃.

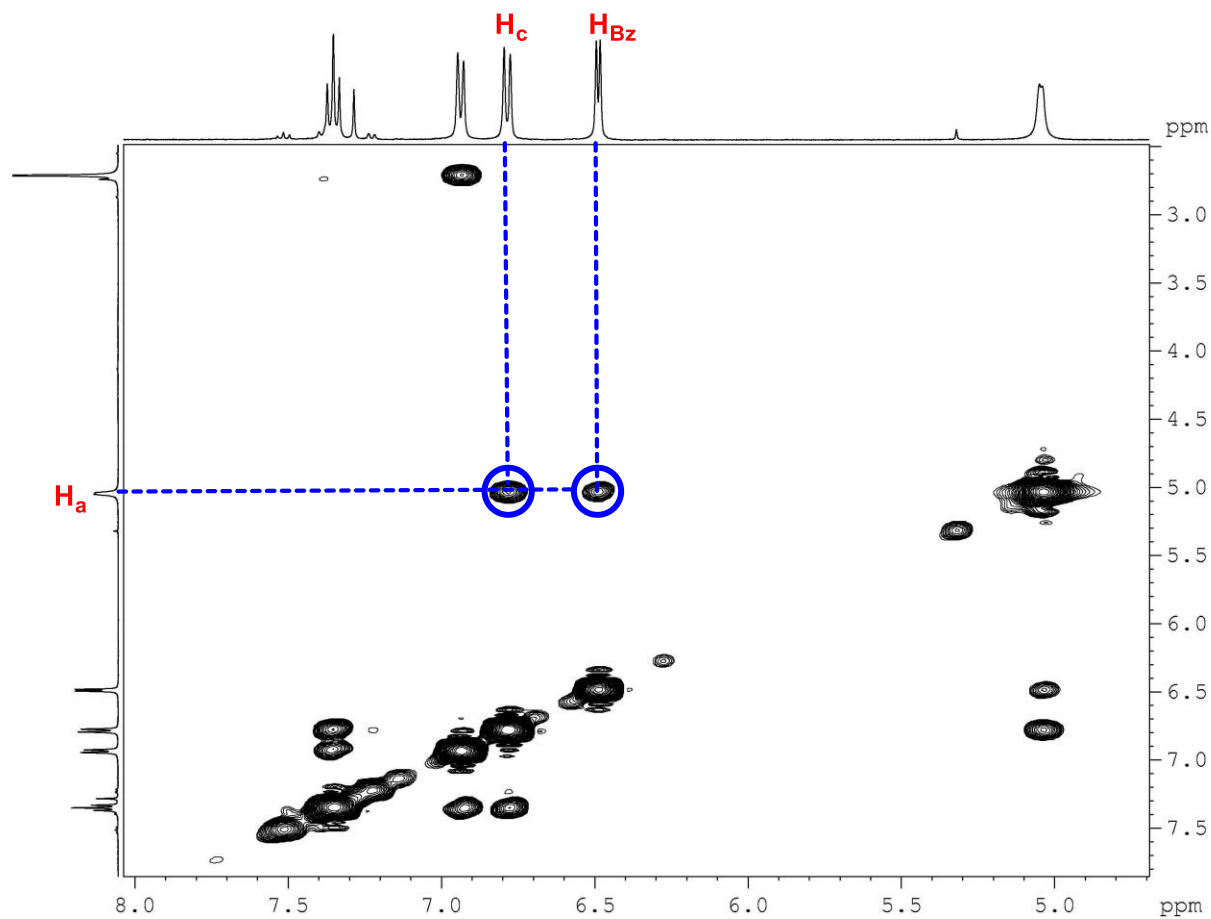


Figure 2.20: NOSY (H-H through space correlation) NMR spectrum of compound **15** in CDCl₃.

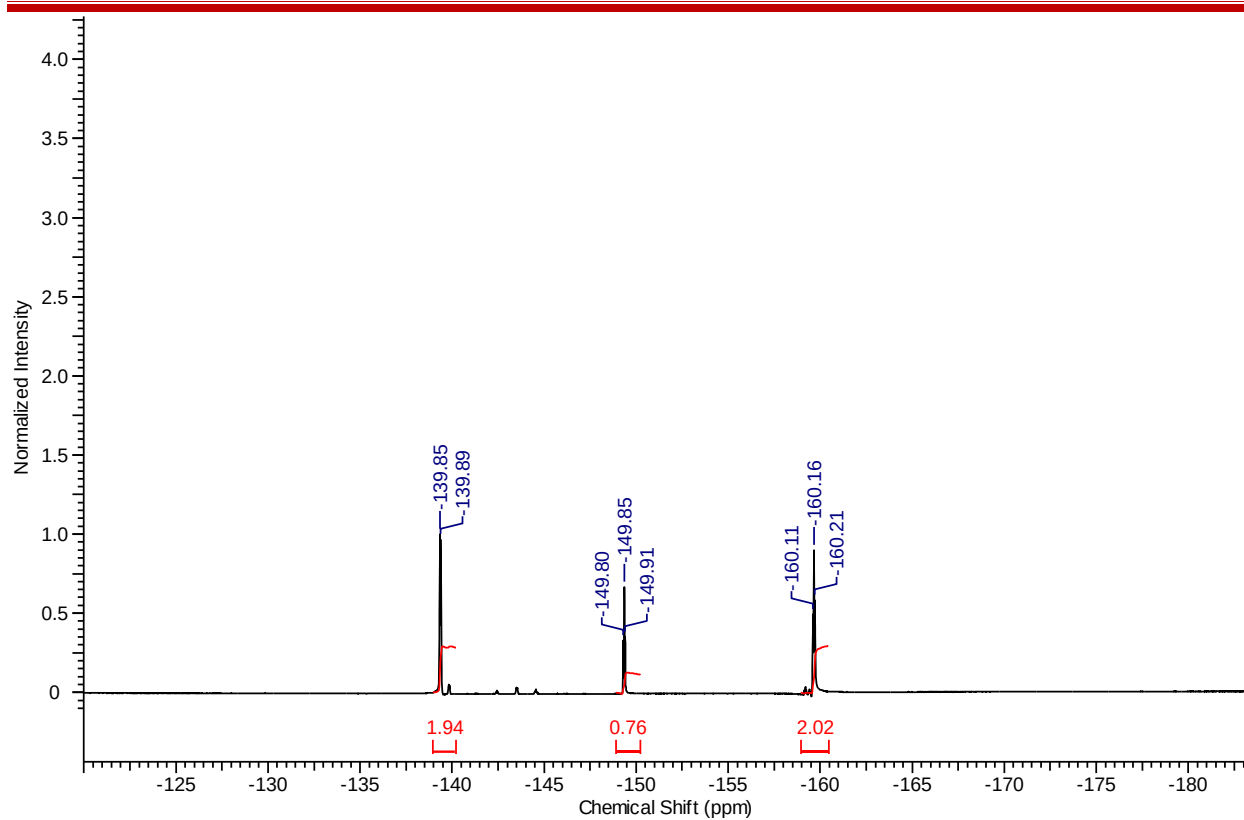


Figure 2.21: ^{19}F NMR spectrum of compound **15** in CDCl_3 .

DVB-08 #113 RT: 0.50 AV: 1 NL: 1.96E9
T: FTMS + p ESI Full ms [100.00-1500.00]

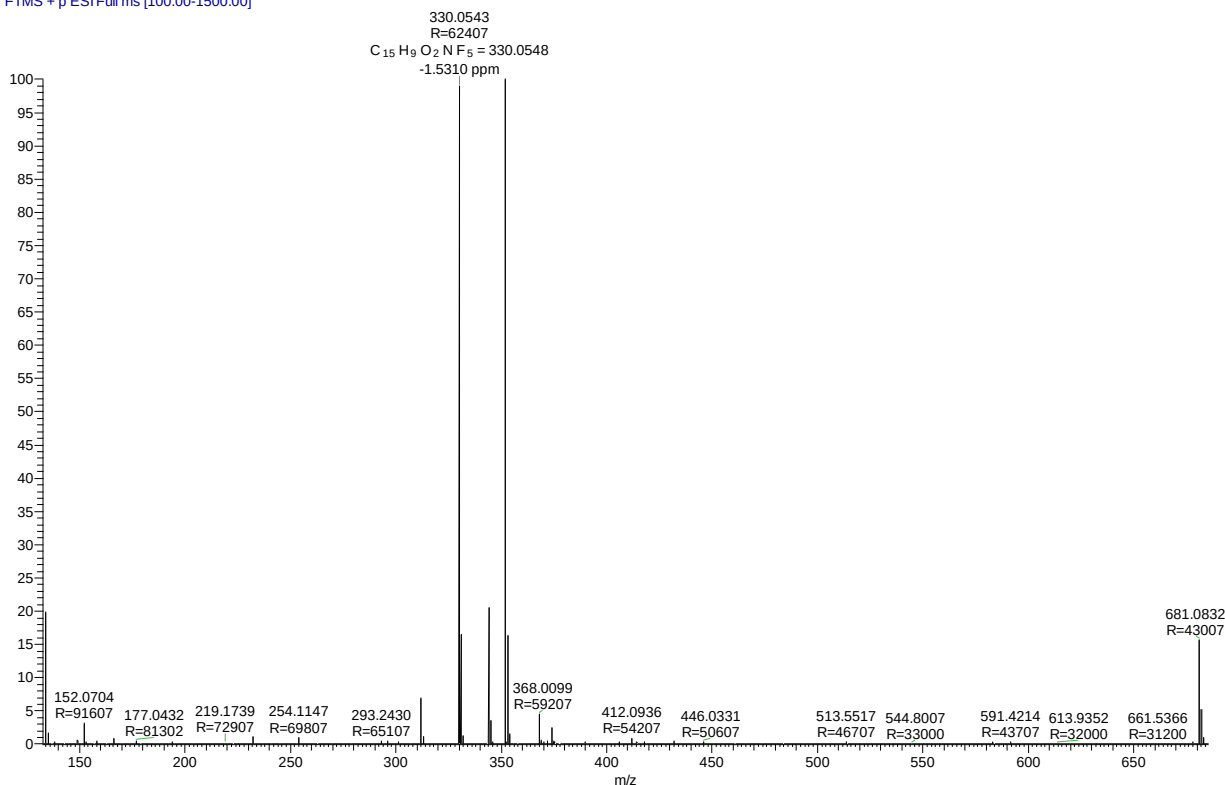


Figure 2.22: HRMS spectrum of compound 15.

2.4.5. Tracking the progress by NMR spectroscopy:

In an NMR tube experiment, 1 μ mol (15 mg, 1equiv.) 2-amino-6-methyl-benzoic acid (**I**) was dissolved in 0.6 mL deuterated acetonitrile and the NMR tube was cooled to -5 $^{\circ}$ C. 0.75 μ mol (14 mg, 0.75 equivalent) of 2,3,4,5,6-pentafluoroaldehyde (**II**) It was put in a cold NMR tube, and at 0 $^{\circ}$ C, a proton NMR was recorded right away. Imine resonance (in the range of 8-9 ppm) could not be observed at 0 $^{\circ}$ C, but even at this low temperature a new resonance at 2.60 ppm appeared, which can be easily assigned to methyl group in benzoxazinone (**IV**). Our attempts to record the NMR at lower temperature (-10 to -25 $^{\circ}$ C) were not very successful as the amine and the aldehyde start precipitating out and very significant signal broadening was observed. Proton NMR was then obtained after the probe's temperature was increased from 0 to 20 degrees Celsius. Likewise, proton NMR of the same sample was recorded at 40 $^{\circ}$ C and 60 $^{\circ}$ C. To obtain full conversion, another 0.25 equivalent of (**II**) was added to the NMR tube and proton NMR

was recorded at 60 °C. Finally excess (another 0.25 equivalent) of aldehyde (II) was necessary to fully convert the (I) and NMR was recorded at 60 °C. Figures 2.23 and 2.24 depicts the variable temperature proton NMR spectra.

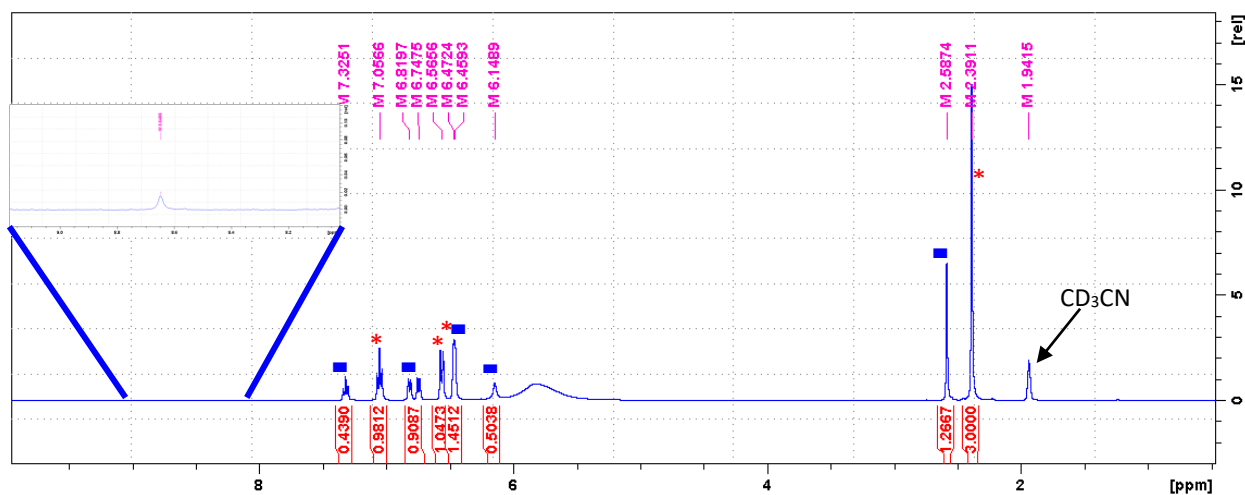
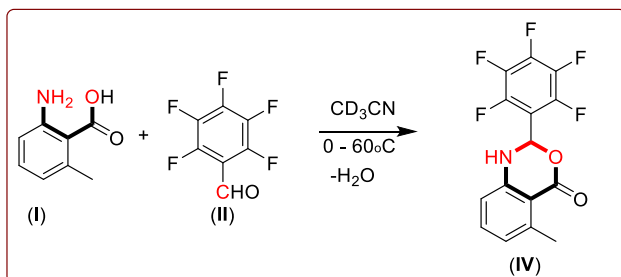


Figure 2.23: ^1H NMR spectrum of a reaction mixture of (I) (*) and (II) at 0°C, product (IV) is denoted with this (■) symbol.

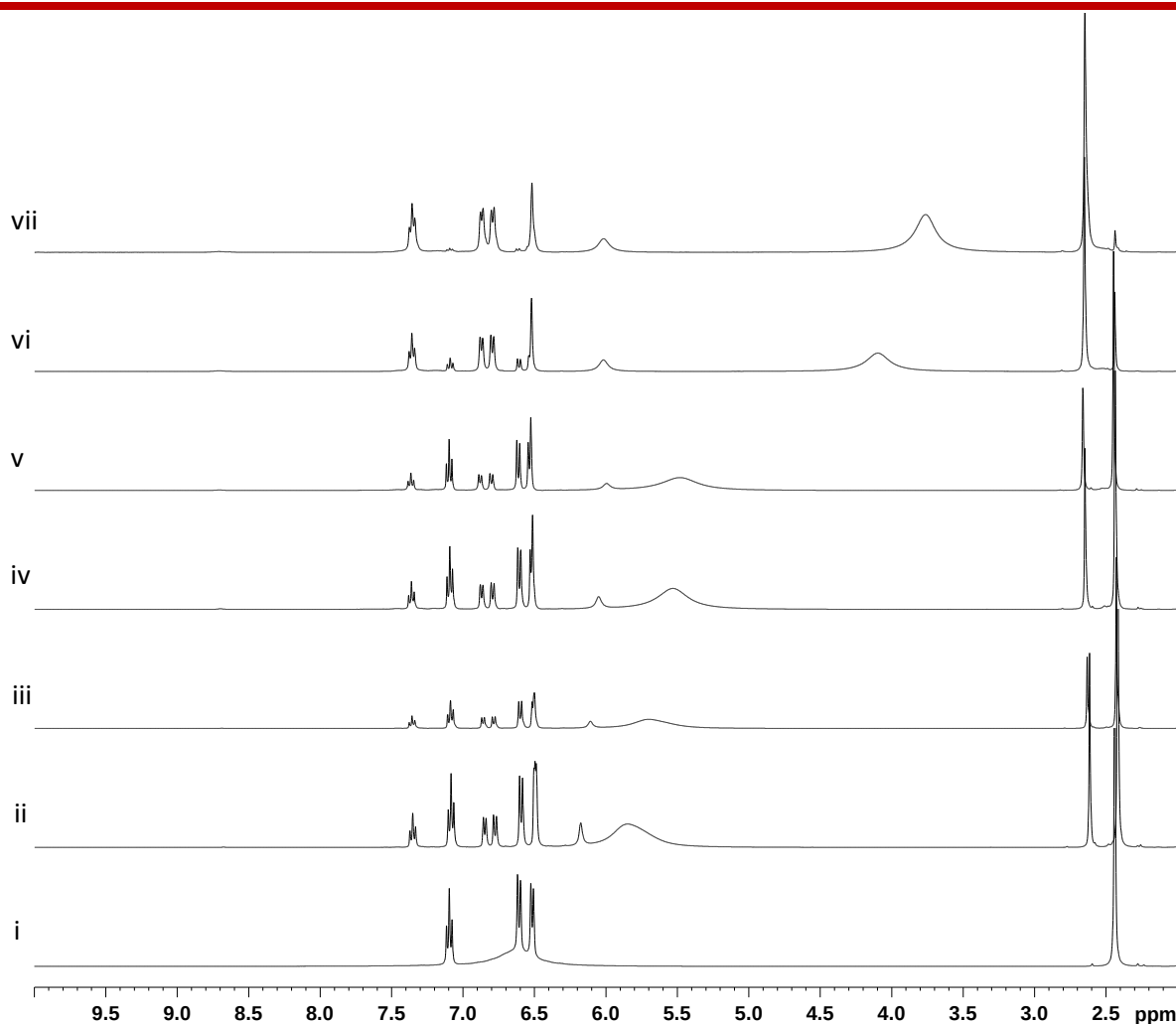


Figure 2.24. Mechanistic investigations. i) ^1H NMR of (I); ii) addition of 0.75 equivalent of II at 0°C ; iii) NMR recorded at 20°C ; iv) NMR recorded at 40°C ; v) NMR recorded at 60°C ; vi) addition of 0.25 equivalent of (II), NMR at 60°C ; vii) addition of 0.25 equivalent of (II), NMR at 60°C .

2.4.6. Isotopic (^{18}O) labeling investigation:

As depicted in figure 2.25, The first step involved converting 2-amino-6-methylbenzoic acid to the equivalent acid-chloride.⁴ An oven dried Schlenk tube was charged with 1 equivalent 2-amino-6-methyl-benzoic chloride (17 mg, 1 μmol , dark red colored) and 2.5 equivalent labeled water (H_2^{18}O) was added. The dark color semisolid chloride immediately turned into light yellow colored precipitate of ^{18}O labeled 2-amino-6-methyl-benzoic acid.⁵ The residue was then dissolved in CD_3CN and 2 equivalent of 2,3,4,5,6-pentafluorobenzaldehyde (40 mg, 2 μmol) was put. NMR spectra were then acquired after the reaction mixture was refluxed for six hours. Due to the presence of ^{18}O , the C-H carbon adjacent to the labelled oxygen shifts up-field and appears

at 77.52 ppm. Similar changes in the chemical shift of ^{18}O labelled C-H carbon have been reported.⁶ The 2D NMR spectroscopy further confirmed the existence of ^{18}O in the cyclized product (**IV**) (Figure 2.27). Figure 2.26 compares the ^{13}C NMR of ^{16}O benzoxazinone (bottom) and that of ^{18}O labelled benzoxazinone (top). Molecular ion peak at $m/z = 332$ $[\text{M}+\text{H}]^+$ was detected by ESI-MS analysis, and it can be attributed to ^{18}O -labeled benzoxazinone. (Figure 2.28).

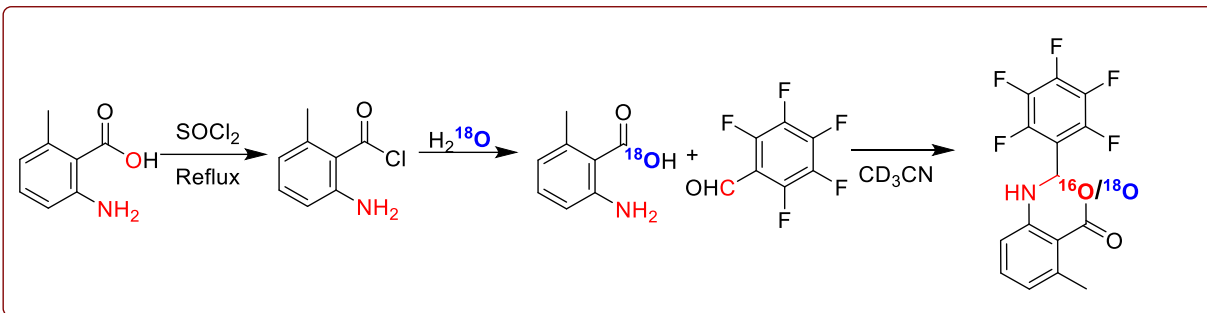


Fig. 2.25. Synthesis of ^{18}O labeled 2-amino-6-methylbenzoic acid.

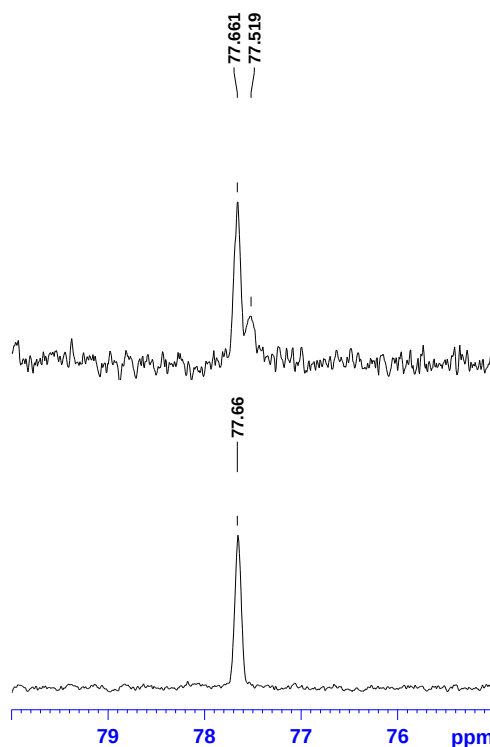


Figure 2.26. ^{13}C NMR spectra of benzoxazinone (**IV**) (bottom) in CD_3CN (500 MHz) and that of ^{18}O labelled benzoxazinone (top).

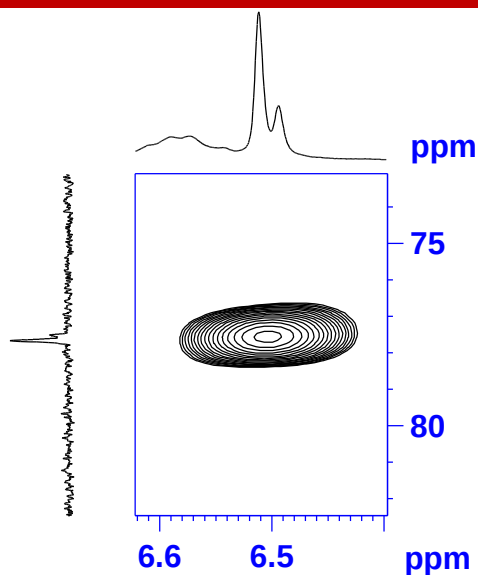


Figure 2.27: Expanded view of a short-range C-H correlation (HSQC) spectrum of ^{18}O labeled benzoxazinone.

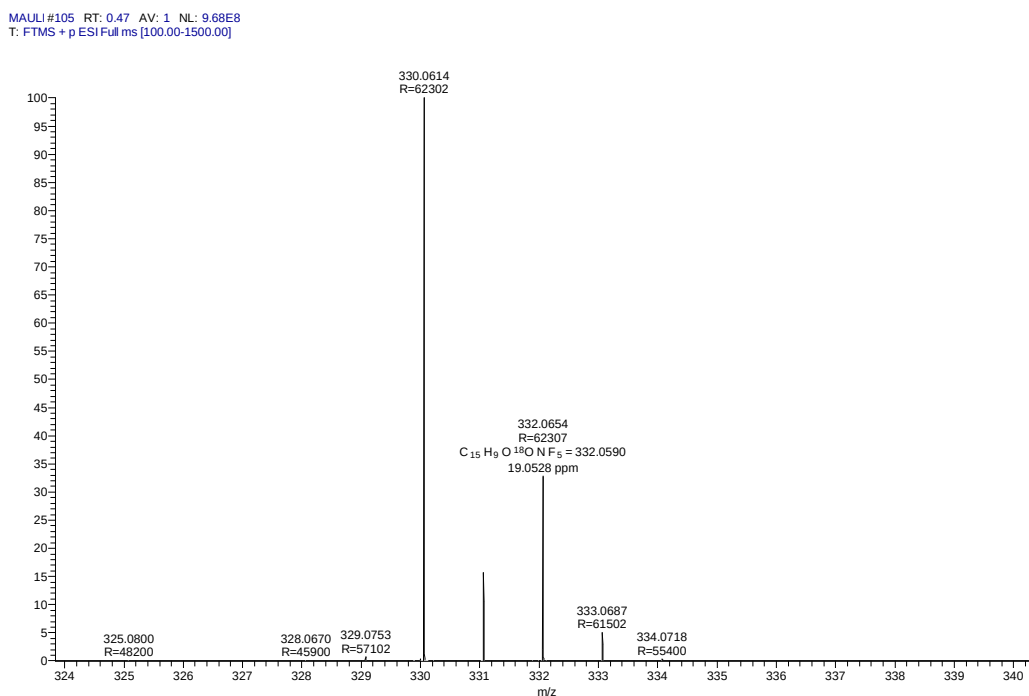


Figure 2.28: ESI-MS spectrum of ^{18}O labelled benzoxazinone (IV) at $m/z = 332.06$ $[\text{C}_{15}\text{H}_8\text{F}_5\text{N}^{16}\text{O}^{18}\text{O}+\text{H}]^+$ and unlabeled (^{16}O) benzoxazinone at $m/z = 330.06$ $[\text{C}_{15}\text{H}_8\text{F}_5\text{N}^{16}\text{O}_2+\text{H}]^+$.

2.4.7. Tracking the reaction by UV-visible spectroscopy:

UV-visible spectroscopy was used as a tool to further investigate the reaction mechanism. Ground state optical absorption of the aqueous solution was measured in a quartz cell on a Perkin Elmer UV-vis spectrophotometer (light path 10 mm) equipped with a PTC-348WI temperature controller. Stock solution of 2,3,4,5,6-pentafluorobenzaldehyde (**I**) and 2-amino-6-methylbenzoic acid (**II**) (1×10^{-3} M) was prepared in ethanol. Dilute solution of (3.8×10^{-5} M) aldehyde and acid were mixed and the reaction mixture was monitored at different time intervals (Figure 2.30). In order to interpret the experimental results of UV-visible spectroscopy, the electronic absorption spectra of the cyclized (**IV**) and imine (**III**) compounds were theoretically calculated using DFT. The calculation has been carried out at the fixed geometry obtained by the geometry minimization with the help of DFT method. DFT calculation suggested the $\lambda_{\text{max}} = 291$ nm for the cyclized structure and 319 nm for the imine (Figure 2.29). Absence of 319 nm band in the reaction mixture (Figure 2.30) clearly suggested that the reaction did not follow Pathway A.

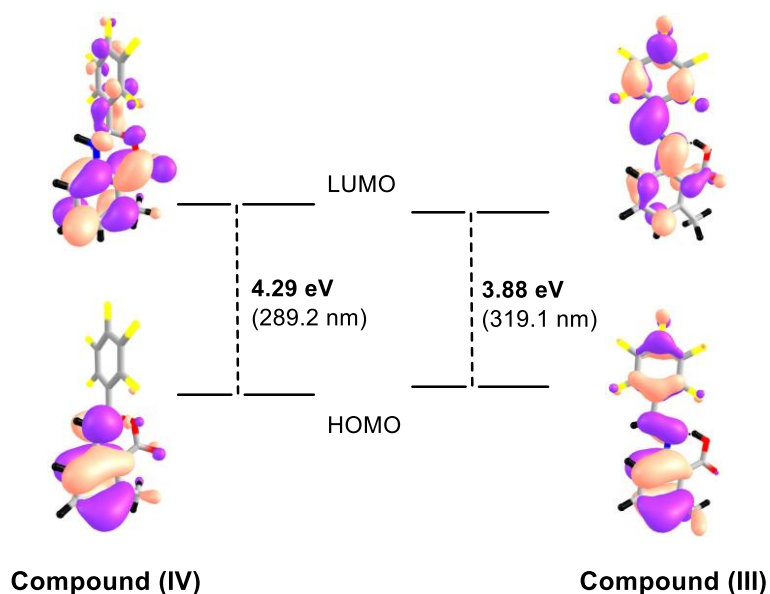


Figure 2.29: Calculated HOMO-LUMO gap in frontier orbitals of (III) and (IV) and λ_{max} .

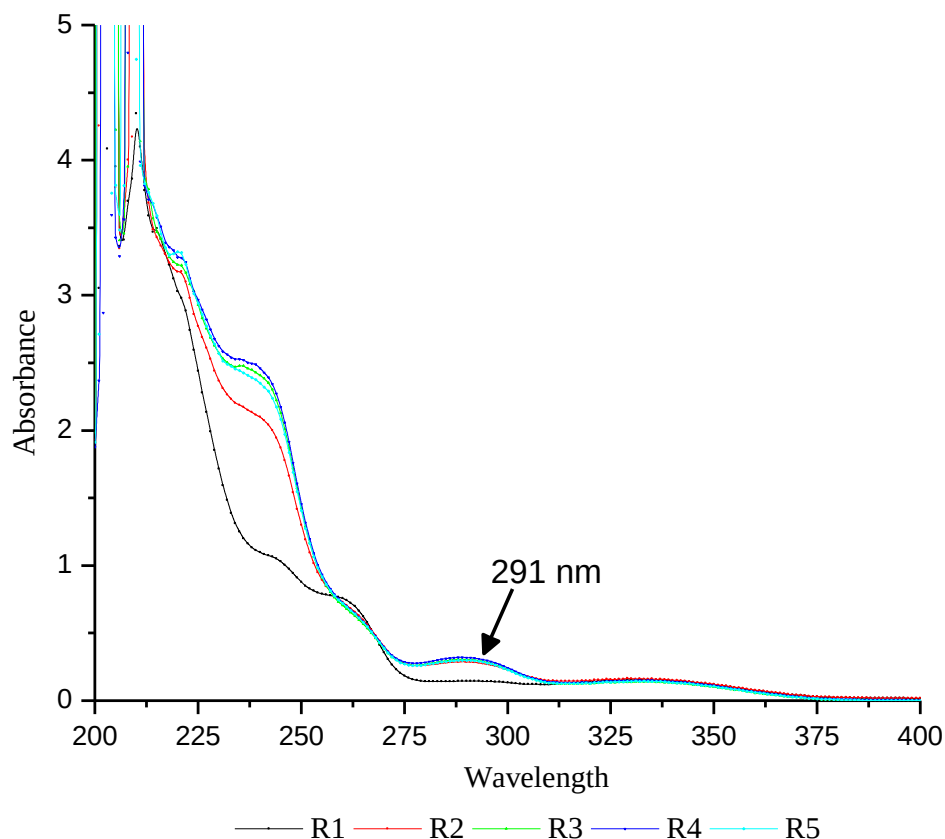


Figure 2.30: UV-Visible spectra of the reaction mixture between (I) and (II) at different time (in seconds) intervals; R1-60, R2-120, R3-180, R4-240, R5-300.

2.4.8. Gram scale experiment:

In order to demonstrate the synthetic utility of present strategy, a gram scale synthesis was attempted. To a stirred reaction mixture of 2-amino-6-methyl-benzoic acid (6.7 mmol, 1.01 g) in dry ethanol (50 mL), and 2,3,4,5,6-pentafluoroaldehyde (13.4 mmol, 2.62 g) was added in presence of catalytic amount of acetic acid at ambient temperature. To obtain a crude semi-solid substance, the resultant reaction mixture was refluxed for six hours while being continuously stirred and then concentrated in a vacuum. Hexane (100 mL $\times$ 3) was used to further wash the residue, resulting in a free-flowing crystalline compound (15) with a 92% isolated yield (2.032 g). In addition, excess aldehyde and solvents (ethanol, hexane) were recovered and reused.

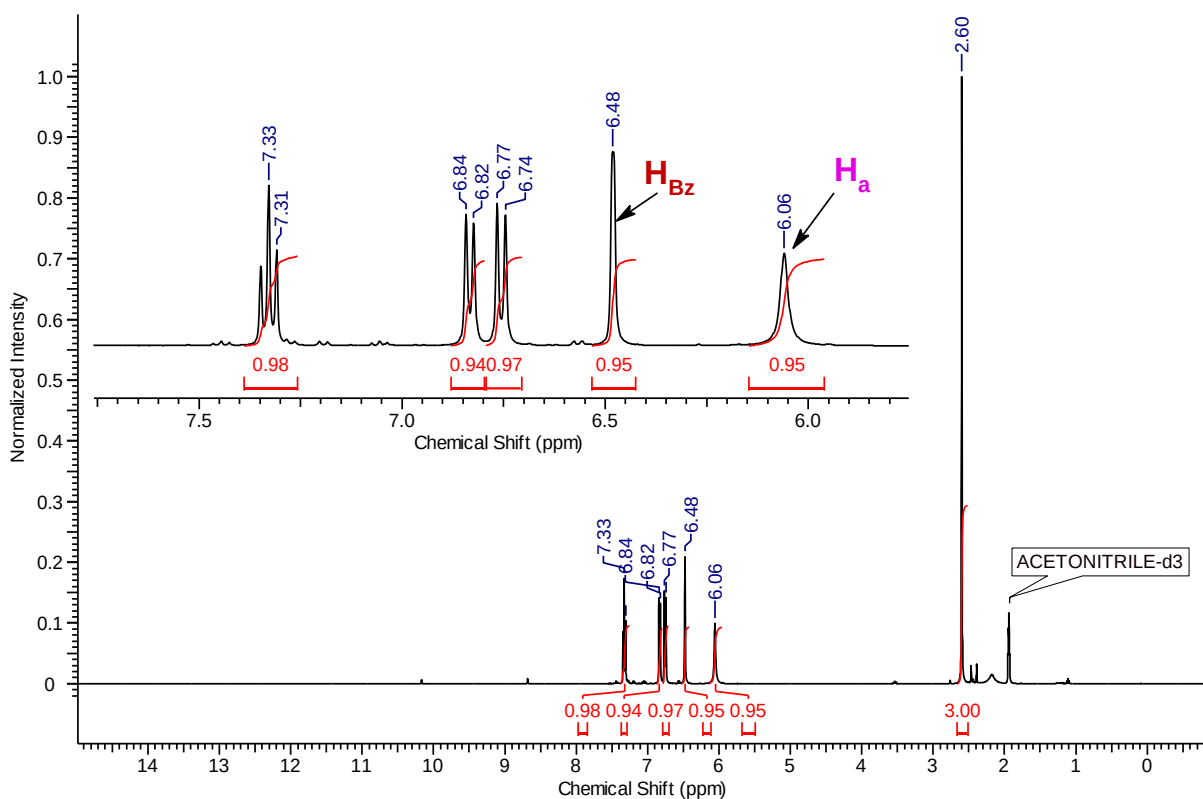
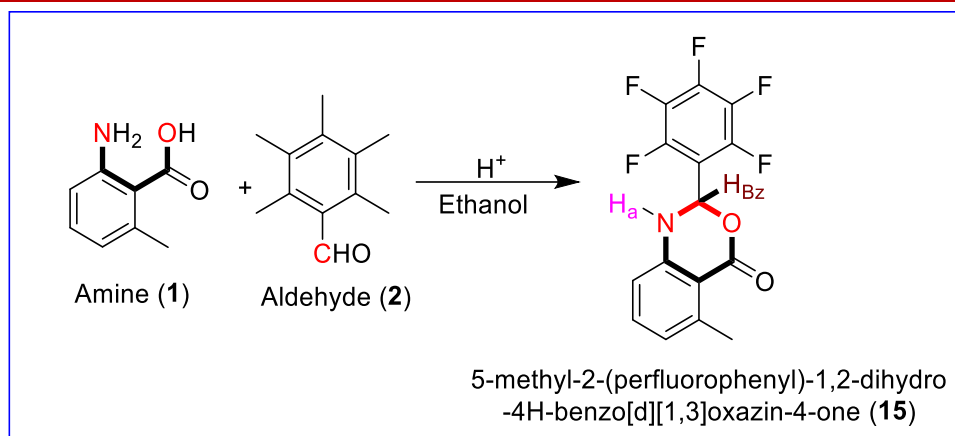


Figure 2.31: ^1H NMR spectrum of isolated **15** from a gram scale experiment.

2.4.9. Computational details:

The manuscript reports the optimized geometries of the structures (the three Cartesian coordinates, in Å, after the atomic symbol).

Ia (2-amino-6-methylbenzoic acid)

20

C	-0.044	0.021	-0.030
C	-0.027	-0.022	1.395
C	1.198	-0.096	2.063
C	2.404	-0.106	1.350
C	2.405	-0.056	-0.033
H	3.354	-0.163	1.887
H	1.208	-0.151	3.153
C	-1.285	-0.033	2.228
C	-1.348	0.129	-0.722
H	3.346	-0.068	-0.587
C	1.191	0.003	-0.759
N	1.268	0.122	-2.128
H	2.167	-0.087	-2.552
H	0.457	-0.141	-2.679
O	-1.364	-0.450	-1.965
O	-2.359	0.663	-0.276
H	-2.251	-0.283	-2.351
H	-2.016	-0.770	1.865
H	-1.038	-0.270	3.271
H	-1.792	0.941	2.203

IIa (2,3,4,5,6-Pentafluorobenzaldehyde)

14

C	-0.082	-0.000	0.054
C	-0.067	-0.000	1.445
C	1.159	0.000	2.113
C	2.355	-0.000	1.389
C	2.319	-0.000	-0.002
F	3.525	0.000	2.045

F	1.190	0.000	3.448
F	-1.209	-0.000	2.149
F	-1.281	-0.000	-0.557
F	3.491	-0.000	-0.650
C	1.100	-0.000	-0.709
C	1.010	0.000	-2.188
O	1.970	-0.000	-2.948
H	-0.027	0.000	-2.582

Int.1 or B

34

C	1.427	-2.953	-2.202
C	0.622	-1.844	-1.927
C	0.691	-0.773	-2.821
C	1.521	-0.786	-3.939
C	2.312	-1.909	-4.187
C	2.264	-2.999	-3.317
C	-0.270	-1.802	-0.698
O	-0.019	-0.624	0.108
F	-0.067	0.329	-2.604
F	1.563	0.264	-4.774
F	3.113	-1.940	-5.261
F	3.021	-4.081	-3.560
F	1.403	-4.026	-1.386
N	-1.645	-1.950	-1.111
C	-2.761	-1.757	-0.272
C	-2.825	-2.092	1.102
C	-4.021	-1.868	1.834
C	-5.136	-1.328	1.185
C	-5.086	-1.029	-0.178
C	-3.915	-1.233	-0.893

C	-1.724	-2.781	1.869
O	-0.661	-2.045	2.264
C	-4.109	-2.207	3.302
O	-1.802	-3.950	2.216
H	-0.344	0.165	-0.365
H	-0.603	-1.203	1.735
H	0.029	-2.623	-0.035
H	-1.823	-1.618	-2.057
H	-3.870	-0.979	-1.955
H	-5.962	-0.617	-0.683
H	-6.048	-1.146	1.756
H	-3.247	-1.823	3.867
H	-5.020	-1.775	3.737
H	-4.140	-3.296	3.459

TS_{im}

43

C	0.475	2.297	2.396
C	-0.603	3.093	1.968
C	-0.356	4.475	1.838
C	0.882	5.042	2.110
C	1.933	4.220	2.523
C	1.727	2.846	2.666
C	-1.971	2.628	1.773
O	-1.908	2.535	-0.411
F	-1.354	5.292	1.448
F	1.074	6.364	1.984
F	3.134	4.748	2.781
F	2.739	2.062	3.068
F	0.329	0.976	2.575
N	-2.368	1.386	2.036

C	-3.716	1.090	2.325
C	-4.537	1.960	3.086
C	-5.886	1.625	3.341
C	-6.375	0.400	2.863
C	-5.554	-0.476	2.151
C	-4.231	-0.138	1.884
C	-3.956	3.167	3.764
O	-4.548	4.320	3.370
C	-6.789	2.521	4.152
O	-3.062	3.126	4.595
H	-7.410	0.126	3.075
H	-2.724	3.417	1.740
H	-1.141	3.069	-0.689
H	-1.515	1.396	-0.281
H	-3.589	-0.821	1.329
H	-5.947	-1.432	1.803
H	-7.722	1.999	4.400
H	-6.315	2.837	5.094
H	-7.043	3.435	3.596
H	-4.176	5.055	3.906
H	-1.817	0.627	1.386
O	-1.240	0.255	0.102
C	-1.911	-0.698	-0.722
C	-1.182	-0.902	-2.045
H	-1.973	-1.659	-0.181
H	-2.952	-0.372	-0.927
H	-1.706	-1.648	-2.663
H	-1.138	0.040	-2.612
H	-0.155	-1.254	-1.874

III

34

C	1.129	-0.653	1.917
C	0.039	-0.075	1.235
C	0.310	0.473	-0.035
C	1.582	0.453	-0.599
C	2.636	-0.132	0.103
C	2.407	-0.689	1.364
C	-1.324	-0.018	1.738
N	-1.657	-0.352	2.941
C	-3.005	-0.322	3.346
C	-4.025	-0.741	2.478
C	-5.343	-0.753	2.921
C	-5.644	-0.351	4.222
C	-4.650	0.070	5.121
C	-3.298	0.078	4.684
C	-2.198	0.518	5.620
O	-2.410	1.114	6.672
F	-0.678	1.044	-0.743
F	1.800	0.990	-1.809
F	3.863	-0.163	-0.426
F	3.421	-1.258	2.033
F	0.970	-1.205	3.130
O	-0.934	0.212	5.277
O	-1.336	2.913	2.002
C	-5.091	0.471	6.505
H	-6.680	-0.372	4.564
H	-6.138	-1.092	2.254
H	-3.771	-1.098	1.479
H	-2.074	0.343	1.025
H	-0.949	-0.173	4.314

H	-1.877	3.004	2.805
H	-0.425	3.021	2.326
H	-6.163	0.265	6.626
H	-4.534	-0.065	7.284
H	-4.913	1.541	6.686

TS_{cy}

34

C	0.464	3.313	0.999
C	-0.891	3.534	1.279
C	-1.270	4.840	1.617
C	-0.340	5.875	1.706
C	1.004	5.617	1.436
C	1.411	4.328	1.078
C	-1.915	2.479	1.160
O	-2.050	2.291	-0.697
F	-2.559	5.118	1.880
F	-0.726	7.112	2.052
F	1.906	6.600	1.526
F	2.700	4.083	0.805
F	0.874	2.083	0.618
N	-1.663	1.282	1.719
C	-2.506	0.140	1.800
C	-3.837	0.072	1.337
C	-4.522	-1.166	1.422
C	-3.878	-2.281	1.972
C	-2.573	-2.191	2.461
C	-1.891	-0.985	2.375
C	-4.644	1.242	0.775
O	-4.375	1.649	-0.426
C	-5.936	-1.298	0.916

O	-5.559	1.697	1.481
H	-4.412	-3.233	2.017
H	-2.941	2.840	1.240
H	-1.425	1.580	-0.945
H	-0.687	1.070	1.926
H	-0.865	-0.904	2.743
H	-2.084	-3.062	2.901
H	-6.232	-2.354	0.868
H	-6.641	-0.770	1.575
H	-6.049	-0.862	-0.087
H	-3.083	1.869	-0.695

IV or compound 15

34

C	-4.280	0.288	2.871
C	-4.079	-0.282	1.609
C	-5.162	-0.957	1.033
C	-6.393	-1.068	1.679
C	-6.561	-0.492	2.938
C	-5.501	0.189	3.537
C	-2.782	-0.175	0.858
N	-1.644	-0.719	1.579
C	-0.493	-0.713	0.778
C	-0.341	0.362	-0.136
C	-1.310	1.477	-0.066
O	-2.500	1.225	0.599
C	0.797	0.410	-0.986
C	1.749	-0.607	-0.867
C	1.608	-1.635	0.072
C	0.493	-1.697	0.901
O	-1.139	2.614	-0.474

F	-5.040	-1.526	-0.181
F	-7.411	-1.723	1.098
F	-7.737	-0.594	3.571
F	-5.664	0.745	4.748
F	-3.290	0.963	3.484
O	-0.343	1.367	3.357
C	1.012	1.500	-2.000
H	2.622	-0.594	-1.523
H	2.375	-2.409	0.146
H	0.365	-2.508	1.620
H	-1.832	-1.601	2.056
H	-2.889	-0.667	-0.124
H	-0.932	2.140	3.338
H	-0.872	0.665	2.920
H	1.843	1.236	-2.666
H	0.112	1.678	-2.605
H	1.247	2.456	-1.508

TS_{Cy'}

34

C	-5.343	-1.218	1.862
C	-4.173	-0.497	2.119
C	-4.027	0.040	3.403
C	-5.003	-0.117	4.385
C	-6.162	-0.839	4.095
C	-6.334	-1.394	2.828
C	-3.141	-0.283	1.032
O	-2.916	1.084	0.807
F	-2.923	0.748	3.728
F	-4.837	0.417	5.607
F	-7.105	-1.000	5.035

F	-7.447	-2.093	2.546
F	-5.546	-1.774	0.649
N	-1.877	-0.959	1.392
C	-0.957	-1.052	0.344
C	-0.269	-2.250	0.099
C	0.635	-2.325	-0.954
C	0.846	-1.222	-1.787
C	0.186	-0.006	-1.572
C	-0.712	0.083	-0.473
C	-1.296	1.398	-0.132
O	-1.442	2.387	-0.791
O	-0.712	1.832	1.459
C	0.477	1.152	-2.489
H	1.544	-1.301	-2.623
H	1.167	-3.259	-1.143
H	-0.468	-3.120	0.729
H	-2.027	-1.848	1.871
H	-3.529	-0.712	0.089
H	-0.285	1.043	1.858
H	-1.950	1.658	1.815
H	1.206	0.853	-3.252
H	-0.432	1.507	-2.992
H	0.885	2.012	-1.938

A

31

C	0.242	-6.316	-0.269
C	-0.150	-5.099	-0.866
C	0.421	-4.752	-2.113
C	1.336	-5.639	-2.710
C	1.722	-6.829	-2.102
C	1.158	-7.170	-0.870
N	-1.145	-4.370	-0.180
C	-1.210	-2.933	-0.133
O	0.064	-2.298	0.163
C	0.098	-3.548	-2.970
O	-0.384	-3.663	-4.077
C	-2.277	-2.498	0.854
C	-2.124	-2.698	2.229
C	-3.055	-2.246	3.162
C	-4.188	-1.561	2.711
C	-4.376	-1.346	1.343
C	-3.422	-1.814	0.434
F	-1.020	-3.346	2.689
F	-3.631	-1.586	-0.873
F	-5.464	-0.692	0.916
F	-5.091	-1.113	3.590
F	-2.873	-2.456	4.473
O	0.464	-2.322	-2.511
H	1.740	-5.368	-3.687
H	2.443	-7.486	-2.589
H	1.435	-8.100	-0.370
H	-0.196	-6.592	0.694
H	-1.389	-4.813	0.701
H	-1.467	-2.525	-1.117

H 0.423 -2.706 0.973

H 0.744 -2.368 -1.562

2.10. Conclusions

Through secondary interactions, a unique synthetic method was established in this study to modulate the reactivity between an aldehyde and an amine. The selective synthesis of the prodrug class benzoxazinones was achieved by favoring dehydration reactions over Schiff-base formation through the careful placement of substituent groups. Through weak secondary contacts, energy-optimized models showed that an ortho-substituent might orient hydrogen bonding motifs at the hemiaminal stage, allowing reversed condensation processes. According to experimental findings, benzaldehyde and 2-amino-6-methylbenzoic acid reacted to produce Benzoxazinone 11 with 86 % selectivity. Furthermore, by reacting electrophilic pentafluoro benzaldehyde with 2-amino-6-methylbenzoic acid, Benzoxazinone 15 was quantitatively formed. This was verified by a number of analytical methods, such as single crystal X-ray diffraction, ESI-MS, and NMR.

The preparation of a library of thirty chemicals and the scaling up of the reaction to gramme scale revealed the synthetic adaptability of this approach. Electron-withdrawing and electron-donating substituents had similar outcomes when the impact of ortho-substitution on the reversed condensation reaction was investigated. It's amazing to note that benzoxazinones might be quantitatively synthesized even with a methyl substituent ortho to the amine group. Furthermore, analogous benzoxazinones were produced in nearly quantifiable yield by aliphatic aldehydes like cyclohexane carboxaldehyde. Extensive mechanistic analyses utilizing UV-vis spectroscopy, isotope labelling, and low-temperature NMR affirmed that pathway B was followed by the process, excluding the possibility of pathways A and C. These experimental results were validated by DFT calculations, which revealed that pathway B has the lowest barrier among them, 20 kcal/mol less than pathway A and 35 kcal/mol less than pathway C.

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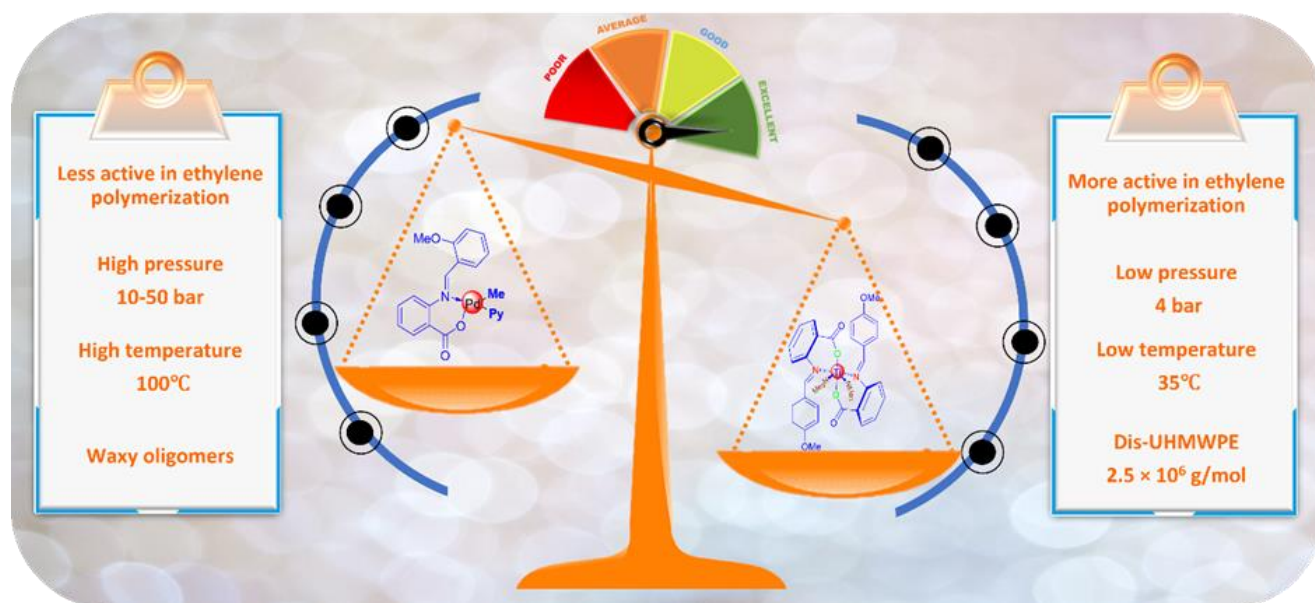
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Chapter 3



Ti-iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene



This chapter is adapted from following publication

European Polymer Journal **2023**, 182, 111725.

3.1. Abstract

Disentangled ultrahigh molecular weight polyethylene (d-UHMWPE) is a niche, highly sought-after, and an emerging class of polyethylene. Nevertheless, d-UHMWPE synthesis is rare and equally difficult. Here, we describe a Ti-iminocarboxylate complex that, in ambient polymerisation conditions, yields d-UHMWPE. Treatment of tetrakis(dimethylamido-titanium) [Ti (NMe₂)₄] with 2-((4-methoxybenzylidene) amino) benzoic acid produced a novel titanium complex Cat.1 [bis-dimethylamido-Ti-(bis-iminocarboxylate)]. Mass analysis and 1-2D NMR spectroscopy were used to definitively determine Cat.1's identification. Cat.1 was activated using various cocatalysts, and MMAO (modified methylaluminoxane) outperformed the others. Screening of polymerization parameters suggested a 1000 Al/Ti ratio, 4 bar of ethylene pressure, The ideal conditions are a temperature of 35 °C and a polymerization time of 30 minutes. Under the optimized polymerization conditions, with an average molecular weight (Mw) of 2.5×10^6 g/mol, Cat.1 polymerizes ethylene to create ultrahigh molecular weight polyethylene. The thermal behavior of the thus prepared material disclosed a highly crystalline [crystallinity χ (DSC) 96 %], strictly linear polyethylene. Using a specially created DSC method, a thorough thermal study of the developing polyethylene showed the presence of a significant melting peak at 139–140 °C. which is a hallmark of disentangled UHMWPE. A single-site, homogenous ethylene polymerization catalyst was therefore created, and when activated with MMAO, it generated extremely crystalline d-UHMWPE.

3.2. Introduction

Within a span of 100 years, polymers have reached every corner of the planet earth. The global annual production of polymers stands at about 380 million tons.^{1,2} Among these, the largest volume polymer is polyethylene (PE),^{3,4} and it is produced mainly using “Mülheim atmospheric polyethylene process” or “low pressure process”.^{5,6} Since the pathbreaking discovery of transition metal-catalyzed olefin polymerization by Ziegler, many academic and industrial centers have pursued olefin polymerization, and today PE is the largest volume polymer in the world. A key to the discovery of “low pressure process” was a catalyst. Thus, a large volume of literature on olefin polymerization deals with the synthesis of metal catalysts. A heterogeneous Ziegler catalyst is used to produce PE, and these catalysts are made of TiCl₄ epitaxially adsorbed on a substrate made of anhydrous MgCl₂.⁷ As the problems associated with investigations of heterogeneous catalysts started surfacing, the community moved to the homogeneous catalysts, and in the process, MAO and metallocenes were discovered by Sinn and Kaminsky.⁸ Metallocenes have slowly entered into the market and about 5-8 % of the total

PE is now produced using metallocene catalysts.⁹ Catalysts which were discovered after metallocenes and which do not meet the criteria of being metallocenes are generally called “Post-metallocenes” or “Non-metallocene’s”.¹⁰ Thus, olefin polymerization has evolved over the years, and slowly, the focus has been shifting to more specialty polyolefins. Among the specialty polyolefins, functional polyethylene,^{11,12,13,14,15,16,17,18} telechelic polyethylene,¹⁹ PE dispersions,²⁰ ultrahigh molecular weight polyethylene,^{21,22,23,24} and polyethylene vitrimers are emerging as a new class of high-end materials.^{25,26}

As defined in ASTM D4020, a polyethylene with viscosity average molecular weight of 2.5 million g/mol is considered as UHMWPE.²⁷ Due to inherent outstanding physical properties, UHMWPE is used in prostheses, body armors, sport wears, battery separators, siding for ships at harbors, etc. However, synthesis of UHMWPE is not trivial and requires careful catalyst tweaking. Control over the rate of propagation (k_p), rate of transfer (k_{tr}) or rate of termination (k_t) is crucial to obtain such high molecular weight polyethylene. The three rates (k_p , k_{tr} , k_t) can be altered by suitable catalyst design that consists of an appropriate metal cation and ligand structure that properly balances the steric and electronic environments. The current understanding of the field allows us to draw the following guidelines to design a catalyst for UHMWPE. The rate of propagation should be much higher than the k_{tr} and k_t . Therefore, the metal centre should be very acidic (oxophilic), which will allow the chain to grow faster. The ligand should force the β -H out of the metal-plan and thus suppress the two rates (k_{tr} , k_t). Thus, a suitable catalyst combined with correct choice of reaction parameters may enable the synthesis of ultrahigh molecular weight PE.²⁸

There are two states of ultrahigh molecular weight polyethylene. The traditional UHMWPE is “entangled”, while another state called “disentangled” (d-UHMWPE) has been identified in the last decade.²⁹ Literature reports suggest that the heterogeneous Ziegler-type catalysts generally produce “entangled” UHMWPE. Entangled UHMWPE is difficult to process, and an additional step of gel-spinning is necessary. While, only homogeneous catalysts have been reported to be capable of producing disentangled UHMWPE (d-UHMWPE). Chikkali and co-workers have reported a recent exception to the rule.³⁰ A heterogeneous catalyst was subjected to controlled reduction of Ti (IV) to Ti (III), which enabled the synthesis of d-UHMWPE. Among the homogeneous catalysts, the titanium bis (phenoxy imine) or the FI-catalysts have been extensively investigated (Figure 3.1,1).^{31,32,33} Under optimized conditions, the FI catalyst can produce d-UHMWPE. Recently, Enders and co-workers reported a naphthyridine cyclopentadienyl chromium catalyst (Figure 3.1,2). The chromium catalysts, upon activation with a suitable cocatalyst, produced d-UHMWPE.^{34,35}

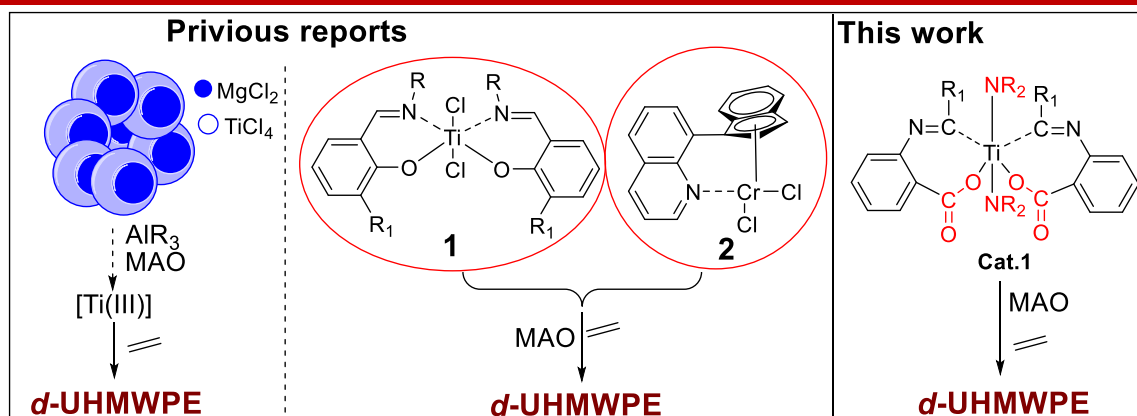


Figure 3.1: State-of-the-art catalysts for the synthesis of d-UHMWPE (left) and the present work (right).

The weak coordination of nitrogen to the metal causes the FI catalyst family to experience structural isomerism.³⁶ Therefore, rational ligands designing approaches have frequently concentrated on creating and altering auxiliary ligands to offer an attractive catalyst.³⁷ A very frequently used parameter in rational designing is steric and electronic control by changing substituents on the ligand framework. Imine ligands are largely favored for three main reasons: (1) easy synthesis, (2) relative stability towards moisture/oxygen, and (3) ease of tailoring electronic and steric by choosing different amine and aldehyde. Metal complexes that produce polyethylene from ethylene have been successfully prepared using a variety of nitrogen-containing ligands. We pondered if an imine-based carboxy ligand can deliver bis-ligated titanium complex and if the Ti-complex can initiate ethylene polymerization.

Here in, we describe a single-step synthesis of iminocarboxylate ligated titanium complex $[(L1)_2Ti(NMe_2)_2]$ (Cat.1) (Figure 3.1). Spectroscopic and analytical techniques unambiguously ascertained the identity of the Ti-complex. The resultant titanium complex $[(L1)_2Ti(NMe_2)_2]$ was employed as a precatalyst for the polymerization of ethylene. To our delight, under defined polymerization conditions, Cat.1 produced highly crystalline, disentangled, ultrahigh molecular weight polyethylene.

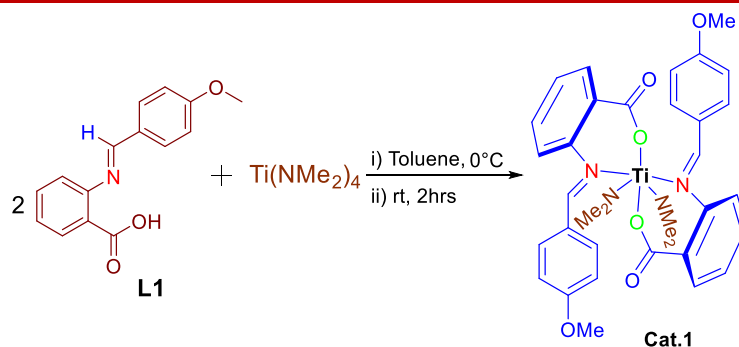
3.3. Results and discussion

3.3.1. Synthesis of imine carboxylate ligand (L1) and its titanium complex

The condensation of amine with an aldehyde to produce imine (Schiff base) is well known for decades. However, condensation of ortho-amino acids with aldehydes is highly challenging and has been found to produce benzoxazinones, instead of expected imines.³⁸ The cyclization to benzoxazinones can be addressed by substituting the acidic proton with a heavy metal cation.³⁹ Therefore, choosing the amine

and aldehyde partners is crucial for condensing the ortho-amino acid compounds. Based on our past experience, we envisaged the condensation of anthranilic acid with anisaldehyde.^{38,39} Thus, 1 g of anthranilic acid was treated with anisaldehyde to obtain the anticipated 2-((4-methoxybenzylidene) amino) benzoic acid (**L1**) in an improved isolated yield of 90 % (2.5 g).⁴⁰ The identity of the resultant compound was ascertained using a combination of spectroscopic and analytical methods, including a single crystal X-ray diffraction.⁴⁰

After establishing a robust ligand synthesis protocol, we examined the coordinating ability of iminocarboxylate ligand with a transition metal. It is necessary to have both, the ligand and the metal precursor, to create a single component metal complex for ethylene polymerization. Our initial effort to obtain the desired metal complex (Cat.1) by treating **L1** with titanium tetrachloride [TiCl₄] as a titanium precursor was not very successful. We could not isolate and characterize the resultant metal complex (Cat.1). The ligand is highly acid sensitive, and one must first prepare ligand-salt before treating it with [TiCl₄]. Thus, after treating the sodium salt of **L1** with [TiCl₄], it was found that the imine bond is cleaved. To address this bottleneck, we were in search of a titanium precursor with less acidity. Marks and co-workers recently reported an unexpected behavior of phenoxy-imine ligated zirconium bis(dimethylamine) precursor on ethylene-olefin copolymerization.⁴¹ Based on this, we anticipated that the titanium congener of the reported zirconium complex might suppress cleavage of **L1** (imine bond) as the by-product is a base (HNMe₂) and may allow coordination of iminocarboxylate ligand to enable the formation of mononuclear titanium complex. With this hypothesis, two equivalents of iminocarboxylate ligand **L1** (1 g, 3.9 mmol) was treated with one equivalent of tetrakis(dimethylamido-titanium) [Ti(NMe₂)₄] (1.9 mmol) at 0 °C. After the addition, the temperature of the reaction mixture was raised to room temperature (~35 °C) and the stirring was continued for 2 hours. After two hours, volatiles were evaporated, and the titanium complex Cat.1 was isolated in 62 % yield (see experimental section for details). The synthesis of the iminocarboxylate-Ti (NMe₂)₂ complex was very straightforward, and the resultant by-product [Me₂NH] was easily evaporated from the reaction mixture. The reddish brown crystalline solid of complex Cat.1 (Scheme 3.1) was subjected to detailed characterization.



Scheme 3.1: Synthesis of amido Ti-iminocarboxylate complex **Cat.1**

The ^1H NMR spectrum of the above reddish brown solid disclosed a resonance at 8.34 ppm, which can be assigned to the imine proton. Compared to the free ligand **L1**, the imine proton is shifted slightly up-field (from 8.65 ppm in the free ligands **L1** to 8.34 ppm for the **Cat.1**) in

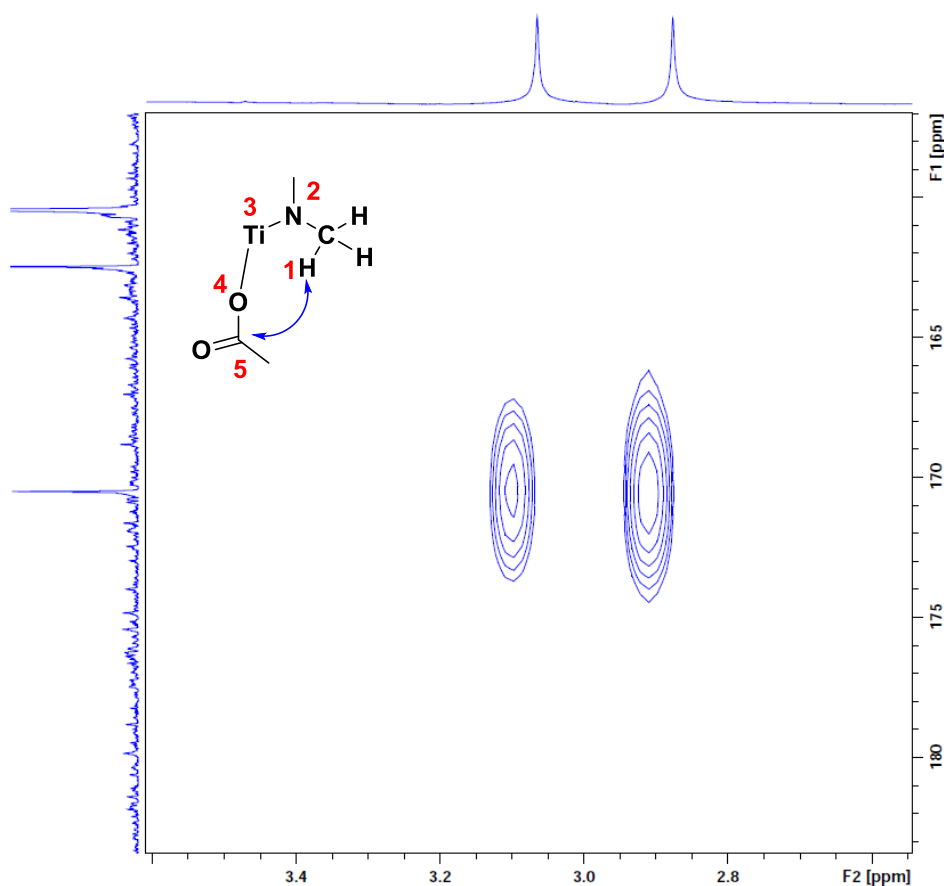


Figure 3.2: Expanded view of a long-range C-H correlation (HMBC) spectrum of **Cat.1** displaying cross peak between the methyl protons ($-\text{TiNMe}_2$) and the carboxylate carbon (in CDCl_3).

the complex **Cat.1**. The change in chemical shift suggests coordination of the imine nitrogen to the titanium. Such up-field shifts are not very common but have been observed for other metal

complexes.^{39,42} Furthermore, the methyl protons in Ti-NMe₂ group could be identified as two sets, one at 3.10 ppm and the other at 2.91 ppm. The ¹³C NMR spectrum of Cat.1 revealed a characteristic imine-carbon resonance at 160.4 ppm. The short-range C-H correlation HSQC spectrum displayed cross-peaks to corresponding carbons. Unambiguous evidence of the existence of Cat.1 was obtained from a long-range C-H correlation HMBC spectrum (Figure 3.2). The methyl proton of the TiNMe₂ group displayed a cross-peak to the acid carbon, confirming chelation of **L1** to Ti-precursor. The NMR findings were further corroborated by mass analysis, and a molecular ion peak was observed at $m/z = 610$ [Cat.1-2NMe₂ + 2H + HNMe₂ + Li]⁺ Da. As the titanium complex, Cat.1, is highly air and moisture-sensitive, fragments with different masses could be observed in the mass spectrum (figure 3.20).

3.4. Ethylene polymerization

After establishing the synthesis, we examined the reactivity of Cat.1 in ethylene polymerization. The ethylene polymerization was conducted in a Büchi high-pressure reactor with a heating/cooling jacket, an overhead mechanical stirrer, and gas inlet/outlet facilities. The reactor was continuously fed with ethylene gas to maintain the necessary pressure.

Table 3.1: Ethylene polymerization catalyzed by Cat.1 in the presence of various cocatalysts.^a

Entry	TMA (equiv.)	BT (equiv.)	MMAO (equiv.)	Yield (g)	Activity ^f	^b M _w	^c Đ	^d Tm	^e Cryst. (%)
1	40	1.2	--	0.250	16.1	1.49 × 10 ⁵	6.4	141.8	67.4
2	100	1.2	--	0.350	22.5	1.12 × 10 ⁵	3.5	141.3	86.8
3	120	1.2	--	0.150	9.6	2 × 10 ⁵	4.4	139.9	91.9
4	40	--	--	0.106	6.8	-	-	136.8	62.7
5	--	1	1000	0.700	-	-	-	-	-

^aConditions: Cat.1-31 μmol of Ti (20 mg), Solvent-Toluene (100 mL), Ethylene-4 bars, Temperature-40 °C, Time-30 minutes, equiv.-equivalent. ND-Not detected. ^{b,c}As obtained from HT-GPC at 160 °C in 1,2,4-

Trichlorobenzene (TCB) against polystyrene standards. ^dObtained from DSC, heating and cooling curves of first heating, cooling, and second heating; ^eCrystallinity was calculated from the melting enthalpy measured by DSC and relative to the theoretical melting enthalpy of 293 J/g for 100 % crystalline polyethylene; ^fActivity in Kg of PE/mol Ti/h.

The titanium complex Cat.1 is just a pre-catalyst and has to be activated to obtain the catalytically active species for ethylene polymerization. Alkyl aluminum or boron compounds are well-known activators and have been commonly used in olefin polymerization.⁴¹ Table 3.1 summarizes the cocatalyst/activator screening and figure 2.2 depicts the performance of various activators in ethylene polymerization. The cocatalyst was used in two lots, see supporting information for details. Please note that 30 minutes stirring with about 70 % cocatalyst was required before the addition of Cat.1. First, the efficiency of trimethyl aluminum (TMA) in the presence of BT (Trityl Borate) was examined. At a TMA (cocatalyst) to catalyst (Cat.1) ratio (Al/Ti) of 40, under 4 bars of ethylene, 250 mg of polyethylene was obtained (Table 3.1, entry 1). The best polymer yield of 350 mg was obtained at a TMA to catalyst ratio (Al/Ti) of 100. While, the yield was reduced to 150 mg when TMA to catalyst ratio (Al/Ti) was increased to 120. Thus, the highest yield was 350 mg under the given polymerization conditions. The difference in crystallinity (67 vs 91 %) can be ascribed to the existence of more crystalline domains, due to which melting enthalpy (area under the peak) increases, leading to higher crystallinity. Next, di-isobutyl aluminum hydride (DiBAI-H) was screened for ethylene polymerization, but no polymer was produced. Subsequently, MMAO was tested as cocatalyst and was found to produce 700 mg of polyethylene under similar conditions (Table 3.1, entry 5). As presented in figure 3.3, MMAO outperformed TMA/BT, DiBAI-H, and DiBAI-H/MMAO, and disclosed the highest activity.

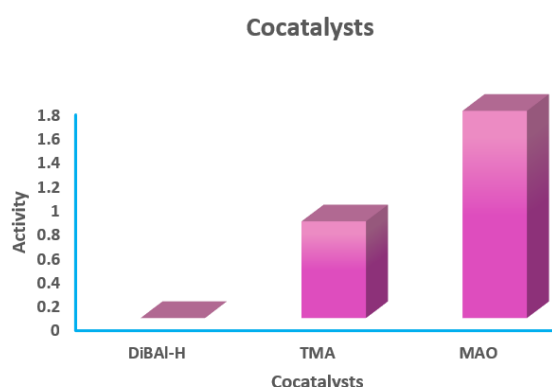


Figure 3.3: Screening of cocatalysts and activity in ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

Thus, MMAO was finalized as the best cocatalyst and further studies were undertaken (Table 3.2). The effect of Al/Ti ratio on the polymerization activity was investigated (Table 3.2, entries 1-4). At an Al/Ti ratio of 500 under 4 bar ethylene pressure, 650 mg of polyethylene was obtained (Table 3.2, entry 1). The melting temperature was found to be 138.7 °C, suggesting high molecular weight, crystalline polyethylene. The Al/Ti ratio was further increased to 1000, 1500, and 2000 (Table 3.2, entries 2-4). The highest TOF and yield of 750 mg was obtained at an Al/Ti ratio of 1000. Increasing the Al/Ti ratio further to 2000, deteriorated the polyethylene yield to 700 mg. Figure 2.3 presents the comparative performance of Al/Ti ratio on polyethylene activity. In our attempts to estimate the life time of the catalyst, ethylene polymerization was carried out for different time period (5, 30, 60 minutes) and the activity was determined. As can be seen in the figure 3.6, the highest activity was obtained after 30 minutes, suggesting existence of active catalyst. While increasing the polymerization time to 60 minutes revealed lower activity, suggesting catalyst decomposition. Thus, the optimized polymerization condition is 20 mg Cat.1, Al/Ti ratio of 1000, 4 bar ethylene pressure, 35 °C temperature, and a polymerization time of 30 minutes.

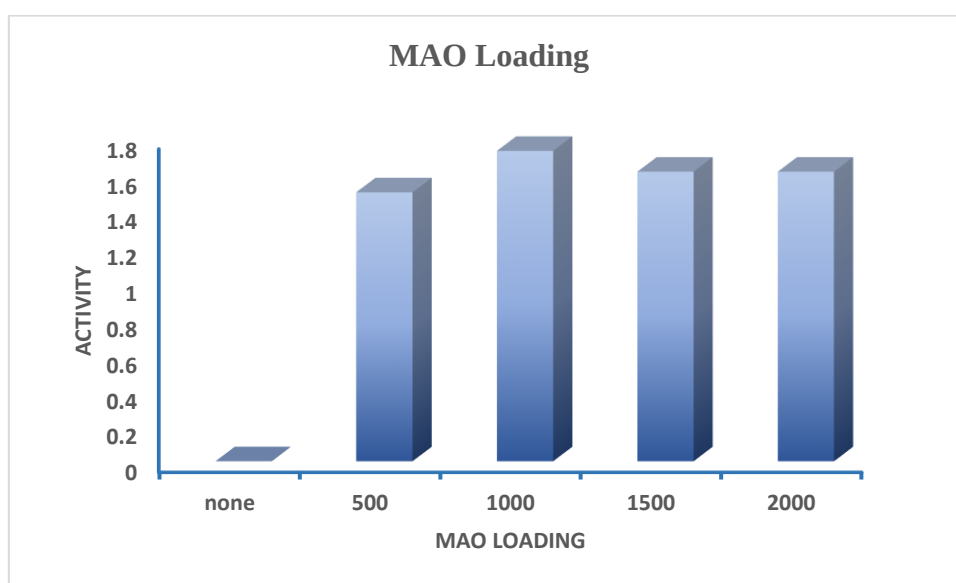


Figure 3.4: Screening of Al/Ti ratio and activity in ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

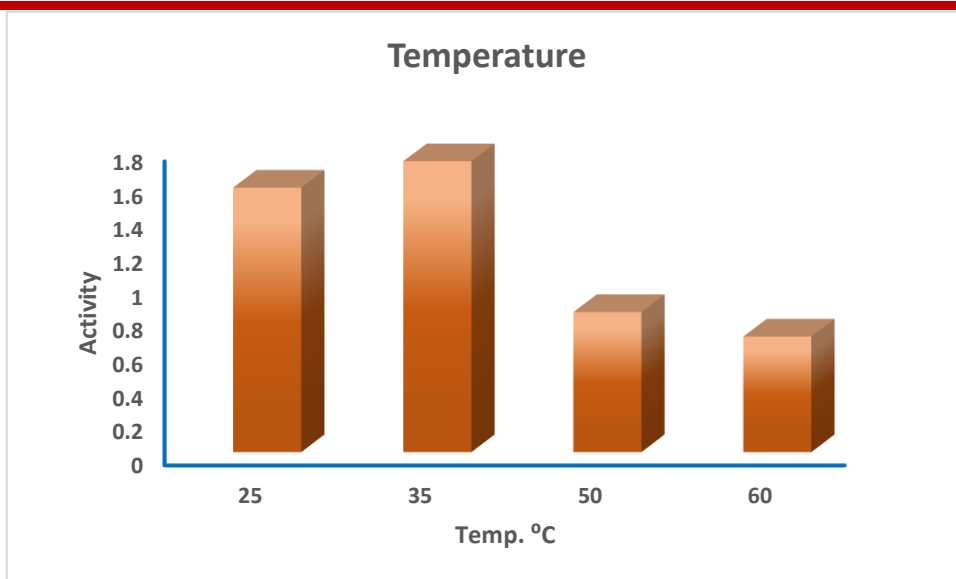


Figure 3.5: Effect of temperature on ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

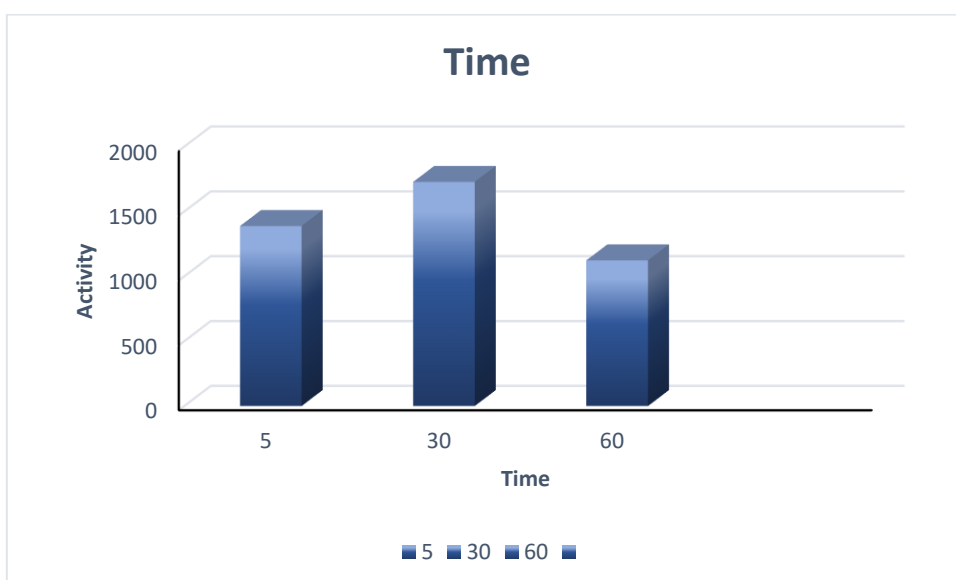


Figure 3.6: Ethylene polymerization at 5, 30 and 60 minutes (Activity = mol of polyethylene/mol of Ti/h).

One of the crucial parameters that influence the activity, molecular weight, polydispersity and entanglement of polyethylene, is the polymerization temperature. Therefore, we investigated the effect of temperature on polymerization, and figure 3.5 summarizes the results. As compared to the optimized temperature of 35 °C, ethylene polymerization at 25 °C disclosed a slight drop in the catalyst activity (1.56×10^3 , 680 mg PE). While increasing the polymerization temperature to 50 °C significantly decreased the catalyst activity (Table 3.2, entry 7, 360 mg PE). Further increasing the polymerization temperature to 60 °C led to a colossal drop-in catalyst activity (Table 3.2, entry 8). Thus, polymerization

temperature significantly influenced catalyst activity, and 35 °C remained the optimal reaction temperature.

Table 3.2: Ethylene polymerization catalyzed by Cat.1 and MMAO.^a

Entry	Precatalyst	Al/Ti	Temp (°C)	^d Poly. (g)	Activity ^b	^e TOF (10 ³)	^f M _v (×10 ⁵)	^f M _w (×10 ⁶)	^g Đ	^h T _m	ⁱ Cryst (%)
1	Cat.1	500	35	0.650	41.9	1.497	4.90			138.7	62.1
2	Cat.1	1000	35	0.750	48.3	1.728	25	2.5	2.4	137.2	87.9
3	Cat.1	1500	35	0.750	48.3	1.612	1.6			139.5	60.8
4	Cat.1	2000	35	0.700	45.1	1.612	1.94			136.5	53.5
5 ^c	Cat.1+ Al ⁱ BuH +MAO	40 + 1000	35	NO		--		--	--	NO	
6	Cat.1	1000	25	0.680	43.8	1.566	7.4			139	96.4
7	Cat.1	1000	50	0.360	23.2	0.829	1.93			138.3	80
8	Cat.1	1000	60	0.297	19.1	0.684	0.54			134	48.6

^aConditions: Catalyst = 31 μmol of Ti (20 mg of catalyst); Solvent = 100 mL of toluene, Time-30 minutes,

^bActivity in Kg of PE/mol Ti/h; ^cAl ⁱBuH 1 Equiv. + MAO 1000, 4 bar ethylene pressure time 30 min; ^dWeight of produced polyethylene (in gm); ^eTOF = mol of polyethylene/mol of Ti/h, ^{f,g} As obtained from HT-GPC at 160 °C in 1,2,4-Trichlorobenzene (TCB) against polystyrene standards, in 10⁶ g/mol. ^hObtained from DSC, heating and cooling curves of first heating, cooling, and second heating; ⁱCrystallinity was calculated from the melting enthalpy measured by DSC and relative to the theoretical melting enthalpy of 293 J/g for 100 % crystalline polyethylene. NO- Not obtained.

3.5. Highly crystalline, disentangled ultrahigh molecular weight polyethylene (d-UHMWPE)

The polyethylene produced under the optimized polymerization conditions was subjected to detailed characterization. The molecular weight of the thus prepared PE was determined using a High-Temperature Gel Permeation Chromatography (HT-GPC). To our delight, HT-GPC analysis of this polyethylene in trichlorobenzene (TCB) at 160 °C disclosed the formation of ultrahigh molecular weight polyethylene (UHMWPE) with a whopping molecular weight of 2.5 million g/mol (Table 3.2, entry 2). Interestingly, the polydispersity index was found to be narrow (2.4), which suggests single-site behavior of the catalyst (Cat.1). Our attempts to record the molecular weight for other entries were not very successful as the PE was only partially soluble and produced a gel even at 160 °C with 1 mg per 10 mL TCB.

The melting temperature of the resultant PE and crystallization data were obtained from differential scanning calorimetry. The melting temperature obtained during the first heating is considered. As compared to regular commodity PE grades (such as LDPE, HDPE), the melting temperature (T_m) of the polyethylene produced using Cat.1 was high (137-140 °C), suggesting a high degree of order or crystallinity. As a representative case, the sample with Mw of 2.5 million g/mol (Table 3.2, entry 2) disclosed a very high crystallinity of 88 % (Table 3.2, entry 2). While, the highest crystallinity of 96 % was observed for polyethylene produced at 25 °C (Table 3.2, entry 6). Such highly crystalline PE is a result of highly active catalyst and polymerization conditions that enable crystallization of the growing polymer chain. If the PE is crystallizing while the chain is growing, there should not be any time for entanglement, and one should expect disentangled ultrahigh molecular weight polyethylene (d-UHMWPE).

Therefore, we anticipated that the resultant UHMWPE would be disentangled in nature. The first melting peak of the reactor PE can be attributed to the melting of single crystal lamellae, which is the signature of the “disentangled” state of UHMWPE. To demonstrate the disentangled nature of UHMWPE prepared using Cat.1, this material was subjected to thermal analysis protocols developed by Rastogi and co-workers.⁴³ A special DSC method was developed, and figure 3.7 presents various steps involved in this protocol.

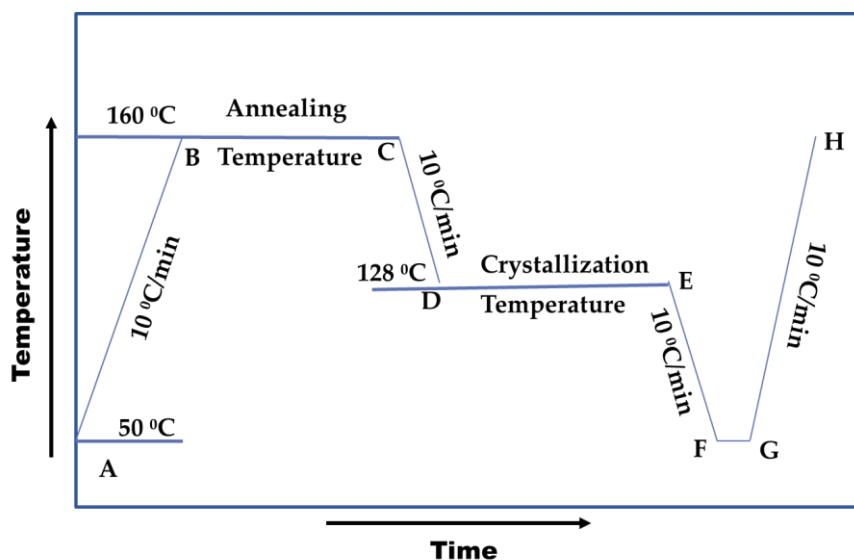


Figure 3.7: Thermal protocol developed to demonstrate disentangled nature of UHMWPE. Thermal protocol: Ramp 1: 50 °C to 160 °C (A-B) @ 10 °C/min. hold @160 °C for 5 min. (B-C). Ramp 2: Cooling to 128 °C @ 10 °C/min. (C-D) and hold at 128 °C for 180 min. (D-E). Ramp 3: Cooling to 50 °C at 10 °C/min. (E-F) and hold at 50 °C for 1 min. (F-G). Ramp 4: Heating from 50 to 160 °C at 10 °C/min. (G-H). The DSC plot shown in figure 8 was obtained during ramp 4 (G-H).

To examine the melt behavior of UHMWPE, Rastogi and co-workers designed a DSC method that can distinguish “entangled” and “disentangled” domains. The method involves heating the UHMWPE from 50 °C to 160 °C (@10 °C per minute) (a-b) (Figure 7) and annealing the sample at 160 °C for a predetermined amount of time (b-c). When the UHMWPE sample is kept at 160 °C, the polymer chains can move to achieve the thermodynamically stable “entangled” state (b-c). Therefore, depending upon the annealing time in step b-c, the polymer sample may show various degrees of “entangled” and “disentangled” domains (heterogeneity in the sample). After that, the sample was cooled to 128 °C (c-d), and was allowed to isothermally crystallize for 180 minutes (d-e), then it was cooled to 50 °C (e-f). Finally, the sample was heated from 50 °C to 160 °C (g-h). The information collected during the g-h heating stage is displayed in figure 8. Figure 8 (blue line) disclosed two distinct melting domains, the initial high melting peak around 139–140 °C is believed to originate from a crystalline domain, representing the “disentangled” state of the UHMWPE. The high melting disentangled domain disappears at 30 minutes of annealing time, and a single melting peak was observed (figure 8, orange line). UHMWPE entangled domains are responsible for the second melting peak, which occurred at about 133–134 °C. The above observations are in line with previous reports on “entangled” and “disentangled” UHMWPE.^{44,45} Thus, the DSC experiment confirms that catalyst Cat.1 polymerizes

ethylene to disentangled UHMWPE. A comparative DSC thermogram of a commercial entangled UHMWPE and our disentangled UHMWPE is presented in experimental section (see figure 3.39).

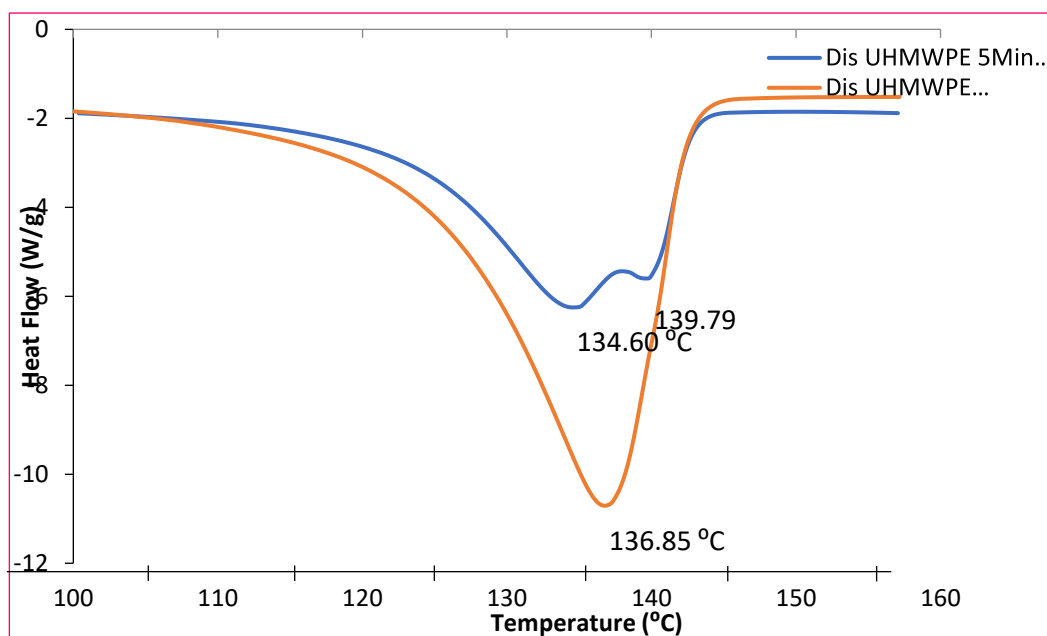


Figure 3.8: DSC plot of the d-UHMWPE sample (Table 3.2, entry 6) annealed for 5 (blue line) and 30 (orange line) min.

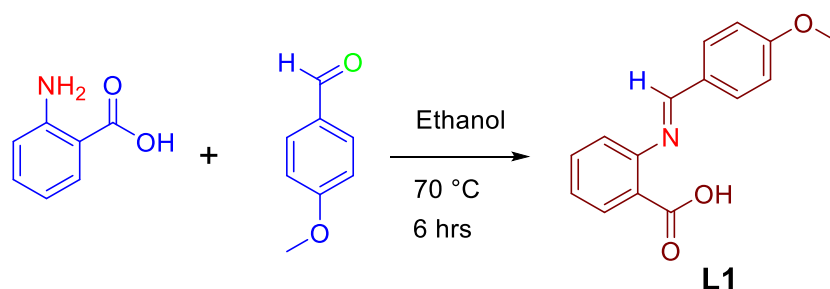
3.6. Experimental section

3.6.1 Materials and methods

All manipulations involving moisture-sensitive compounds were carried out under an inert gas atmosphere using standard Schlenk or glove box techniques. Toluene was distilled from sodium/benzophenone under an argon atmosphere. Chloroform or CDCl_3 , ethanol, dichloromethane, etc. were dried and distilled as per reported procedures.⁴⁶ Ethylene (purity; 99.95 %, 3.5 grade) was supplied by Ms. Vadilal Chemicals Ltd, Pune, India. 2-aminobenzoic acid, 4-methoxy benzaldehyde, $[\text{Ti}(\text{NMe}_2)_4]$, TiCl_4 , Trityl tetrakis (pentafluoro phenyl) borate, MMAO-12 (7 Wt % Aluminum in Toluene), Diisobutyl aluminum hydride (DiBAI-H), deuterated 1,1,2,2-tetrachloroethane were procured from sigma-aldrich and used without further purification. Ethanol was purchased from Spectrochem Pvt. Ltd. Trimethyl aluminum (TMA) was supplied by Schering AG, Germany and was used as received. NMR spectra were recorded on a Bruker Avance 200, 400, 500 and JEOL 600 MHz instruments. The

polymerization was run in a Büchi picoclave mini pressure reactor equipped with overhead mechanical stirrer, heating/cooling jacket and pressure regulators. High temperature NMR (HT-NMR) of the polymers was recorded in $C_2D_2Cl_4$ solvent at 130 °C. Chemical shifts are referenced to external reference TMS (1H and ^{13}C). Mass spectra were recorded on Agilent Q-ToF mass spectrometer. FT-IR spectra were recorded on a Bruker α -T spectrophotometer in the range of 4000-400 cm^{-1} . Differential scanning calorimeter (DSC) was carried out on DSC Q-10 equipment from TA instruments with a heating and cooling rate of 10 K min^{-1} , unless mentioned otherwise. High temperature Gel Permeation Chromatography (HT-GPC) of the PE was recorded in 1,2,4- trichlorobenzene at 160 °C on a Viscotek GPC (HT-GPC module 350A) instrument equipped with triple detector system. The columns were calibrated with linear polystyrene standards and the reported molecular weights are with respect to polystyrene standards. Weight-average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) of the synthesized UHMWPE was recorded using HT-GPC.

3.6.2. Synthesis of 2-((4-methoxybenzylidene) amino) benzoic acid (L)



An improved process to prepare **L1** was developed.⁴⁷ 2-aminobenzoic acid (1 gm, 7.2 mmol) was dissolved in ethanol (50 mL) and 4- methoxy benzaldehyde (1 mL, 7.2 mmol) was added to the above solution. The reaction mixture was refluxed at 70 °C for 6 hours. Volatiles were evaporated under reduced pressure to obtain a residue. The yellow-colored residue was washed with hexane (50 mL $\times$ 3) to yield 2.5 gm of **L1** (90 %).

A 1H NMR spectrum of the isolated compound disclosed a distinctive imine proton at 8.65 ppm (Figure 3.9) and the corresponding carbon was observed at 159 ppm in a ^{13}C NMR spectrum (Figure 3.10). The short-range through bond C-H correlation spectrum (HSQC) confirmed that the proton at 8.65 ppm shows a cross peak to carbon at 159 ppm (Figure 3.12). The NMR findings were further corroborated by mass analysis, which disclosed a molecular ion peak at $m/z = 256.09$ $[M+H]^+$ Da, that can be assigned to **L1** (Figure 3.13). The observed mass and isotopic pattern exactly match with the simulated pattern. An IR spectrum of the compound revealed a C=N stretching band at 1618 cm^{-1} , further authenticating the presence of imine groups.

In order to help the reader, the following data and figures are reproduced below.

^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 15.07 (br s, 1H), 8.65 (s, 1H, $-\text{CH}=\text{N}-$), 8.32 (d, J = 7.58 Hz, 1H, Ar H), 7.85 (d, J = 8.59 Hz, 2H, Ar H), 7.61 (m, 1H, Ar H), 7.48-7.40 (m, 2H, Ar H), 7.02 (d, J = 8.46 Hz, 2H, Ar H), 3.90 (s, 3H, OCH_3). **^{13}C NMR** (125 MHz, CDCl_3 , 298 K): δ = 167.5, 164.2, 159.9 ($-\text{CH}=\text{N}$), 147.2, 133.9, 132.6, 131.9, 127.7, 126.5, 124.0, 116.6, 114.9, 55.9 ($-\text{OCH}_3$). **Elemental analysis:** Calculated C 70.58; H 5.13; N 5.49; found C 70.40; H 5.0; N 5.27. IR (cm^{-1}): 3396 ($-\text{COOH}$), 1708 ($-\text{C}=\text{O}$), 1618 ($-\text{CH}=\text{N}$, stretching vibration). **ESI-MS** (+ve) m/z for $\text{C}_{15}\text{H}_{14}\text{NO}_3$: Calculated: 255 Da, Observed: 256.0970 Da $[\text{M}+\text{H}]^+$.

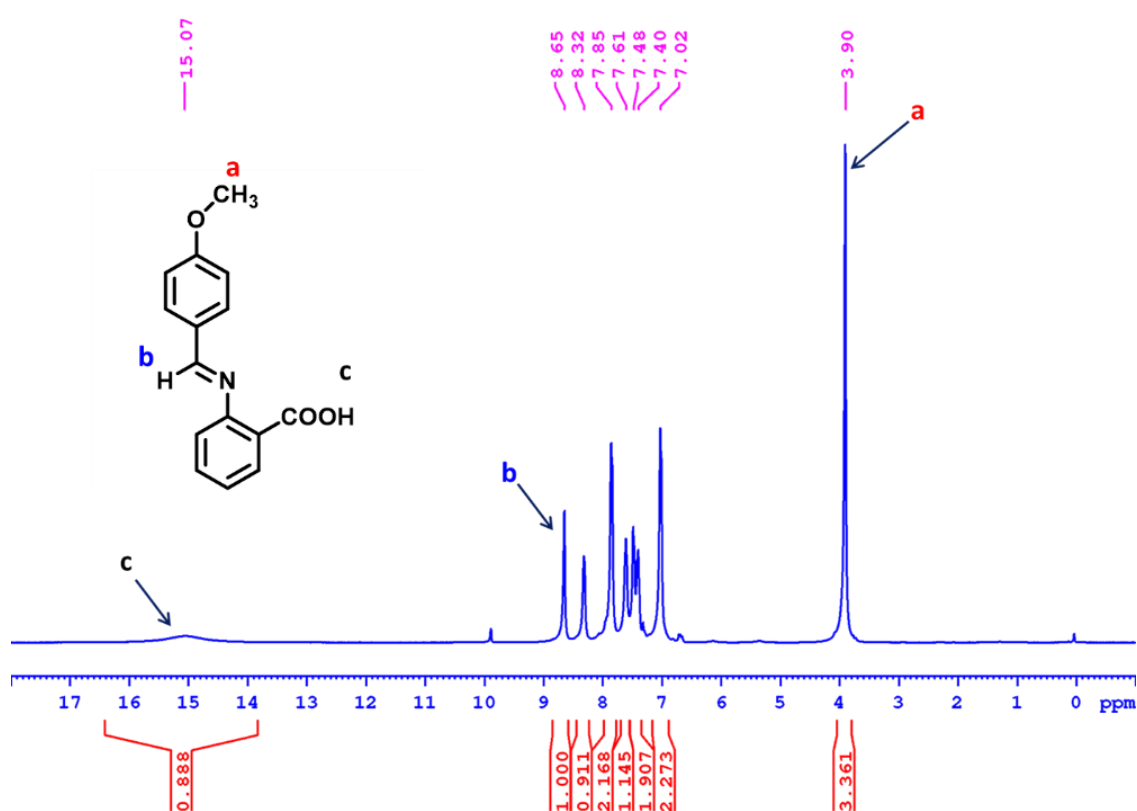


Figure 3.9: ^1H NMR spectrum of L1 in CDCl_3 (500 MHz).

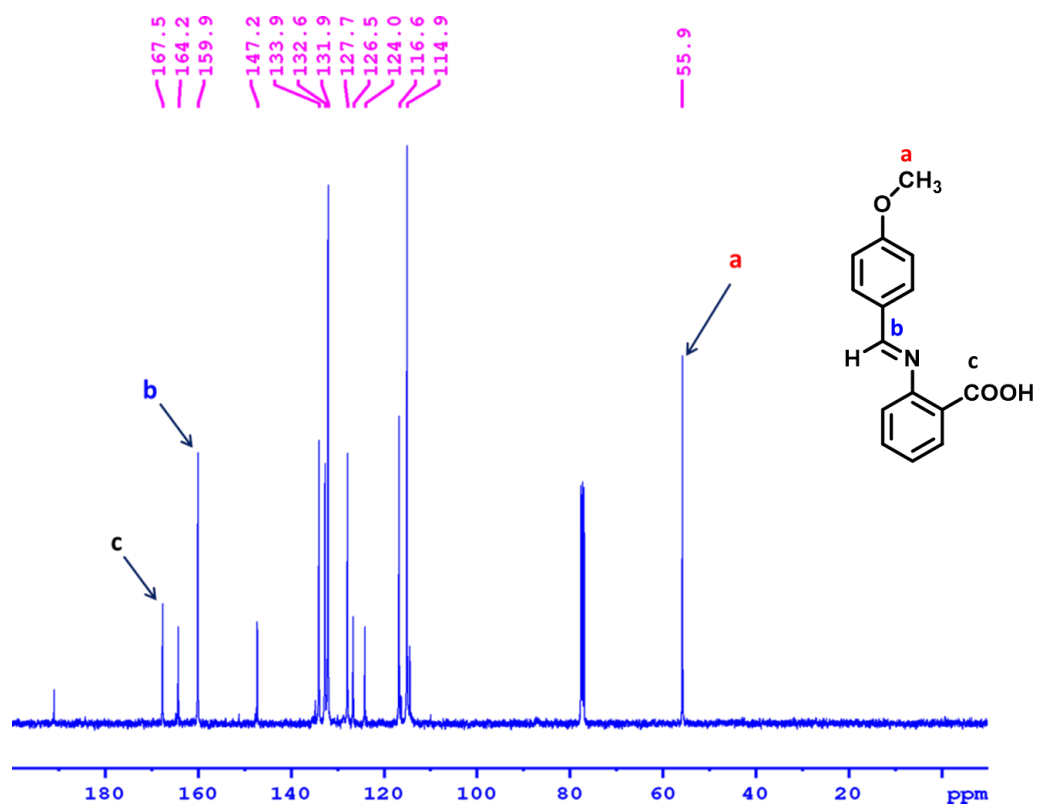


Figure 3.10: ¹³C NMR spectrum for L1 in CDCl₃ (125 MHz).

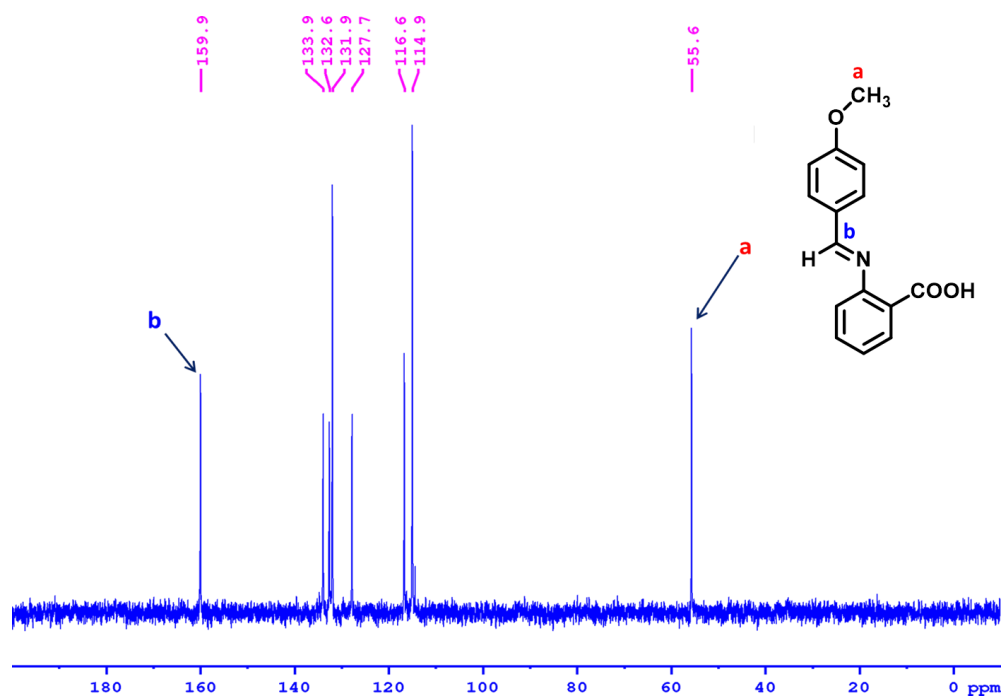


Figure 3.11: DEPT NMR spectrum of L1 in CDCl₃ (125 MHz).

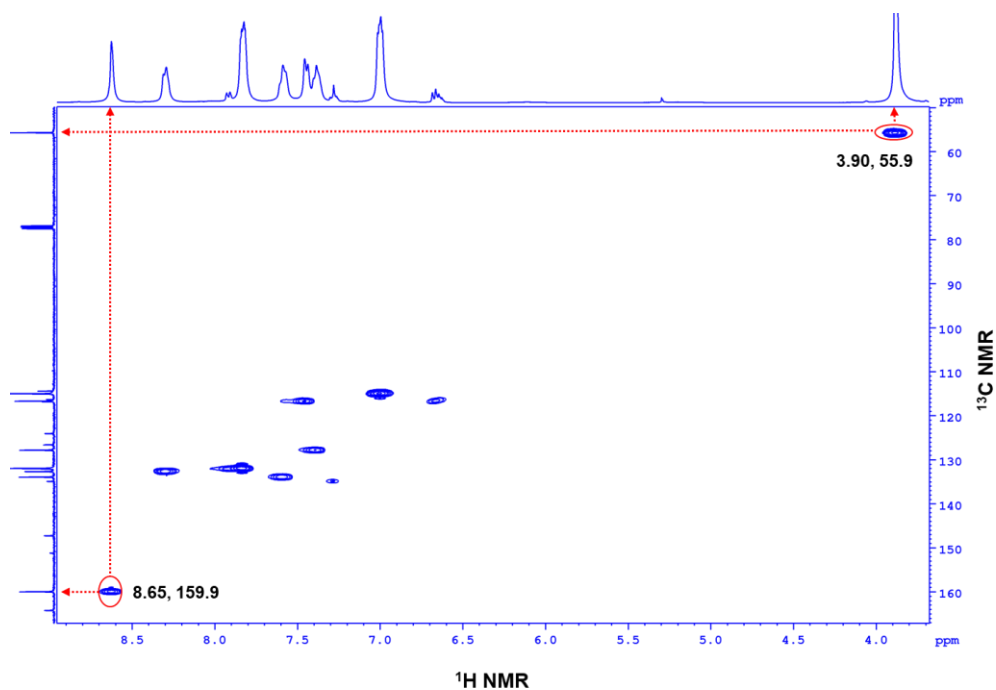


Figure 3.12: Expanded view of a short-range C-H correlation (HSQC) NMR spectrum of L1 in CDCl_3 (400 MHz).

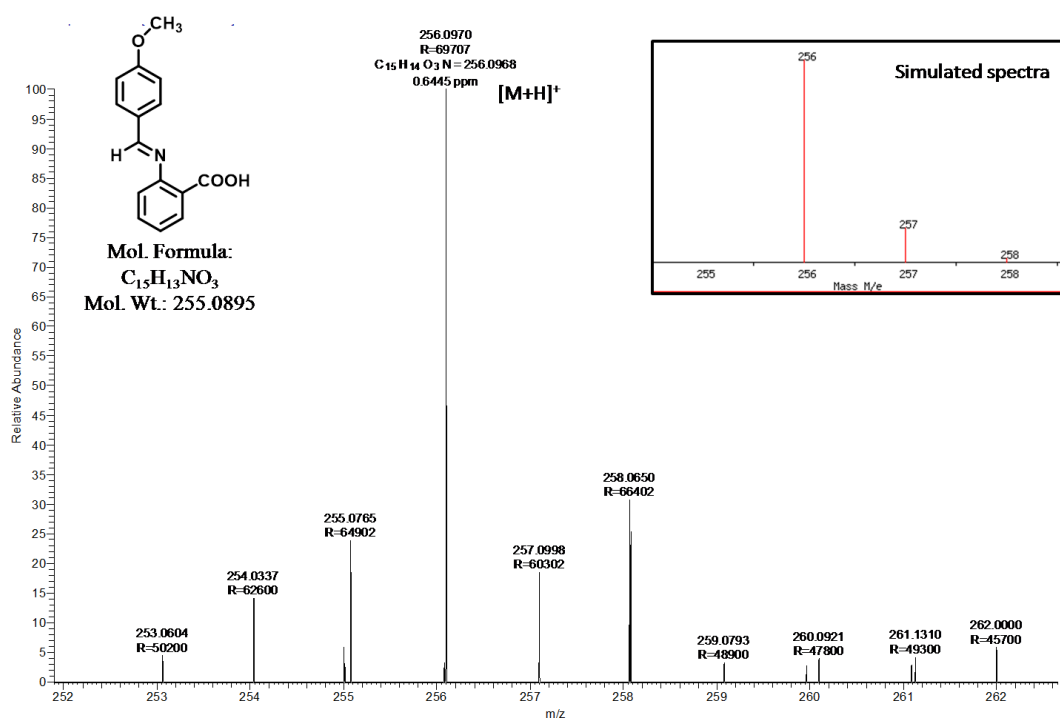


Figure 3.13: ESI-MS (+ve mode) spectrum of L1.

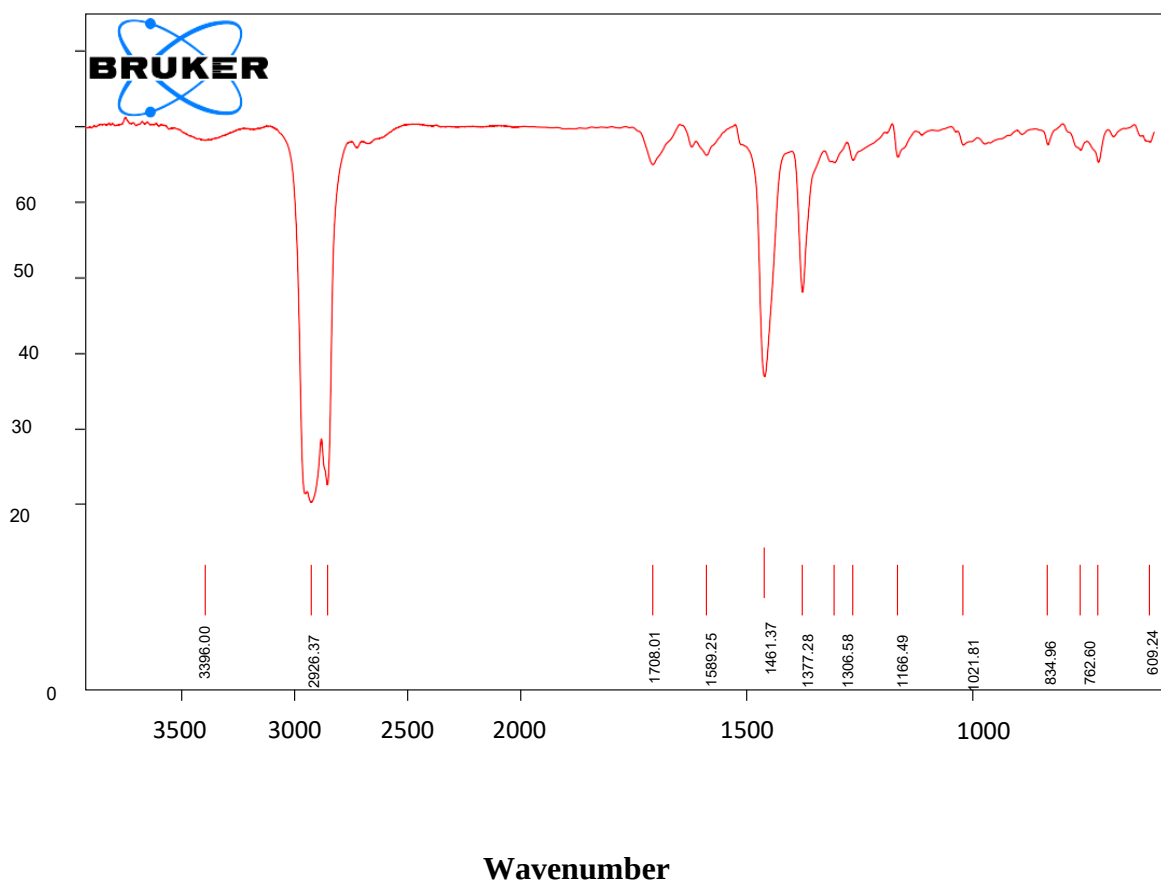


Figure 3.14: IR spectrum of L1

3.6.3. Synthesis of [bis-dimethylamido-Ti-(bis-iminocarboxylate)] (Cat.1)



A 250 mL oven-dried Schlenk flask was cooled under vacuum, and argon gas was purged. The Schlenk flask was heated and cooled three times under vacuum to reduce the moisture content. Under the positive flow of argon, 1 g (3.9 mmol.) of **L1** was added to the above Schlenk flask. Subsequently, toluene (40 mL) was added, the mixture was stirred for 5 minutes. The Schlenk was cooled to 0 °C and Ti (NMe₂)₄ (0.4 mL, 1.9 mmol) was added gradually over a period of 5 minutes. A turbid yellow solution turned to a clear reddish brown one. Subsequently, the ice bath was then replaced with a water bath and the temperature of the reaction mixture was raised from 0 °C to about 30 °C. The mixture was then stirred for additional two hours at room temperature. After another 30 minutes of stirring, volatiles were evaporated under vacuum. A reddish-brown residue was obtained. This crude complex was further purified by washing with freshly distilled hexane (20 mL × 3). The content was stirred for 5 minutes to let the solid settle, and the supernatant liquid was separated. The solid was then vacuum-dried and stored in the glove box for future use.

¹H NMR (400 MHz, CDCl₃) δ = 8.35 (s, 2H, HC=N-), 7.80 (d, J = 8.58 Hz, Ar, 4H), 7.36 (t, J = 6.38, 7.50, Ar, 5H), 7.06 (d, J = 7.88, Ar, 3H), 6.97 (d, J = 8.75, Ar, 4H), 3.86 (s, 6H), 3.07 (s, 6H) and 2.88 (s, 6H, -NMe₂). **¹³C NMR (125 MHz, CDCl₃)** δ = 170.4 (-COOH), 162.4, 160.4(-C=N), 148.5, 131.3, 129.8, 127.4, 125.6, 118.7, 114.7, 55.4 (OCH₃), 38.2 and 34.7 (-N(CH₃)₂).

ESI-MS (+ve) m/z for C₃₄H₃₆N₄O₆Ti [M+H]⁺ + Calculated: 644.21 Da, observed: m/z = 610.18 [Cat.1-2NMe₂ + 2H + HNMe₂ + Li]⁺ Da.

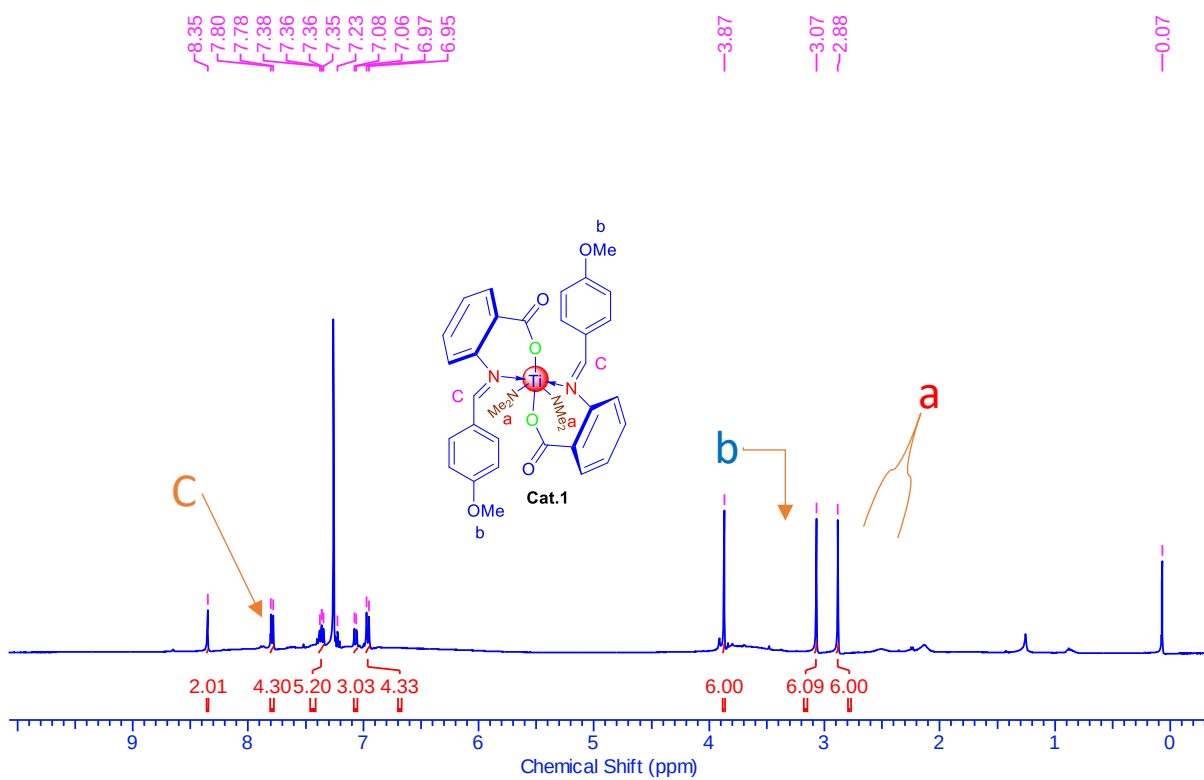


Figure 3.15: ¹H NMR spectrum of Cat.1 in CDCl₃(400 MHz).

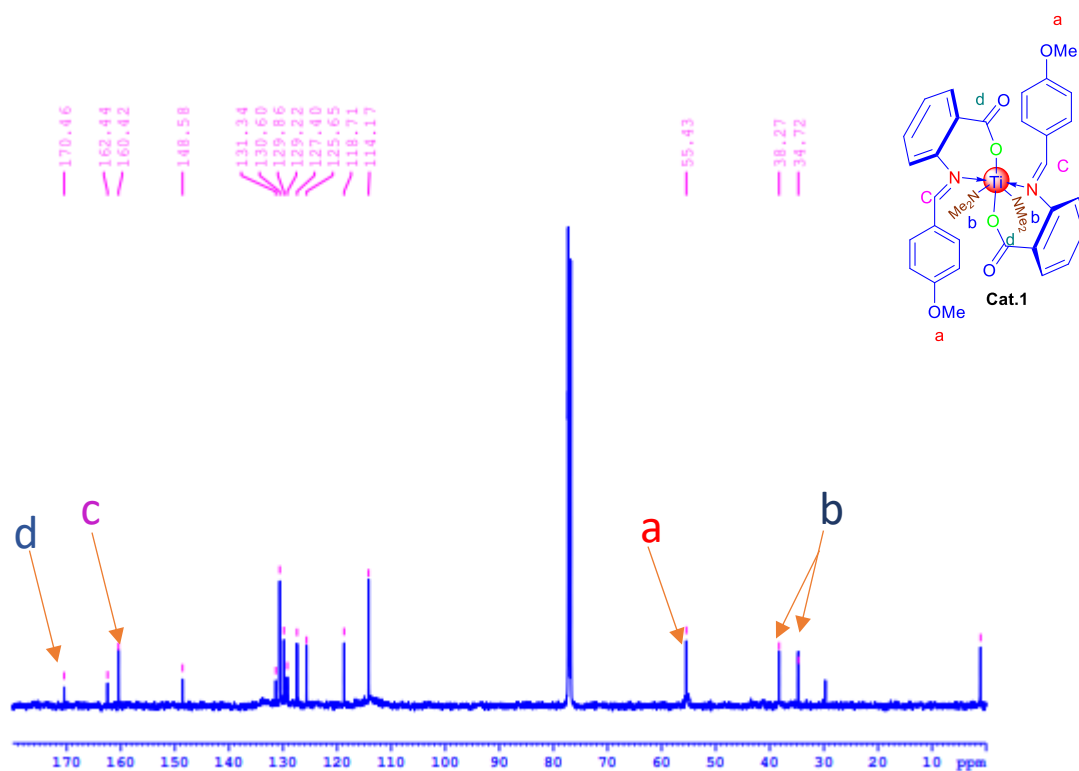


Figure 3.16: ^{13}C NMR spectrum of Cat.1 in CDCl_3 (100 MHz).

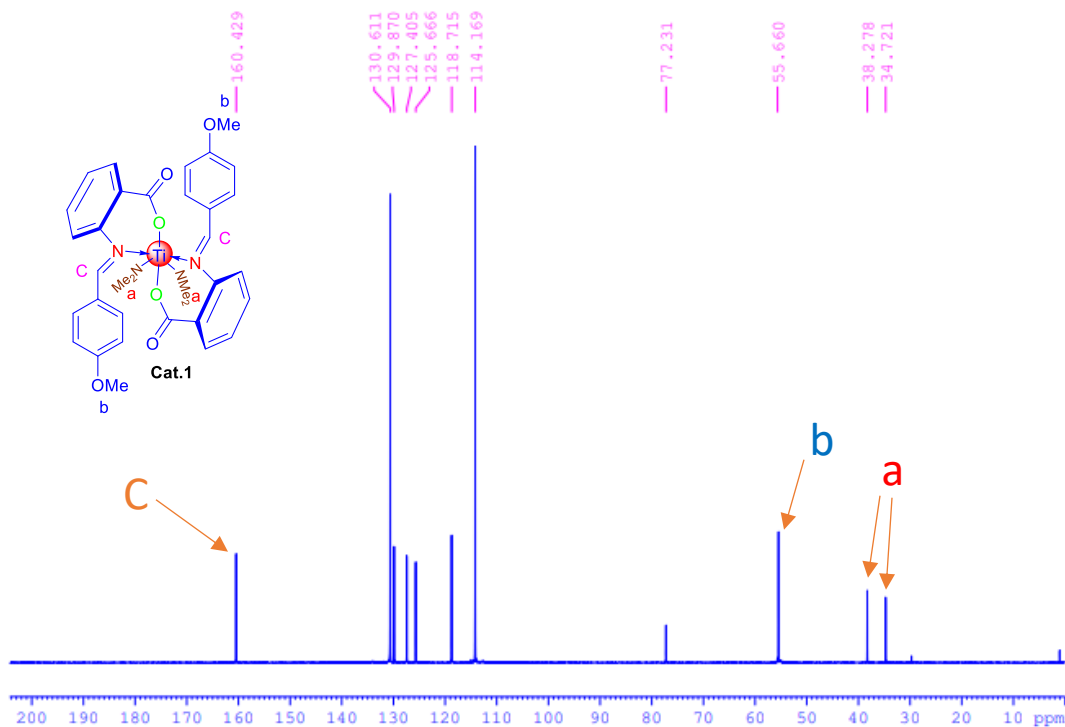


Figure 3.17: DEPT NMR spectrum of Cat.1 in CDCl₃ (100 MHz).

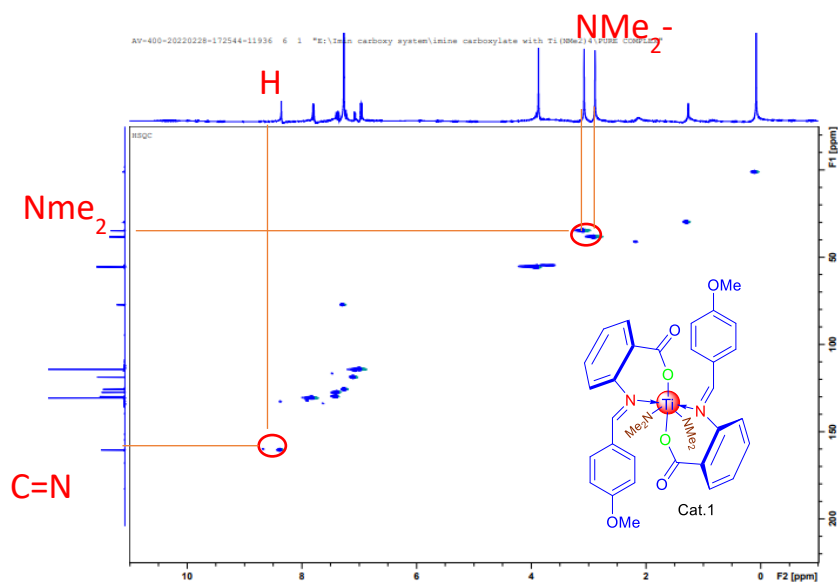


Figure 3.18: HSQC NMR spectrum of Cat.1 in CDCl₃ (400 MHz).

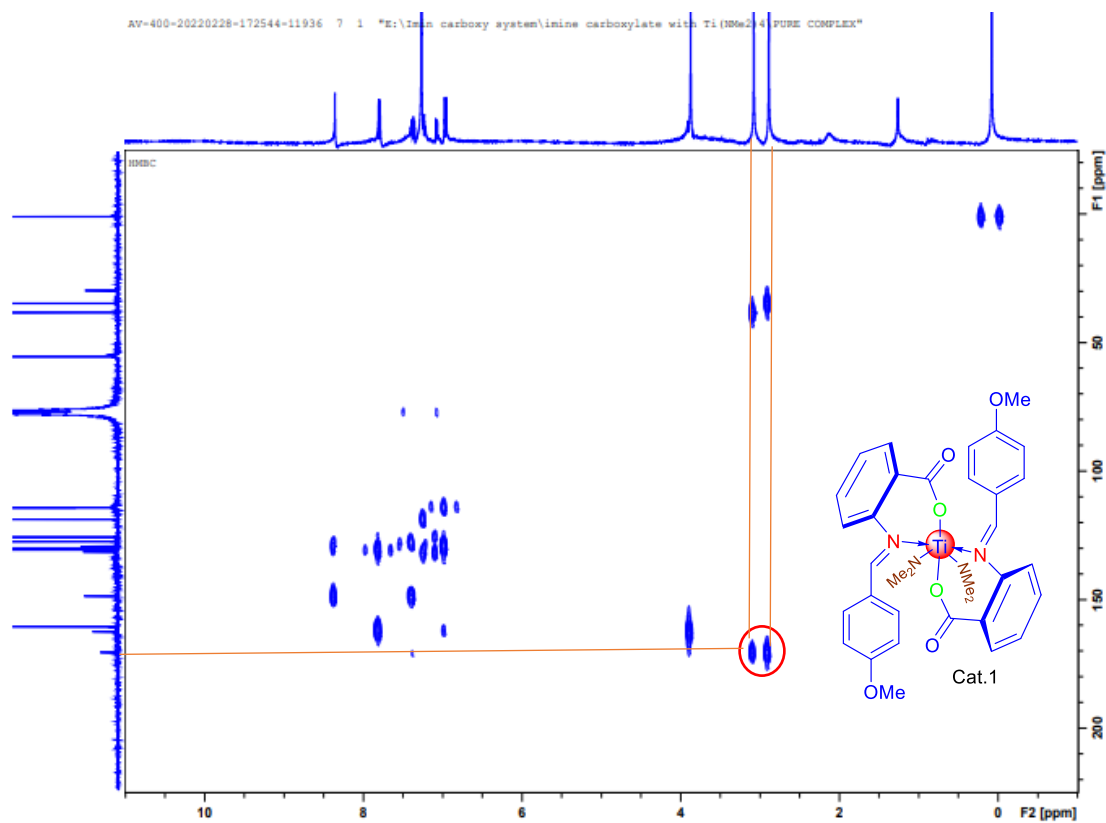


Figure 3.19: HMBC NMR spectrum of Cat.1 in CDCl₃ (400 MHz).

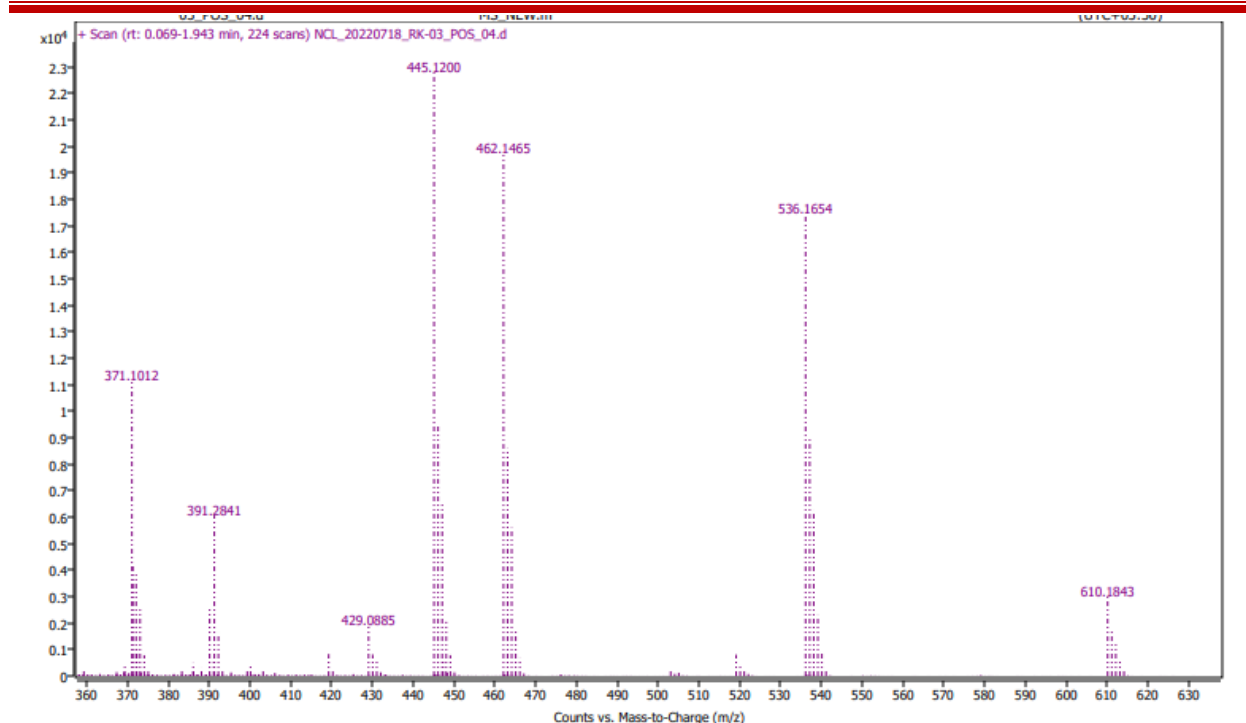


Figure 3.20: Mass-spectrum (+ ve mode) of Cat.1.

3.6.4. General procedure for ethylene polymerization

The ethylene polymerization reaction was carried out in a Büchi glasuster cyclone 075 high-pressure reactor, equipped with an overhead mechanical stirrer, heating/cooling jacket, and pressure regulators. A pre-dried 250 mL Büchi reactor was kept under vacuum at 90 °C for 30 minutes before usage. After cooling down, the reactor was filled with argon, and after 3 cycles of vacuum/argon, the reactor was filled with ethylene gas (20 bar) and flushed 3 times. It was charged with 100 mL of dried freshly distilled toluene at room temperature under the positive flow of ethylene gas. The reaction temperature was set to the desired range using Julabo temperature controller and after the thermal equilibrium was reached, 70 % of the total amount of cocatalyst (MMAO-12) was added, and the mixture was stirred for about 30 minutes. Simultaneously, in a separate Schlenk tube, 10 mL of dried, freshly distilled toluene was taken and the remaining amount of cocatalyst (MMAO-12) (30 %) was added, and the content was stirred for 30 minutes.

After 30 min. a suitable amount of catalyst was injected into the reactor along with 10 mL of dry toluene containing cocatalyst (MMAO-12), and the polymerization was initiated by pressuring the reactor with ethylene. The polymerization was carried out for the required time under vigorous stirring and a constant feed of ethylene and then terminated by the addition of acidified methanol. The polymer was filtered out, washed with a copious amount of methanol/acetone, and dried overnight under vacuum at 60 °C to obtain a free-flowing powder. The polymerization results have been summarized in table no 3.3, 3.4, 3.5 and 3.6.

Table 3.3: Polymerization of ethylene catalyzed by Cat.1 in the presence of TMA and BT (Trityl tetrakis (pentafluoro phenyl) borate)^a

Entry	Catalyst	TMA (eqv.)	BT (eqv.)	Time (Min)	Yield ^b (gm)	Tm (°C) ^c
1.	Cat.1	40	1.2	30	0.250	141.8
2.	Cat.1	100	1.2	30	0.350	141.3
3.	Cat.1	120	1.2	30	0.150	139.9
4.	Cat.1	40	--	30	0.106	-
5.	TDMAT	40	1.2	30	-	-

^aConditions: Catalyst = 31 μmol of Ti (20 mg of catalyst); Solvent = 100 mL of toluene; ethylene-4 bars; ^bObtained from polyethylene produced, ^cObtained from DSC, heating and cooling curves of first heating cycle; TDMAT-Tetrakis (dimethylamino) Titanium (IV).

Table 3.4: Polymerization of ethylene catalyzed by Cat.1 in the presence of DiBAL-H.^a

Entry	Catalyst	DBAL-H(eq.)	MMAO (eq.)	BT (eq.)	Time (Min)	^b Yield (gm)
1.	Cat.1	40	100	--	30	--
2.	Cat.1	40	1000	--	30	--
3.	Cat.1	40	--	1	30	--
4.	Cat.1	--	1000	1	30	0.700

^aConditions: Catalyst = 31 μmol of Ti (20 mg of catalyst); Solvent = 100 mL of toluene; ethylene-4 bars; ^bObtained from polyethylene produced.

Table 3.5: Polymerization of ethylene catalyzed by Cat.1 in the presence of MMAO12.

Entry	Catalyst	MAO Al/Ti Ratio	Temp. (°C)	Yield gm ^b	^c M _w	T _m ^d	^e Cryst. (%)
1.	Cat.1	100	35	NA	-	-	-
2.	Cat.1	500	35	0.650	-	138.7	62.1
3.	Cat.1	1000	35	0.750	2.5×10 ⁶	137.2	87.9
4.	Cat.1	1500	35	0.750	-	139.5	60.8
5.	Cat.1	2000	35	0.700	-	-	
6.	Cat.1	1000	25	0.680	-	139	96.4
7.	Cat.1	1000	50	0.360	-	138.3	80
8.	Cat.1	1000	60	0.297	-	134	48.6

^aConditions: Catalyst = 31 μmol of Ti (20 mg of catalyst); Solvent = 100 mL of toluene; ethylene-4 bars;

^bObtained from polyethylene produced; ^cAs obtained from HT-GPC at 160 °C in 1,2,4-Trichlorobenzene (TCB) against polystyrene standards, in g/mol. ^d Obtained from DSC, heating and cooling curves of first heating cycle; ^eCrystallinity calculated from the melting enthalpy measured by DSC and relative to the theoretical value (293 J/g) for 100 % crystalline polyethylene.

Ethelene polymerization for different time periods (5 Min, 30 Min, 60 Min) Procedure:

A pre-dried 250 mL Büchi reactor was kept under vacuum at 90 °C for 3 hours before usage. A general procedure for ethylene as mentioned above, was followed. The polymerization was carried out for 5 minutes time under vigorous stirring and a constant feed of ethylene and then terminated by the addition of acidified methanol. The resultant mixtures were filtered, washed with a copious amount of acetone, and dried overnight under vacuum at 60 °C to obtain a white solid. Same procedure has been followed for 30 Min and 60 Min time periods.

Table 3.6: Ethylene polymerization catalyzed by Cat.1 and MMAO

Entry	Precatalyst	Al/Ti ^b	Time (Min)	Yield ^c	Activity ^d (Mol of PE/Mol of T/h)
1	Cat.1	1000	5	0.100	1188
2	Cat.1	1000	30	0.750	1728.1
3	Cat.3	1000	60	0.975	1123.2

^aConditions: Cat.1 = 31 μ mol of Ti (20 mg of catalyst); Solvent = 100 mL toluene, ^bAl (MAO)/Ti = 1000; 4 bar ethylene pressure; ^cWeight of produced polyethylene (in gm); ^dActivity = (mol of polyethylene/mol of Ti/h

3.7. Polymer characterization

3.7.1 DSC (Differential Scanning Calorimetry)

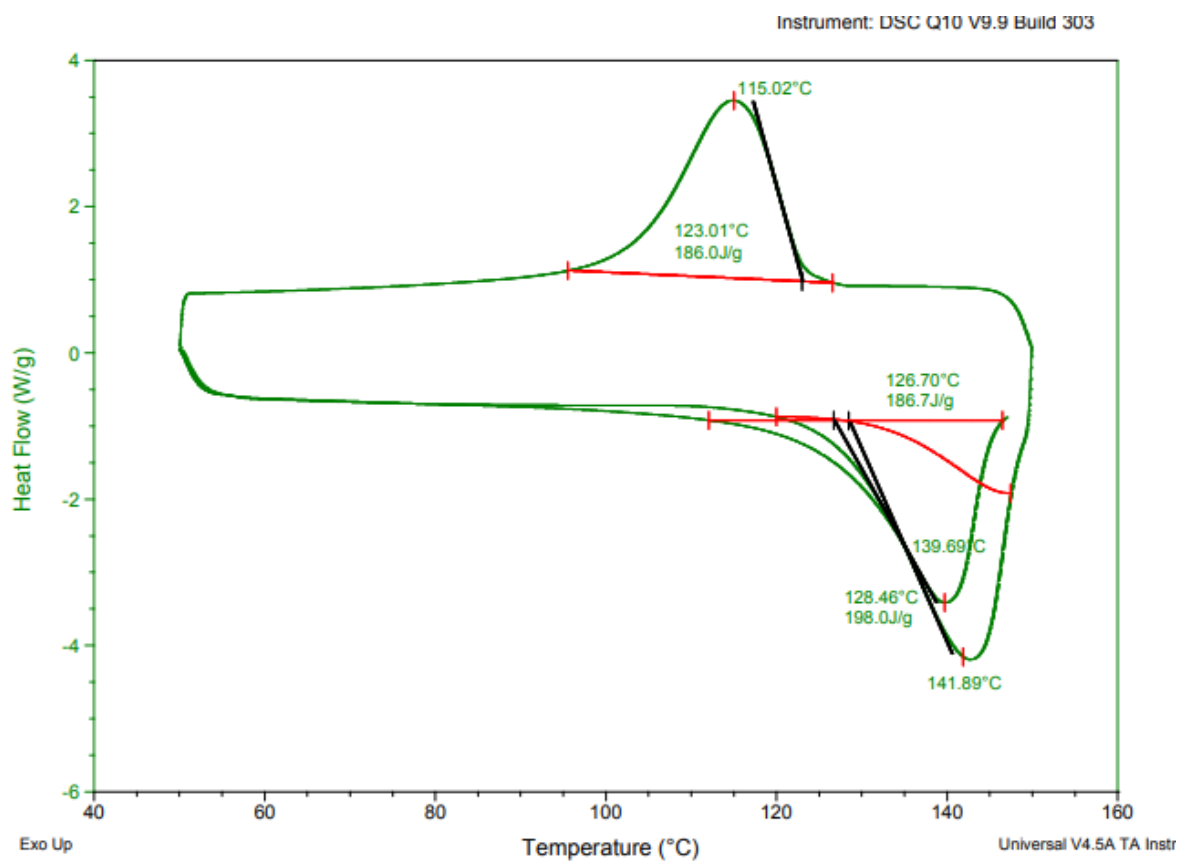


Figure 3.21: DSC curves for the first heating, cooling and second heating cycle (Table 3.3, entry 1)

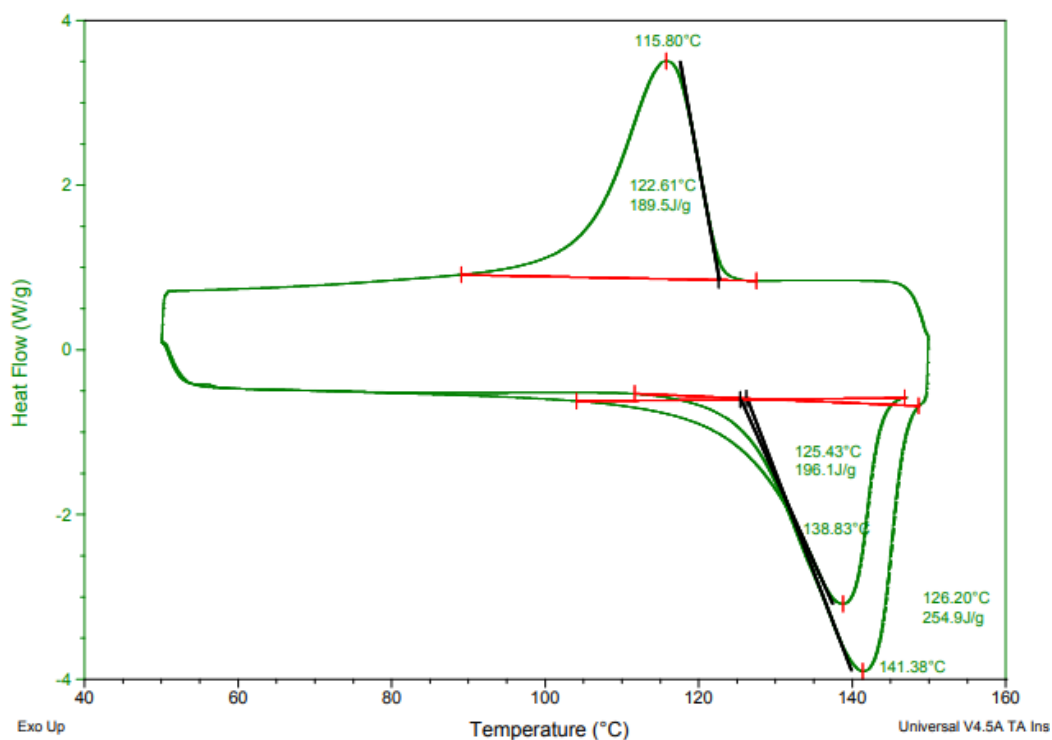


Figure 3.22: DSC curves for the first heating, cooling and second heating cycle (Table 3.3, entry 2)

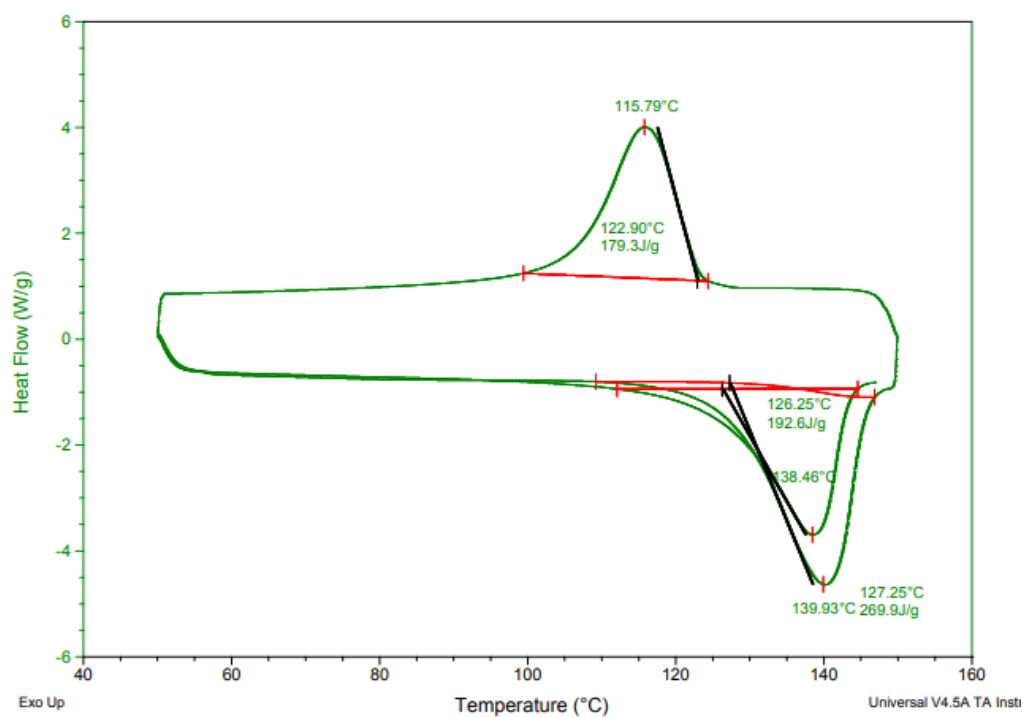


Figure 3.23: DSC curves for the first heating, cooling and second heating cycle (Table 3.3, entry 3)

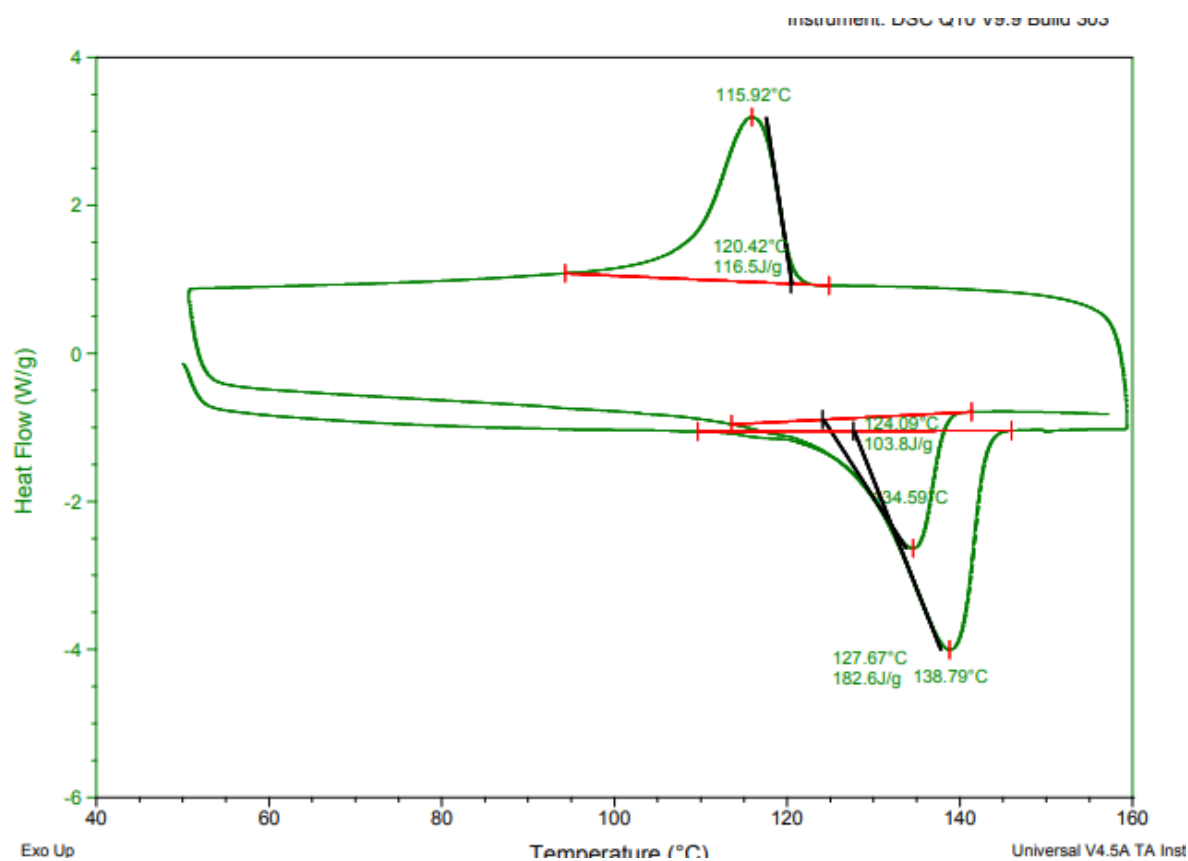


Figure 3.24: DSC heating curve for the first heating, cooling and second heating cycle (Table 3.5, entry 2).

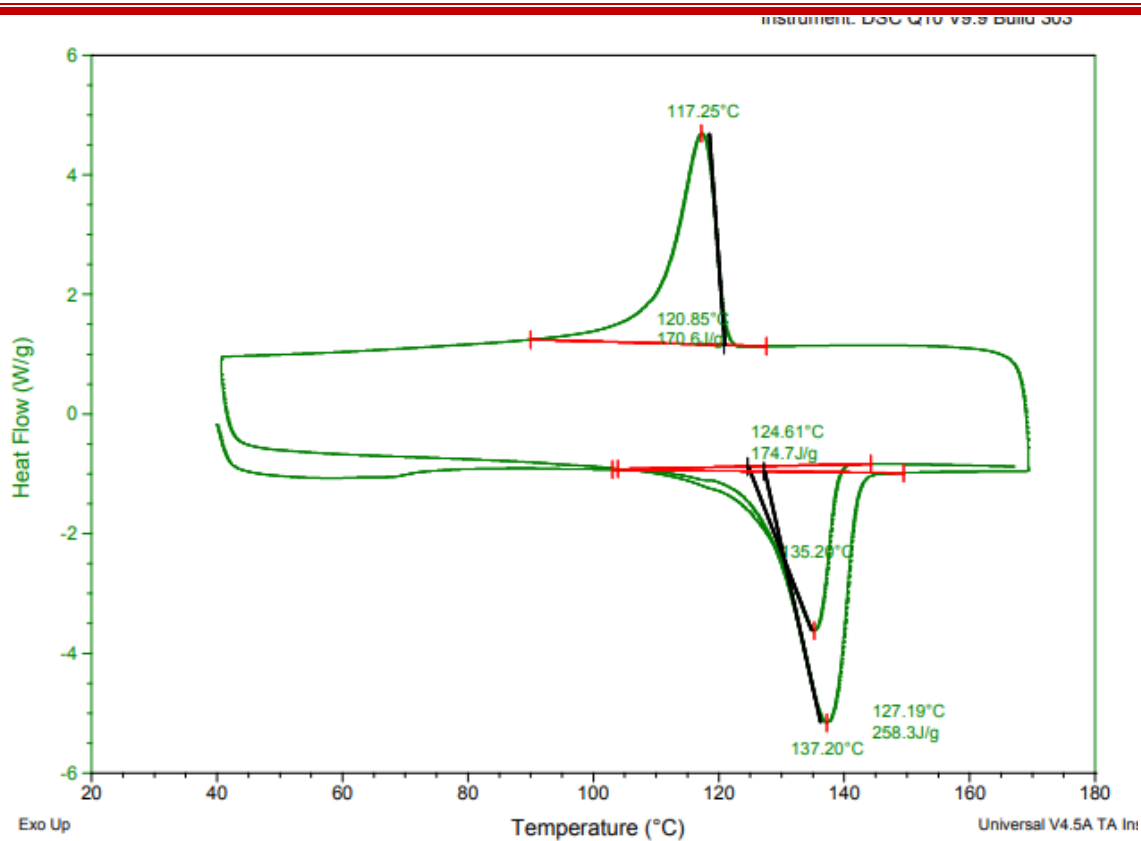


Figure 3.25: DSC heating curves for the first heating, cooling and second heating cycle (Table 3.5, entry 3).

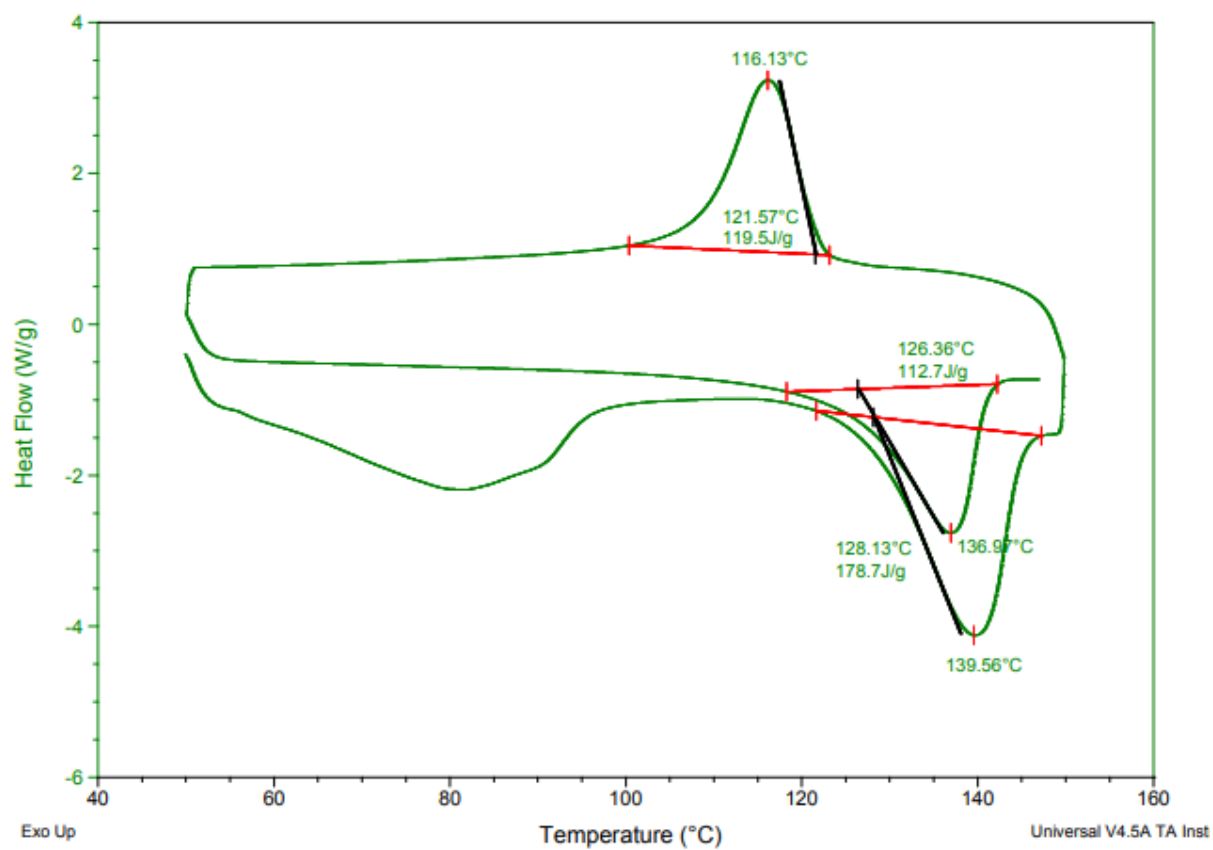


Figure 3.26: DSC heating curves for the first heating, cooling and second heating cycle (Table 3.5, entry 4).

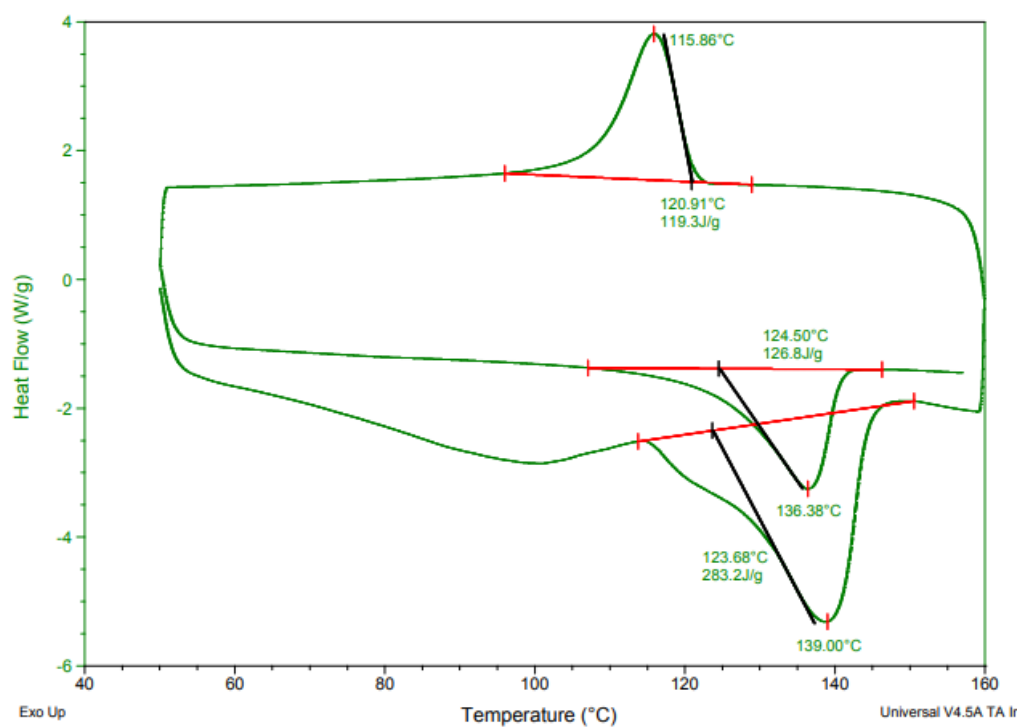


Figure 3.27: DSC heating curves for the first heating, cooling and second heating cycle (Table 3.5, entry 6).

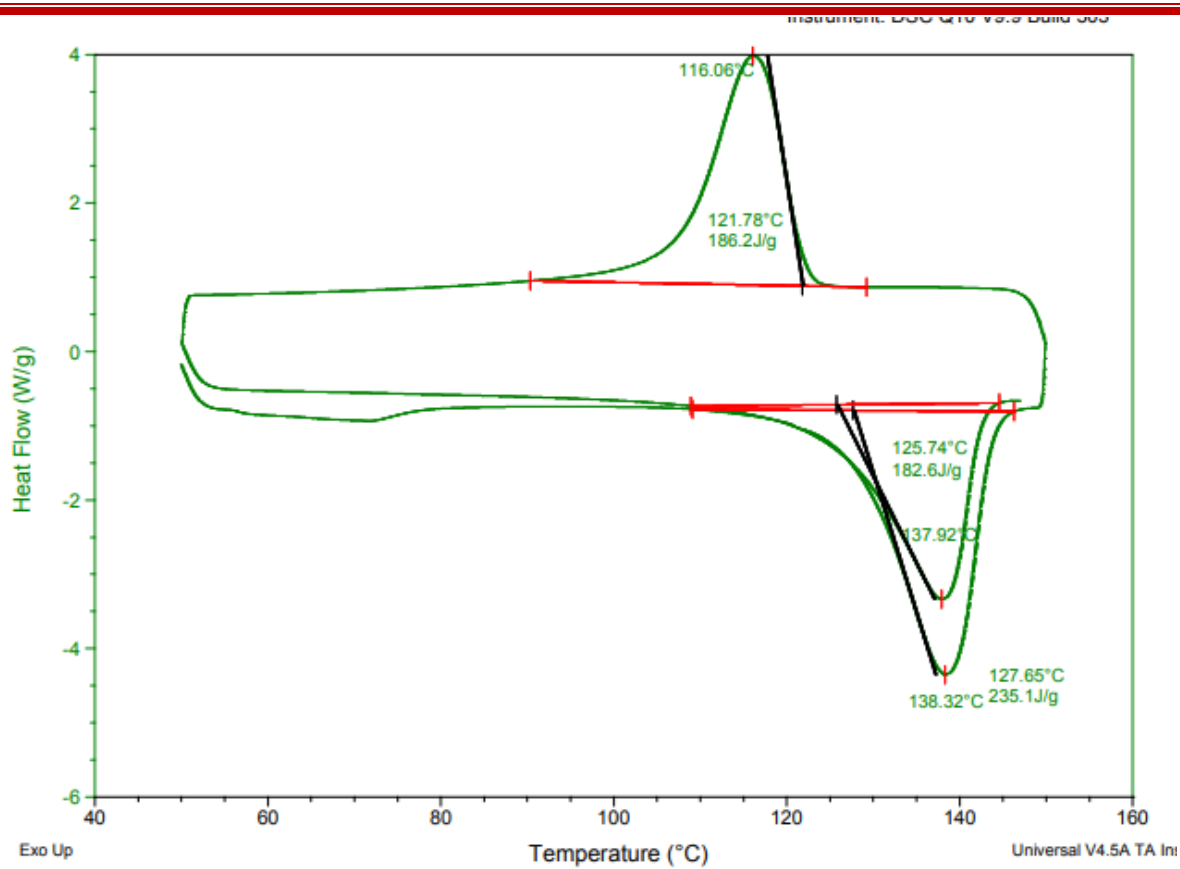


Figure 3.28: DSC heating curves for the first heating, cooling and second heating cycle (Table 3.5, entry 7).

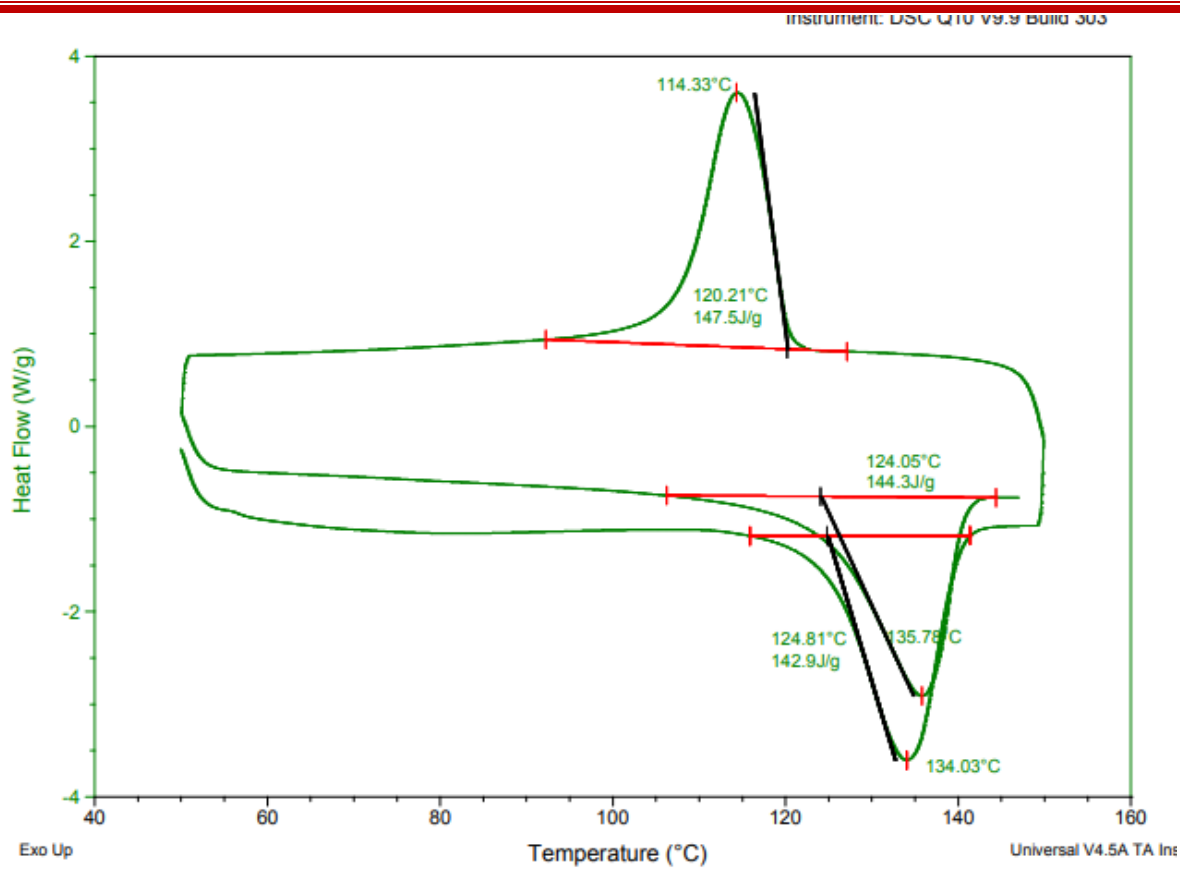
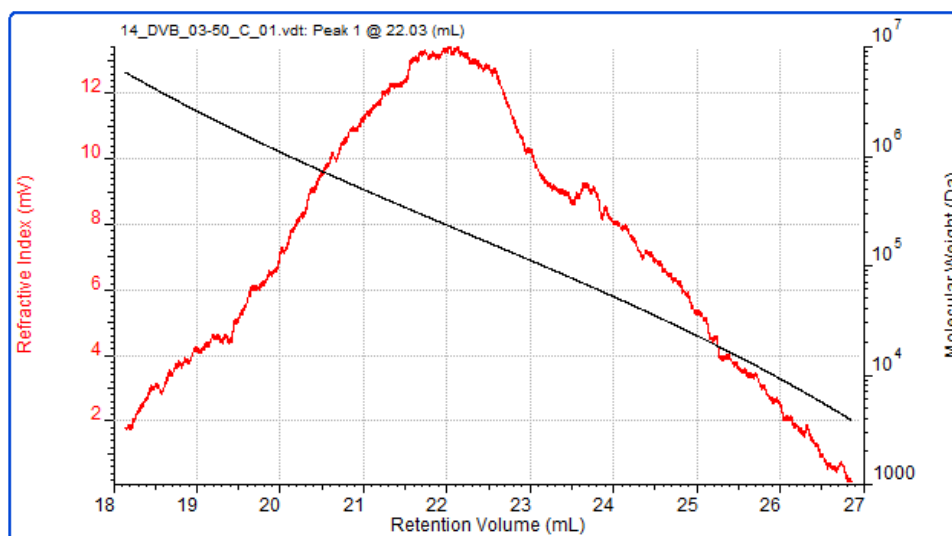


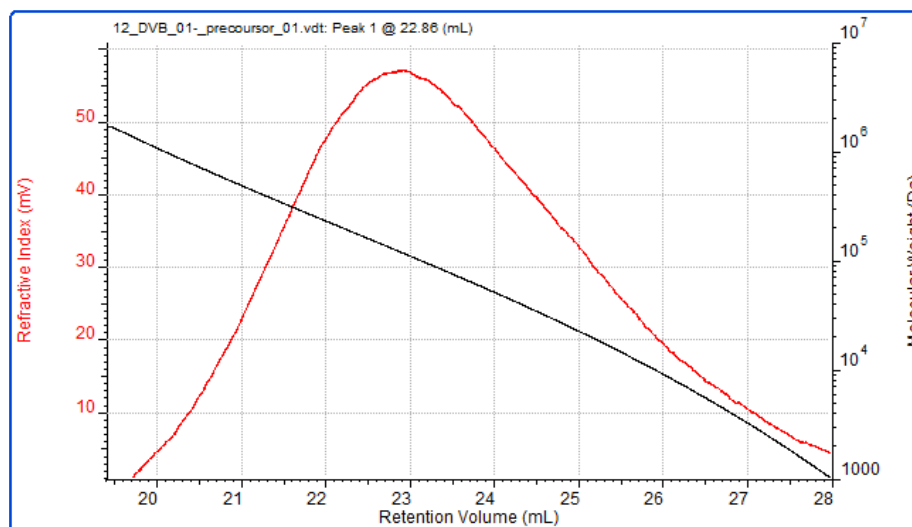
Figure 3.29: DSC heating curves for the first heating, cooling and second heating cycle (Table 3.5, entry 8).

3.7.2 High-temperature gel permeation chromatography (HT-GPC)



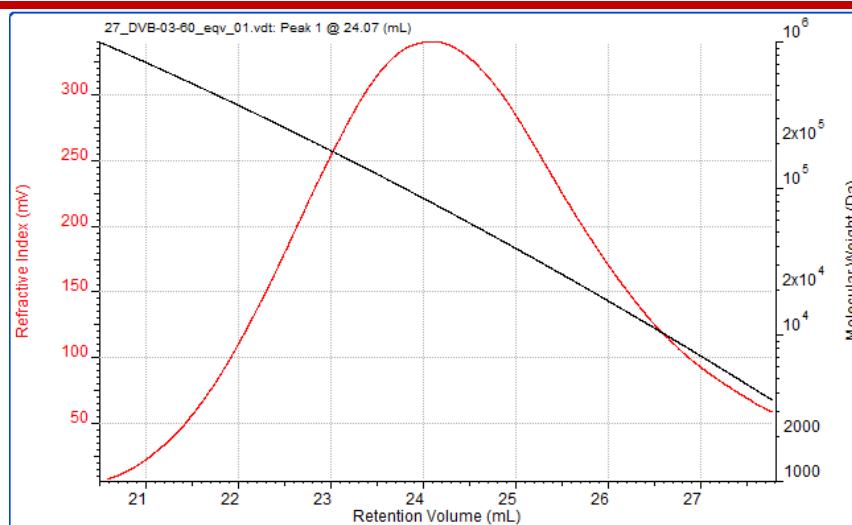
Ret Vol (mL)	18.967
Mn (Da)	1.033 e 6
Mw (Da)	2.544 e 6
Mz (Da)	5.121 e 6
Mp (Da)	2.574 e 6
Mw/Mn	2.462

Figure 3.30: HT-GPC chromatogram of PE (for Table 3.5, entry 3).



Ret Vol (mL)	22.863
Mn (Da)	23,116
Mw (Da)	149,706
Mz (Da)	375,725
Mp (Da)	120,384
Mw/Mn	6.476

Figure 3.31: HT-GPC chromatogram of PE (for Table 3.5, entry 1).



Ret Vol (mL)	24.073
Mn (Da)	31,406
Mw (Da)	112,016
Mz (Da)	253,368
Mp (Da)	79,251
Mw/Mn	3.567

Figure 3.32: HT-GPC chromatogram of PE (for Table 3.5, entry 2).

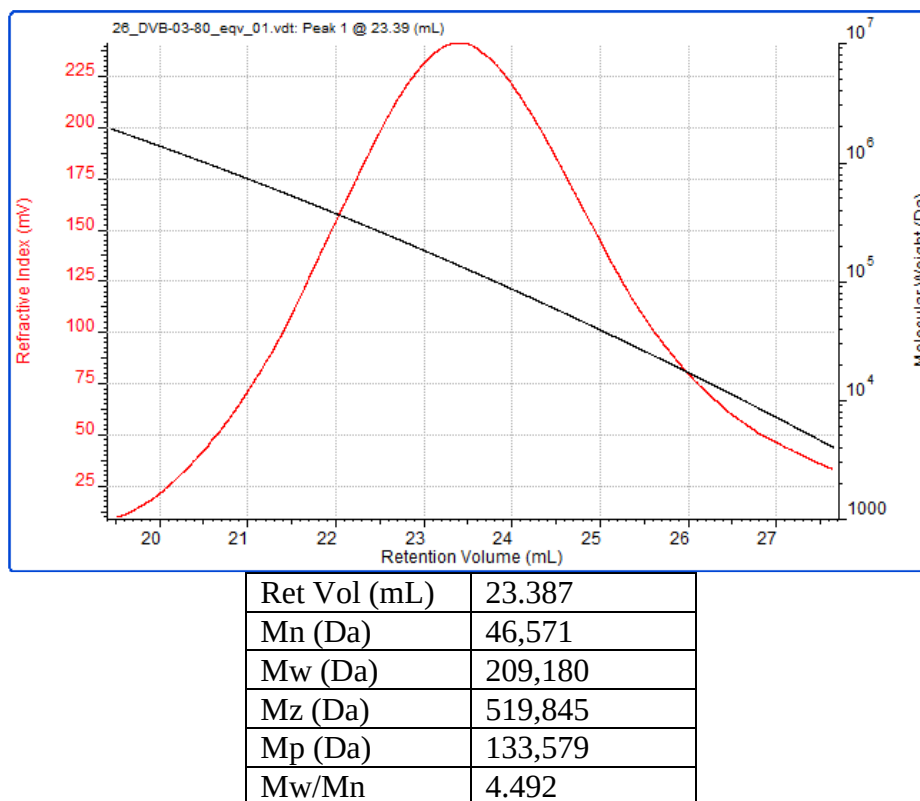


Figure 3.33: HT-GPC chromatogram of Polymer (for Table 3.3, entry 3).

3.7.3. High-temperature NMR spectroscopy

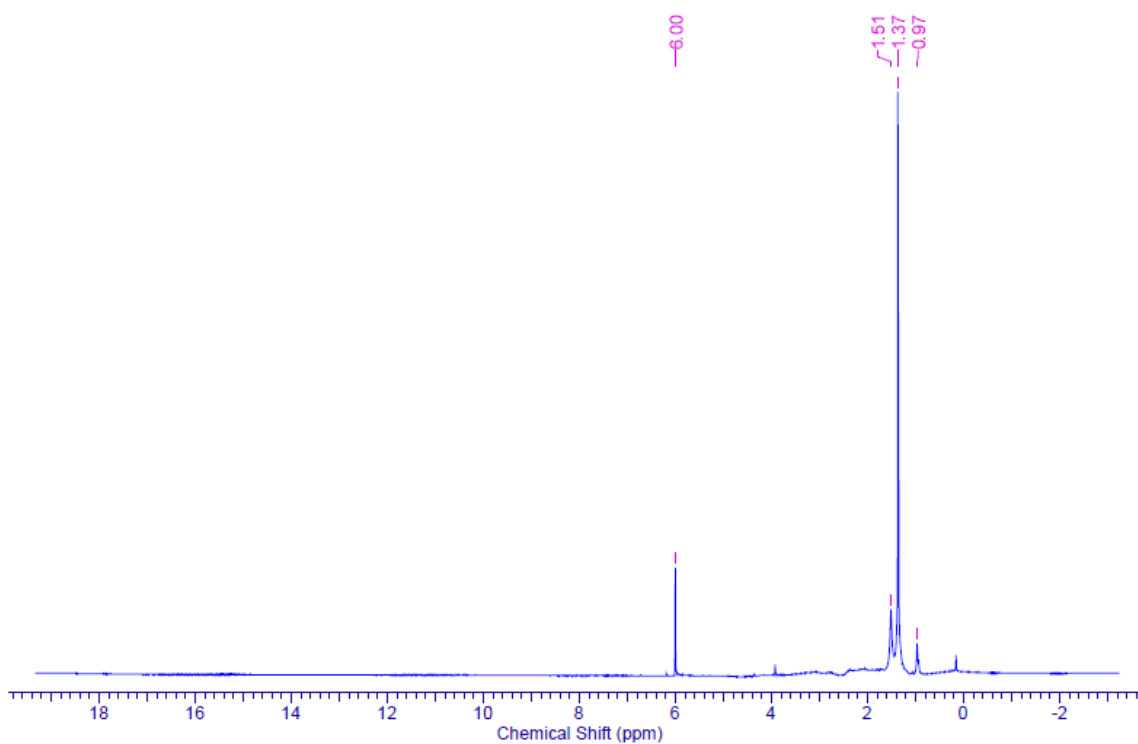


Figure 3.34: ^1H HT-NMR spectrum of polyethylene recorded at 130 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ (for Table 3.5, entry 3).

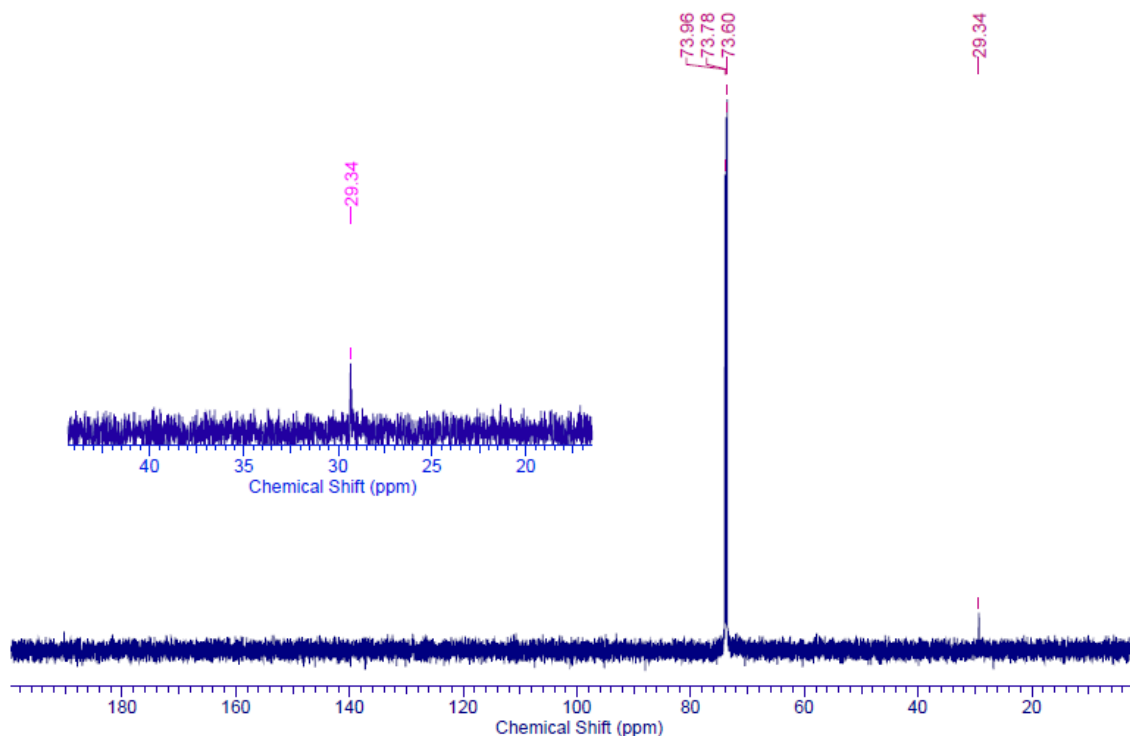


Figure 3.35: ^{13}C HT-NMR spectrum of polyethylene recorded at 130 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ (for Table 3.5, entry 3).

3.8. Determination of percentage crystallinity and disentanglement in UHMWPE

3.8.1. % Crystallinity

The crystallinity of the resultant polyethylene was calculated from the melting enthalpy measured by DSC and relative to the theoretical value 293.6 J/g for 100 % crystalline polyethylene (Table 3.5).

The term ΔH_m° is a reference value and represents the heat of melting, if the polymer were 100% crystalline. This reference heat of melting has been established for each of the commonly used polymers and some of these are listed below in table 3.6.

Table 3.6. Melting enthalpy for 100% crystalline polymers

Polymer	ΔH_m° (J/g)
Nylon 6	230.1
PET	140
Nylon 6, 6	255.8
Polypropylene	207.1
Polyethylene	293.6

The DSC software directly provides melting enthalpy values to make the assessment of the percent crystallinity more convenient and easier.⁴⁸ Crystallinity for one of the polyethylene samples (Table 3.5, entry 6) is determined using the following method.

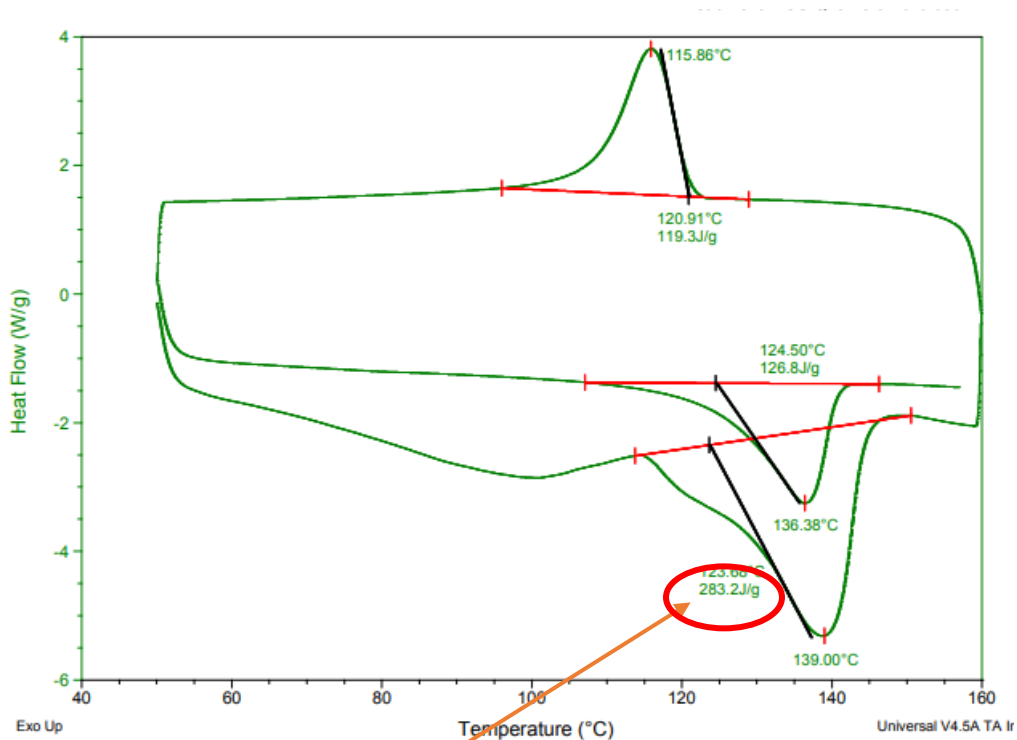
$$\% \text{ Crystallinity} = \Delta H_m / \Delta H_m^\circ \text{ (J/g)} \times 100$$

Therefore,

$$\Delta H_m = 283.2 \text{ J/g}$$

$$\Delta H_m^\circ = 293.6 \text{ J/g}$$

$$\begin{aligned} \% \text{ Crystallinity} &= 283.2 / 293.6 \times 100 \\ &= 96.4 \end{aligned}$$



3.8.2. Disentanglement studies by DSC

A TA instrument Q-10 Differential Scanning Calorimeter (DSC) was utilized to obtain the melting temperatures (T_m) and subsequent melt enthalpies. To minimize the thermal lag caused by the samples, the weight is kept within $6 \text{ mg} \pm 0.1 \text{ mg}$ for each sample. During the measurement, nitrogen was continuously purged at 50 mL/min . A DSC method has been devised to obtain different entanglement densities by following a literature reported protocol as depicted in Figure S29.⁴⁹ The sample was heated from 50°C to an annealing temperature which is higher than PE's equilibrium temperature (145°C) at 10°C/min . to 160°C . At this temperature, the sample was annealed for a fixed time (5 and 30 min.). Two different annealing times were chosen to vary entanglement density in melt. Next, the sample was cooled to an isothermal crystallization

temperature of 128 °C, at 10 °C/min. rate. The sample was kept on hold at isothermal crystallization temperature for a fixed time of 180 min. Next, the sample was cooled to 50 °C at 10 °C/min. rate and second heating was resumed from 50 to 160 °C at 10 °C/min. The DSC plots depicted in Figure 3.37 and 3.38 were obtained during this second heating ramp.

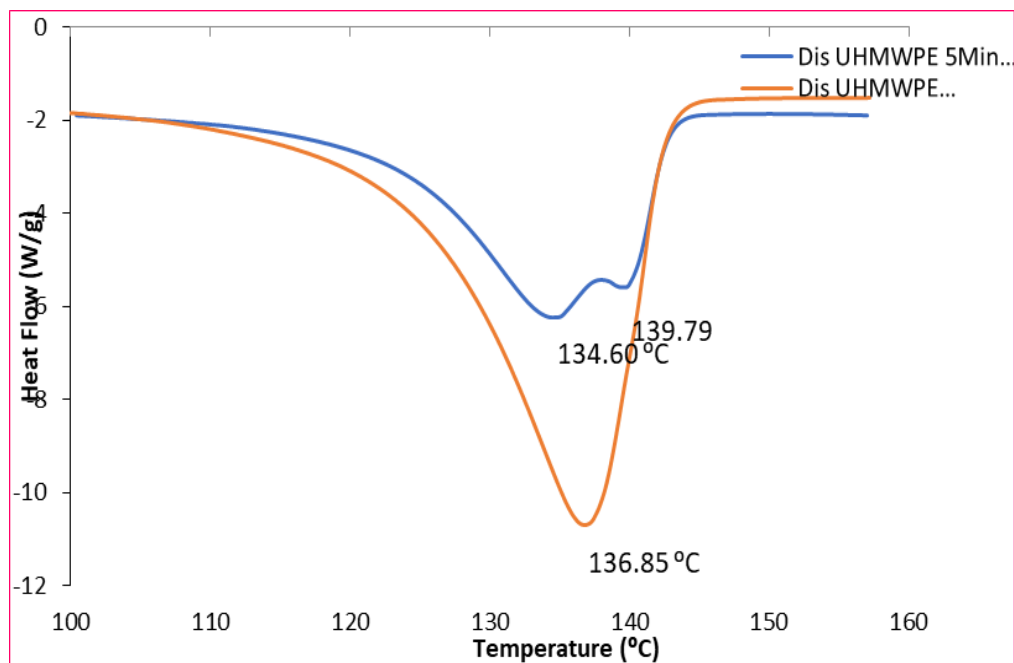


Figure 3.36: Thermal protocol followed to demonstrate disentangled nature of UHMWPE.

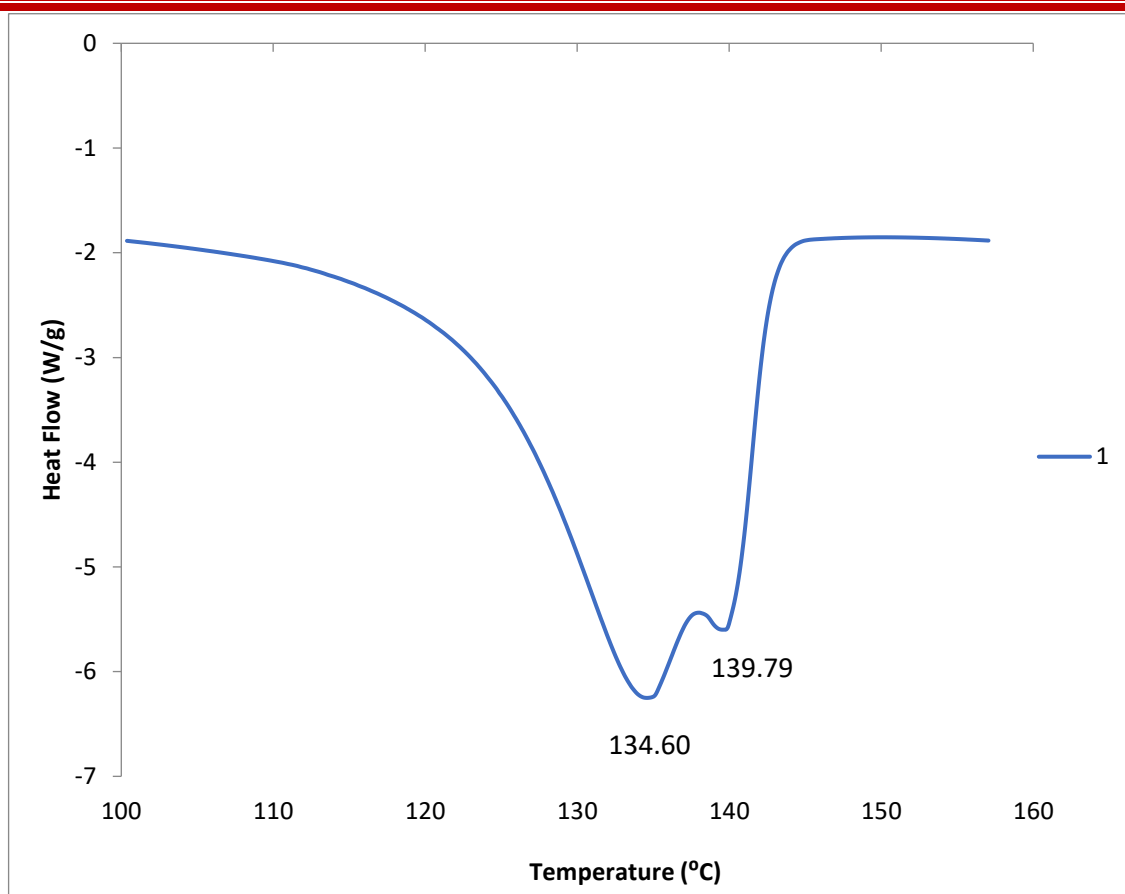


Figure 3.37: DSC plot of the *d*-UHMWPE sample annealed for 5 minutes using the thermal protocol displayed in figure 3.36. (Table 3.5, entry 6).

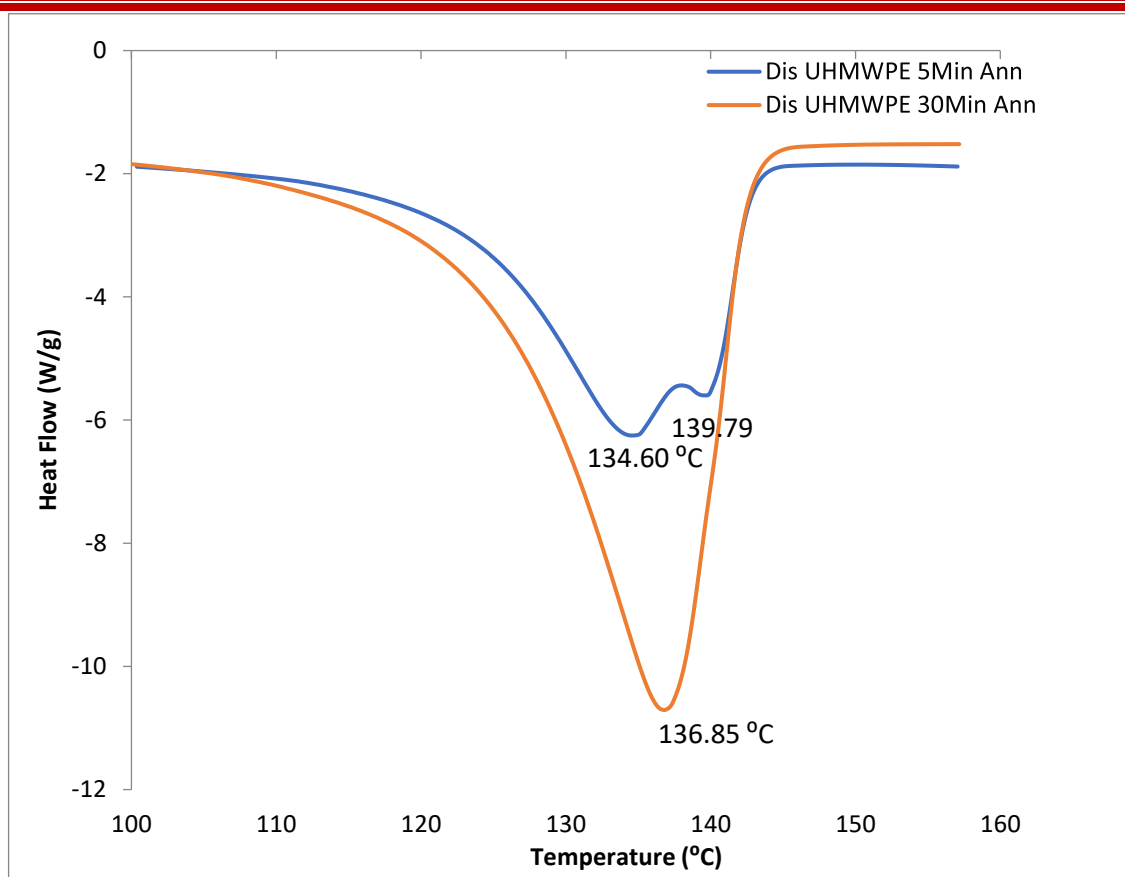


Figure 3.38: DSC plot of the *d*-UHMWPE sample annealed for 5 (blue line) and 30 (orange line) minutes using the thermal protocol displayed in figure S29. (Table 2.5, entry 6).

3.8.3. Commercial UHMWPE studies by DSC for comparison

We procured commercial Sigma-Aldrich UHMWPE (CAS 9002-88-4) with Mw 3,000,000-6,000,000 g/mol and subjected it to DSC analysis using DSC method presented in figure S28. This type of comparative analysis has already been reported by Prof. Rastogi.⁴ The authors state that “The comparative example of commercial sample also shows the presence of two peaks on crystallization at lower supercooling. However, unlike the disentangled sample, the high temperature endothermic peak is found to be around 134 °C, which is not surprising and is in agreement with earlier findings on linear polyethylene’s).” Our DSC experiment reconfirms the

above finding by Rastogi. The commercial Sigma-Aldrich UHMWPE with Mw of 3,000,000-6,000,000 g/mol displayed a peak at 132.4 °C with a shoulder around 136.5 °C (see figure 3.39).

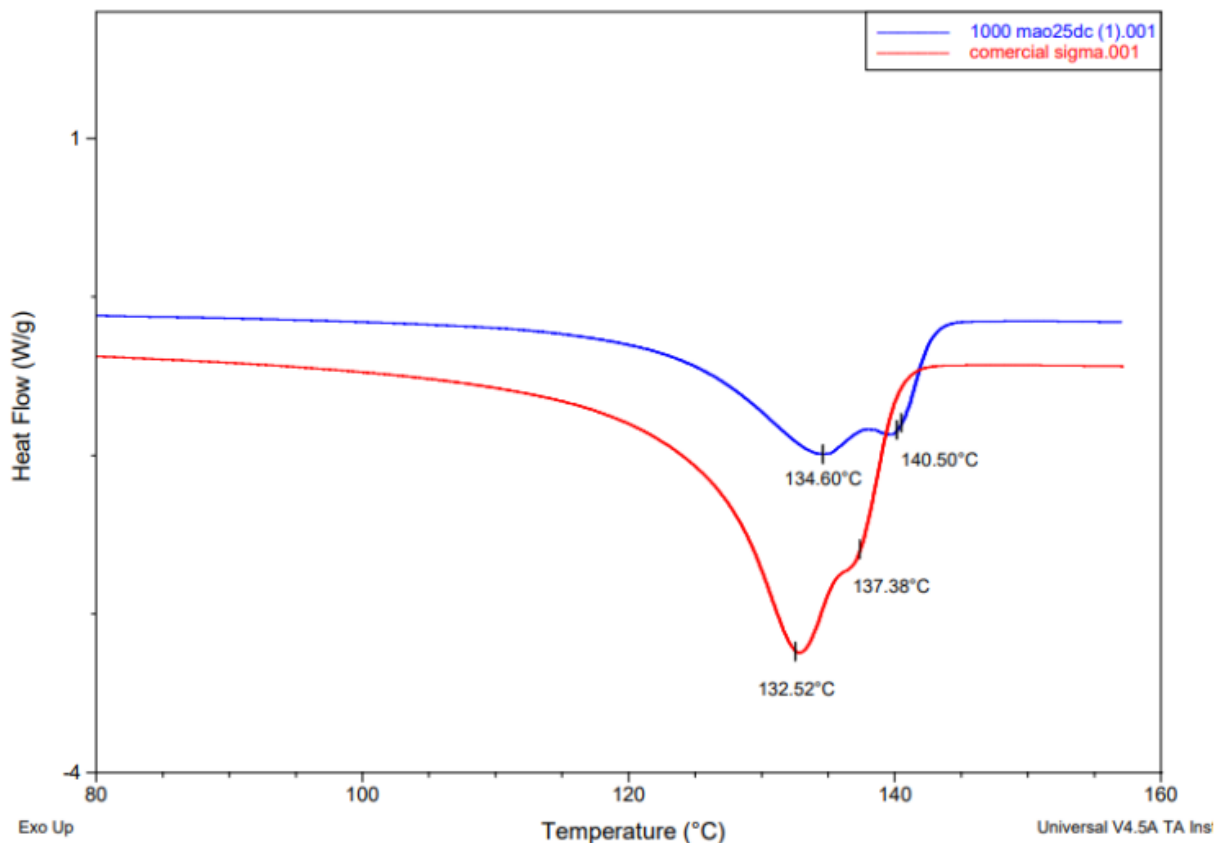


Figure 3.39: DSC plot of the d-UHMWPE sample annealed for 5 (blue line) and commercial entangled UHMWPE (red line) sample annealed for 5 minutes using the 30 thermal protocols displayed in figure 3.38.

While our disentangled UHMWPE, with a much lower molecular weight of (Mv) 7,00,000 g/mol, under identical conditions, disclosed two distinct peaks at 134.6 °C and 140.5 °C (see DSC figure 3.39). These findings are in line with the literature report and clearly demonstrate that our reactor PE is disentangled UHMWPE.

3.9. Conclusions

In summary, an iminocarboxylate ligand L1 was treated with a $[\text{Ti}(\text{NMe}_2)_4]$ to produce [bis-dimethylamido-Ti-(bis-iminocarboxylate)] in good yield (62 %). ^1H , ^{13}C , HSQC, HMBC NMR and mass analysis conclusively proved the existence of a bis-ligated Titanium complex Cat.1.

Preliminary screening of cocatalysts suggested MMAO to be the best activator. The effect of Al/Ti ratio on the activity of Cat.1 was investigated and an Al/Ti ratio of 1000 was found to be the optimal ratio. Temperature screening suggested 35 °C as the optimal temperature, while, either lowering the temperature to 25 °C or increasing it to 50 and 60 °C displayed reduced activity. The resultant polyethylene was examined by using DSC, high temperature GPC, high temperature NMR (HT-NMR) spectroscopy. High temperature proton (^1H) and carbon (^{13}C) NMR of the polymer suggested the formation of linear polyethylene. High temperature gel permeation chromatography revealed a molecular weight of 2.5 million g/mol, which can be classified as UHMWPE as per ASTM-D4020. DSC analysis of the resultant PE revealed a very high degree of crystallinity (96 %). A specially designed DSC method disclosed that the thus formed UHMWPE exists in a “disentangled” state. Thus, [bis-dimethylamido-Ti-(bis-iminocarboxylate)] complex catalyzed polymerization of ethylene in the presence of MMAO to disentangled ultrahigh molecular weight polyethylene (d-UHMWPE). Further investigations to improve the activity by tweaking the ligand structure are in progress.

3.10. References

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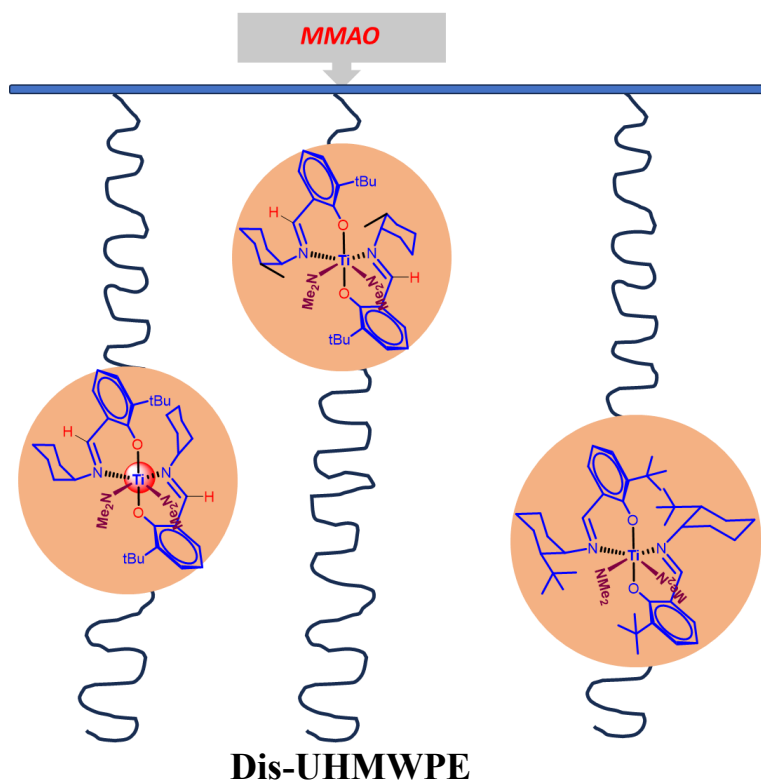
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Chapter 4



Sterically Tailored Phenoxy-imine Titanium Complexes as Catalysts for the Preparation of Ultrahigh Molecular Weight Polyethylene



4.1. Abstract

In this study, three distinct substituted phenyl cyclohexylimine titanium complexes were synthesized and characterized using various spectroscopic techniques. These complexes were activated with methyl aluminoxane (MMAO), triisobutylaluminum (TIBA), and tetrakis (pentafluoro phenyl) borate (BT), and were systematically examined in ethylene polymerization. Notably, the introduction of steric bulk near the active site generally enhanced catalytic activity, except for Cat. 3. However, an investigation into excessive steric congestion, exemplified by Cat. 3, revealed a reduction in catalytic activity. This phenomenon suggests a potential hindrance to monomer access to the active site or impeding polymer chain growth. Among these MMAO and the combination of TIBA and BT, MMAO was able to produce ultrahigh molecular weight polyethylene (UHMWPE). The Al/Ti ratio of 2000 equivalent, an ethylene pressure of 2 bar, a temperature of 40 °C, and a polymerization period of 10 minutes were found to be the optimal parameters for polymerization. Cat.2 produced UHMWPE with molecular mass of 2.75×10^6 g/mol under optimized conditions. High crystallinity (95 %) and a distinctive melting peak at 140-143 °C were observed in the resultant material, suggestive of disentangled ultrahigh molecular weight polyethylene (d-UHMWPE). The findings of this work provide valuable insights into the intricate interplay between steric effects and catalytic activity, offering considerations for the rational design of efficient catalysts for ethylene polymerization.

4.2. Introduction

Ultrahigh molecular weight poly(ethylene)s (UHMW-PE) is an engineering polymer with high modulus/high strength, toughness, lightweight and chemical inertness. These exceptional features find unique applications for UHMWPE.^{1,2,3} Since the discovery of Ziegler catalysts for ethylene polymerization, extensive literature has elucidated C-C bond processes in these reactions.⁴ The key strategy for high molecular weight polyethylene production involves enhancing propagation rates relative to transfer and termination or reducing transfer/termination rates.⁵ Critical to this strategy is the design of metal catalysts, focusing on transition metal and ligand selection, homogeneous catalysts with defined active sites, and optimizing propagation while minimizing transfer mechanisms like β -hydride elimination or transfer to aluminum co-catalyst numerous transition metal catalysts, such as Group 4 metallocene's, constrained-geometry catalysts, and post-metallocene's, particularly bis(phenoxy imine) Group 4 Schiff's base metal complexes, yield

a diverse range of linear or branched polyethylenes with medium to high molecular weights and narrow distributions.⁶

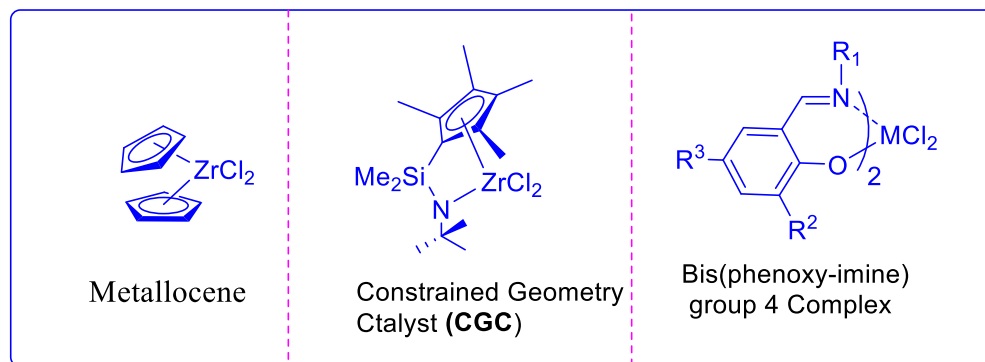


Figure 4.1: High-performance catalysts for olefin polymerization.

Post-metallocene complexes, particularly Group 4 metal bis(phenoxy–imine) complexes, offer an attractive framework for synthesizing high molecular weight polyethylenes (PEs) (Figure 4.1).⁷ However, these complexes often exhibit fluxional behavior, making it challenging to definitively identify the active complex in polymerization, whether with two homo- or heteronuclear bidentate ligands.⁸ The objective of this study is to deepen our understanding of the structure-catalyst-activity relationship in metal complexes, facilitating the design of superior catalysts for the production of ultrahigh molecular weight polyethylenes. Since the 1990s, there has been a proliferation of early and late transition metal catalysts. Notably, the catalysts discovered by Fujita and coworkers at Mitsui in Japan, based on Group 4 bis (phenoxy imine) Schiff's base complexes, have attracted widespread interest.^{9,10} Fujita investigated the use of various cycloalkanes at the imine nitrogen, revealing a significant increase in activity with an enlarged steric environment around the metal center, ranging from cyclopropane to cyclohexane.¹¹

Interestingly, a remarkable and unexpected enhancement in molecular weight was observed with 2-methylcyclohexane compared to cyclohexane.¹² This anomalous behavior might be attributed to the chair-boat conformational equilibrium of the cyclohexane ring. The catalytic ability was significantly enhanced by introducing sterically demanding substituents at the cyclohexyl ring and the ortho position of the phenol ring. Motivated by this discovery, our interest lies in investigating how steric factors around the metal center can suppress β -hydride elimination in polymerization, potentially contributing to the attainment of ultrahigh molecular weight polyethylene.

4.3. Results and discussion

4.3.1. Rational ligand design

Ligands play a pivotal role as essential components in homogeneous catalysis, functioning as molecular tools to finely adjust and govern the behavior of metal complexes.¹³ The meticulous selection and design of ligands enable the customization of catalysts for polymerization reactions. In various instances, it has been demonstrated that ethylene dimerization/oligomerization catalysts able to be controlled to produce polyethylene (PE), a high molecular weight by purposefully modifying the ligand's electronical and steric properties (Figure 4.2). For instance, Fujita investigated the use of various cycloalkanes at the imine nitrogen, revealing a significant increase in activity with an enlarged steric environment around the metal center, ranging from cyclopropane to cyclohexane. Interestingly, a remarkable and unexpected enhancement in molecular weight was observed with 2-methylcyclohexane compared to cyclohexane.¹⁴ This anomalous behavior might be attributed to the chair-boat conformational equilibrium of the cyclohexane ring.

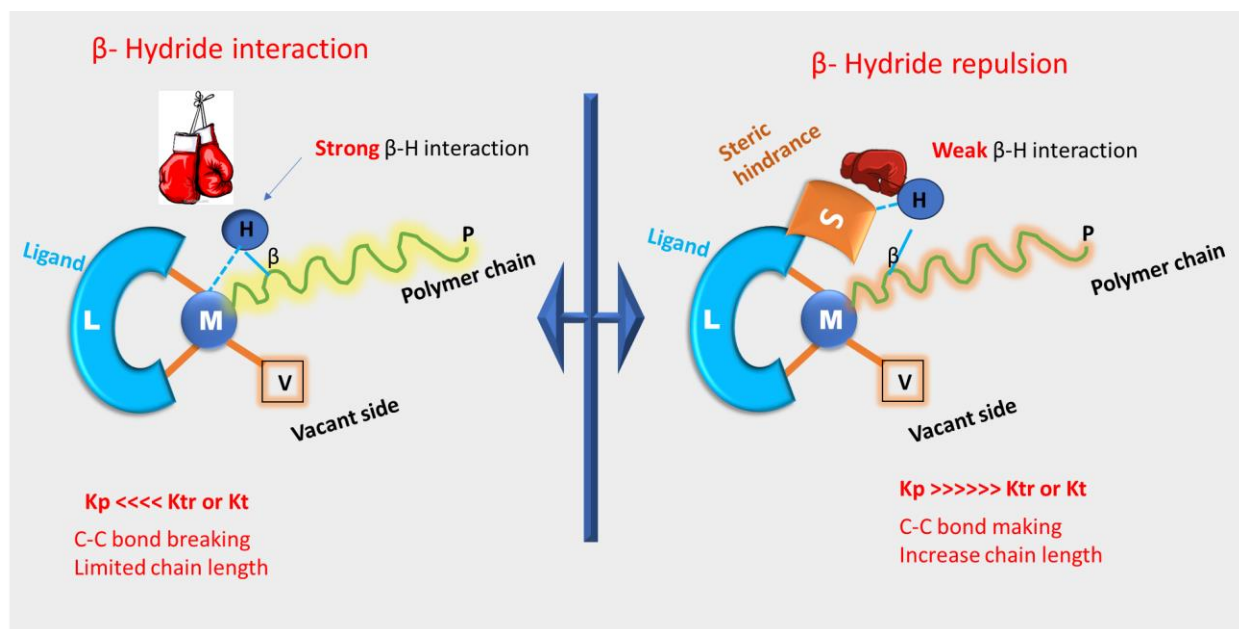


Figure 4.2: Ligand design aimed at suppressing β -hydrogen elimination in catalysis for enhanced control of polymerization reactions.

It is well established that a methyl substituent on the cyclohexyl ring prefers the sterically less demanding equatorial position, evidenced by an equilibrium constant of 19 and an energy

difference of 7.3 kJ/mol between the equatorial and axial conformers. Placing a 2-methyl group in the equatorial position leads to increased steric crowding around the metal center. This arrangement reduces the likelihood of forming a four-membered transition state, a critical element for the β -agnostic interaction mechanism. To support this concept, we have calculated the energy difference between axial and equatorial positions using Density Functional Theory (DFT). The results indicate that in the chair conformation, equatorial methyl and t-butyl substituents are more stable in the imine ligand (Figure 4.3, Table no 4.1)

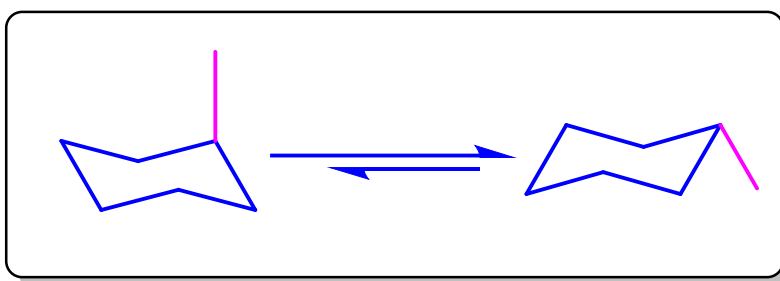


Figure 4.3: Axial -equatorial conformation of substituted hexane.

Table 4.1 Energy difference between axial and equatorial position

Sr. no	Conformations	E _{axial} - E _{equatorial} of cyclohexyl kJ/mol ⁻¹	E _{axial} - E _{equatorial} of imine ligands kJ/mol ⁻¹	% with equatorial substituents
1.	H	0	0	50
2.	Axial_2_Methyl - Equi_2_Methyl	7.29	12.36	95
3.	Axial_2-t-Bu - Equi_2_t-Bu	23.98	26.42	> 99.9

Our objective is to produce ultrahigh molecular weight polyethylene. After an in-depth examination of phenoxy-imine ligand, we were motivated to enhance the ligand's bulk by substituting the methyl group with a tert-Bu group. This modification creates a more crowded environment around the metal, potentially suppressing β -hydride elimination and promoting the

polymer propagation rate, thereby increasing the likelihood of obtaining UHMWPE. The inclusion of the tert-butyl group in the equatorial position introduces significant steric hindrance, influencing the accessibility and favorability of the specific transition state required for β -agnostic interaction. This insight underscores the critical role that ligand substitution patterns and conformational preferences play in shaping the reactivity and mechanism of metal-catalyzed polymerization. Our hypothesis, focused on augmenting bulk at the 2-position on the cyclohexyl ring, is aimed at suppressing β -hydrogen elimination during polymerization, with the ultimate goal of producing UHMWPE (Figure 4.4).

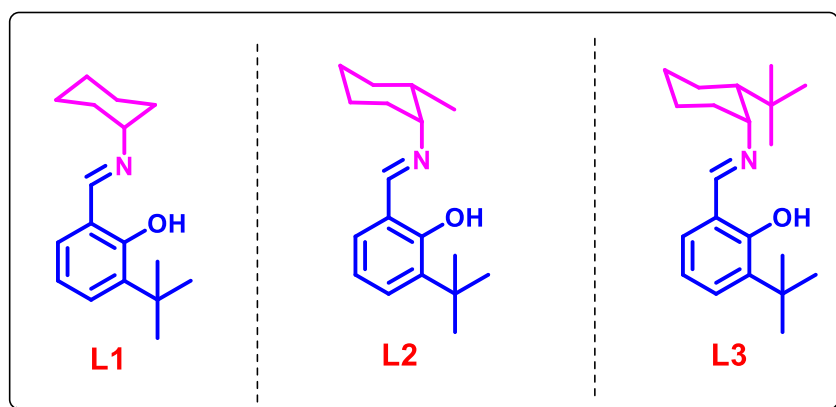


Figure 4.4: Ligands L1-L3 displaying increasing steric.

4.3.2. Rationale for titanium complex

The FI catalysts, utilizing salicylaldimine ligands in group 4 transition metal complexes, show promise. Titanium and zirconium salicylaldimine complexes exhibit notable catalytic efficiency in olefin polymerization, producing high molecular weight and narrow molecular weight distribution for polyethylene or polypropylene.¹⁵ Titanium's superior activity in UHMWPE production stems from its unique catalytic properties, with bulky ligands creating increased steric hindrance around the metal center, suppressing undesired reactions like β -H elimination. This results in improved control over polymerization and higher molecular weights in UHMWPE. Inspired by Fujita's work, we observed a surprising increase in molecular weight with 2-methylcyclohexane compared to cyclohexane. Encouraged by the unique properties of cyclohexylamine ligands,¹⁴ We embarked on the development of group 4 metal complexes incorporating these ligands, specifically focusing on

the synthesis and molecular structures of titanium complexes with cyclohexylamine ligands featuring tertiary butyl substituents. Utilizing DFT, we calculated the energy difference between the axial and equatorial positions of H, 2-Me, and 2-tert-butyl in the titanium complex. The results indicate that the 2-tert-butyl substituent is more stable in the equatorial position, with energy values of $0 < 41.06 < 377.40$ kJ/mol⁻¹, respectively. Additionally, energy calculations between stable conformations in the fractional conformation suggest that the C1 cis complex is more stable (Table 4.2).

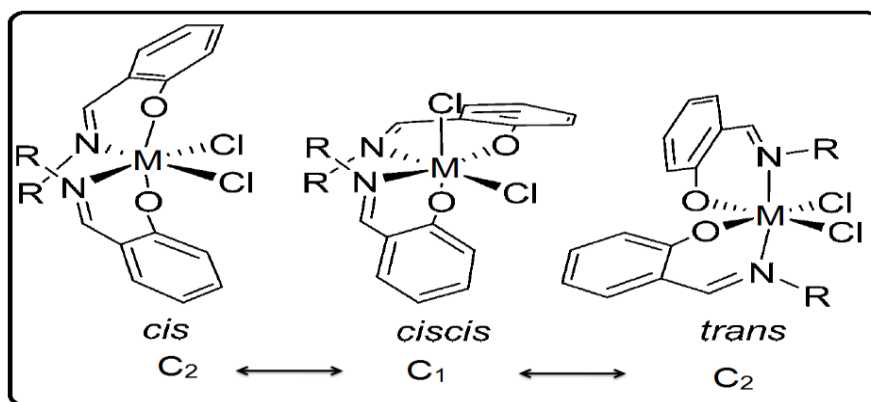


Table 4.2. Energy difference of various isomer in Oh geometry.

Conformations	Energy profile of an overall reaction = -E (kcal/mol)		
	C2 cis imine	C1 Ciscis	C2 Trans imine
Ti_Axial_2_Methyl_Cy6	165.32	164.80	131.57
Ti_Equi_2_Methyl_Cy6	169.01	158.52	135.47
Ti_Axial_tert_butyl_Cy6	169.87	160.35	78.42
Ti_Equi_tert_butyl_Cy6	165.42	92725.39	155.99

As we increased the bulk on the ligand backbone, our curiosity turned to the steric bulk around the metal center. To investigate this, we examined the volume buried (%V Bur), a measurement of the ligand's area in the metal's initial coordination sphere for the suggested titanium complexes. The findings suggest that with the transition from a methyl (Me) to a tert-butyl (tert) substituent, there is an increase in the percentage of buried volume 69.1 to 71.3. (Figure no. 4.5).

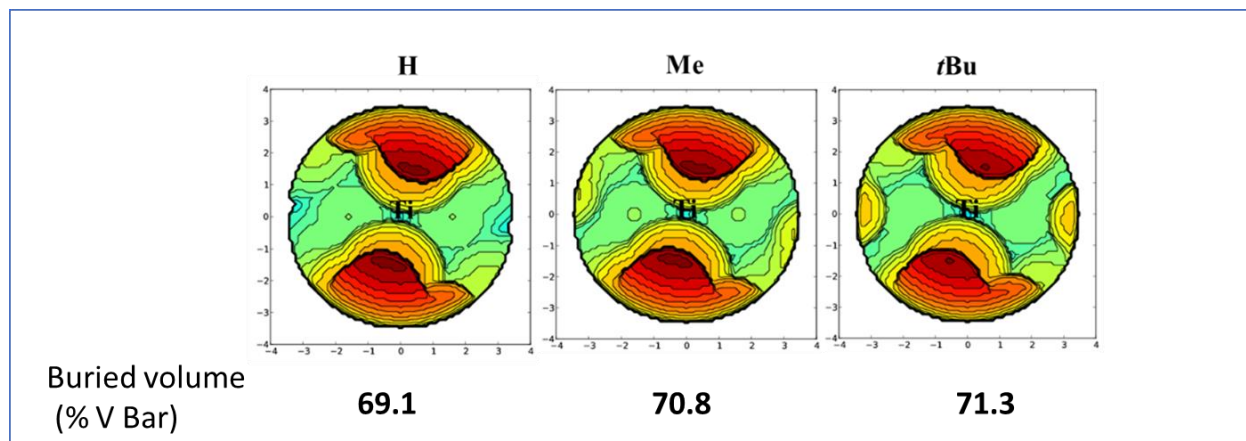


Figure 4.5: Steric quantification of Ti complexes (Buried volume (%V_{bur})).

This study aims to enhance the suppression of β -H hydride elimination, consequently increasing the rate of propagation in polymerization. Our primary focus is to explore the catalytic behaviors of these complexes, specifically in relation to β -H hydride elimination, with the ultimate goal of achieving UHMWPE. Typically, phenoxy systems undergo a two-step treatment with TiCl_4 , forming the lithium/sodium salt followed by reaction with the precursor. However, because TiCl_4 is acidic and imine ligands are intolerant of acidic environments, this approach frequently results in a moderate catalyst yield. In our investigation, seeking a titanium precursor with reduced acidity, we drew inspiration from the work of Marks and co-workers,¹⁶ particularly their prior report involving the use of $[\text{Ti}(\text{NMe}_2)_4]$ with an imino carboxylate ligand. Building on their findings, we successfully activated the system using modified methyl aluminoxane (MMAO).¹⁷

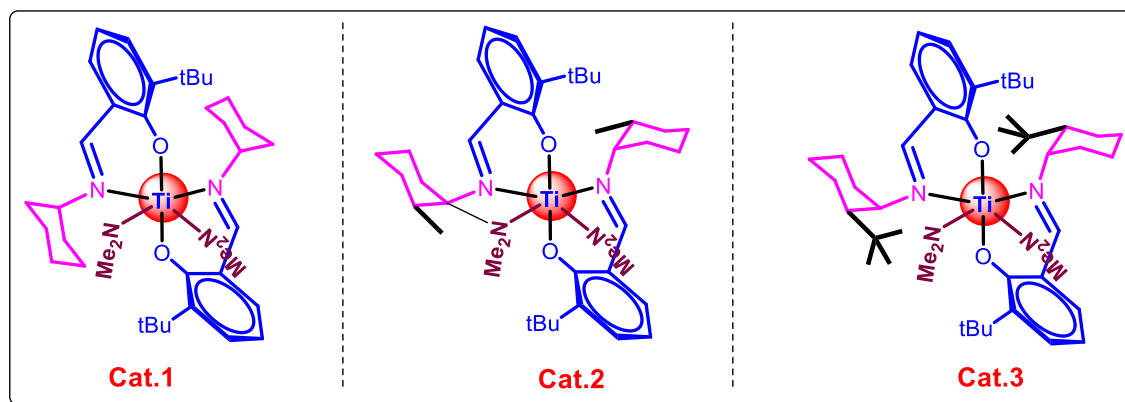
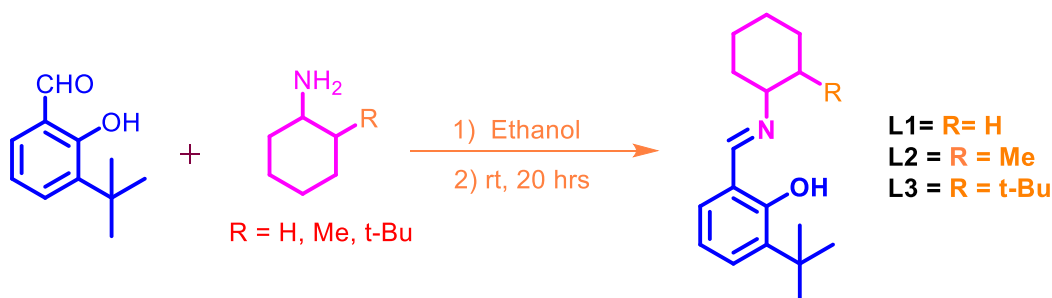


Figure 4.6: Titanium complexes Cat.1- Cat.3.

We hypothesized that the titanium congener of the reported zirconium complex could potentially suppress the cleavage of L1-L3 (imine bond). This is because the by-product of the reaction is a base (HNMe_2), and this suppression may allow the coordination of phenoxy-cycloalkyl-imine ligands, enabling the formation of a mononuclear titanium complex (Fig. 4.6).

4.3.3. Synthesis of phenoxy-cycloalkyl-imine ligands and their Ti-complexes

To elaborate further, the salicylaldehyde derivatives employed for ligand synthesis were obtained using established procedures¹⁴ (Scheme 1). In particular, the ligands of phenoxy-cycloalkyl-imine Synthesis of compounds L1–L3 was accomplished with essentially quantifiable yields (> 99%). This synthetic method used the condensation of Schiff bases, where the matching cycloalkyl amine reacted with the derivative of salicylaldehyde. Consequently, the ligands were thoroughly characterized using various spectroscopic techniques,



Scheme 4.1: Synthesis of phenoxy-cycloalkyl-imine ligands L1-L3.

In the experimental procedure, (5.6 mmol) 3-tert-butylsalicylaldehyde at room temperature, cyclohexylamine (8.4 mmol) was added gradually after 30 mL of ethanol had been used to dissolve it. Under normal circumstances, the resultant mixture was agitated for eighteen hours. Following the reaction time, volatiles were removed under reduced pressure, leaving behind a crude imine **L1** with a sticky consistency. Subsequently, using n-hexane as a mobile phase, the unrefined imine product was purified using column chromatography on silica gel. This purification process afforded imine 2-(tert-butyl)-6-((cyclohexyl imino) methyl) phenol **L1** in the form of a yellow oil, with a yield of 90 %, representing an impressive 99 % efficiency.

A spectrum of ^1H NMR of the isolated compound revealed a distinctive proton of imine at 8.39 ppm and a ^{13}C NMR spectra showed the matching carbon at 162.3 ppm. The short-range through bond C-H correlation spectrum (HSQC) confirmed that the proton at 8.39 ppm shows 162 ppm is the cross peak to carbon. Mass analysis further supported the NMR results, The peak of molecular ions at $m/z = 260 [\text{M}+\text{H}]^+$ Da was revealed. This can be attributed to **L1**. The simulated pattern and the observed mass and isotopic pattern are exactly the same. The compound's infrared spectra showed a C=N stretching band at 1618 cm^{-1} , further authenticating the presence of imine phenol groups. Along the same line **L2**, 2-(tert-butyl)-6-(((2-methylcyclohexyl) imino) methyl) and **L3**, 2-(tert-butyl)-6-(((2-tert butyl cyclohexyl) imino) methyl) phenol formed readily upon mixing with 3-tert-butyl salicylaldehyde and 2-methyl cyclohexylamine or 2-tert-butyl cyclohexylamine. Both ligands were isolated in excellent yields (90-95%). NMR, IR, and mass spectroscopy methods were used in combination to definitively confirm their identity. **L3** Ligand was meticulously characterized through single crystal X-ray diffraction, with an in-depth examination of its molecular structure (refer to Figure 4.30a). Crystals suitable for single crystal measurements were obtained using the slow evaporation method from a hexane solution. The between the carbon and nitrogen atoms in the ligand analysis uncovered a C=N distance of 1.28 Å, signifying a stable and well-defined bond.

Additionally, specific details regarding the spatial arrangement of atoms were revealed. The distance between the two tert-butyl groups on the cyclohexyl ring and the imine nitrogen was

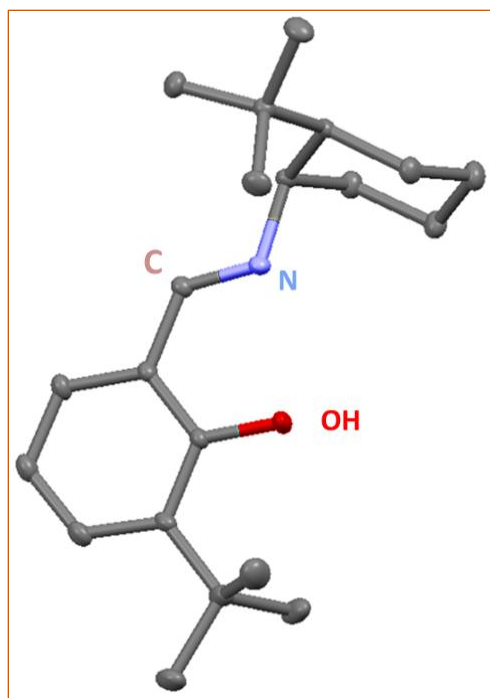
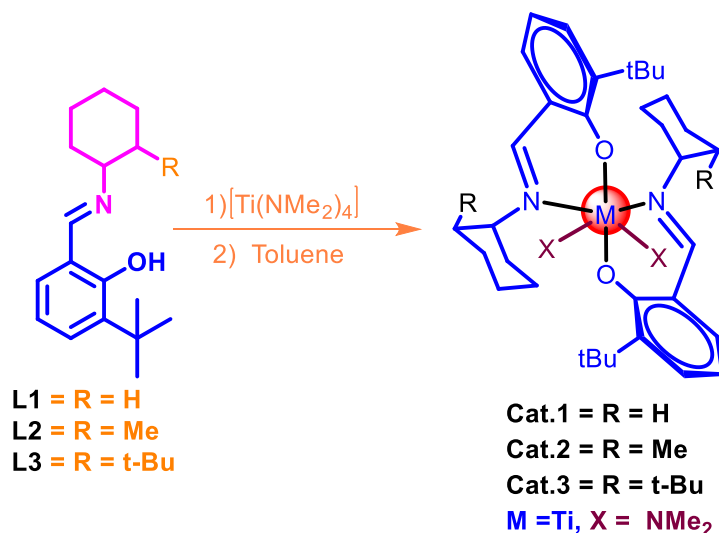


Figure 4.7: Molecular structure of ligand **L3** 2-(tert-butyl)-6-(((2-tert butyl cyclohexyl) imino) methyl) phenol (H-atoms omitted for clarity, except the imine C–H atom; 50% probability thermal ellipsoids).

found to be 3.4 Å, with these groups positioned in the equatorial position (bond angle 116.1°). The imine group was found in the axial position (angle between 109°), and both were cis to each other. Notably, the imine nitrogen, OH group, and tert-butyl group on the salicylic ring were on the same side and other information is as: space group $P 2_1/c$, Cell lengths- **a** 11.3140(4) **b** 12.9007(4) **c** 13.6816(4), Cell Angles- α 90 β 110.1330(10) γ 90, Cell Volume-1874.93, R-factor (%) -9.47.

Following the successful synthesis and characterization of all imine ligands, the subsequent step involved treating these ligands with a titanium metal precursor for complexation. This critical stage aimed at forming complexes by combining the imine ligands with the titanium metal precursor. The treatment with the titanium metal precursor served as a pivotal phase in further exploring the reactivity and coordination chemistry of the synthesized imine ligands. In our investigation, inspired by the work of Marks and co-workers, particularly in our previous study involving $[\text{Ti}(\text{NMe}_2)_4]$ with an imino carboxylate ligand, we sought a titanium precursor with reduced acidity. Building on their findings, we successfully activated the system using MMAO. This strategic modification was aimed to mitigate the adverse effects of acidic conditions on imine ligands, and

provide a more favorable environment for the synthesis of phenoxy systems and enhancing the overall catalyst performance. Synthesis of the [bis-dimethyl amido-Ti-(bis-[N-(3-tert-butylsalicylidene) cyclohexylaminato]] complexes outlined in this study is presented in Scheme 4.3.



Scheme 4.2: Synthetic procedure for complexes Cat.1- Cat.3

According to this approach, two equivalents of phenoxy-cycloalkylimine ligands **L1** was treated with one equivalent of tetrakis (dimethyl amido-titanium) $[Ti(NMe_2)_4]$ at 0 °C. Following the addition, the temperature of the reaction solution was brought up to ambient (about 35 °C), and stirring was maintained for two hours. Subsequently, volatiles were evaporated, and the titanium complex **Cat.1** were isolated in a 56 % yield. The synthesis of the phenoxy-cycloalkylimine-Ti $(NMe_2)_2$ complex was a straightforward process, and the resulting by product $[Me_2NH]$ could be readily evaporated from the reaction mixture. The reddish-brown crystalline solid of complex **Cat.1** (Scheme 4.3) was then subjected to detailed characterization. A 1H NMR spectrum of the isolated compound disclosed a up field shift of imine proton at 8.37 ppm to at 8.09 ppm and in a ^{13}C NMR spectra, the matching carbon was detected at 165.0 ppm, and the cyclohexyl proton moved from 3.22 ppm to 3.44 ppm. The short-range through bond C-H correlation spectrum (HSQC) confirmed that the proton at 8.09 ppm shows carbon at a cross peak 165.0 ppm (Fig. 4.8). Mass analysis provided additional confirmation of the NMR results, this revealed a signal for molecular ions at $m/z = 608.3 [Cat.1-NMe_2]^+ Da$, that can be assigned to **Cat.1**. The simulated pattern and the observed mass and isotopic pattern are exactly the same.

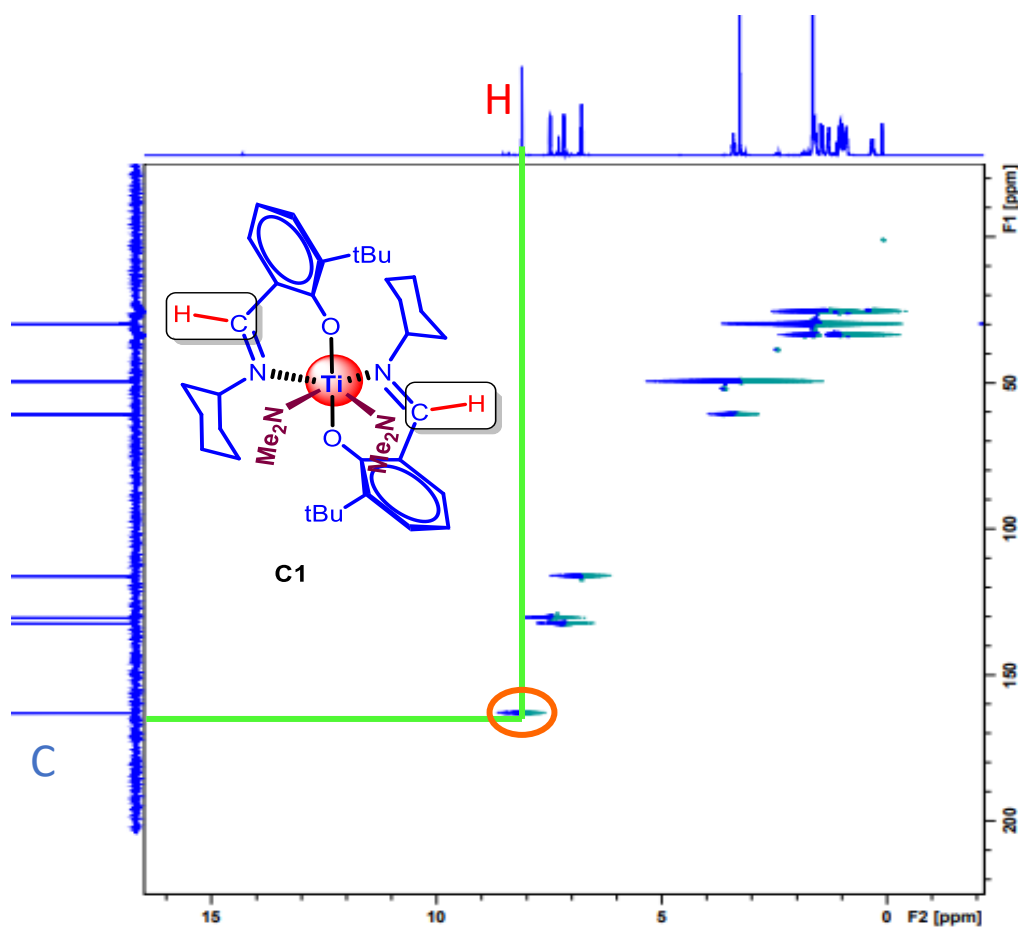


Figure 4.8: ^1H - ^{13}C HSQC NMR spectrum of Cat.1 in CDCl_3 (500 MHz).

A similar synthesis protocol, as employed in the preparation of **Cat.1**, was followed for the treatment of ligands **L2** and **L3** with $[\text{Ti}(\text{NMe}_2)_4]$. The resulting products, namely **Cat.2** and **Cat.3**, were successfully isolated in good yield.

Table 4.3: Characteristic NMR chemical shifts for L1-L3 and Cat.1-Cat.3.

Complex functional group	Cat. 1 (ppm)		Cat. 2 (ppm)		Cat. 3 (ppm)	
	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C
HC=N	8.0	163.0	8.0	163.3	8.7	
-OH	NA	162.1	NA	163.0	NA	138.7
CH C-NH₂	3.4	60.7	2.2	67.3	2.4	52.3
Free ligand	L1		L2		L3	
HC=N	8.36	162.9	8.2	166.6	8.39	163.4
-OH	14.3	160.6	14.1	163.6	14.4	160.7
CH C-NH₂	3.22	67.6	2.6	76.4	3.8	66.5

NA: Not applicable. NMR was recorded in CDCl₃ at room temperature.

The noted up-field shift among the imine proton within the three complexes, as indicated in Table 4.3, compared to the free ligand, indicates that the titanium centre is being coordinated with the imine nitrogen's lone pair. This shift is indicative of changes in the electronic environment surrounding the imine group upon complexation, providing clear evidence for the formation of coordination bonds between the imine nitrogen and the titanium center in the synthesized complexes. The coordination induced changes in chemical shift are a common phenomenon in NMR spectroscopy and are consistent with the imine ligands' coordination with the titanium metal centre in the complexes under investigation. In addition to NMR spectroscopy, characterization of **Cat.2** and **Cat.3** was conducted using ESI-MS. Pseudo-molecular ion peaks were observed at $m/z = 636.4$ for $[\text{Cat.2-NMe}_2]^+$ and 765.5 for $[\text{Cat.3} + \text{H}]^+$. These findings provide additional confirmation for the existence of the titanium complexes **Cat.2** and **Cat.3**. The observed mass-to-charge ratios align with the expected molecular ions, supporting the formation of the desired complexes and adding further analytical evidence to the comprehensive characterization of the synthesized compounds. All complexes have characterized by X-ray photoelectron microscopy (fig.no 4.9) in it the all complex show the binding energy Ti2p 1/2 from 457.9 eV to 458.5 eV and Ti 2p 3/2 from 463.6 eV to 464.2 eV, X-ray photoelectron spectroscopy (XPS) is a technique used to analyze the elemental composition

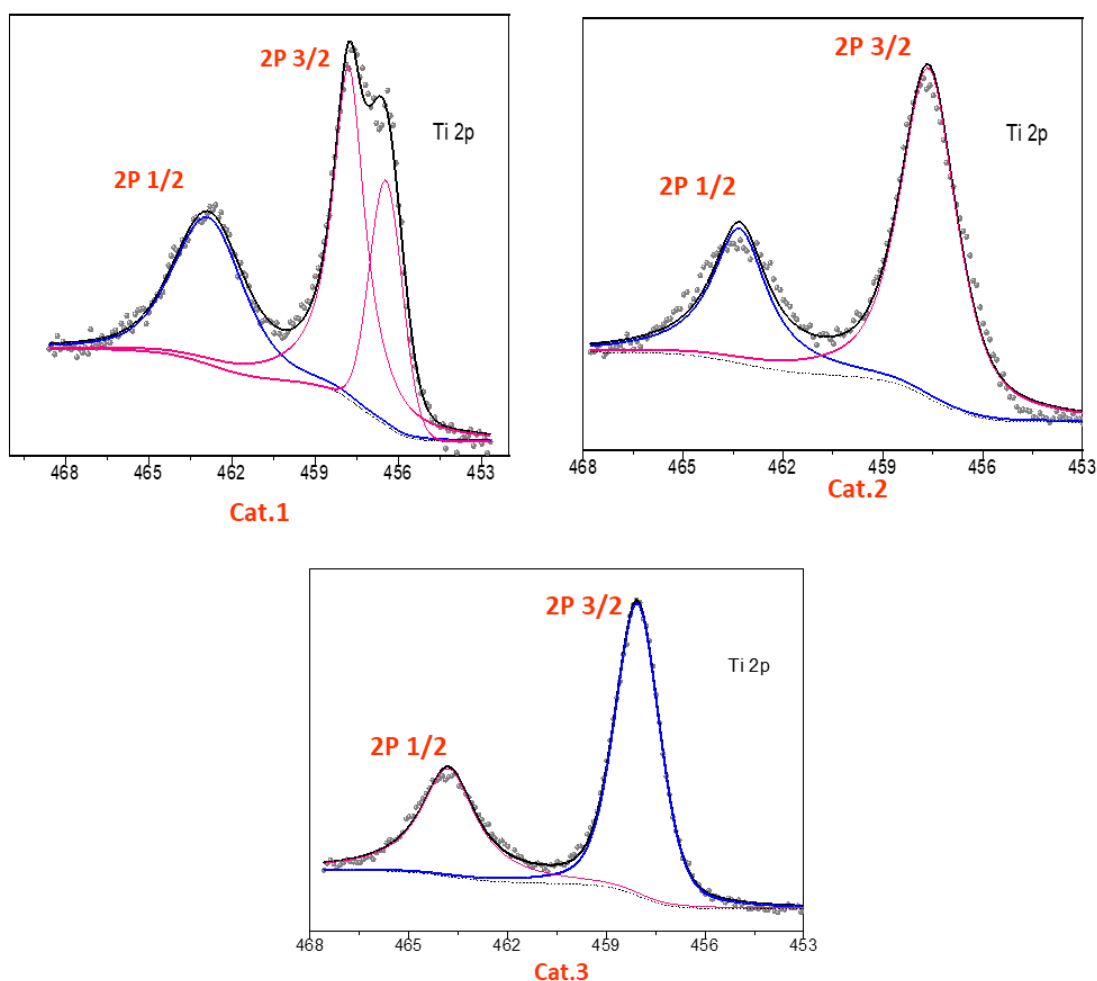


Figure 4.9: XPS analysis of Cat.1 - Cat.3.

and chemical state of materials by measuring the binding energies of core-level electrons. In this study, XPS was employed to characterize the complexes synthesized. The XPS spectra showed characteristic peaks corresponding to the binding energies of the Ti2p core-level electrons.

For the Ti2p core-level electrons, the binding energy values observed ranged from 457.9 eV to 458.5 eV for Ti2p 1/2 and from 463.6 eV to 464.2 eV for Ti 2p 3/2 across all complexes. These binding energy values are indicative of the oxidation state of titanium, specifically Ti^{+4} . The consistency in these binding energy values across all complexes suggests that the oxidation state of titanium remains constant within the synthesized compounds. This information is crucial for confirming the chemical composition and structural properties of the complexes, providing

valuable insights into their electronic structure and potential reactivity in catalytic processes or other applications

4.4. Ethylene polymerization using Cat.1 – Cat.3

Having successfully established the synthesis of phenylcyclohexylimine titanium complexes, our focus shifted to investigate their reactivity towards ethylene. In the context of insertion polymerization reactions, the rates of ethylene insertion and termination play crucial roles in determining the final outcome. To achieve a high molecular weight polymer, it is essential for the rate of ethylene insertion to far exceed the rate of termination of the growing chain. This careful balance in reactivity is key to obtaining a polymer with the desired molecular weight and properties. Our exploration aimed to understand and optimize these reaction kinetics for effective ethylene polymerization as per our hypothesis, our goal is to investigate the steric effects in polymerization. To mitigate these effects, we propose employing β -hydrogen elimination. A rise in the rate of propagation, exceeding the rates of termination and transfer, is the expected result. It is worth noting that these catalysts have been activated by MMAO, and we expect this activation to play a crucial role in enhancing their reactivity. By strategically managing steric effects through β -hydrogen elimination and leveraging the catalyst activation, we aim to achieve a polymerization process where the rate of propagation significantly outpaces termination and transfer reactions, leading to the synthesis of high molecular weight polymers with desirable properties. The ethylene polymerization data is summarized in table no 4.4 and 4.5.

Table 4.4: Polymerization of ethylene catalyzed by Cat.1-3 in the presence of MMAO12.

Sr. No.	Catalysts - Loading (mg)	MAO Al/Ti Ratio	Temp. (°C)	Time (Min)	Yield g ^b	^f Activity Kg of PE/Mol of Ti/h	^c M _w (g/mol)	^c Đ M _w /M _n	T _m ^d	^e Cryst. (%)
1.	Cat.1-20	500	40	30	1.5	93.7	1.01×10^5	2.0	141	95.3

2.	Cat.1-20	1000	40	30	4	250	9.15×10^5	2.3	140.7	90.9
3.	Cat.1-20	1500	40	30	5.5	343.7	9.57×10^5	1.5	139.7	86.1
4.	Cat.1-20	2000	40	30	4	250	9.39×10^5	1.7	138.5	68.6
5.	Cat.2-20	500	40	30	0.900	62.0	2.75×10^6	2.1	143.1	82.5
6.	Cat.2-20	1000	40	30	3	206.8	1.56×10^6	2.2	142.1	87.5
7.	Cat.2-20	1500	40	30	3.8	262	2.25×10^6	1.7	142	89.6
8.	Cat.2-20	2000	40	30	7.4	510.3	1.66×10^6	1.8	139.3	57.2
9.	Cat.3-20	1000	40	30	0.72	55.3	6.8×10^5	1.8	138.3	77.9
10.	Cat.3-20	2000	40	30	0.993	76.3	1.04×10^6	1.5	134.9	65.8
11.	Cat.2-5	2000	40	30	1	293.9	2.19×10^6	1.6	142.3	90.7
12.	Cat.2-10	2000	40	30	3.2	457.1	1.59×10^6	1.7	141.4	81.4
13.	Cat.2-15	2000	40	30	5.2	472.7	1.76×10^6	2.3	142.4	70.9
14.	Cat.2-5	2000	40	5	0.100	165	6.69×10^5	2.3	139.2	86.7
15.	Cat.2-5	2000	40	10	0.900	742.6	2.09×10^6	2.1	141.6	78.4
16.	Cat.2-5	2000	40	15	0.400	219	1.45×10^6	3.0	141.8	93.2
17.	gCat.2-5	2000	40	10	0.320	274	1.81×10^6	1.9	140.7	91.1
18.	hCat.2-5	2000	40	10	0.373	319	2.25×10^6	2.1	141.9	56.5
19.	Cat.2-5	2000	25	10	0.120	102	1.79×10^6	1.8	140.6	78
20.	Cat.2-5	2000	60	10	0.860	736.3	1.0×10^6	2.3	140.4	69.2
21.	Cat.2-5	2000	80	10	1.75	1498	5.88×10^5	1.8	140.4	69

22.	Cat.2-20	2000	25	30	3.4	245.5	2.63×10^6	1.9	140.6	44.8
23.	Cat.3-20	1000	25	30	0.225	17.3	1.19×10^6	1.8	138.2	82.6
24.	Cat.1-5	2000	40	10	0.537	459.7	1.01×10^6	2.1	140.9	90
25.	Cat.3-5	2000	40	10	0.050	42.8	2.0×10^6	1.8	137.9	43
26.	Cat.3-5	2000	60	10	0.085	81.7	9.24×10^5	1.9	138.2	43.2
27.	Cat.3-5	2000	80	10	0.090	86.5	5.2×10^5	2.3	138/13 1	-
28.	Cat.1-5	2000	60	10	0.397	629.3	6.85×10^5	2.1	140.6	90
29.	Cat.1-5	2000	80	10	0.430	353.6	2.87×10^5	1.9	135.2	39.5

^a Conditions: Catalyst = 31 μ mol; Solvent = 100 mL of toluene; ethylene-2 bars; ^b Obtained from polyethylene produced; ^c Mw = Wt. average molecular weight and PDI were determined at 160 °C in TCB using HT-GPC. ^d Obtained from DSC, heating and cooling curves of first heating cycle; ^e Crystallinity calculated from the melting enthalpy measured by DSC and relative to the theoretical value (293 J/g) for 100% crystalline polyethylene; ^f Activity in Kg of PE/mol Ti/h, ^{g,h} ethylene press. 4 bar and 6 bar.

The Ti-complexes Cat.1 to Cat.3 were treated with varying equivalents of MMAO under 2 bar ethylene pressure at 40 °C (entry no 1-10). The systematic evaluation of reaction activities revealed that, **Cat. 2**, particularly with 2000 equivalents of MMAO, exhibited superior activity of 510.3 Kg of PE/mol Ti/h (Mw = 1.01×10^5 to 2.75×10^6 g/mol which UHMWPE), surpassing the activities of complexes 1 (250 Kg of PE/mol Ti/h) and 3 (76.3 Kg of PE/mol Ti/h). This suggests that the specific conditions and the combination of **Cat. 2** with MMAO contribute to a more efficient catalyst for ethylene polymerization.

A higher steric bulk of the cycloalkyl group on the imine-N results in increased activity for catalysis, according to the overall trend in catalytic activity that has been observed, with the exception of **Cat. 3**. However, it is notable that, in the case of **Cat. 3** (entry no 10), Catalytic activity (76.3 Kg of PE/mol Ti/h) can be reduced by excessive steric congestion brought about by

the substituent at the active site, however UHMWPE may result with $M_w = 1.04 \times 10^6$ g/mol. This reduction in activity is likely because it prevents the monomer from reaching its active location and/or stops the polymer chain from growing. These results imply that there may be two conflicting impacts on catalytic activity when steric bulk is introduced close to the active site. While moderate steric effects enhance activity, excessive steric hindrance near the active site may impede the polymerization process. This observation underscores the delicate balance required in designing catalyst structures, considering the influence of steric factors on the efficiency of the catalytic reaction. Further exploration and optimization of catalyst structures can contribute to a nuanced understanding of how steric effects impact catalytic activity in ethylene polymerization.

Moreover, **Cat. 2** was further utilized for additional parameter optimization. Catalyst loading was screened from 7.3 μmol to 22 μmol , and at 22 μmol of catalyst loading (entry no.11-13) with 2000 equivalents of MMAO, at 472.7 kg of PE/mol Ti/h ($M_w = 1.76 \times 10^6$), the maximum activity was recorded. Further, while keeping the catalyst loading constant at 7.3 μmol , the polymerization time was varied from 5 to 30 minutes (entry no 14-16), with the optimum activity of 724 Kg of PE/mol Ti/h ($M_w = 2.09 \times 10^6$ g/mol) achieved at a 10-minute reaction time. These additional parameter optimizations contribute to a more detailed understanding and fine-tuning of the ethylene polymerization process using **Cat. 2**. Furthermore, we optimized the pressure (entries 15, 17, 18) from 2 bar to 6 bar. Interestingly, at 2 bars of pressure, ethylene exhibited higher activity (742.6 Kg of PE/mol Ti/h and $M_w = 2.09 \times 10^6$ g/mol) compared to both 2 and 6 bars. Subsequently, using cat. 2, we fine-tuned the temperature. Considering that higher temperatures promote Beta hydride elimination, in our investigation, we explored a temperature range spanning from 25 to 80 °C to assess its impact on catalytic performance. Remarkably, at a temperature of 80 °C, we observed superior performance, yielding 1498 Kg of PE/mol Ti/h, compared to other temperature settings (entries 19, 20, 21). This finding suggests that the increased temperature enhances catalytic activity, indicating that, Cat.2 exhibits high thermal stability and effectively suppresses β -hydride elimination. This inference is supported by its relatively high molecular weight (6×10^5 g/mol), indicative of efficient polymer chain growth. Motivated by these results, we conducted further investigations on Cat.1 and Cat.3 despite displaying increased activity with rising temperature, Cat.1 exhibits a lower molecular weight ($M_w = 2.8 \times 10^5$ g/mol), indicating a propensity for β -hydride elimination. On the other hand, cat.3 demonstrates the ability to suppress β -hydride

elimination. However, due to the presence of high steric bulk around the metal center, it has less catalytic activity than cats 1 and 2. Furthermore, we calculated the molecular weight using the HT-GPC technique for the obtained polyethylene, yielding a range of $M_w = 1.01 \times 10^5$ to 2.75×10^6 .

To our surprise, transitioning from MMAO to a combination of triisobutylaluminum ($i\text{Bu}_3\text{Al}$) (250 μmol) and tetrakis(pentafluorophenyl)borate ($\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$) (2 equiv.) resulted in the production of exceptionally high molecular weight polyethylenes (PEs). Specifically, under these conditions, **Cat.2** exhibited a remarkable molecular weight (M_w) of 5.53×10^5 g/mol. Although the activity was moderate compared to MMAO (entry no 6), subsequent optimization efforts were undertaken. Upon adjusting the polymerization time from 5 minutes to 30 minutes, we observed an increase in both yield (0.293 g) and activity (483.5 kg of PE/mol of Ti/h), with the optimal activity achieved at 5 minutes (entry no 1-3).

Table 4.5: Polymerization of ethylene catalyzed by Cat.1-3 in the presence of triisobutylaluminium (TiBA) and Triphenylmethylium tetrakis (per fluorophenyl) borate (BT).

Sr. No.	Catalysts-Loading (mg)	TiBA and Borate (2 equiv.) Al/Ti Ratio (μmol)	Temp. ($^{\circ}\text{C}$)	Time (Min)	Yield g^{b}	$^{\text{f}}$ Activit y Kg of PE/Mol of Ti/h	$^{\text{c}}$ M_{w}	$^{\text{d}}$ Mw/Mn	T_{m}^{d}	$^{\text{e}}$ Cyst. (%).
1	Cat.2- 5	250	40	30	0.833	228.2	1.25×10^5	1.9	142.9	92.4
2	Cat.2-5	250	40	15	0.596	326.5	1.0×10^6	2.1	142.7	85.4
3	Cat.2-5	250	40	5	0.293	483.5	4.15×10^5	2.2	141.9	82.5
4	Cat.2-5	500	40	5	0.263	434.0	8.04×10^5	1.5	142.1	94.8
5	Cat.2-5	125	40	5	0.143	244.8	7.53×10^5	1.8	141.4	90.2
6	Cat.2-5	250	50	5	0.367	605.7	5.53×10^5	2.1	142.2	95
7	Cat.2-5	250	80	5	0.960	821.9	9.52×10^5	2.0	143	89.5
8	Cat.2-5	250	25	5	0.078	133	5.63×10^5	2.5	140.8	89.7
9	Cat.2-5	250	50	5	0.290	248.2	7.13×10^5	2.3	143.9	99.6
10	Cat.2-5	250	50	5	0.360	308.2	5.14×10^5	2.5	142.9	96.2
11	Cat.1-5	250	50	5	0.109	172.7	4.33×10^5	2.7	142.7	44.6
12	Cat.3-5	250	50	5	0.006	11.1	ND	NA	141.7	85.8

^a Conditions: Catalyst = 7 μmol ; TiBA and BT 250 μmol and 2 eq. Solvent = 100 mL of toluene; ethylene = 2 bars; ^b Obtained from polyethylene produced; ^c M_{w} = Weight average molecular weight and PDI were determined by HT-GPC at 160 $^{\circ}\text{C}$ in TCB solvent against PS standards. ^d Obtained from DSC, heating and cooling curves of first heating cycle; ^e Crystallinity calculated from the melting enthalpy measured by DSC

and relative to the theoretical value (293 J/g) for 100% crystalline polyethylene; ^f Activity in Kg of PE/mol Ti/h, ^{g,h} ethylene press. 4 bar and 6 bar., ND = Not determined.

Maintaining the polymerization time constant at 5 minutes and catalyst loading at 7 μmol , we further optimized the temperature from 25 to 80 °C. Remarkably, increasing the temperature resulted in enhanced activity, reaching 821.9 kg of PE/mol of Ti/h and molecular weight as well ($M_w = 9.52 \times 10^5$ g/mol). This optimization allowed us to achieve significant improvements in the polymerization process, demonstrating the potential for fine-tuning reaction conditions. These results suggest that Zr-FI catalysts, when combined with $i\text{Bu}_3\text{Al}$ / $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ co-catalyst systems, are also suitable for the production of UHMWPE.

4.4.1. Disentangled ultrahigh molecular weight polyethylene with high crystallinity (d-UHMWPE)

Detailed characterization was conducted on the polyethylene generated under optimized polymerization conditions. HT-GPC was used to determine the molecular weight of the produced PE. The HT-GPC analysis of polyethylene in trichlorobenzene (TCB) at 160 °C revealed the formation of ultrahigh molecular weight polyethylene (UHMWPE) with a molecular weight of more than 2 million g/mol. Interestingly, the narrow polydispersity index (2-4) indicates catalytic behavior at a single location. The melting temperature and crystallization data of the PE were measured using differential scanning calorimetry. The melting temperature from the first heating is considered. The melting temperature (T_m) of polyethylene manufactured using **Cat.1** to **Cat.3** was higher (137-140 °C) than standard commercial PE grades, indicating high order or crystallinity. A representative sample with M_w of 1.1 million g/mol (Table 4.4, entry 23) showed a high crystallinity of 82.6 %. Active catalysts and polymerization conditions enable highly crystalline PE by crystallizing the expanding polymer chain. PE crystallization during chain growth prevents entanglement, resulting in disentangled ultrahigh molecular weight polyethylene (d-UHMWPE). Thus, we expected the resulting UHMWPE to be disentangled. First melting peak observed for reactor PE is due to melting of single crystal lamellae, indicating the “disentangled” state of UHMWPE. Literature procedures were used to demonstrate the disentangled nature of UHMWPE produced using Cat.2 and 3. A unique DSC method was created, with Fig. 4.97 illustrating its processes. Rastogi and colleagues developed a DSC approach to analyze UHMWPE melt behavior, distinguishing between “entangled” and “disentangled” domains. Heat UHMWPE from 50°C to

160°C (@10°C/min) (Fig. 4.97) and anneal the sample at 160 °C for a set time (Fig.4.97). Staying at 160 °C allows UHMWPE polymer chains to reach the thermodynamically stable “entangled” state (b and c).

The polymer sample may exhibit different degrees of “entangled” and “disentangled” domains (heterogeneity) depending on the annealing time in steps b-c. Following cooling to 128 °C (c and d), the sample undergoes isothermal crystallization for 180 minutes (d and e) prior to cooling to 50 degrees Celsius (e and f). The specimen was heated from 50 °C to (g-h) 160 °C. The data from the g-h heating stage is shown in Fig. 4.9.1. Fig. 4.9.1 (blue line) shows two melting domains. The initial high melting peak at 134-140 °C is believed to arise from a crystalline domain, indicating the “disentangled” condition of UHMWPE. The high melting disentangled domain vanishes at 60 min of annealing, revealing a single melting peak (Fig. 4.9.1, pink line). UHMWPE entangled domains caused the second melting peak at 133-134 °C. The observations align with prior reports on “entangled” and “disentangled” UHMWPE.¹⁸

The DSC experiment reveals that catalyst, Cat.3 disentangles UHMWPE by polymerizing ethylene. We compared the DSC thermogram of commercial entangled UHMWPE to our disentangled version.

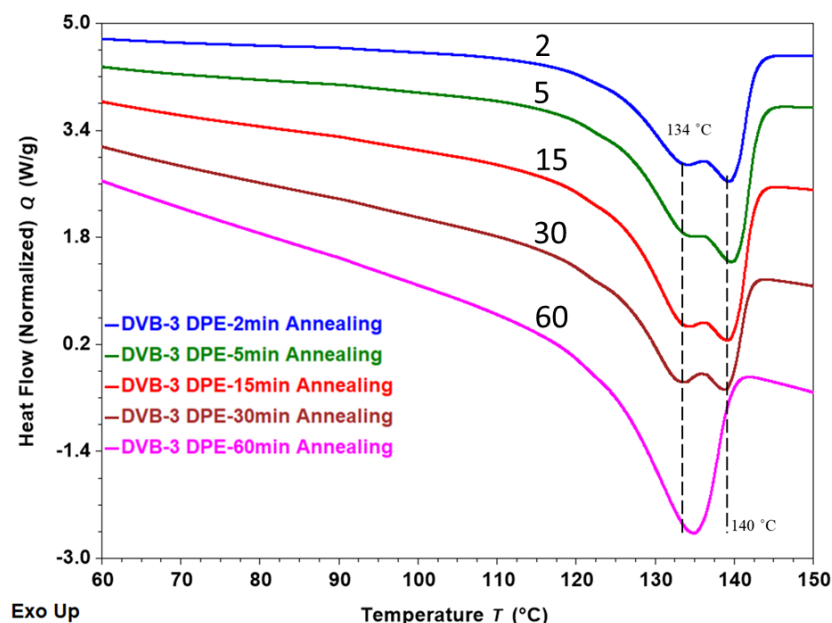


Figure 4.10: DSC plot of the d-UHMWPE sample (Table 4.4, entry 23) annealed for 2 (blue line), 5 (green line), 15 (red line), 30 (brown line) and 60 (pink line) minutes.

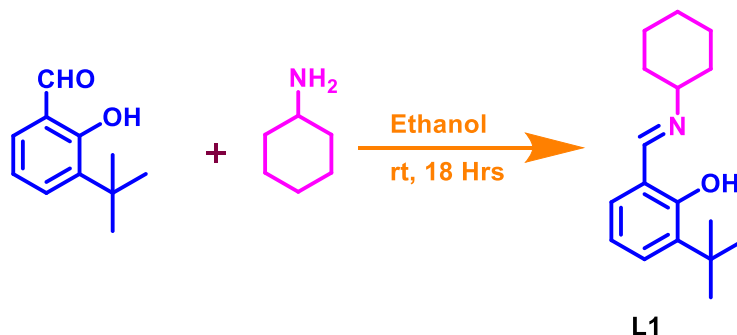
4.5. Experimental section

4.5.1. Materials and methods

Unless noted otherwise, all manipulations were carried out under an inert atmosphere of argon using standard Schlenk line techniques or M-Braun glove box. Hexane and toluene were distilled from sodium/benzophenone under argon atmosphere. Methylene chloride was distilled on calcium-hydride. 3-tert-butylsalicylaldehyde was purchased from Sigma Aldrich Pvt. Ltd. Cyclohexyl amin and 2 me cyclohexyl amine and $(\text{TiNMe}_2)_4$ procured from Sigma-Aldrich. Ethanol (commercial grade, 99.9%) was obtained from Brampton, Canada. All other solvents were purchased from local suppliers (Spectrochem Pvt. Ltd.; Avra Synthesis Pvt. Ltd.). Ethylene (99.95%; 3.5 grade) was supplied by Ms. Vadilal Chemicals Ltd., Pune, India. Ethylene polymerization was carried out in a 250 mL stainless steel high pressure Büchi (glasuster cyclone 075) reactor equipped with a mechanical stirrer and a heating/cooling jacket. NMR was recorded on Bruker Avance 400 and 500 MHz instruments. Chemical shifts are referenced to external reference TMS (1 H and 13 C). Coupling constants are given as absolute values. Multiplicities are given as follows: br s: broad singlet, s: singlet, d: doublet, t: triplet, m: multiplet. Mass spectra were recorded on a Thermo scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150×4.6 mm diameter 8 μm particle size, and the mobile phase used is 90% methanol + 10% water + 0.1% formic acid. IR spectra were recorded on Bruker VERTEX 80 spectrophotometer. The samples were prepared as Nujol mull. C, H, and N analyses were carried out using PerkinElmer 2400 instrument. The X-ray diffraction measurements were carried out using a Bruker SMART APEX CCD diffractometer with graphite-monochromatized ($\text{Mo K}\alpha = 0.71073 \text{ \AA}$) radiation. Differential scanning calorimeter (DSC) was carried out on DSC Q-10 equipment from TA instruments with a heating and cooling rate of 10 K min^{-1} , unless mentioned otherwise. Molecular weight was determined using high-temperature GPC (HT-GPC) at 160°C with a Polymer Char instrument, IR-4 detector, and GPC control software. Calibration was performed using polystyrene standards.

4.6. Ligand synthesis

4.6.1. 3-(tert-butyl)-6((cyclohexylimino)methyl) phenol (L1)



3-tert-butylsalicylaldehyde 40 mL of ethanol was used to dissolve 1 g, 5.6 mmol, Cyclohexylamine (0.84 mL, 8.4 mmol) was then gradually added at room temperature. Under normal circumstances, the resultant mixture was agitated for 18 hours. After the reaction period, volatiles were removed under reduced pressure, leaving behind a crude imine with a sticky consistency. After that, n-hexane was used as the eluent in column chromatography (silica gel) to purify the crude imine chemical. This purification process afforded imine in the form of a yellow sticky solid, with a yield of (89 %), representing an impressive 99 % efficiency.

In order to help the reader, the following data and figures are reproduced below.

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 14.30 (br s, 1H, OH), 8.36 (s, 1H, -CH=N-), 6.80 (t, 1H, aromatic-H), 7.10 (d, 1H, aromatic-H), 7.31 (d, 1H, aromatic-H), 3.22 (m, cyclohexyl-CH, 1H), 1.28-1.84 (m, cyclohexyl-CH₂, 10H), 1.44 (t-Bu, 9H, s). **¹³C NMR** (CDCl₃, 298 K, 125 MHz): δ = 162.3 (-CH=N), 160.6, 137.3, 129.4, 129.0, 118.7, 117.5, 67.6, 34.4, 29.3 (t-Butyl), 25.5, 24.5. IR (cm⁻¹): 3443 (-OH), 1624 (-CH=N, stretching vibration). **ESI-MS** (+ve) for C₁₇H₂₅NO: Calculated: m/z = 259.19 Da, Observed: m/z = 260.2007 Da [M+H]⁺.

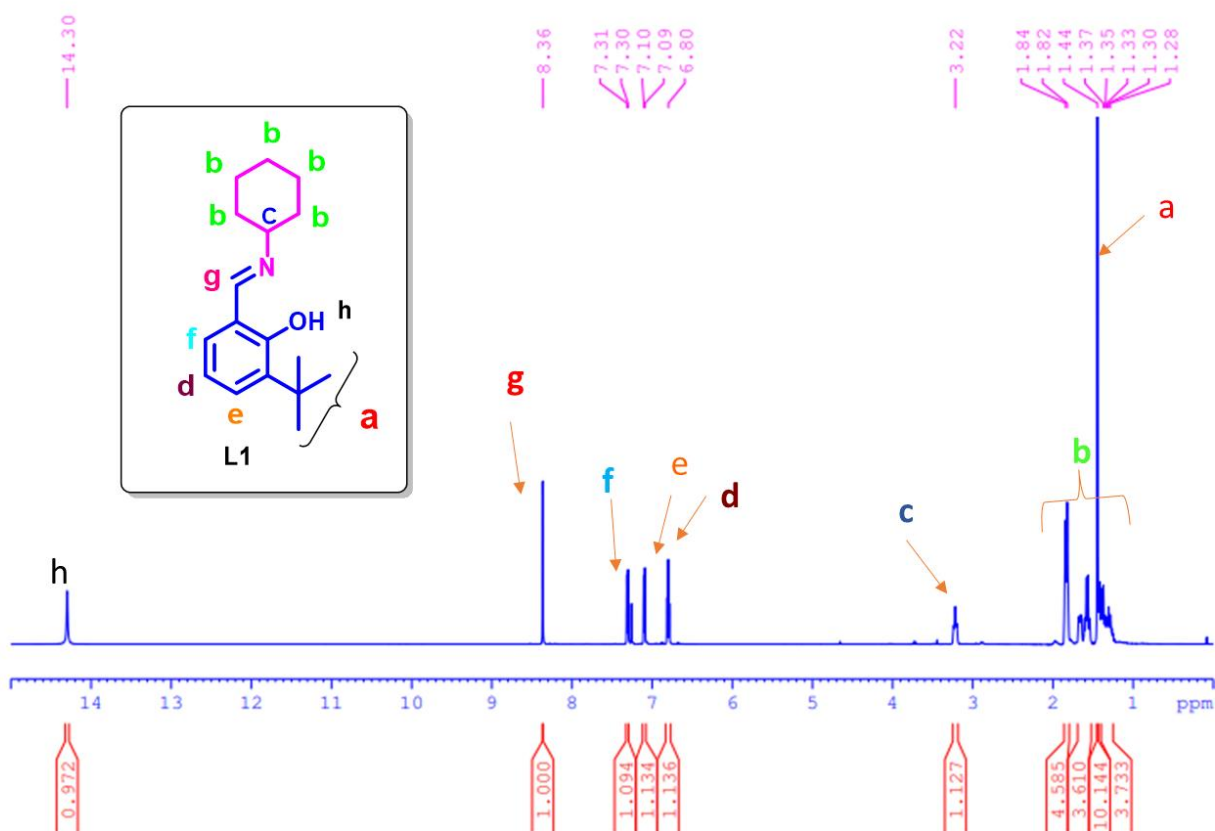


Figure 4.11: ^1H NMR spectrum of L1 in CDCl_3 (500 MHz).

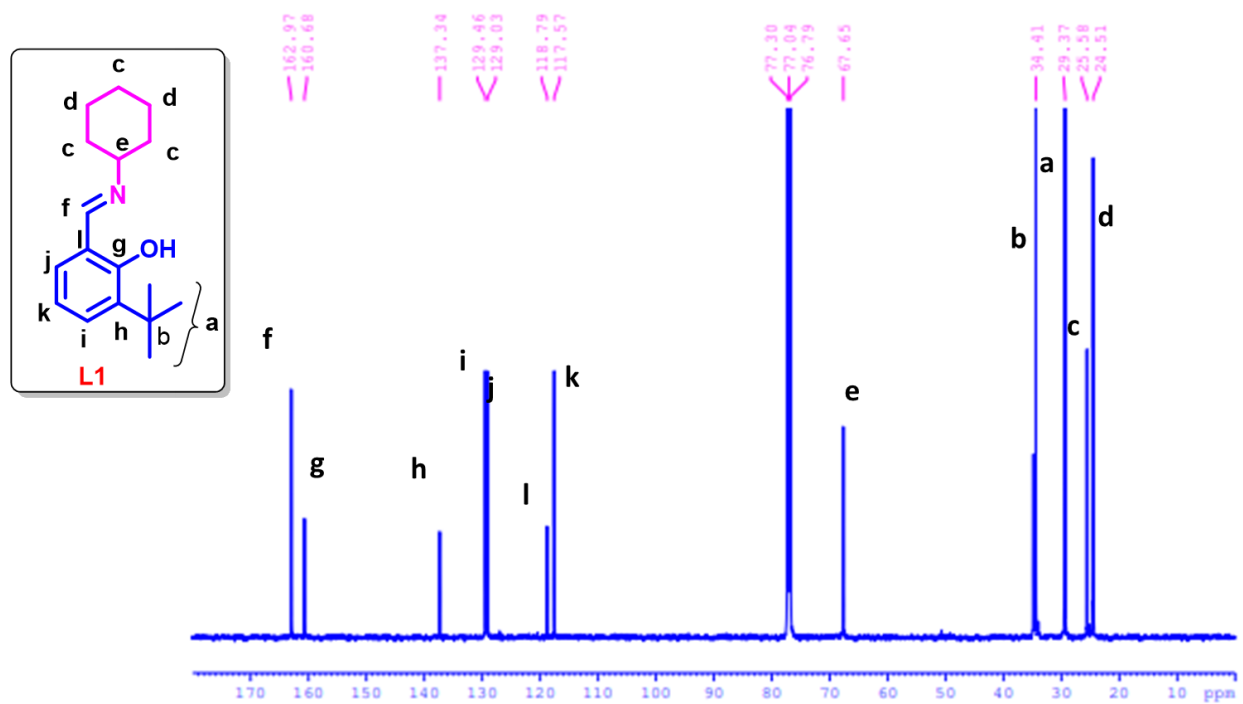


Figure 4.12: ^{13}C NMR spectrum for L1 in CDCl_3 (125 MHz).

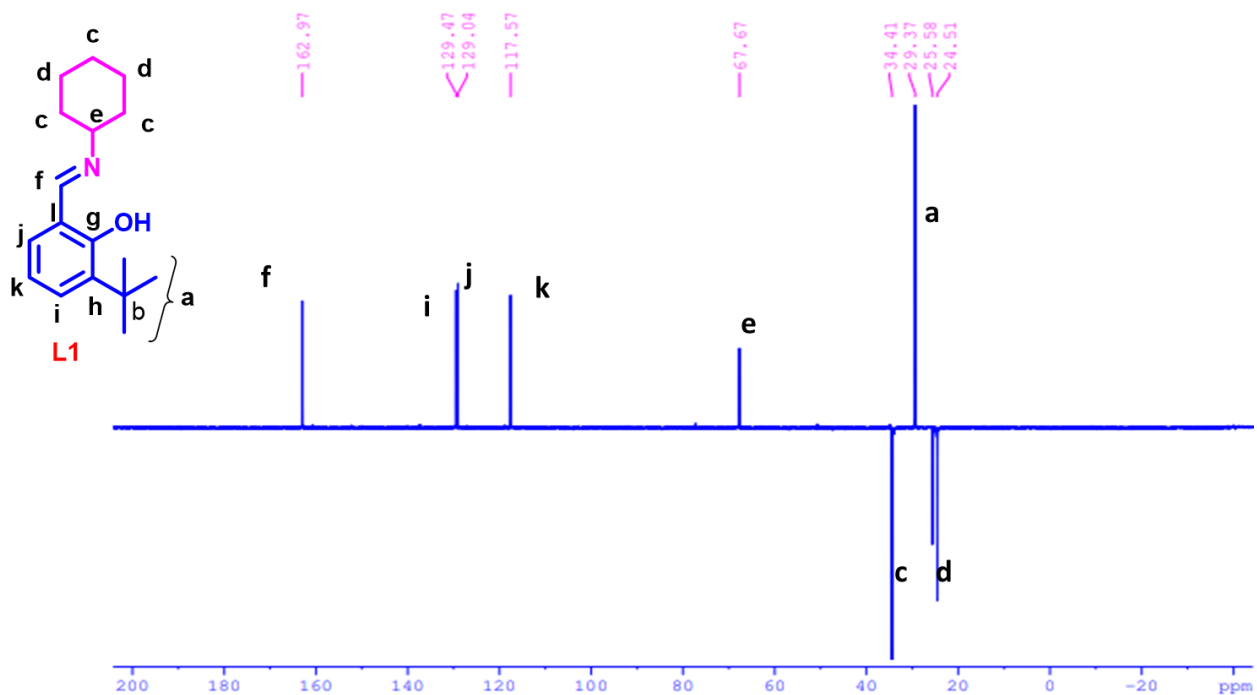


Figure 4.13: DEPT NMR spectrum of L1 in CDCl_3 (125 MHz).

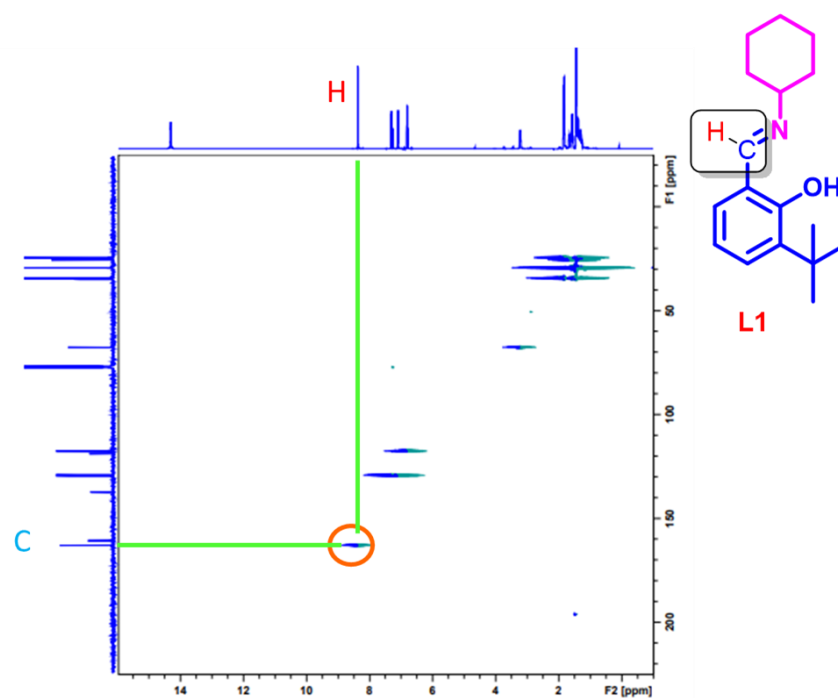


Figure 4.14: Expanded view of a short-range C-H correlation (HSQC) NMR spectrum of L1 in CDCl_3 (500 MHz).

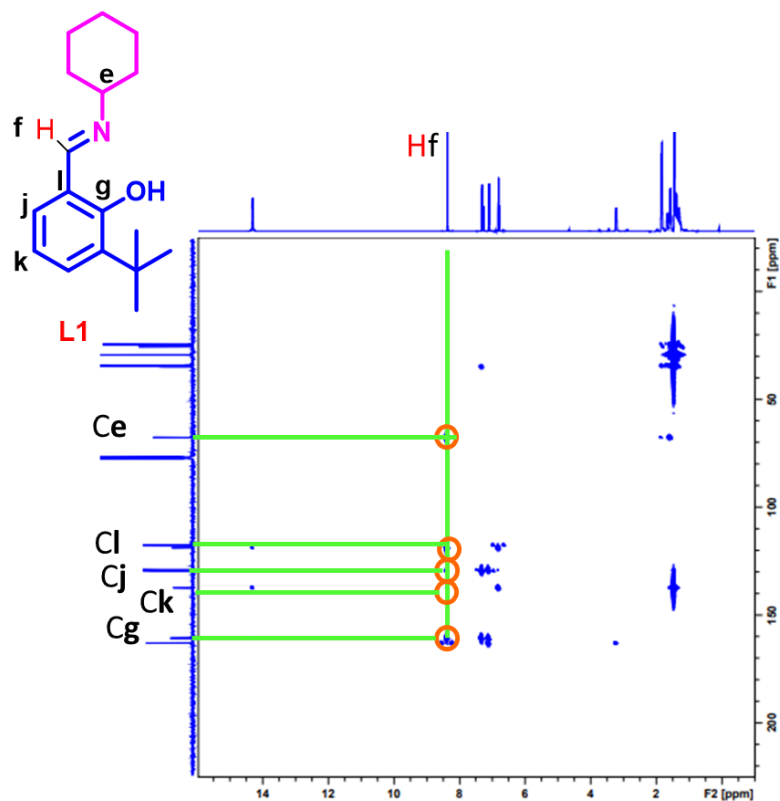


Figure 4.15: Expanded view of a long-range C-H correlation (HMBC) NMR spectrum of L1 in CDCl_3 (500 MHz).

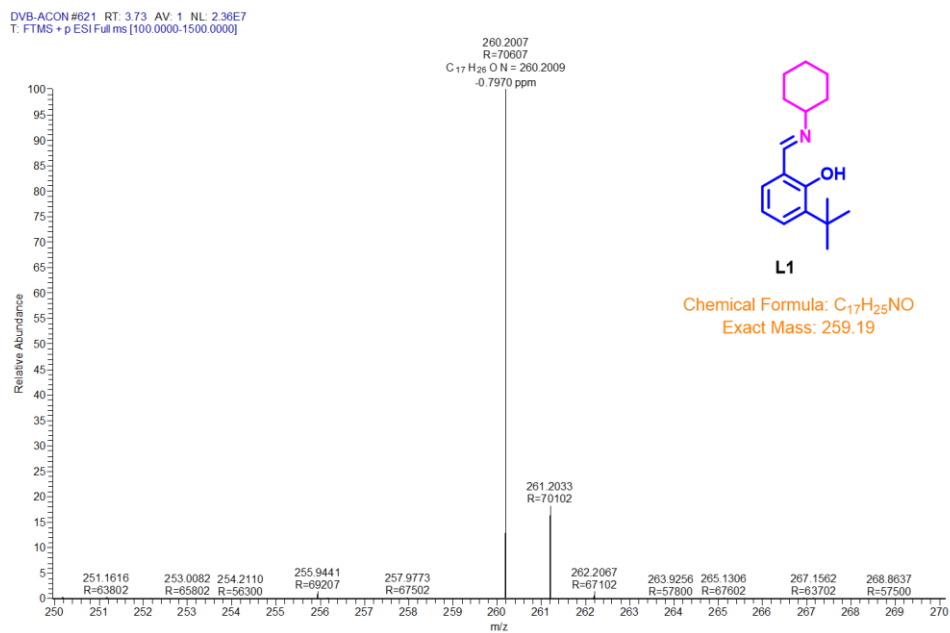


Figure 4.16: ESI-MS (+ve mode) spectrum of L1.

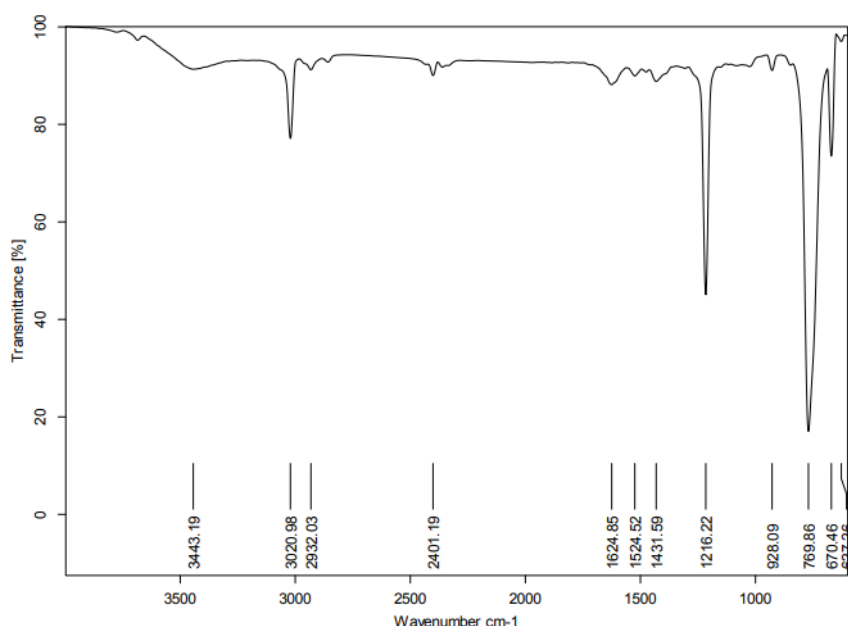
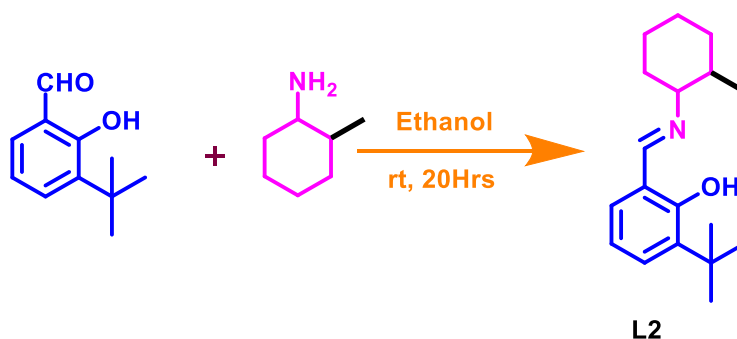


Figure 4.17: IR spectrum of L1.

4.6.2. 2-(tert-butyl)-6-(((2-methylcyclohexyl) imino) methyl) phenol (L2)

2-Methyl cyclohexylamine (1.1 mL) was poured into a 40 mL suspension of 3-tert-butylsalicylaldehyde (1 g, 5.6 mmol) at room temperature dropwise. When at room temperature, the mixture was then agitated for 20 hours. Crude imine sticky substance was obtained by evaporating volatiles under low pressure. Imine **L2** was obtained as a yellow oil with a 95% yield through column chromatographic purification with n-hexane as the eluent.



In order to help the reader, the following data and figures are reproduced below.

^1H NMR (CDCl_3 , 298 K, 500 MHz): δ = 14.11 (OH, 1H, br s), 8.21 (s, 1H, -CH=N-), 6.73 (t, aromatic-H, 1H), 7.03 (d, aromatic-H, 1H), 7.23 (d, aromatic-H, 1H), 2.58 (m, 1H, cyclohexyl-CH), 0.75-1.76 (m, 9 H, cyclohexyl- CH_2), 1.36 (s, 9H, t-Bu), 0.74 (s, 3H, methyl). **^{13}C NMR** (125 MHz, CDCl_3 , 298 K): δ = 166.6 (-CH=N), 163.6, 140.1, 132.5, 132.1, 78.0, 40.8, 37.8, 36.7, 32.5 (t-Butyl), 28.9, 22.6. IR (cm^{-1}): 3684 (-OH), 1629 (-CH=N, stretching vibration). **ESI-MS** (+ve) for $\text{C}_{18}\text{H}_{27}\text{NO}$: Calculated: m/z = 273.2 Da, Observed: m/z = 274.2 Da $[\text{M}+\text{H}]^+$.

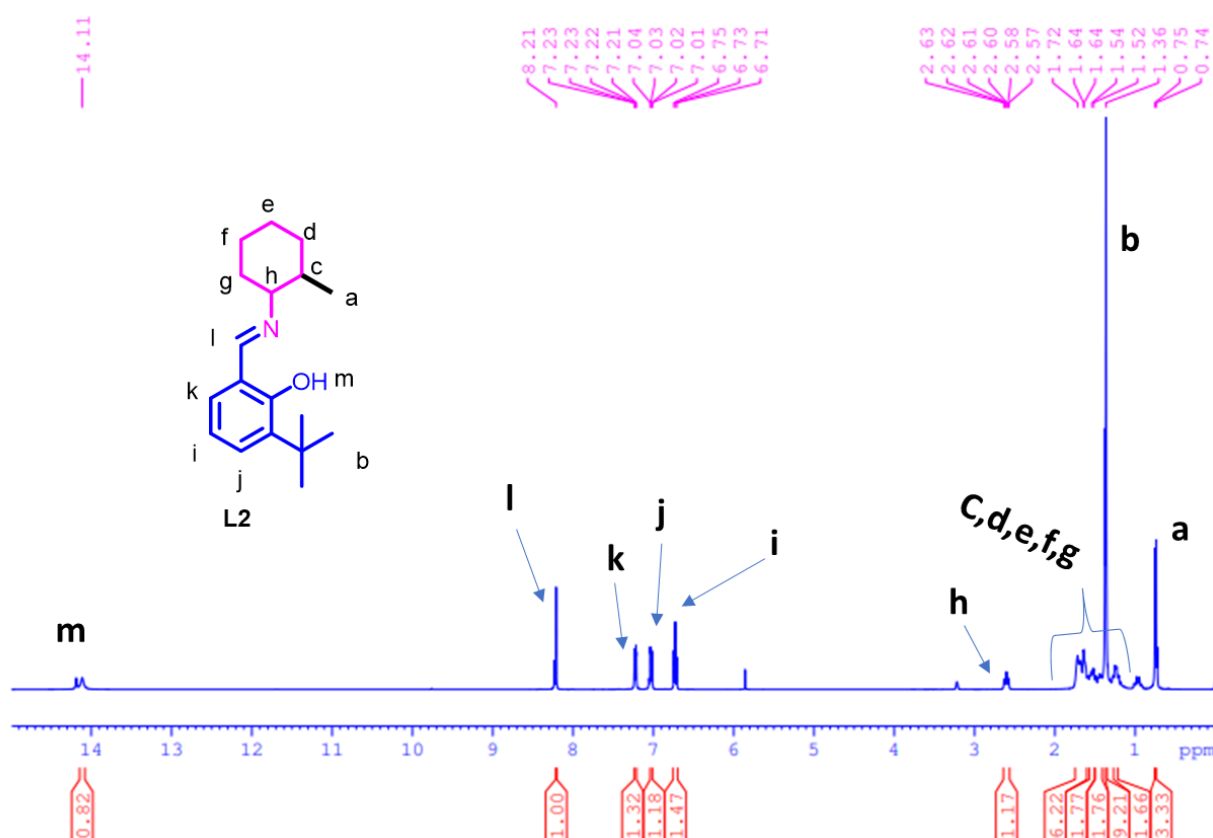


Figure 4.18: ^1H NMR spectrum of L2 in CDCl_3 (500 MHz).

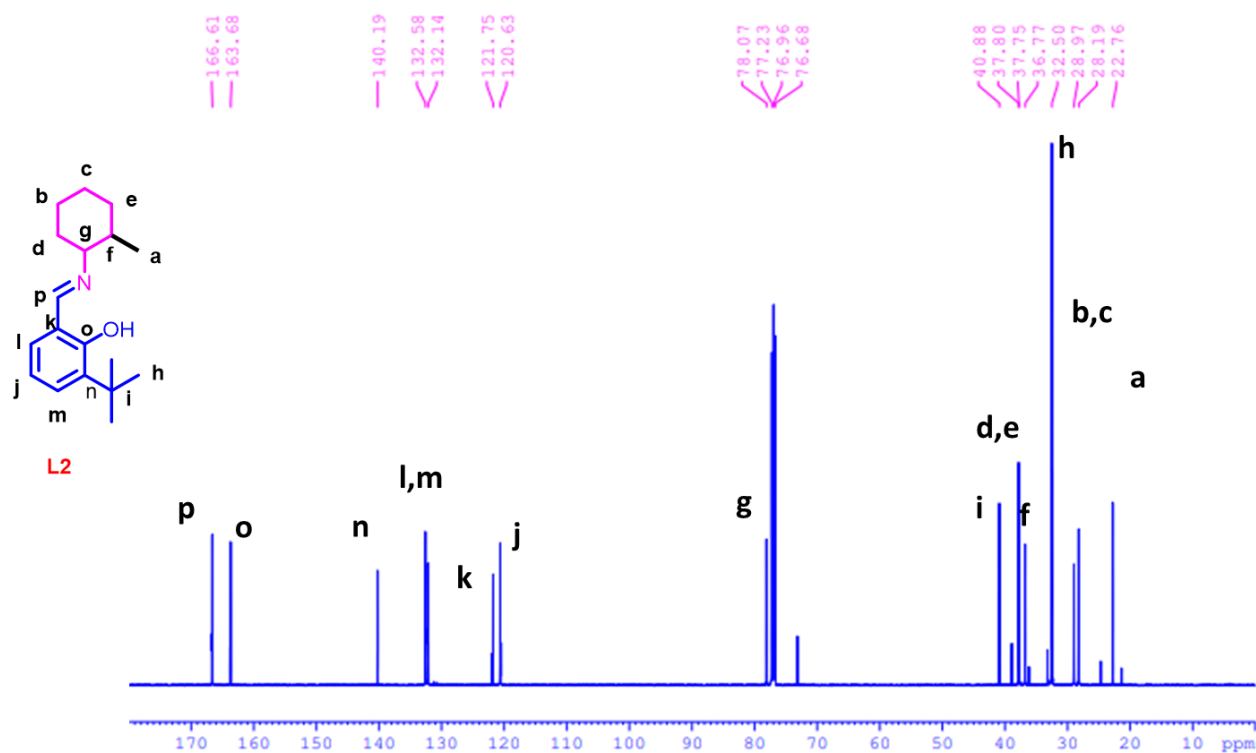


Figure 4.19: ^{13}C NMR spectrum for L2 in CDCl_3 (125 MHz).

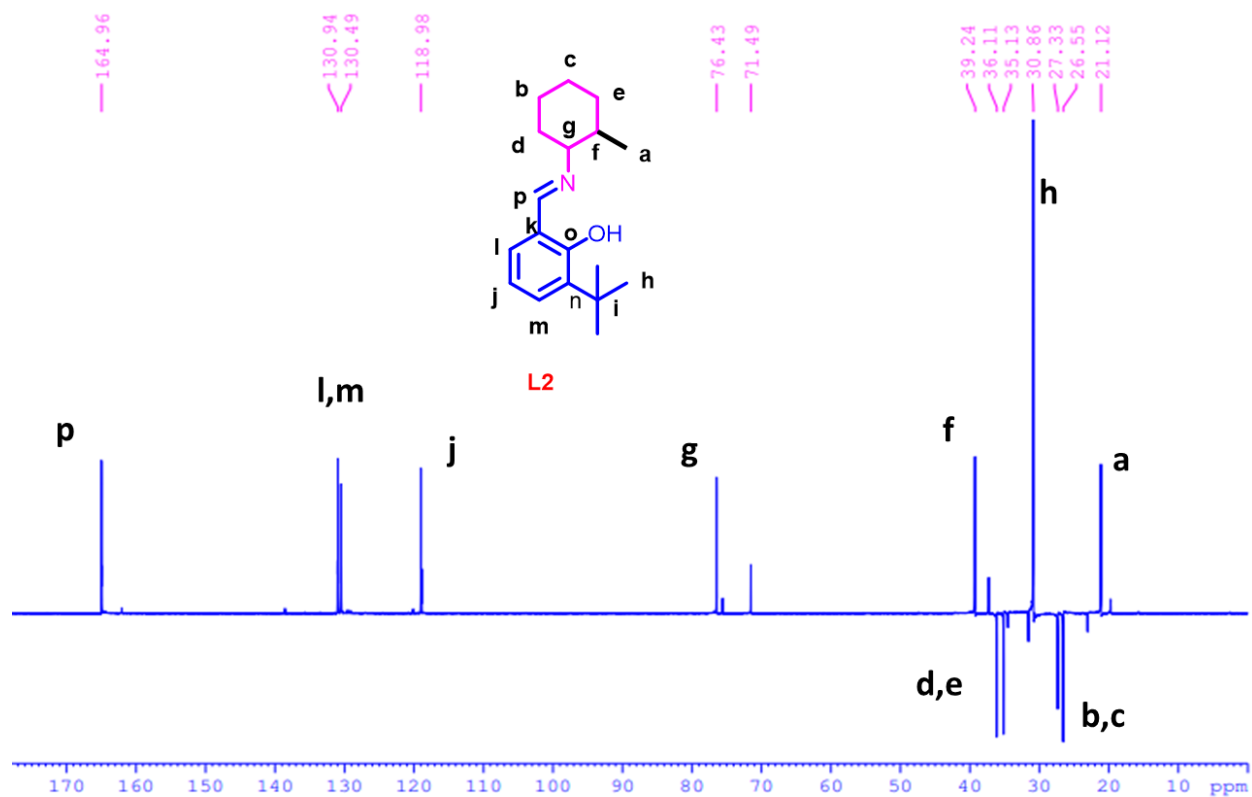


Figure 4.20: DEPT NMR spectrum of L2 in CDCl_3 (125 MHz).

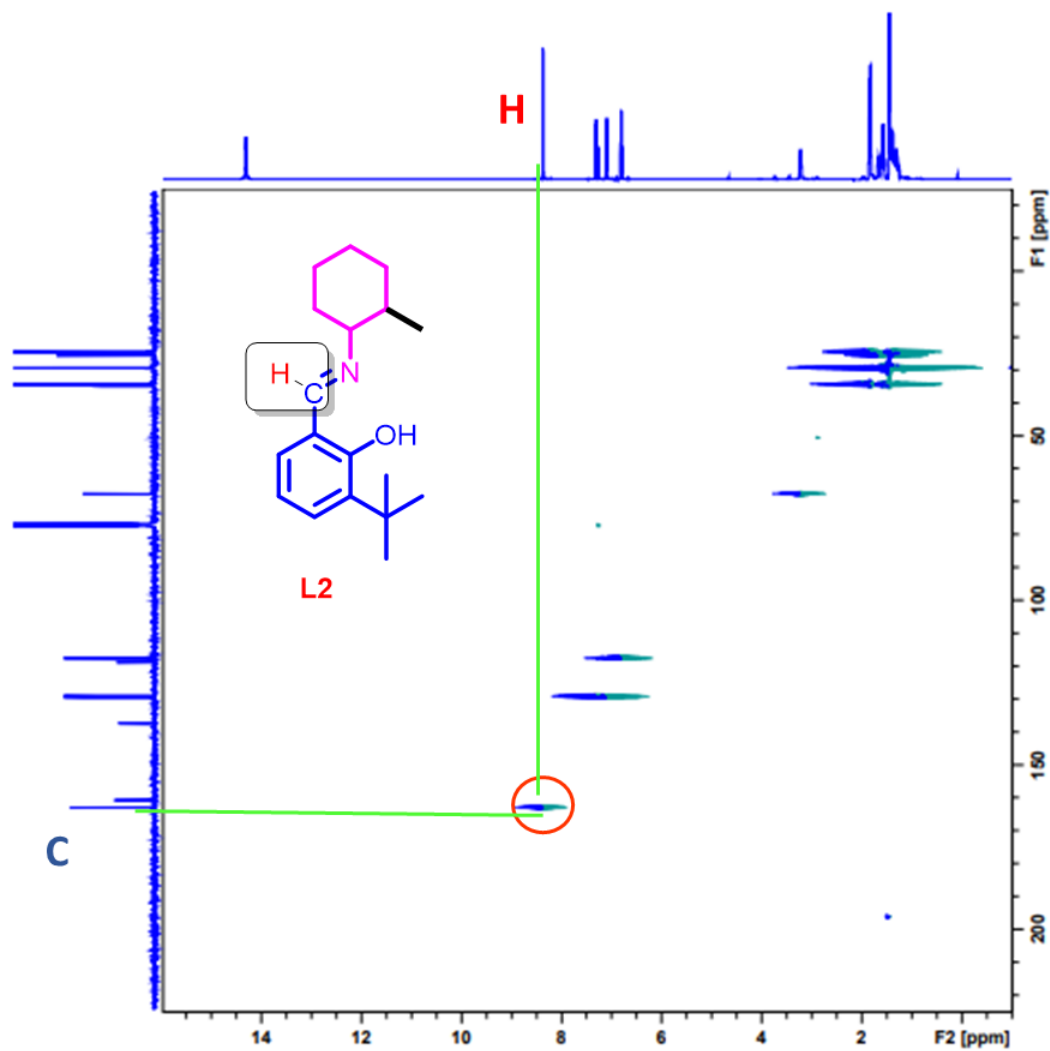


Figure 4.21: Expanded view of a short-range C-H correlation (HSQC) NMR spectrum of L2 in CDCl_3 (500 MHz).

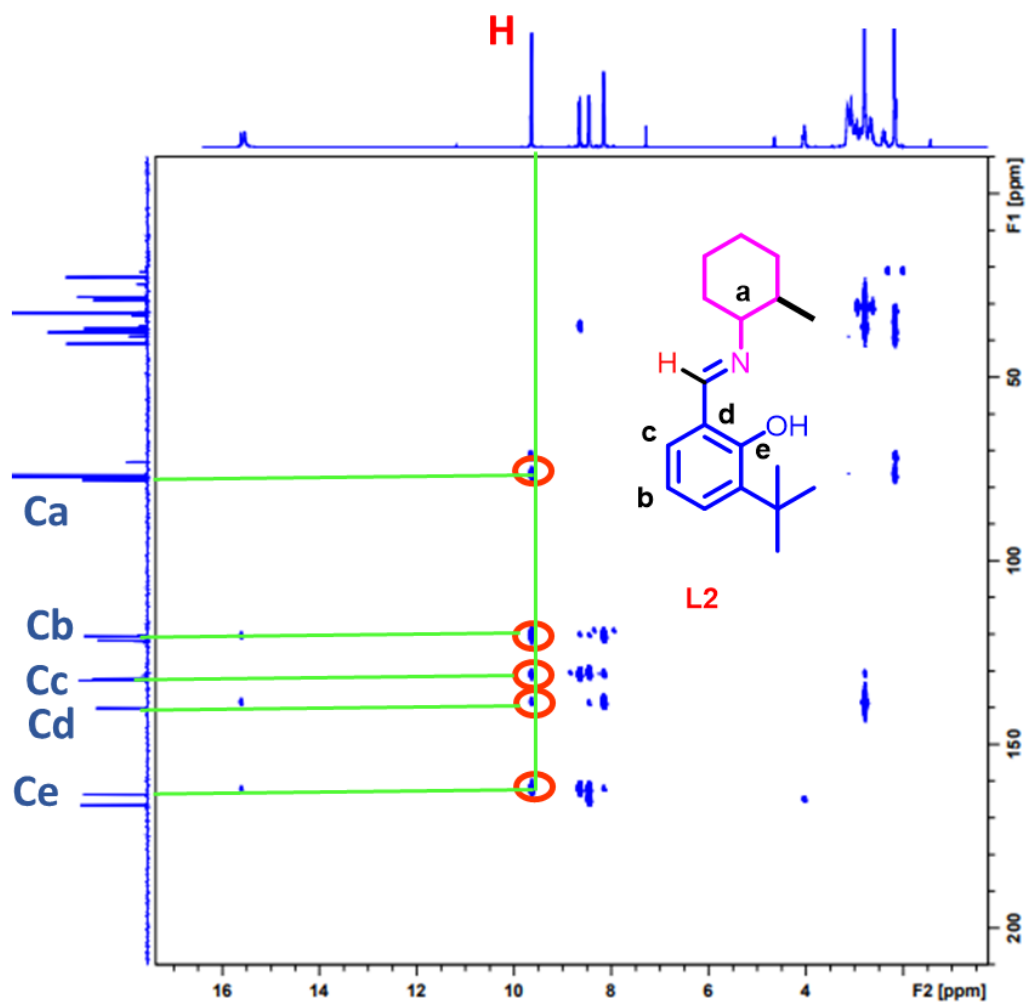


Figure 4.22: Expanded view of a short-range C-H correlation (HMBC) NMR spectrum of L2 in CDCl₃ (500 MHz).

DVB-ACON #648 RT: 3.89 AV: 1 NL: 1.04E9
T: FTMS + p ESIFull ms [100.0000-1500.0000]

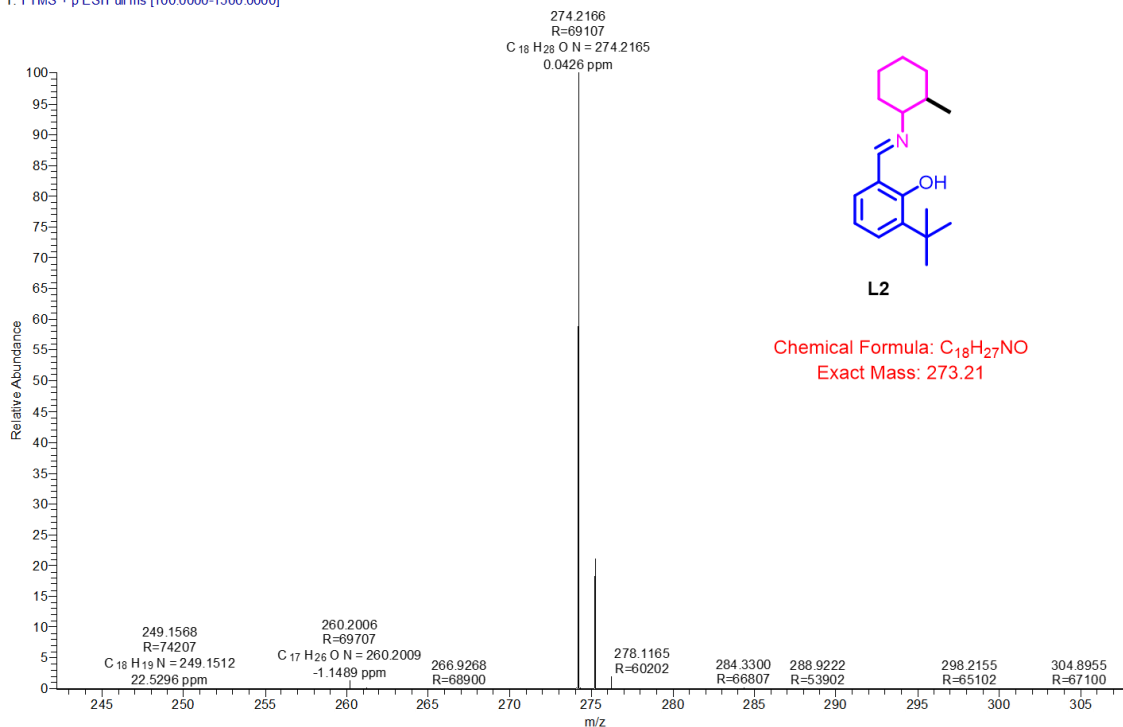


Figure 4.23: ESI-MS (+ve mode) spectrum of L2.

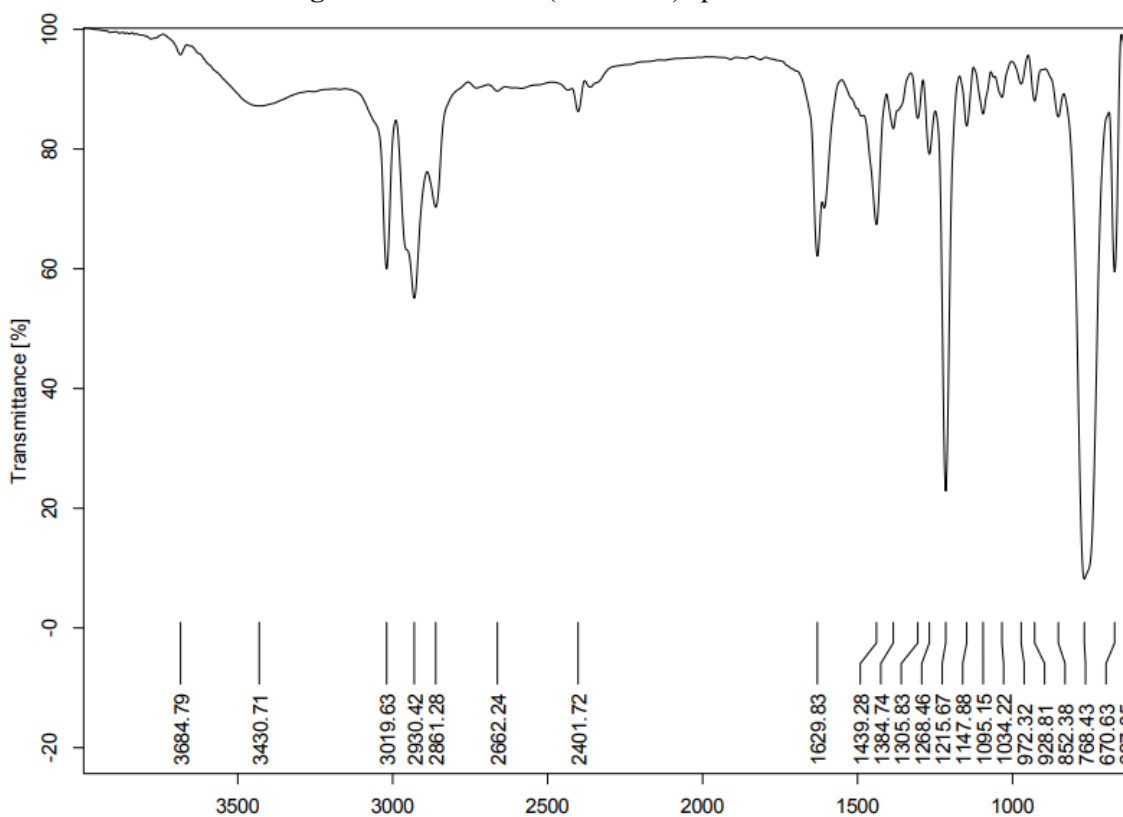
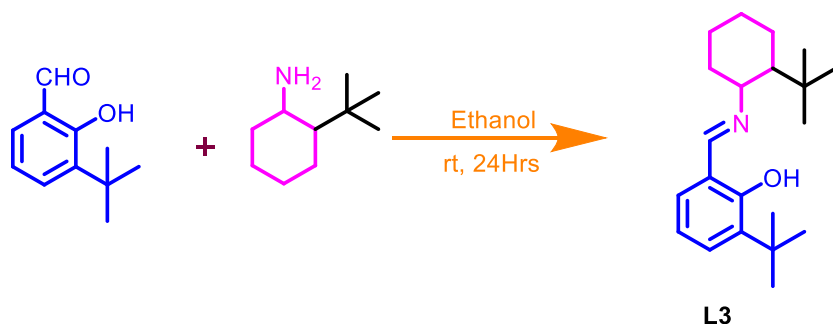


Figure 4.24: IR spectrum of L2.

4.6.3. 2-(tert-butyl)-6-(((2-(tert-Butyl) cyclohexyl) imino) methyl) phenol (L3)

2-Tert-butyl cyclohexylamine (1.4 mL, 8.4 mmol) was gradually added at ambient temperature. After 3-tert-butylsalicylaldehyde (1 g, 5.6 mmol) was added to ethanol (40 mL). When at room temperature, the entire mixture was then agitated for 24 hours' time period. Crude imine sticky substance was obtained by evaporating volatiles under low pressure. Purification by column chromatography with n-hexane as the eluent produced **L3** as yellow solid in 95% isolated yield.



In order to help the reader, the following data and figures are reproduced below.

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 14.30 (OH, 1H, br s), 8.36 (-CH=N-, s, 1H), 6.80 (t, 1H, aromatic-H), 7.10 (d, 1H, aromatic-H), 7.31 (d, 1H, aromatic-H), 3.22 (m, cyclohexyl-CH, 1H), 1.28-1.84 (m, cyclohexyl-CH₂, 10 H), 1.44 (t-Bu, 9H, s). **¹³C NMR** (CDCl₃, 298 K, 125 MHz): δ = 162.3 (-CH=N), 160.6, 137.3, 129.4, 129.0, 118.7, 117.5, 67.6, 34.4, 29.3 (t-Butyl), 25.5, 24.5. IR (cm⁻¹): 3484 (-OH), 1627 (-CH=N, stretching vibration). **ESI-MS** (+ve) for C₂₁H₃₃NO: Calculated: m/z = 315.26 Da, Observed: m/z = 316.30 Da [M+H]⁺.

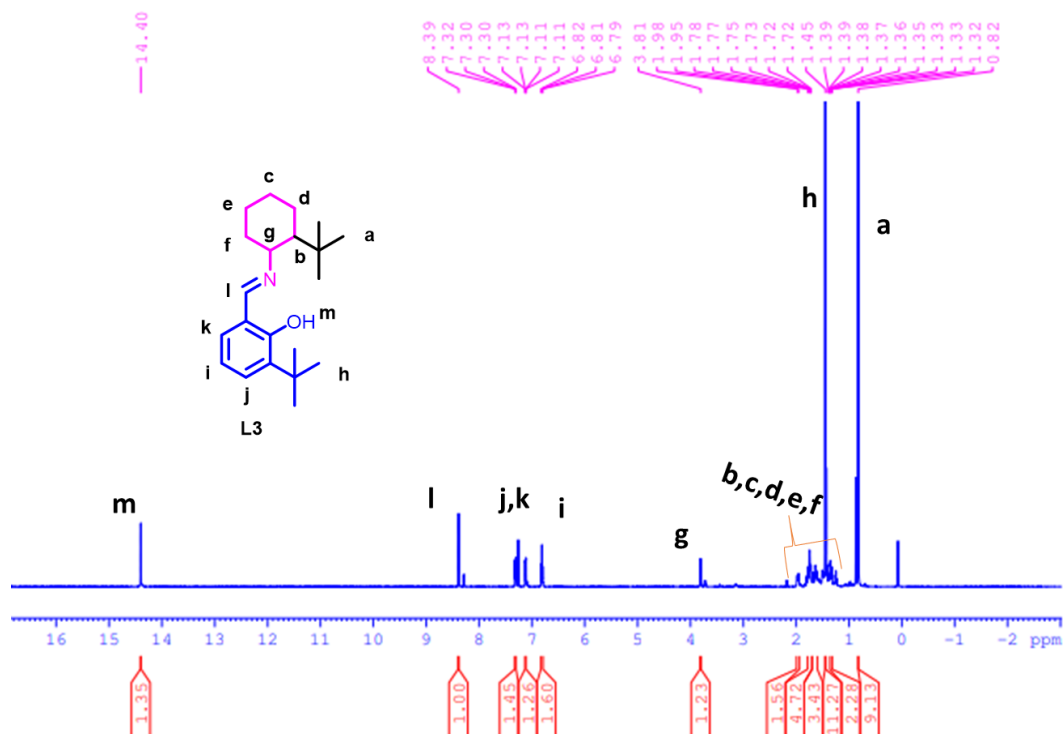


Figure 4.25: ¹H NMR spectrum of L3 in CDCl₃ (500 MHz).

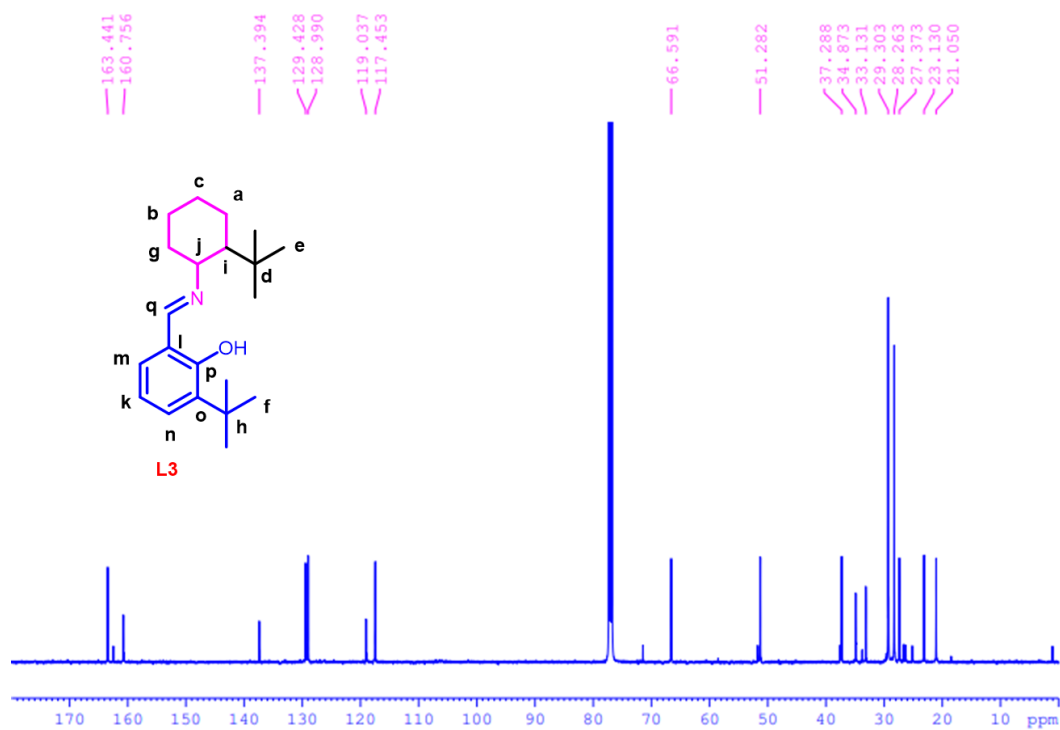


Figure 4.26: ¹³C NMR spectrum for L3 in CDCl₃ (125 MHz).

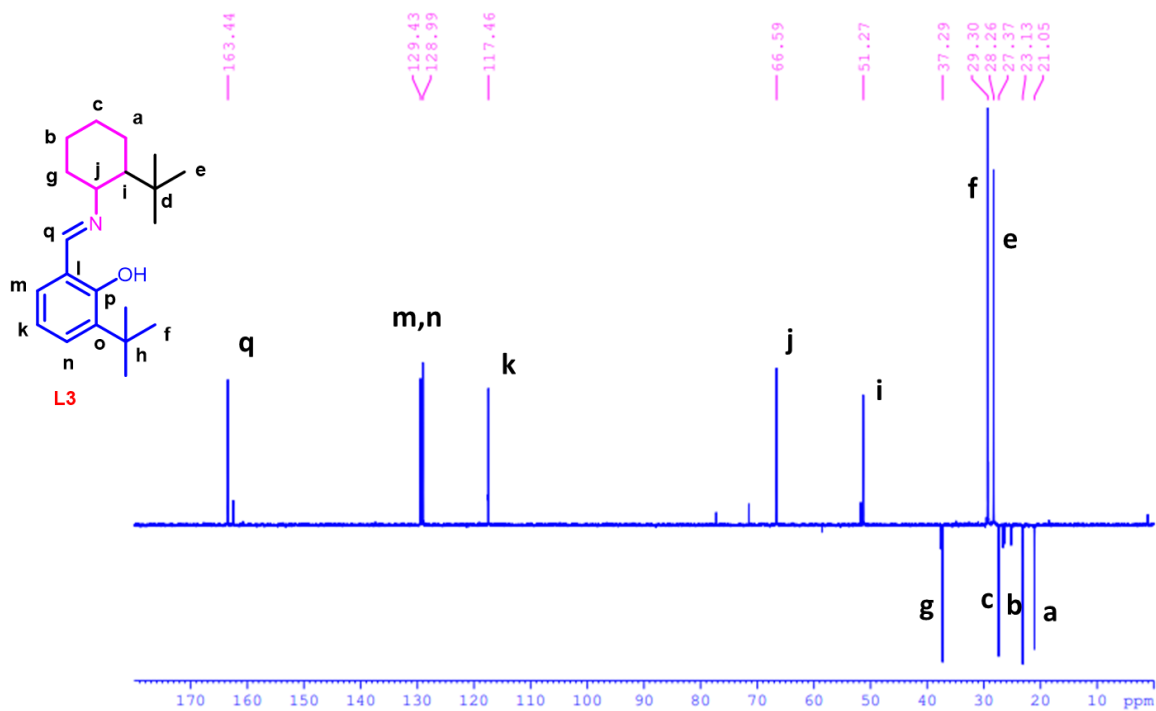


Figure 4.27: DEPT NMR spectrum of L3 in CDCl_3 (125 MHz).

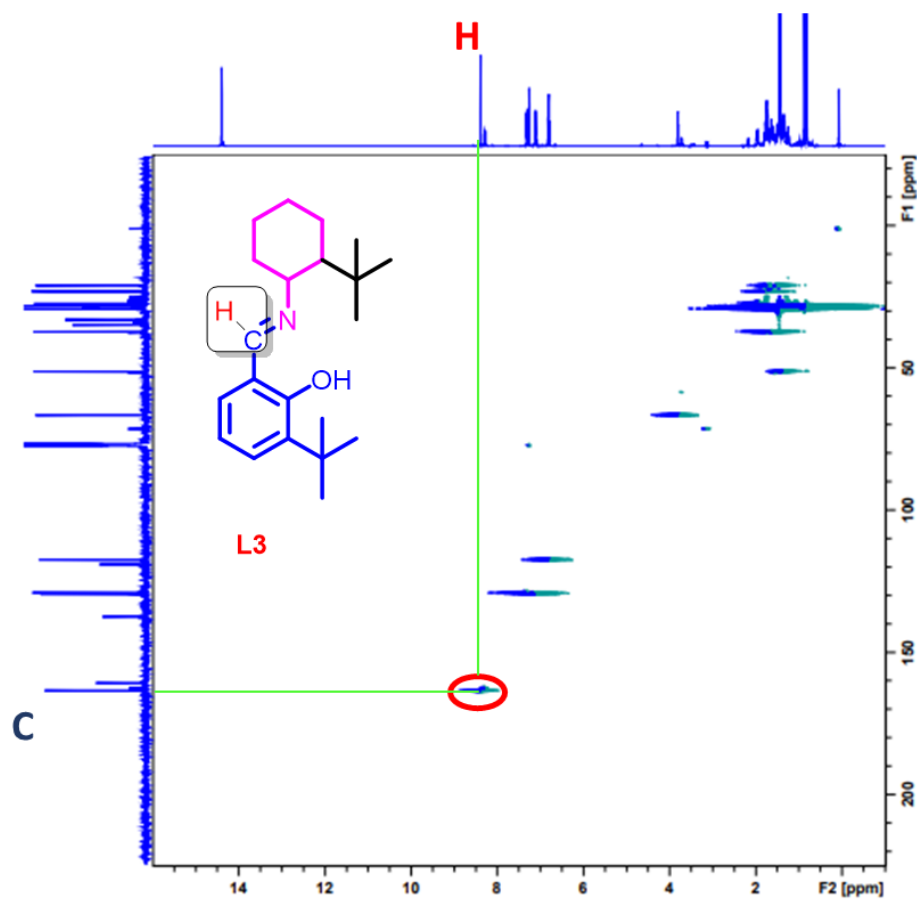


Figure 4.28: Expanded view of a short-range C-H correlation (HSQC) NMR spectrum of L3 in CDCl_3 (500 MHz).

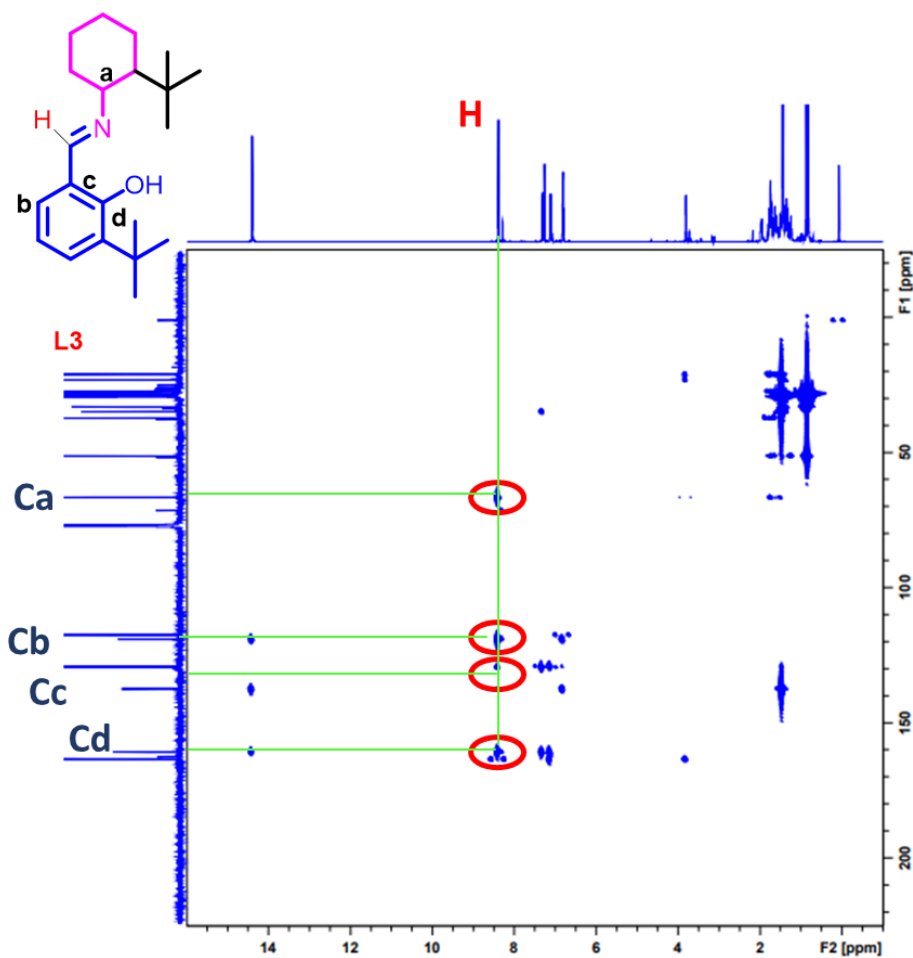


Figure 4.29: Expanded view of a long-range C-H correlation (HMBC) NMR spectrum of L3 in CDCl₃ (500 MHz).

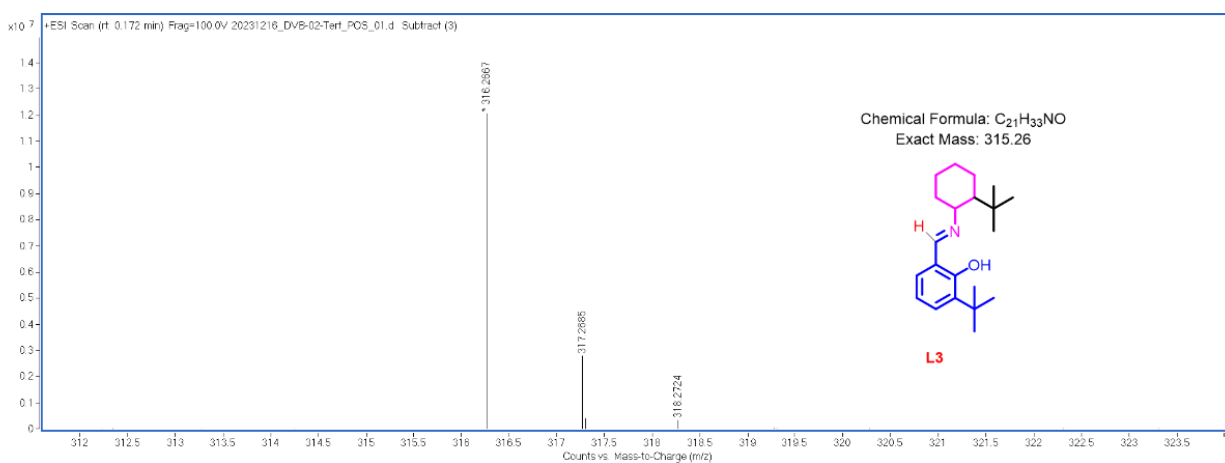


Figure 4.30: ESI-MS (+ve mode) spectrum of L3.

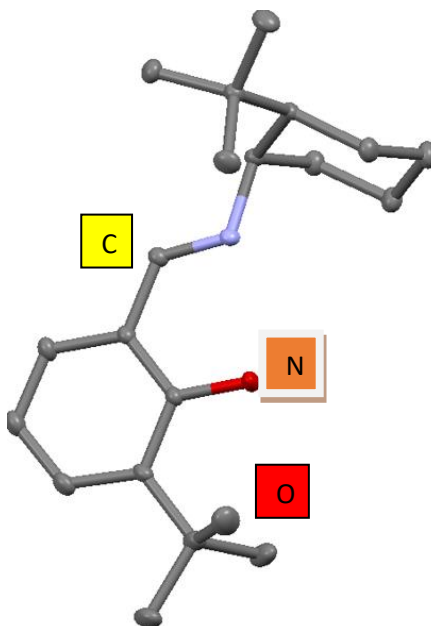


Figure 4.30 a: Molecular structure of ligand **L3** 2-(tert-butyl)-6-(((2-tert butyl cyclohexyl) imino) methyl) phenol (H-atoms omitted for clarity, except the imine C–H atom; 50% probability thermal ellipsoids)

Formula	C H N O
Space group	P 2 ₁ /c
Cell lengths	a 11.3140(4) b 12.9007(4) c 13.6816(4)
Cell Angles	α 90 β 110.1330(10) γ 90
Cell Volume	1874.93
Z, Z'	Z : 37 Z' : 0
R-factor (%)	9.47

	Number	Atom1	Atom2	Atom3	Angle
1		C009	N002	C00C	117.2(2)
1		C00C	N002	C009	117.2(2)
2		C004	C003	C006	117.1(2)
2		C006	C003	C004	117.1(2)
3		C004	C003	C00K	121.2(2)
3		C00K	C003	C004	121.2(2)

4	C006	C003	C00K	121.7(2)
4	C00K	C003	C006	121.7(2)
5	O001	C004	C003	120.1(2)
5	C003	C004	O001	120.1(2)
6	O001	C004	C008	119.3(2)
6	C008	C004	O001	119.3(2)
7	C003	C004	C008	120.7(2)
7	C008	C004	C003	120.7(2)
8	C007	C005	C009	109.9(2)
8	C009	C005	C007	109.9(2)
9	C007	C005	C00A	113.5(2)
9	C00A	C005	C007	113.5(2)
10	C009	C005	C00A	116.2(2)
10	C00A	C005	C009	116.2(2)
11	C003	C006	C00H	123.1(2)
11	C00H	C006	C003	123.1(2)
12	C005	C007	C00J	111.8(2)
12	C00J	C007	C005	111.8(2)
13	C004	C008	C00C	121.6(2)
13	C00C	C008	C004	121.6(2)
14	C004	C008	C00D	119.9(2)
14	C00D	C008	C004	119.9(2)
15	C00C	C008	C00D	118.5(2)
15	C00D	C008	C00C	118.5(2)
16	N002	C009	C005	112.6(2)
16	C005	C009	N002	112.6(2)
17	N002	C009	C00G	109.1(2)
17	C00G	C009	N002	109.1(2)

18	C005	C009	C00G	110.1(2)
18	C00G	C009	C005	110.1(2)
19	C005	C00A	C00B	112.4(2)
19	C00B	C00A	C005	112.4(2)
20	C005	C00A	C00E	110.8(2)
20	C00E	C00A	C005	110.8(2)
21	C005	C00A	C00I	108.4(2)
21	C00I	C00A	C005	108.4(2)
22	C00B	C00A	C00E	109.0(2)
22	C00E	C00A	C00B	109.0(2)
23	C00B	C00A	C00I	109.0(2)
23	C00I	C00A	C00B	109.0(2)
24	C00E	C00A	C00I	107.0(2)
24	C00I	C00A	C00E	107.0(2)
25	N002	C00C	C008	123.5(2)
25	C008	C00C	N002	123.5(2)
26	C008	C00D	C00H	120.2(2)
26	C00H	C00D	C008	120.2(2)
27	C00G	C00F	C00J	111.2(2)
27	C00J	C00F	C00G	111.2(2)
28	C009	C00G	C00F	112.4(2)
28	C00F	C00G	C009	112.4(2)
29	C006	C00H	C00D	119.0(2)
29	C00D	C00H	C006	119.0(2)
30	C007	C00J	C00F	110.6(2)
30	C00F	C00J	C007	110.6(2)
31	C003	C00K	C00L	111.5(2)
31	C00L	C00K	C003	111.5(2)

32	C003	C00K	C00M	110.0(2)
32	C00M	C00K	C003	110.0(2)
33	C003	C00K	C00N	109.4(2)
33	C00N	C00K	C003	109.4(2)
34	C00L	C00K	C00M	108.2(2)
34	C00M	C00K	C00L	108.2(2)
35	C00L	C00K	C00N	107.0(2)
35	C00N	C00K	C00L	107.0(2)
36	C00M	C00K	C00N	110.7(2)
36	C00N	C00K	C00M	110.7(2)

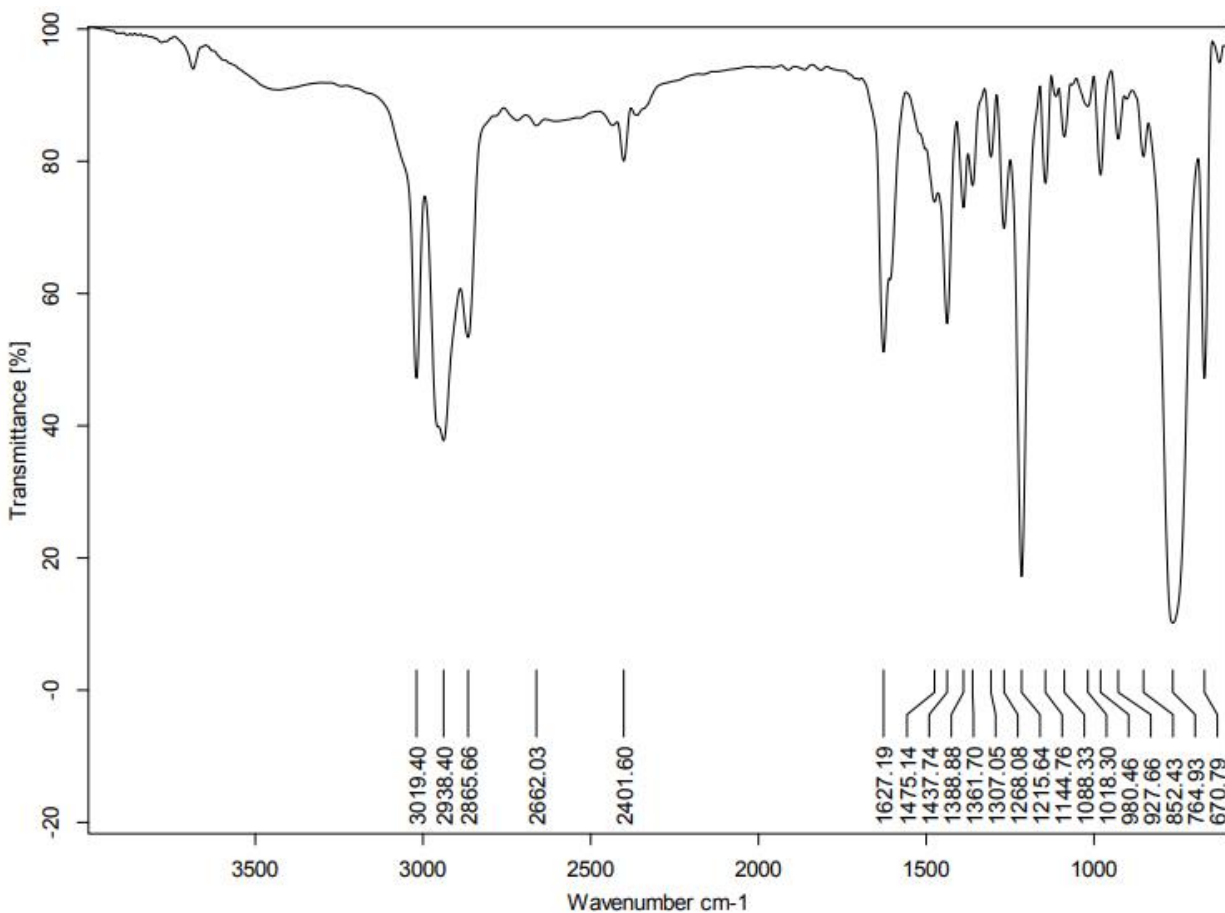
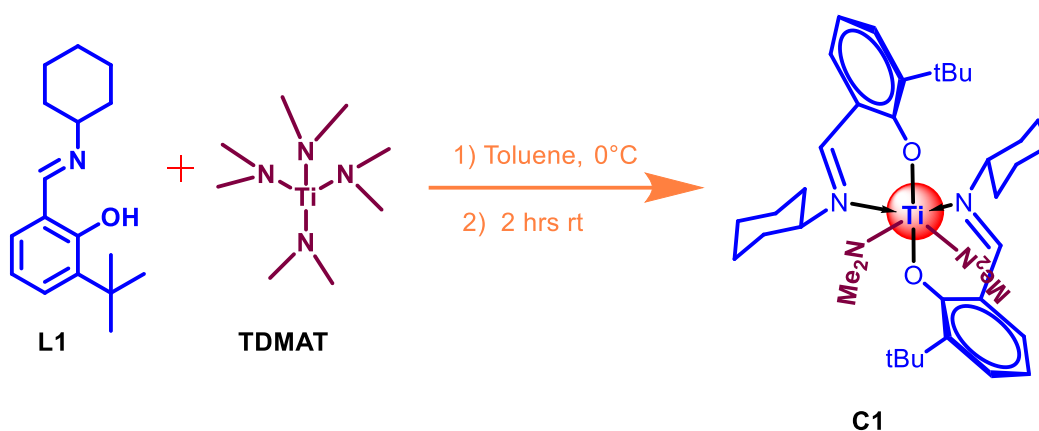


Figure 4.31: IR spectrum of L3.

4.7. Titanium complex synthesis

4.7.1. [Bis-dimethylamido-Ti-(bis-[N-(3-tert-butylsalicylidene)cyclohexylaminato])] (Cat.1)



After cooling under vacuum, argon gas was purged from a 250 mL dried in the oven Schlenk flask. The Schlenk flask was heated and cooled three times under vacuum to reduce the moisture content. Under the positive flow of argon, 1 g (3.8 mmol) of **L1** was added to the above Schlenk flask. Subsequently, after adding 30 mL of toluene, the liquid was agitated for five minutes. $\text{Ti}(\text{NMe}_2)_4$ (0.7 mL, 1.9 mmol) was added gradually over the course of five minutes after the Schlenk had been cooled to 0 °C. A turbid yellow solution turned to a clear reddish brown one. A water bath was then used in place of the ice bath, raising the reaction mixture's temperature from 0 °C to roughly 30 °C. After that, the mixture was agitated for two more hours at room temperature. After another 30 minutes of stirring, volatiles were evaporated under vacuum. A reddish-brown sticky residue was obtained. This crude complex was further purified by dissolving it in freshly distilled hexane (5 mL) and was kept at low temperature overnight. The settled solid, and the supernatant liquid was separated. The solid (yield 56 %) was then vacuum-dried and stored in the glove box for future use.

In order to help the reader, the following data and figures are reproduced below.

^1H NMR (500 MHz, CDCl_3) δ = 8.08 (s, 2H, HC=N-), 7.46 (d, J = 7.32 Hz, Ar, 2H), 7.16 (d, J = 7.63 Hz, Ar, 2H), 7.75 (t, J = 7.32, 7.63 Hz Ar, 2H), 3.44 (m, cyclohexyl-N, 2H), 3.24 (s, -NMe₂ 12H), 1.62 (s, Ar-tert butyl 18H) and 0.87 to 1.57 (19H, Cyclohexyl CH₂). **^{13}C NMR (125 MHz, CDCl_3)** δ = 170.4 (-COOH), 162.4, 160.4(-C=N), 148.5, 131.3, 129.8, 127.4, 125.6, 118.7, 114.7, 55.4 (OCH₃), 38.2 and 34.7 (-N(CH₃)₂).

ESI-MS (+ve) for $\text{C}_{46}\text{H}_{76}\text{N}_4\text{O}_2\text{Ti}$ $[\text{M}+\text{H}]^+$ Calculated: m/z = 652 Da, observed: m/z = 608.3 [Cat.1-NMe₂]⁺ Da.

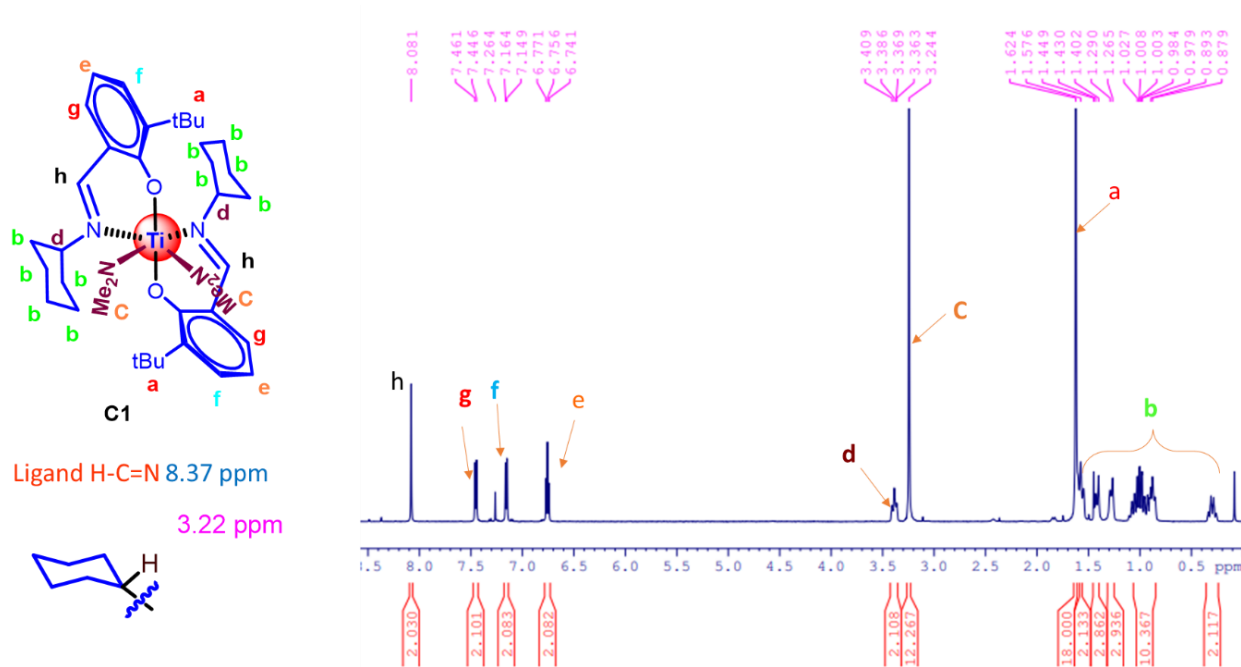
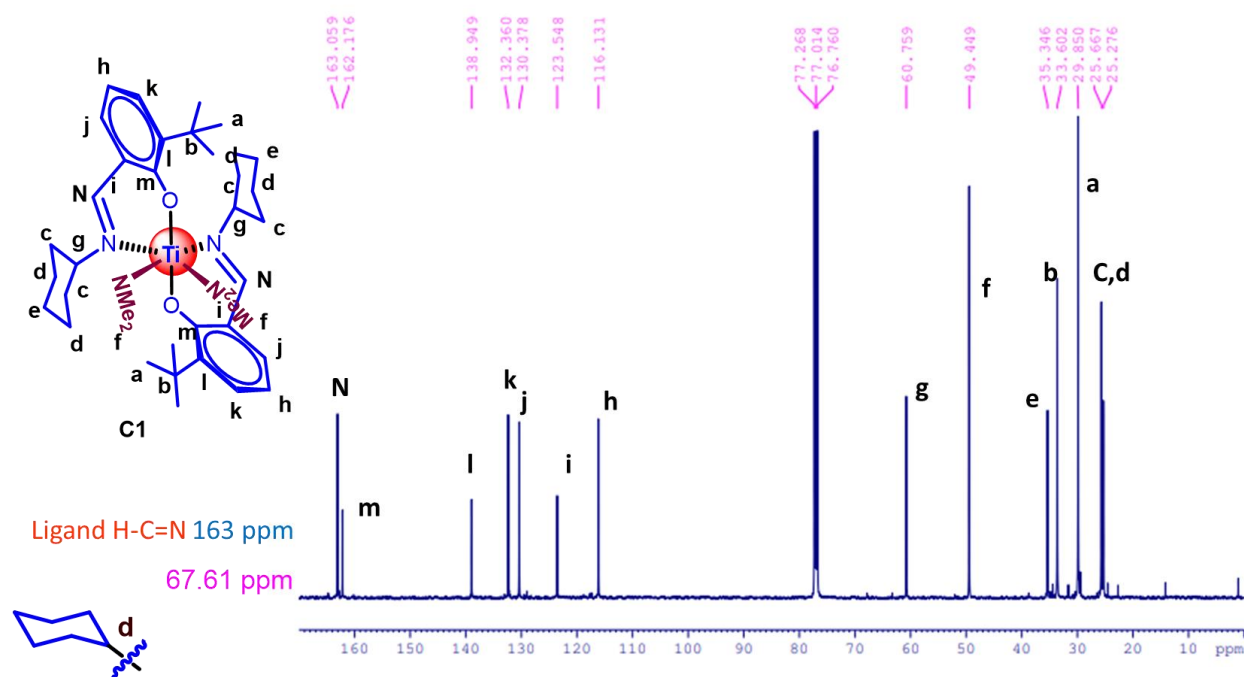
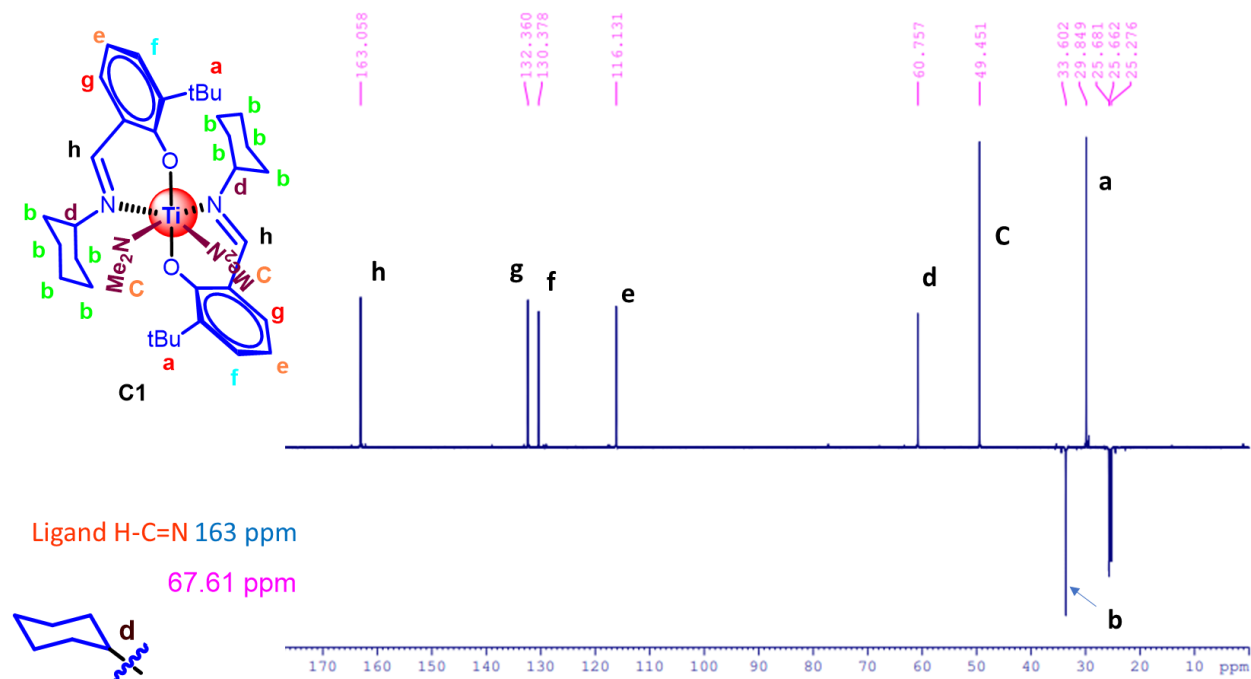


Figure 4.32: ^1H NMR spectrum of Cat.1 in CDCl_3 (500 MHz).

Figure 4.33: ^{13}C NMR spectrum of Cat.1 in CDCl_3 (125 MHz).Figure 4.34: DEPT NMR spectrum of Cat.1 in CDCl_3 (125 MHz).

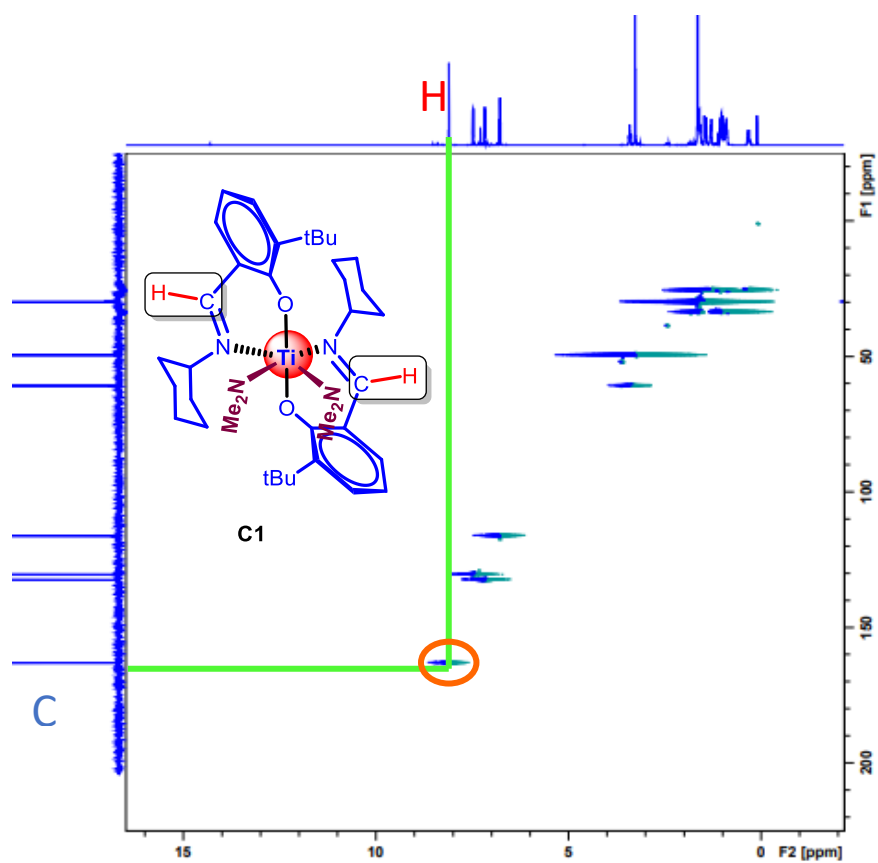


Figure 4.35: HSQC NMR spectrum of Cat.1 in CDCl₃ (500 MHz).

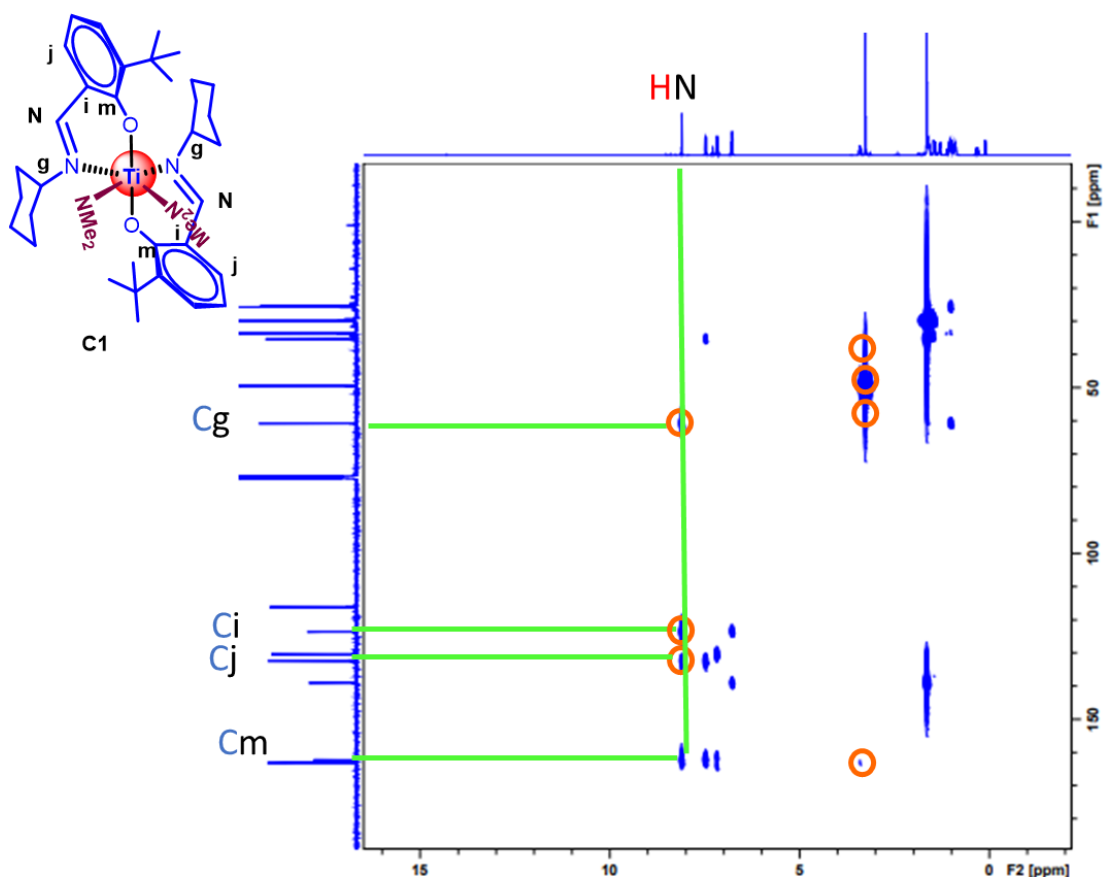


Figure 4.36: HMBC NMR spectrum of Cat.1 in CDCl_3 (500 MHz).

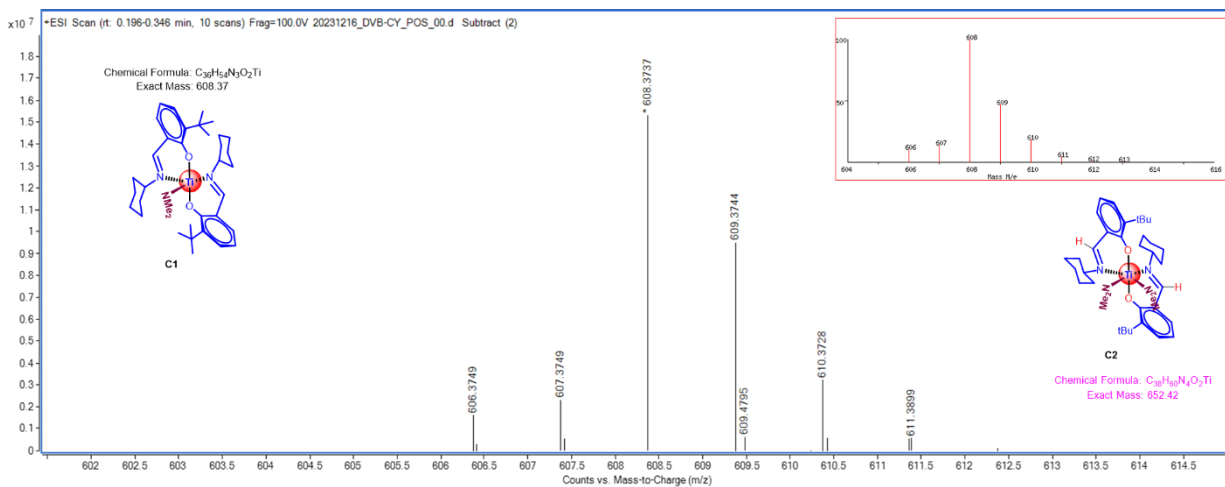


Figure 4.37: ESI-MS spectrum (+ve mode) of Cat.1.

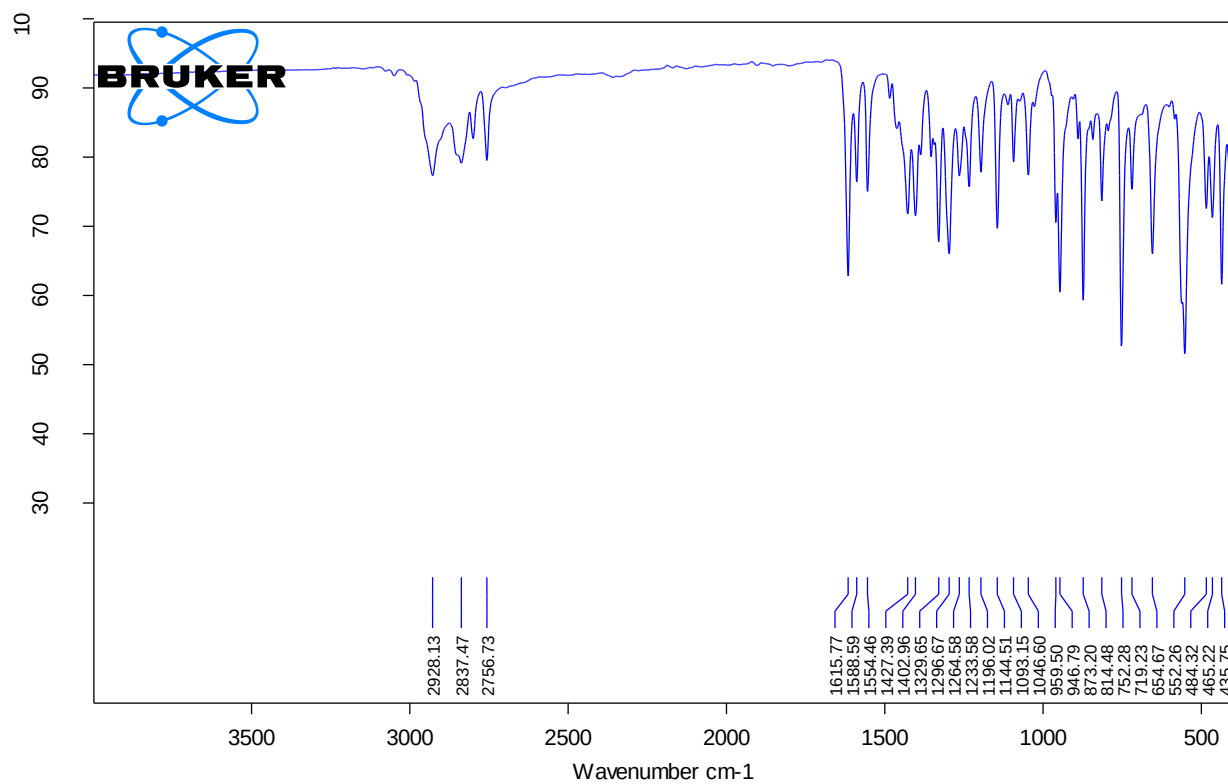
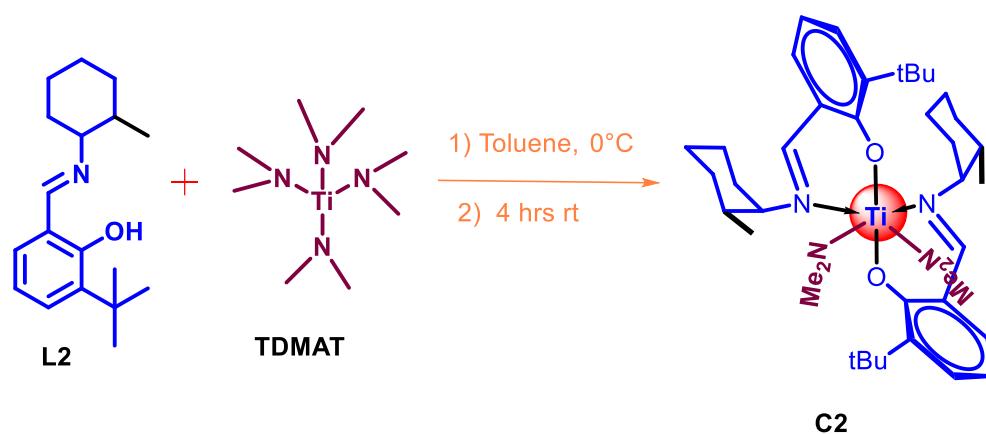


Figure 4.38: IR spectrum of Cat.1.

4.7.2. [Bis-dimethylamido-Ti-(bis-[N-(3-tert-butylsalicylidene)2-methylcyclohexylaminato])] (Cat.2):



After cooling under vacuum, argon gas was purged from a 250 mL dried in an oven Schlenk flask. The Schlenk flask was heated and cooled three times under vacuum to reduce the moisture content. Under the positive flow of argon, 1 g (3.6 mmol.) of **L2** was added to the above Schlenk flask. After adding 40 mL of toluene, the liquid was agitated for five minutes. The Schlenk was cooled to 0 °C and Ti (NMe₂)₄ (0.65 mL, 1.8 mmol) was progressively introduced during a five-minute period. A turbid yellow solution turned to a clear reddish brown one. The temperature of the reaction mixture was then increased from 0 °C to roughly 30 °C by substituting a water bath for the ice bath. After that, the mixture was agitated for four more hours at room temperature. After another 30 minutes of stirring, volatiles were evaporated under vacuum. A reddish-brown sticky residue was obtained. This crude complex was further purified by dissolving freshly distilled hexane (5 mL) and kept it for low temperature overnight to let the solid settle, and the supernatant liquid was separated. After a 70% yield from vacuum drying, the solid was put away in the glove box for later use.

In order to help the reader, the following data and figures are reproduced below.

¹H NMR (CDCl₃, 500 MHz): δ = 8.09 (m, 7.20, 5.43 Hz 2H, HC=N-), 7.48 (d, J = Ar, 2H, 7.45 Hz), 7.16 (d, J = Ar, 2H, 7.45 Hz), 6.78 (t, J = 7.58, Ar, 2H, 7.58 Hz), 3.23 (m, 12H -NMe₂), 2.25 (m, cyclohexyl-N, 2H), 1.65 (s, Ar-tert butyl 18H) and 0.63 to 1.28 (m, 18H, Cyclohexyl CH₂),

0.90 (s, 6H cyclohexyl-Me). ^{13}C NMR (125 MHz, CDCl_3) δ = 163.3(-C=N), 148.5, 131.3, 129.8, 127.4, 125.6, 118.7, 114.7, 55.4 (OCH_3), 38.2 and 34.7 ($-\text{N}(\text{CH}_3)_2$).

ESI-MS (+ve) for $\text{C}_{40}\text{H}_{64}\text{N}_4\text{O}_2\text{Ti}$ $[\text{M}+\text{H}]^+$ Calculated: m/z = 680.26 Da, observed: m/z = 636.4030 $[\text{Cat.2} - \text{HNMe}_2]^+$ Da.

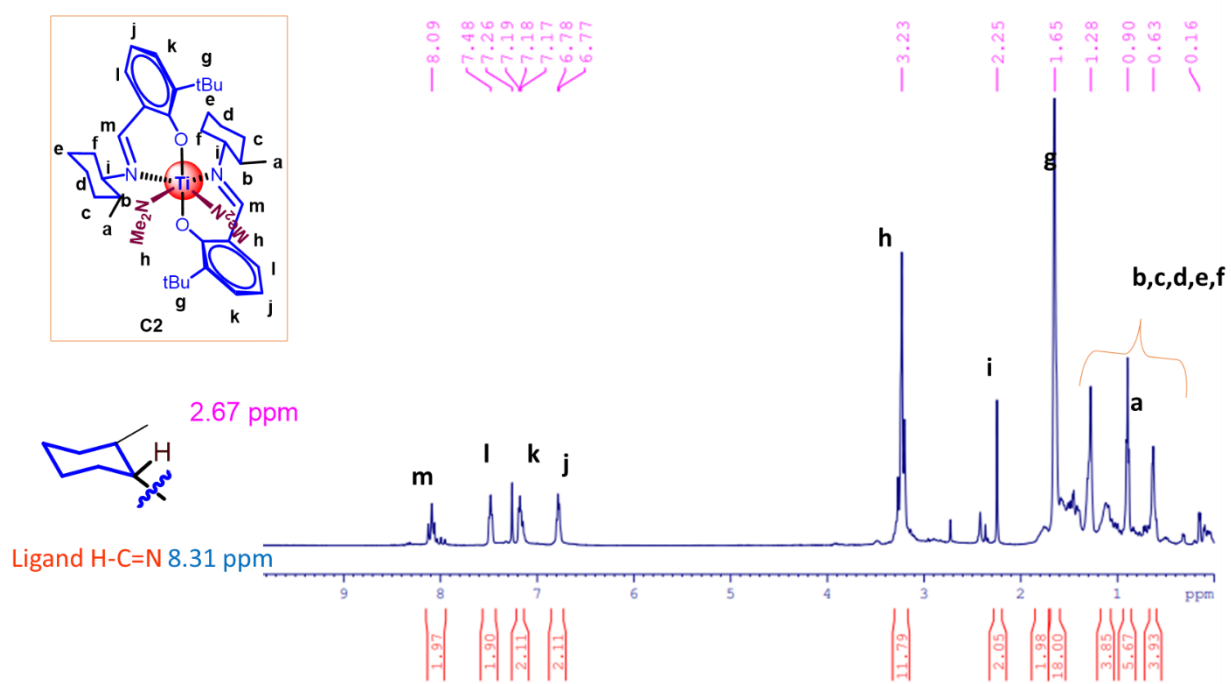


Figure 4.39: ^1H NMR spectrum of Cat.2 in CDCl_3 (500 MHz).

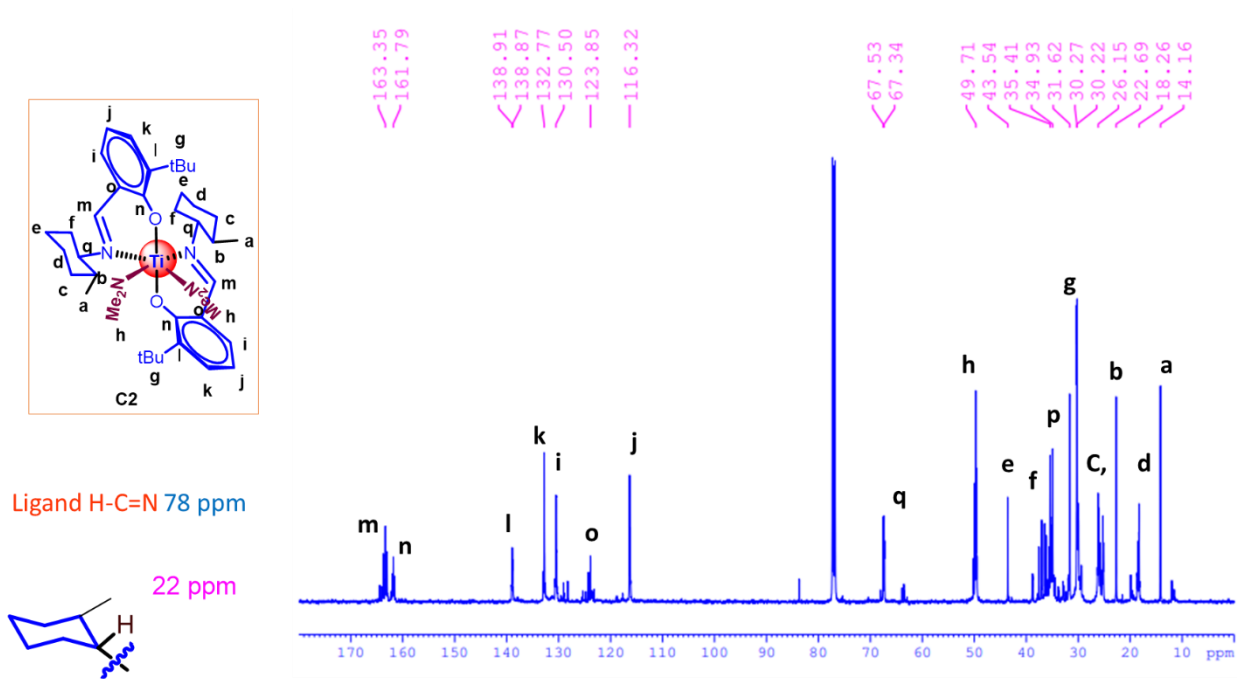


Figure 4.40: ^{13}C NMR spectrum of Cat.2 in CDCl_3 (125 MHz).

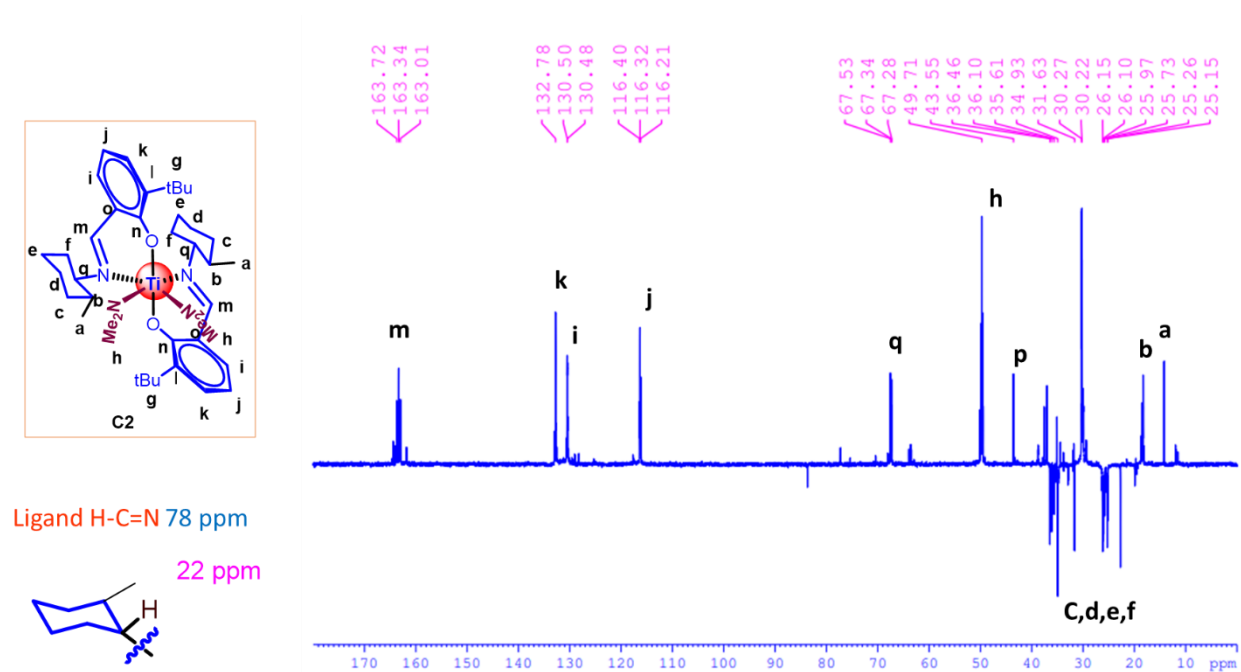


Figure 4.41: DEPT NMR spectrum of Cat.2 in CDCl_3 (125 MHz).

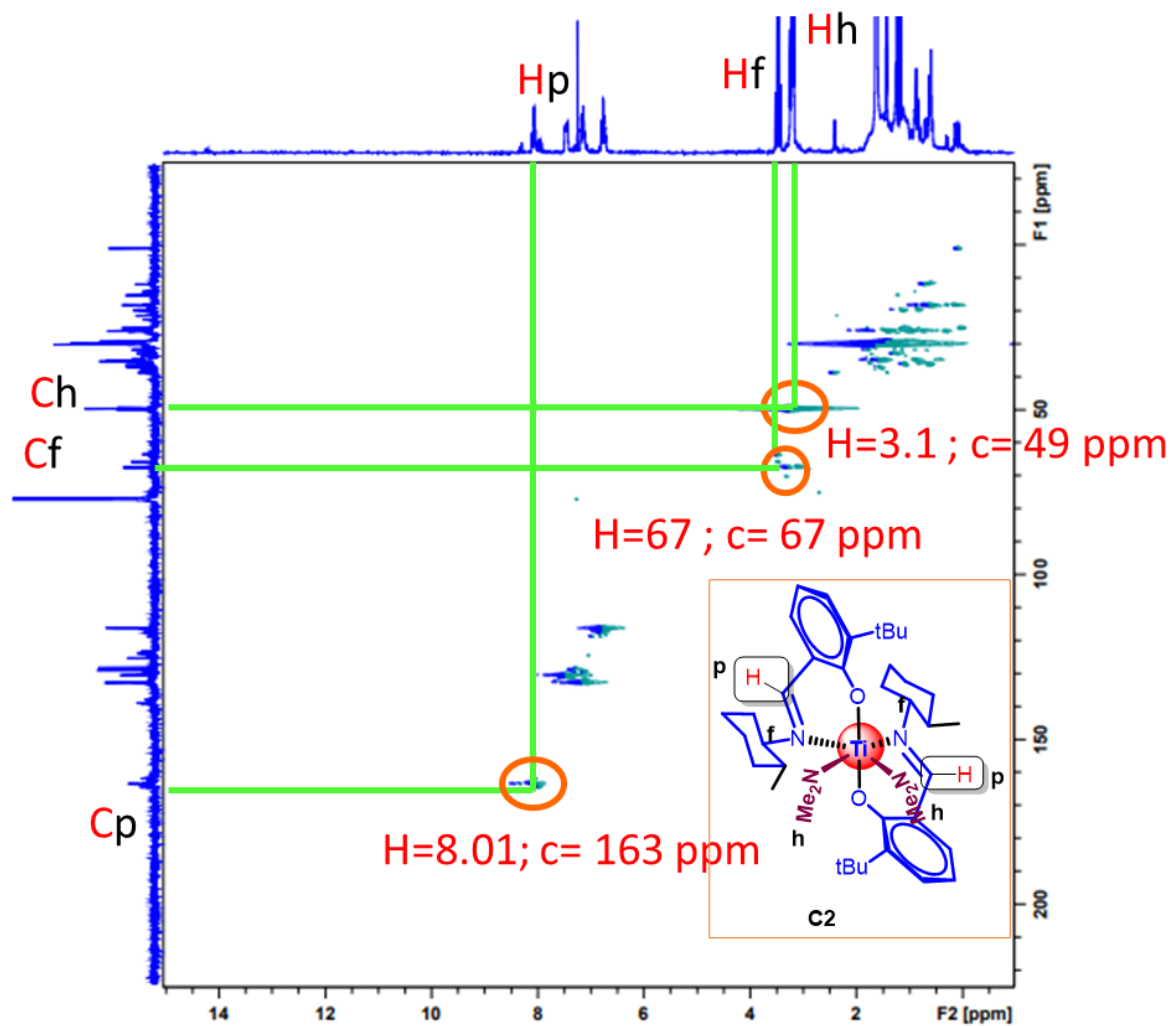


Figure 4.42: Expanded view of a short-range C-H correlation (HSQC) NMR spectrum of Cat.2 in CDCl_3 (500 MHz).

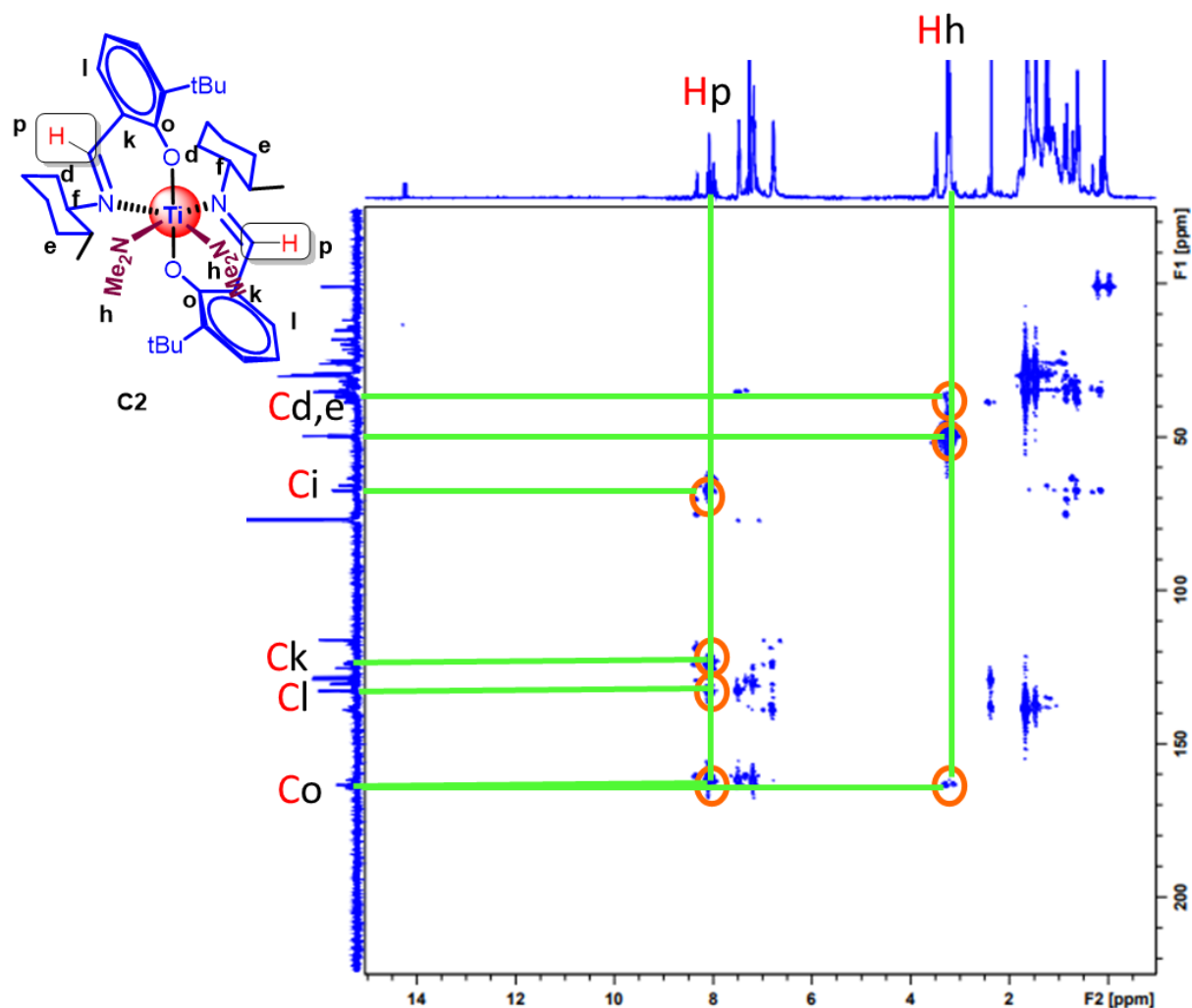


Figure 4.43: Expanded view of a long-range C-H correlation (HMBC) NMR spectrum of Cat.2 in CDCl₃ (500 MHz).

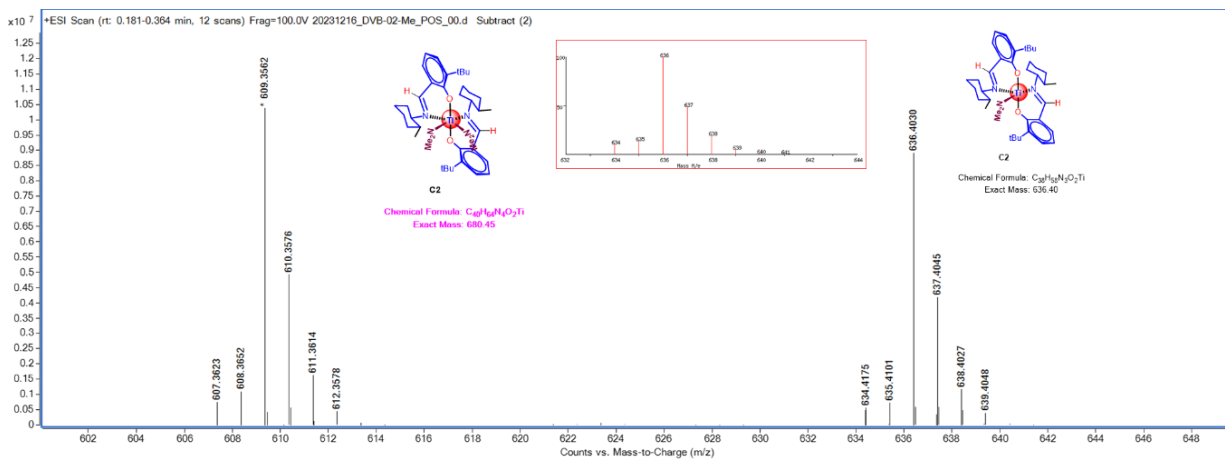


Figure 4.44: ESI-MS spectrum (+ ve mode) of Cat.2.

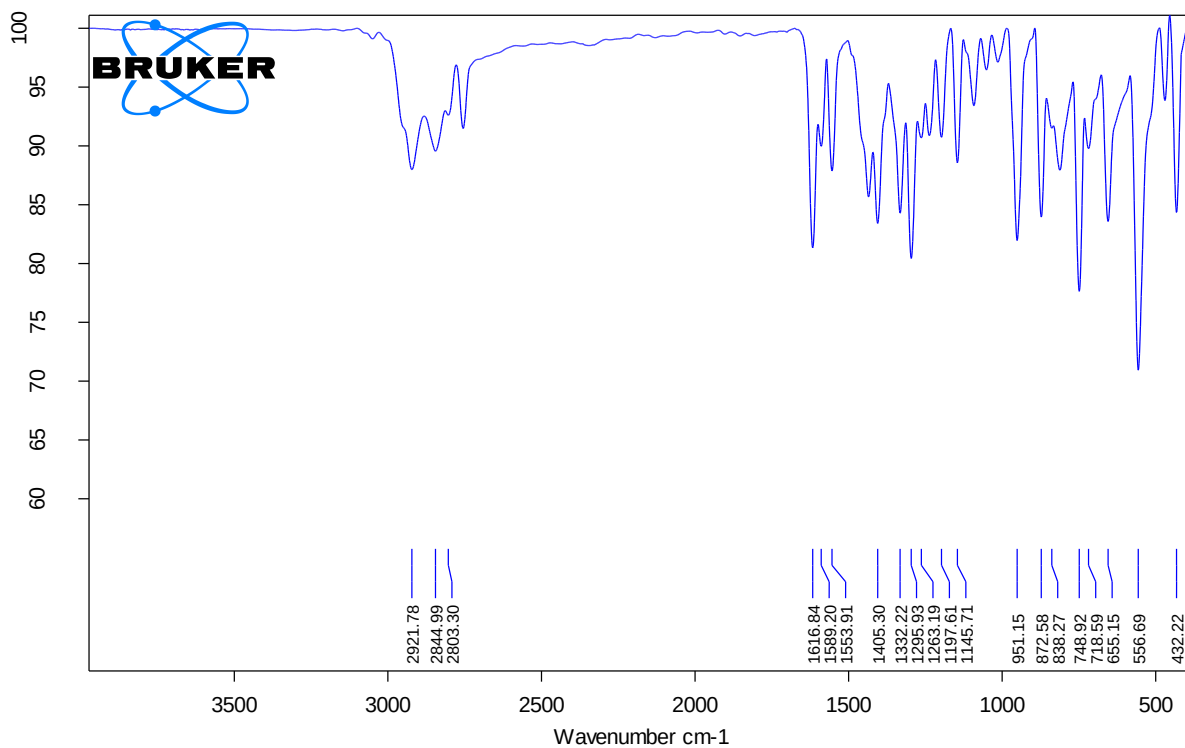
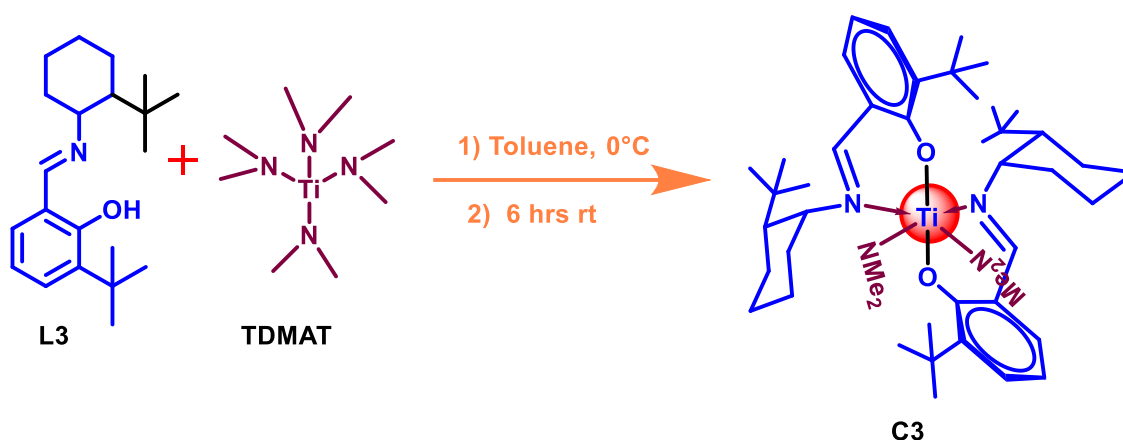


Figure 4.45: IR-spectrum of Cat.2.

4.7.3. [Bis-dimethyl amido-Ti-(bis-[N-(3-tert-butylsalicylidene) 2-tert-butylcyclohexylaminato])] (Cat.3)



After cooling under vacuum, argon gas was purged from a 250 mL drying in the oven Schlenk flask. The Schlenk flask was heated and cooled three times under vacuum to reduce the moisture content. Under the positive flow of argon, 1 g (3.2 mmol.) of **L3** was added to the above Schlenk flask. After that, 40 mL of toluene was added, and the mixture was agitated for five minutes. Ti (NMe₂)₄ (0.54 mL, 1.6 mmol) was added gradually over the course of five minutes after the Schlenk had been cooled to 0 °C. A turbid yellow mixture turned to a clear reddish-brown solution. Subsequently, the ice bath was then replaced with a water bath and the temperature of the reaction mixture was raised from 0 °C to about 30 °C. After then, the mixture was stirred for six more hours at room temperature. Vacuum was used to evaporate the volatiles after another half hour of stirring. A reddish-brown residue was obtained. This crude residue was further purified by dissolving it in freshly distilled hexane (5 mL) and low temperature overnight precipitation to obtain the solid. The solid was separated from the liquid supernatant. The solid (1 gm, 41%) was then vacuum-dried and stored in the glove box for future use.

In order to help the reader, the following data and figures are reproduced below.

¹H NMR (CDCl₃, 500 MHz): δ = 8.62 (s, 2H, HC=N-), 7.45 (d, J = Ar, 2H, 7.63 Hz), 7.17 (d, J = Ar, 2H, 7.00 Hz), 6.76 (t, J = 5.88, Ar, 2H, 7.50 Hz), 3.15 (s, -NMe₂ 12H), 3.19 (m, cyclohexyl-N, 2H), 1.57 (s, Ar-tert butyl 18H), 0.80 (s, Cy6 tert butyl 18H), 0.80 to 1.64 (m, 18H, Cyclohexyl

CH₂), 0.90 (s, cyclohexyl-Me). ¹³C NMR (125 MHz, CDCl₃) δ = 155 (-C=N), 148.5, 131.3, 129.8, 127.4, 125.6, 118.7, 114.7, 30.3 (Ar t-butyl) 29.2 (Cyclohexyl t-CH₃), 40.5 (-N(CH₃)₂).

ESI-MS (+ve) for C₄₆H₇₇N₄O₂Ti [M+H]⁺ Calculated: m/z = 765.5 Da, observed: m/z = 765.5 [Cat.3+H]⁺ Da.

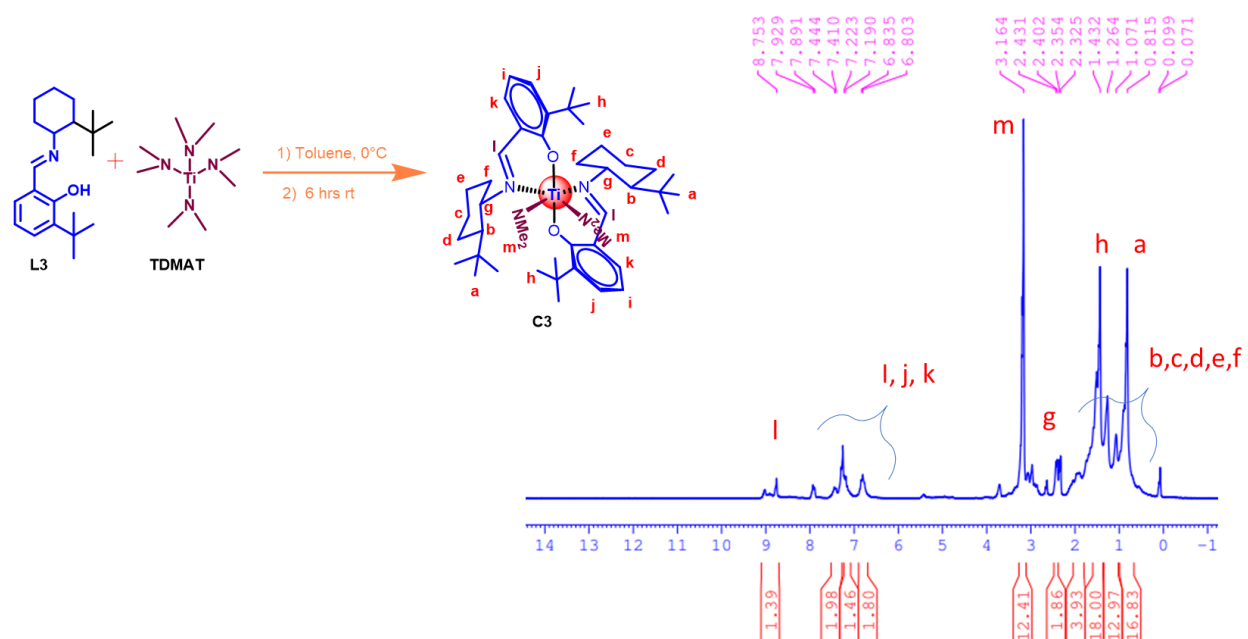


Figure 4.46: ¹H NMR spectrum of Cat.3 in CDCl₃ (400 MHz).

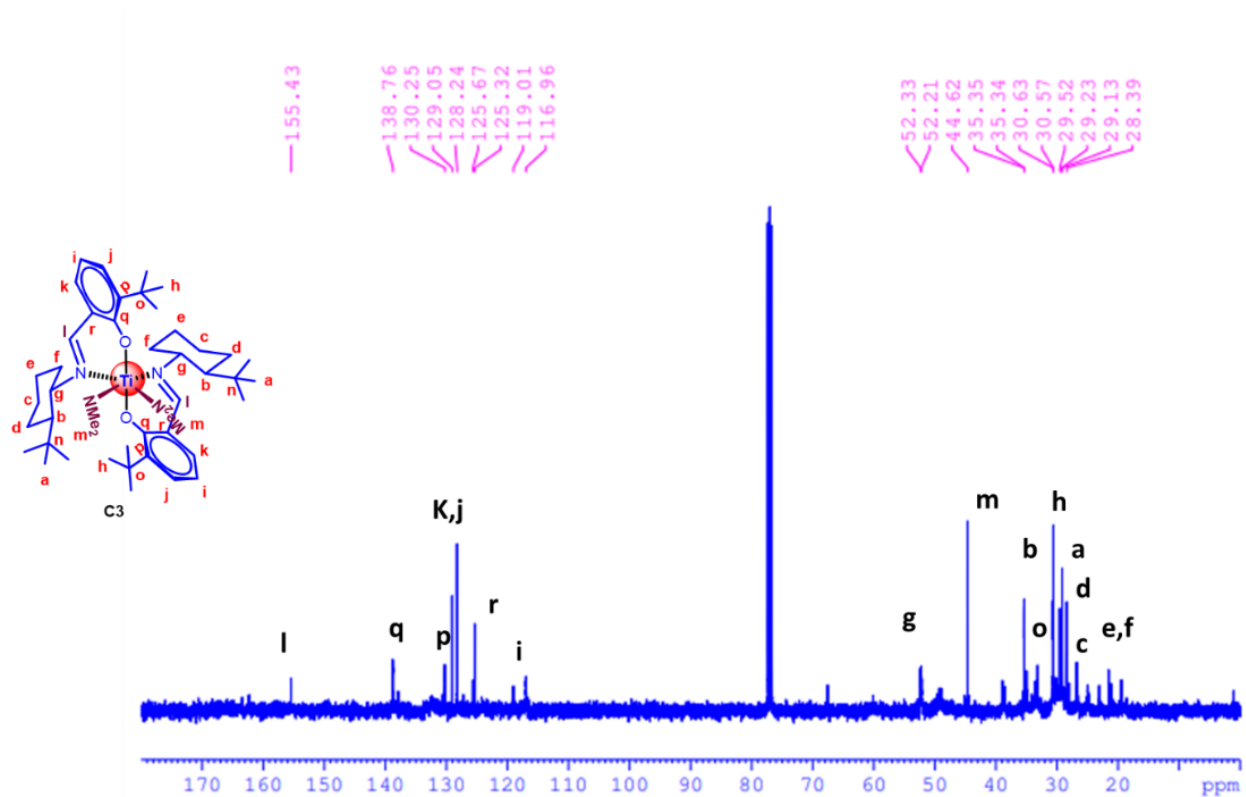


Figure 4.47: ^{13}C NMR spectrum of Cat.3 in CDCl_3 (100 MHz).

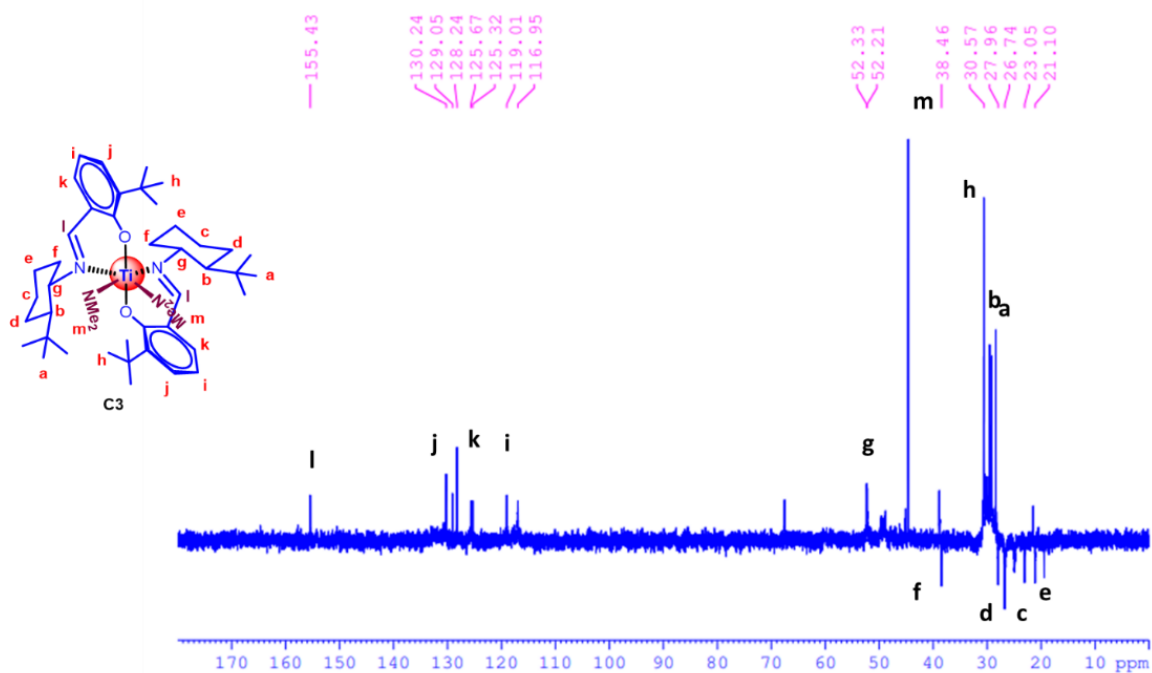


Figure 4.48: DEPT NMR spectrum of Cat.3 in CDCl_3 (100 MHz).

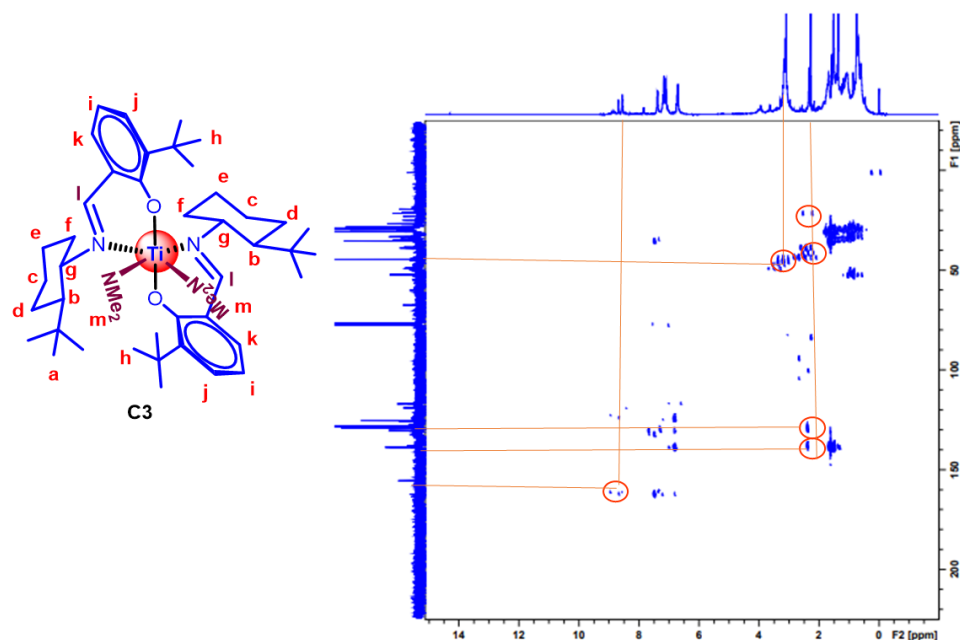


Figure 4.49: HMBC NMR spectrum of Cat.3 in CDCl_3 (100 MHz).

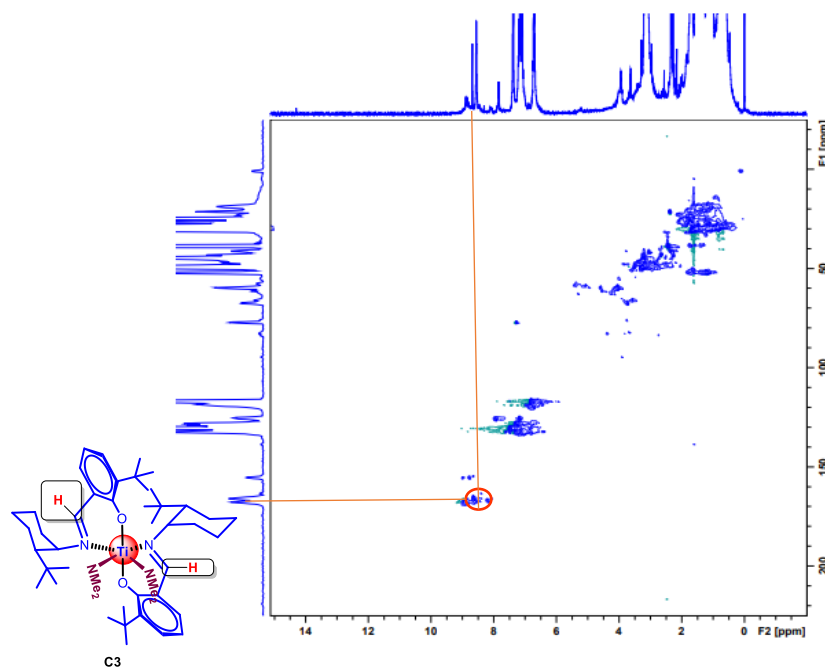
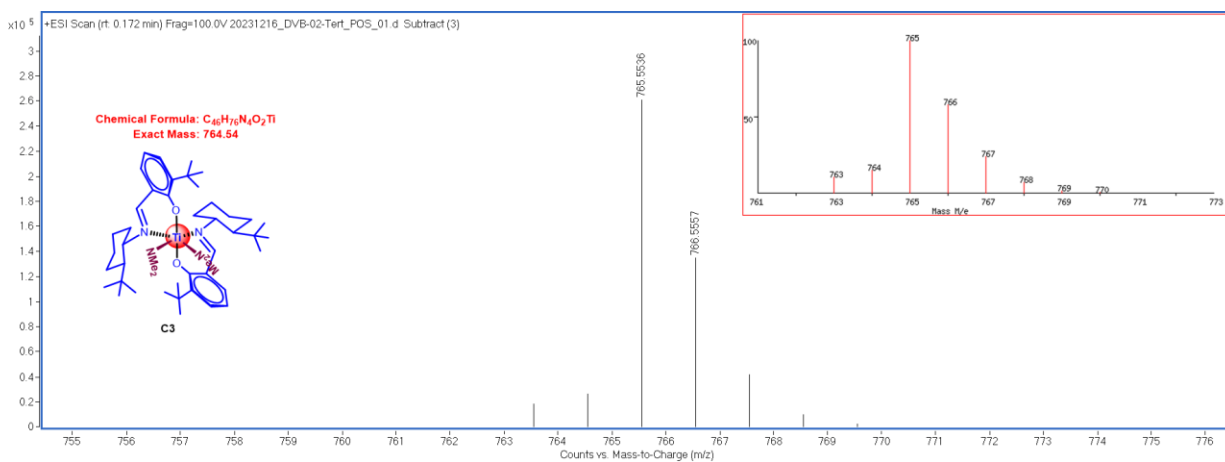
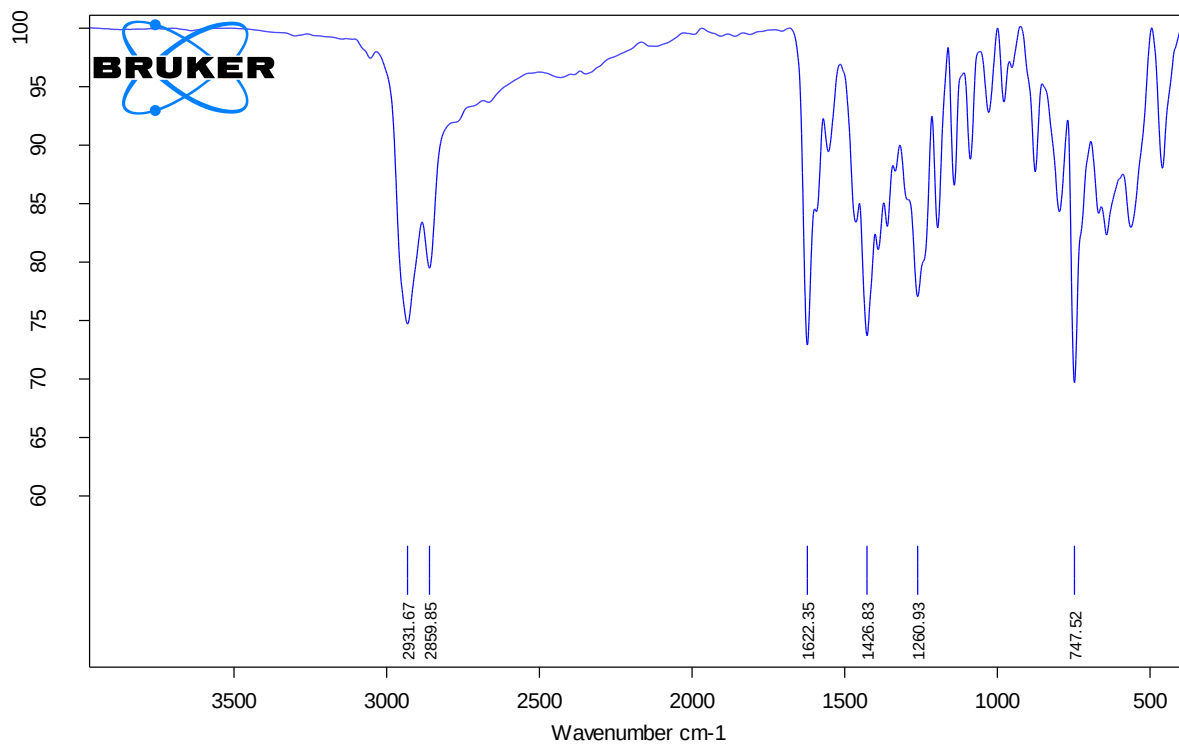


Figure 4.50: HSQC NMR spectrum of Cat.3 in CDCl₃ (100 MHz).**Figure 4.51:** ESI-MS spectrum (+ ve mode) of Cat.3.**Figure 4.52:** IR of Cat.3.

4.8. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a Thermo Scientific K-Alpha+ X-ray Photoelectron

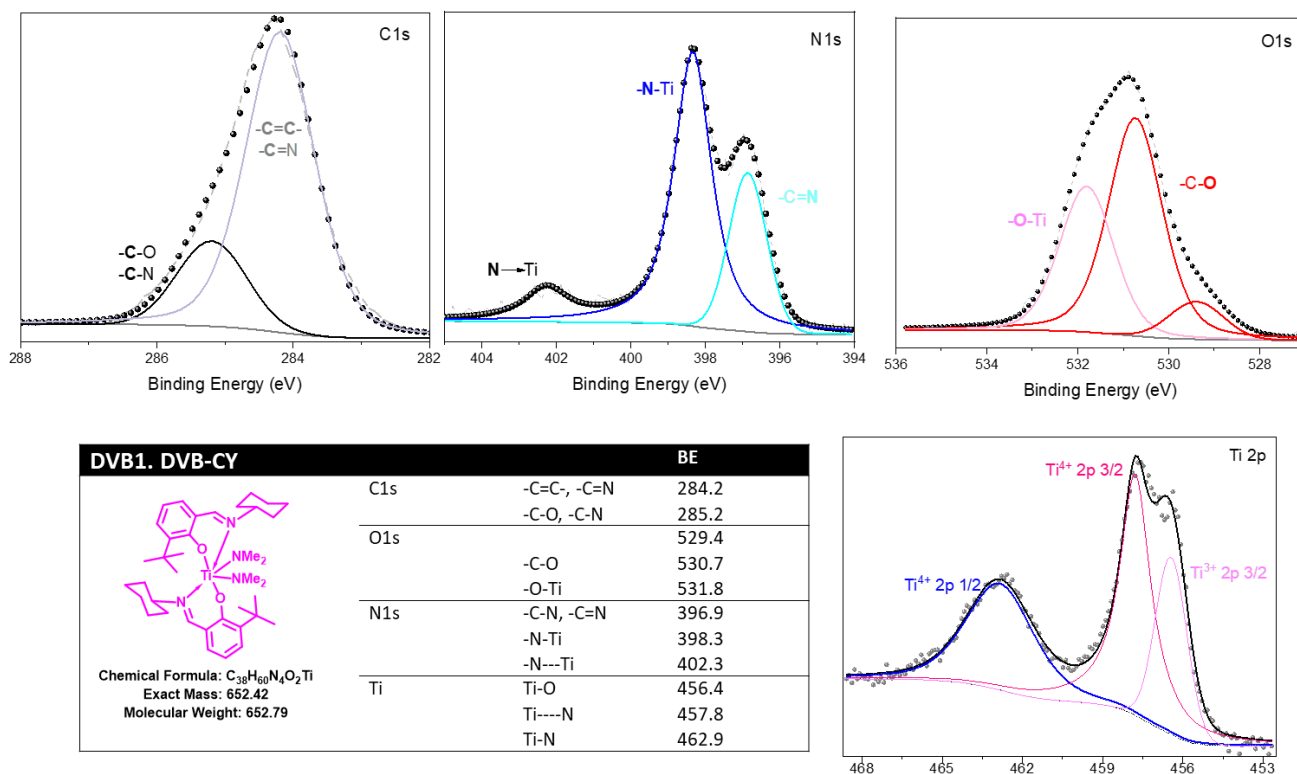


Figure 4.53: XPS analysis of Cat.1.

Spectrometer System (XPS). A vacuum transfer module was used to move samples from the glove box to the K-Alpha+ system without exposing them to air because the catalyst is sensitive to both moisture and air. The vacuum transfer module components cover, base, to avoid device sealing during antechamber evacuation cycles, the clamp and device were put into the glove box separately. Carbon tape was used to mount the samples on the base. Once the samples were mounted, the vacuum transfer module was sealed and kept in a small antechamber under vacuum for 20 minutes to lock it under vacuum. The module was then transferred to the K-Alpha for XPS analysis, where it was automatically opened in the load lock chamber once the pressure reached better than 10^{-6} torr. During analysis, the base pressure was 10^{-9} torr. As per XPS analysis all the complex observed in +4 oxidation state.

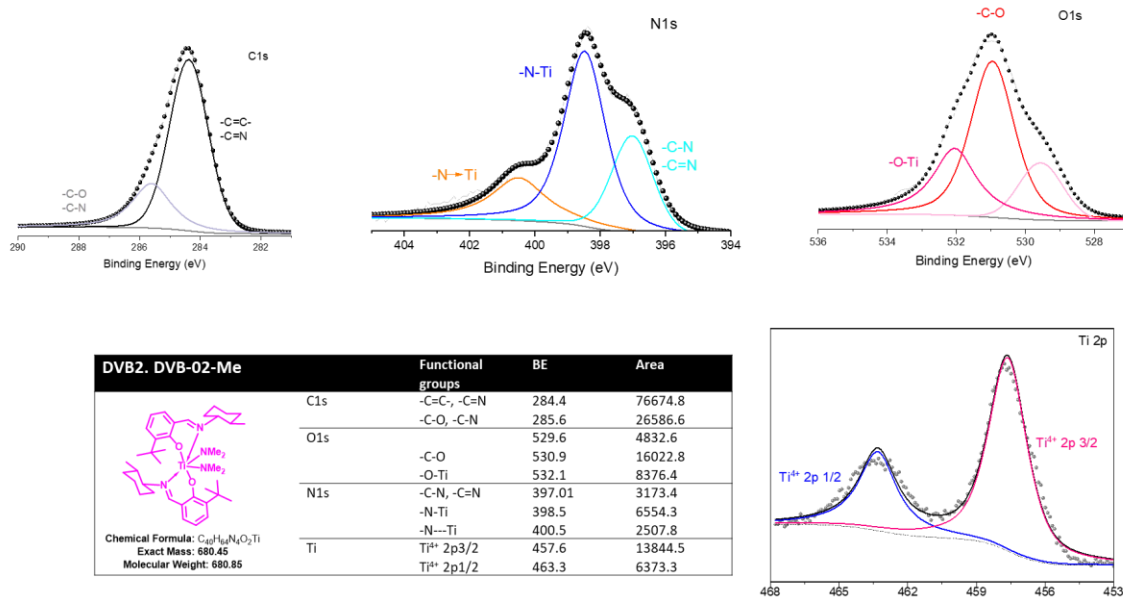


Figure 4.54: XPS analysis Cat.2.

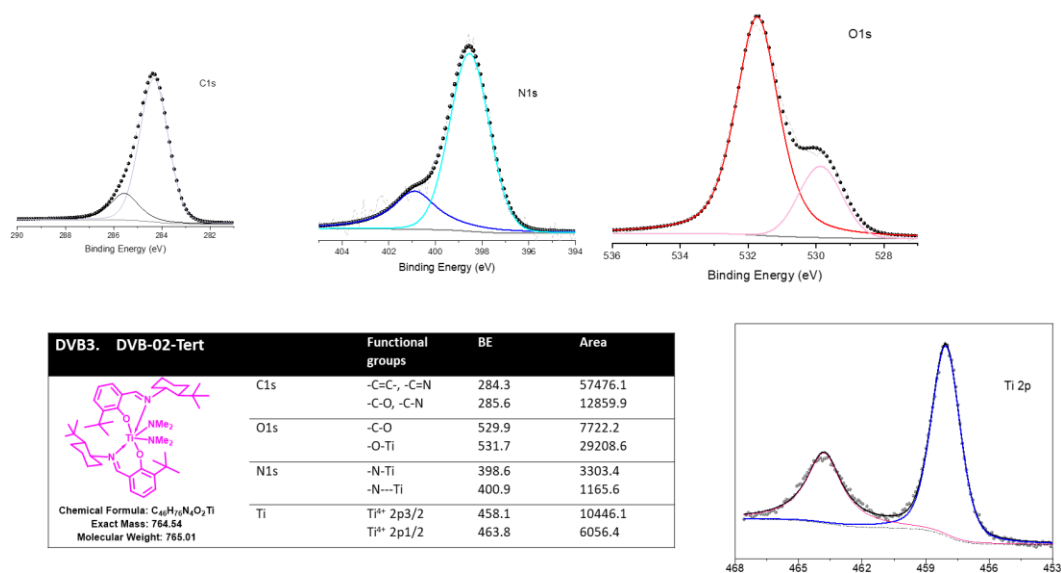
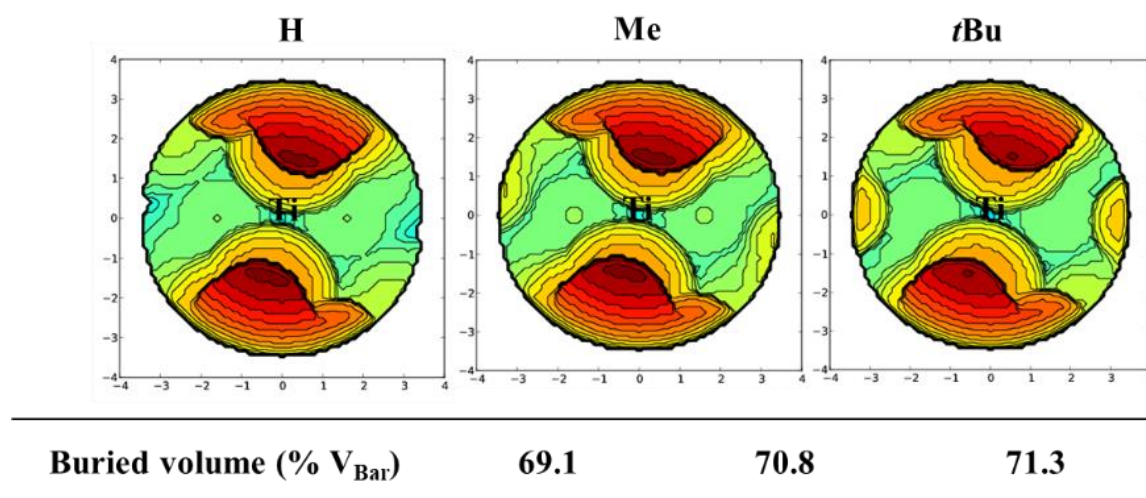


Figure 4.55: XPS analysis Cat.3.

4.9. Buried volume quantification



Stearic quantification of Ti complexes (Buried volume (% V_{bur}))

Figure 4.56: Buried volume (% V_{bur}) for Cat.1, Cat.2 and Cat.3.

4.10. Procedure for ethylene polymerization

A Büchi glasuster cyclone 075 high-pressure reactor with a heating/cooling jacket, pressure regulators, and an overhead mechanical stirrer was used to conduct the ethylene polymerisation reaction. Before use, a 250 mL Büchi reactor that had been previously dried was vacuum-sealed at 90 °C for half an hour. Following cooling, argon was pumped into the reactor, followed by three cycles of argon and vacuum, ethylene gas (20 bar), and three flushes. It was charged with 100 millilitres of newly distilled, dried toluene at room temperature while ethylene gas was flowing positively. Using a Julabo temperature controller, the reaction temperature was adjusted to the correct range. Once thermal equilibrium was achieved, 70% of the total cocatalyst (MMAO-12) was added, and the mixture was swirled for roughly ten minutes. The remaining 30% cocatalyst (MMAO-12) was added concurrently to 10 mL of dried, newly distilled toluene in a different Schlenk tube, and the mixture was swirled for half an hour. After 30 minutes, 10 mL of dry toluene-containing cocatalyst (MMAO-12) and an appropriate quantity of catalyst were put into the reactor. The polymerisation process was then started by applying ethylene pressure to the reactor. The addition of acidified methanol ended the polymerisation after it had been vigorously stirred and fed ethylene continuously for the necessary amount of time. To create a free-flowing powder, the polymer was filtered out, thoroughly cleaned with methanol/acetone, and vacuum-dried for an entire night at 60 °C.

4.10.1. Polymer characterization

4.10.2. DSC (Differential Scanning Calorimetry)

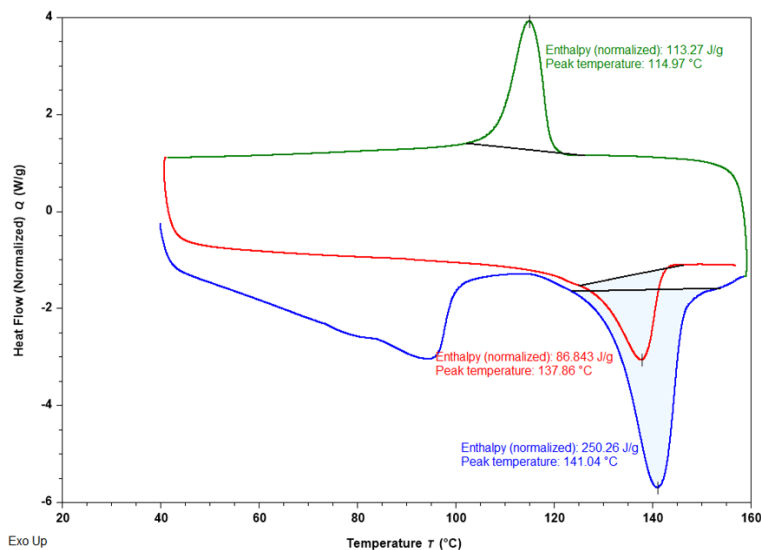


Figure 4.57: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 1).

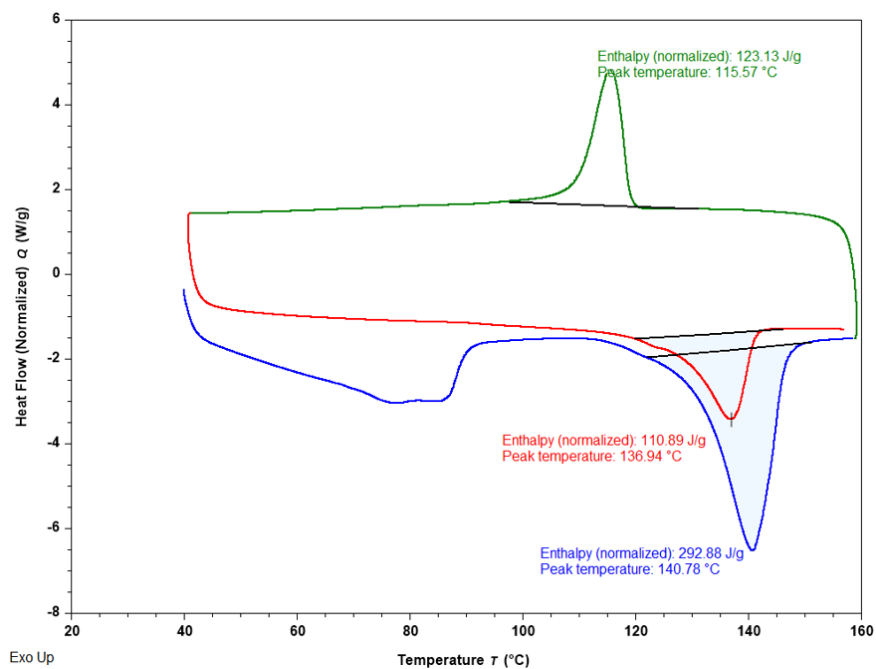


Figure 4.58: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 2).

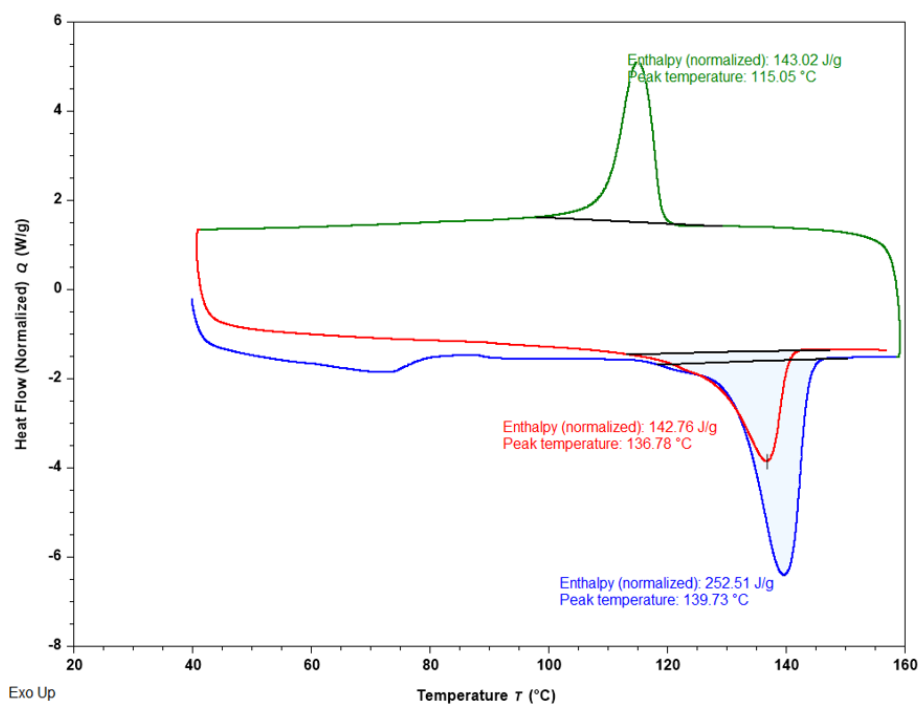


Figure 4.59: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 3).

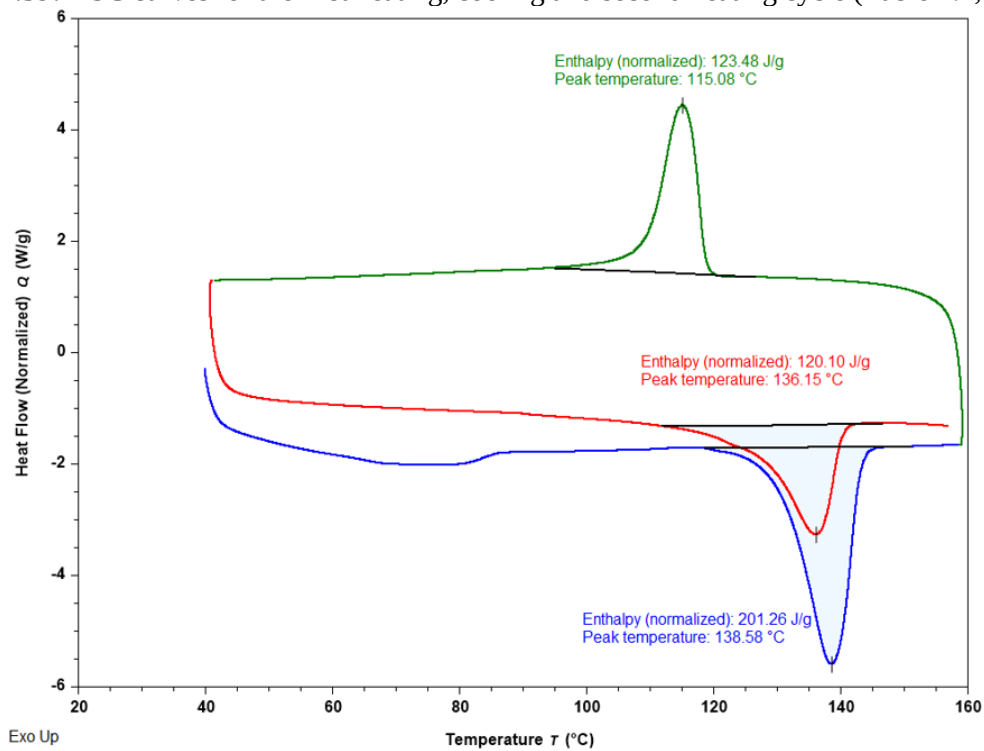


Figure 4.60: DSC curve for the first heating, cooling and second heating cycle (Table 4.4, entry 4).

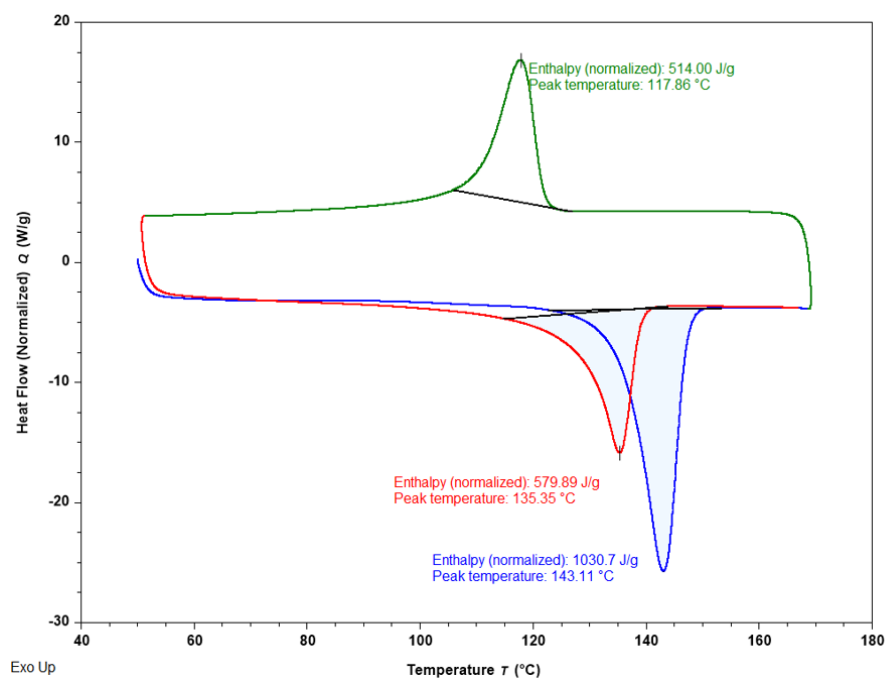


Figure 4.61: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 5).

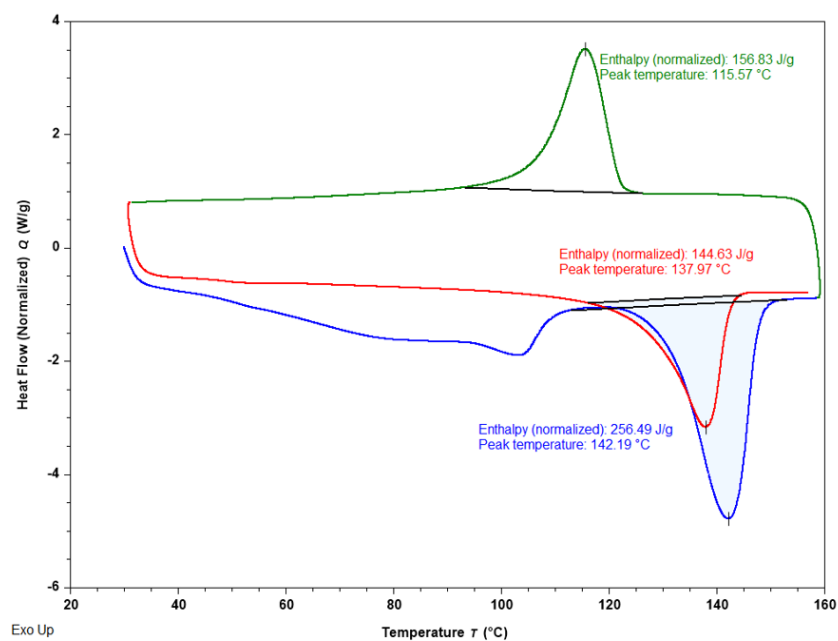


Figure 4.62: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 6).

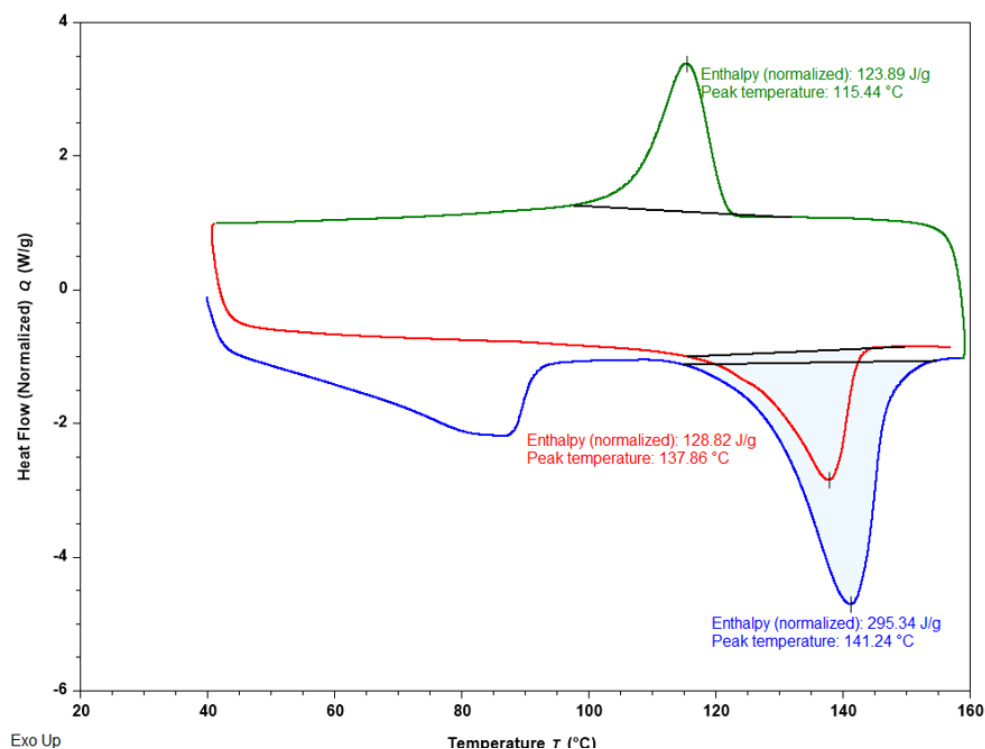


Figure 4.63: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 7).

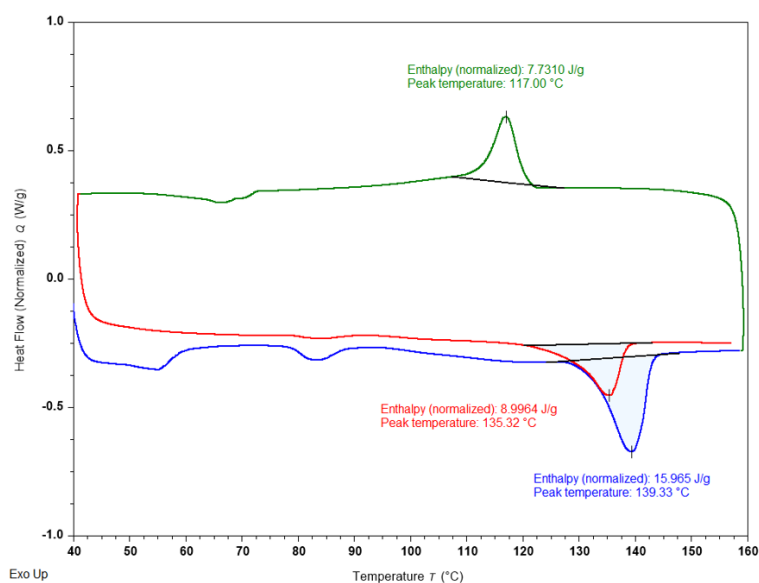


Figure 4.64: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 8).

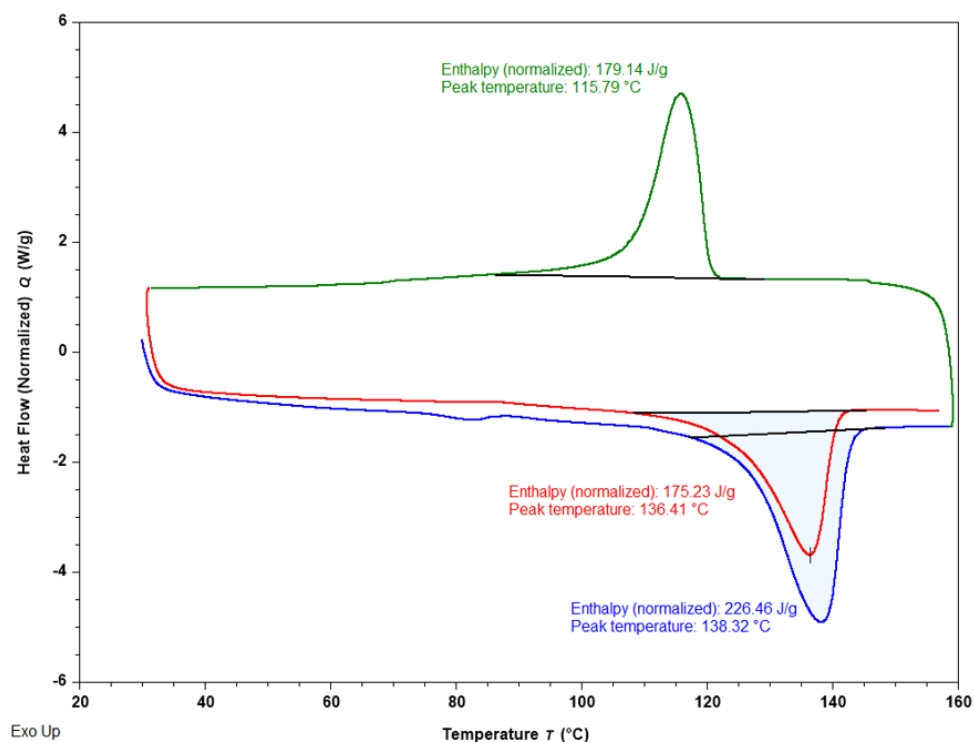


Figure 4.65: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 9).

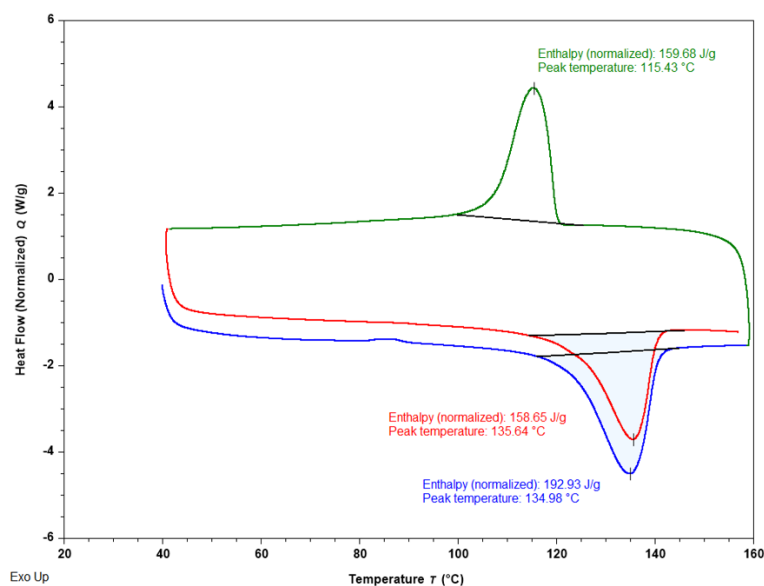


Figure 4.66: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 10).

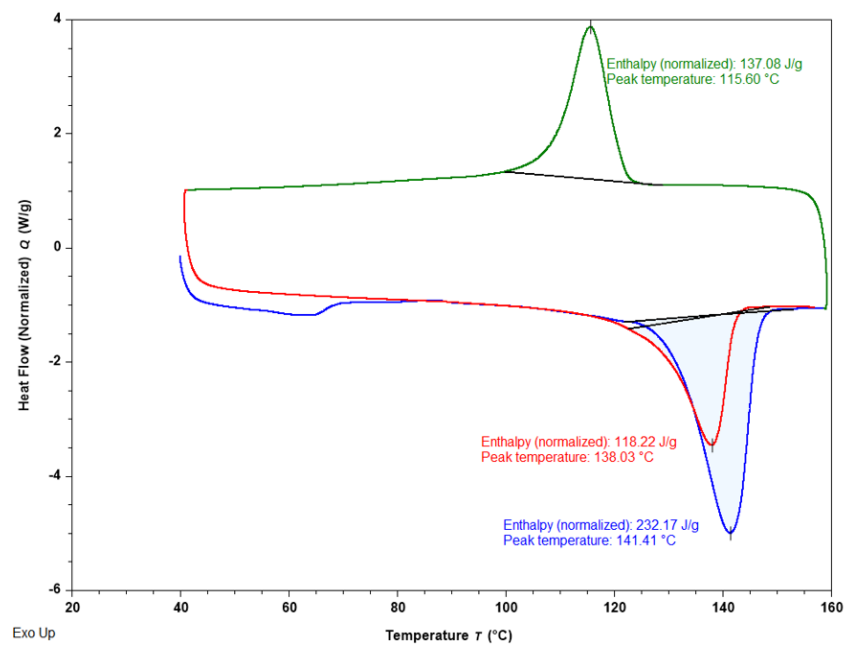


Figure 4.67: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 11).

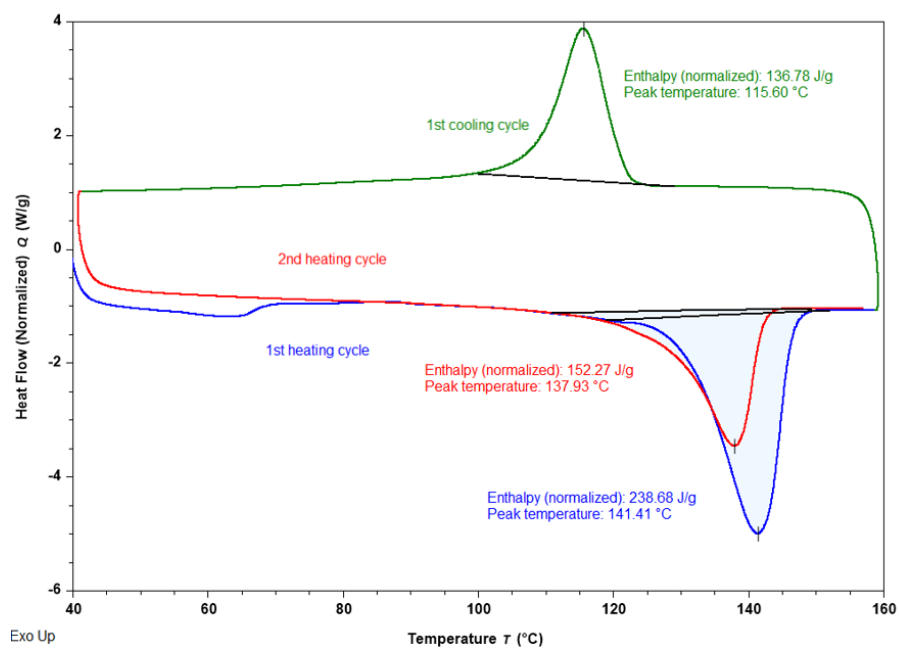


Figure 4.68: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 12).

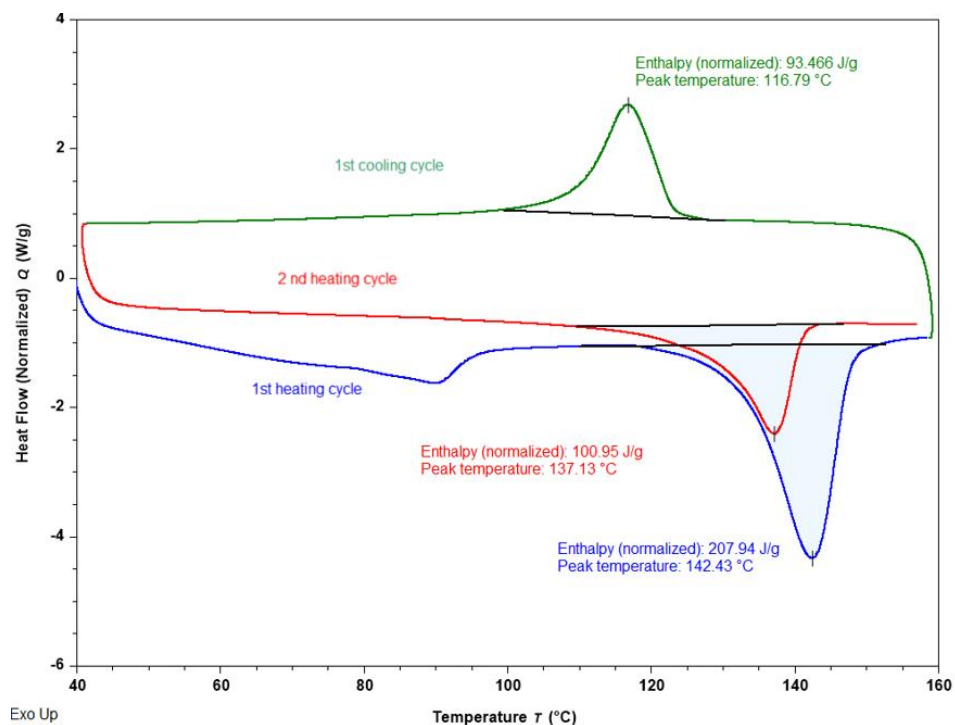


Figure 4.69: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 13).

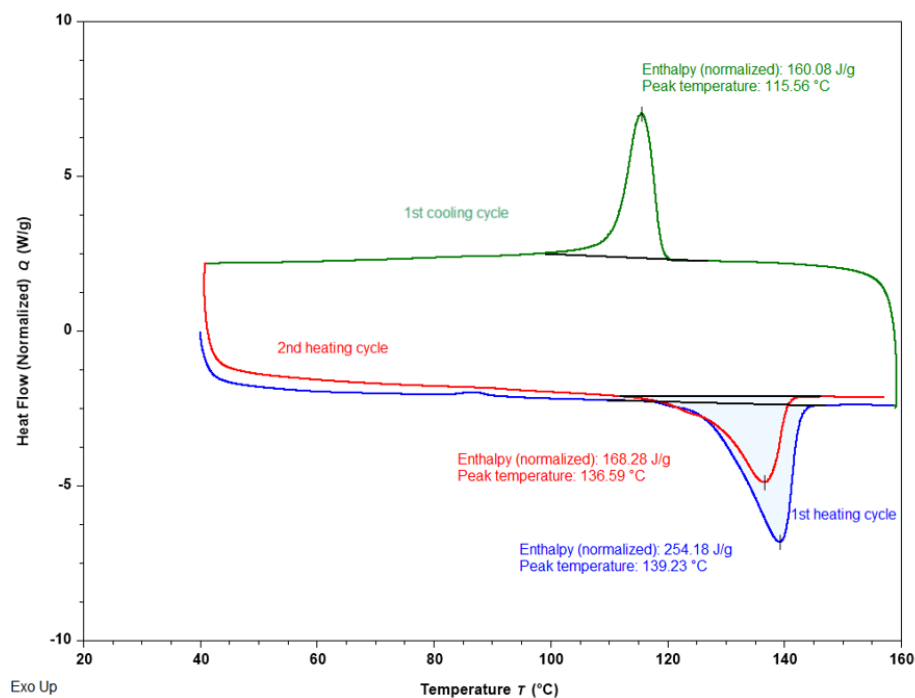


Figure 4.70: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 14).

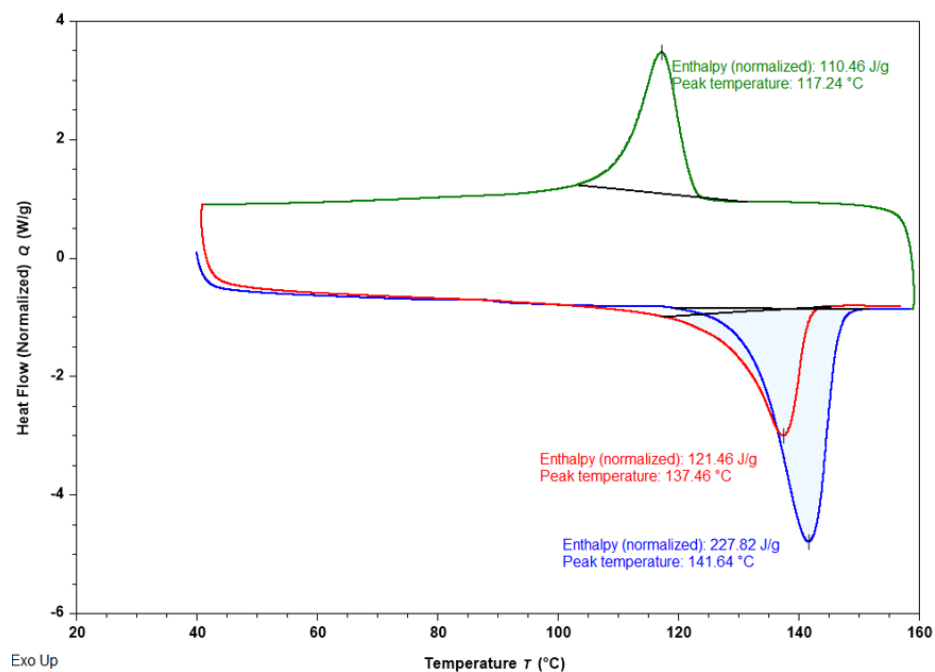


Figure 4.71: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 15).

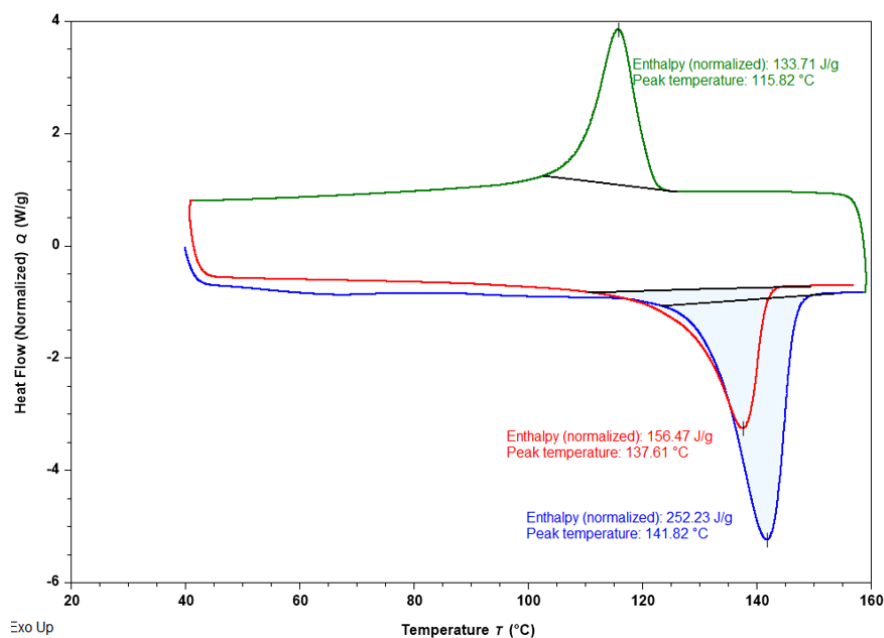


Figure 4.72: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 16).

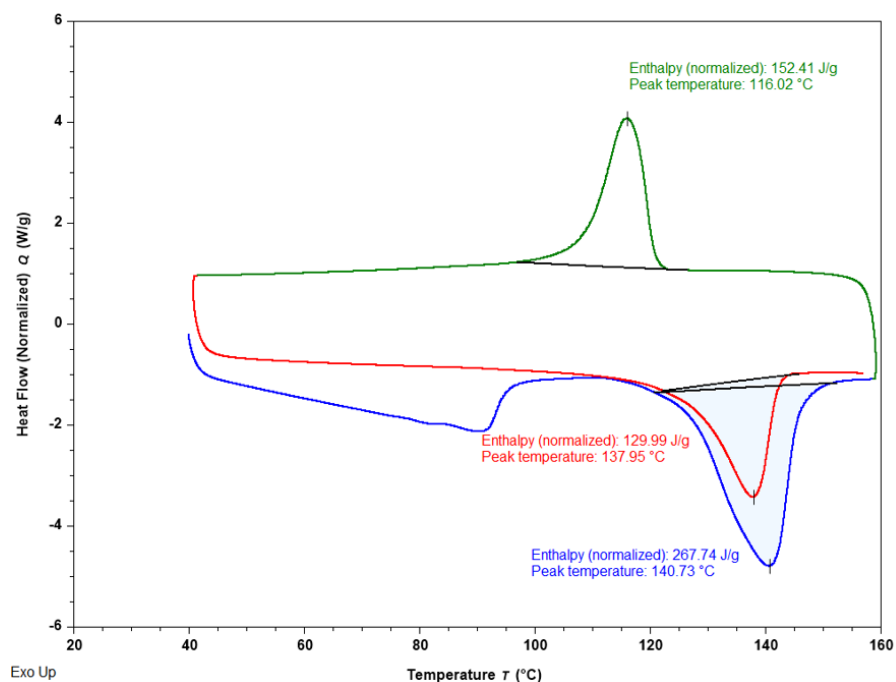


Figure 4.73: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 17).

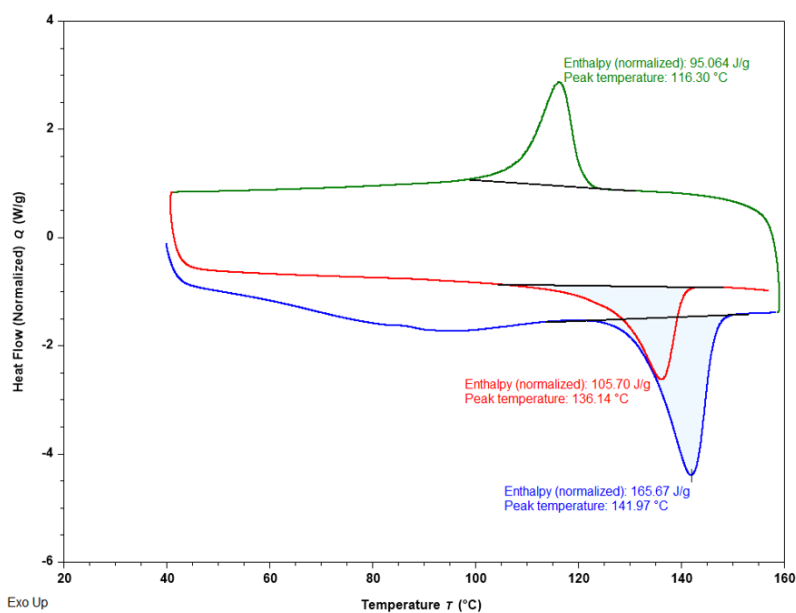


Figure 4.74: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 18).

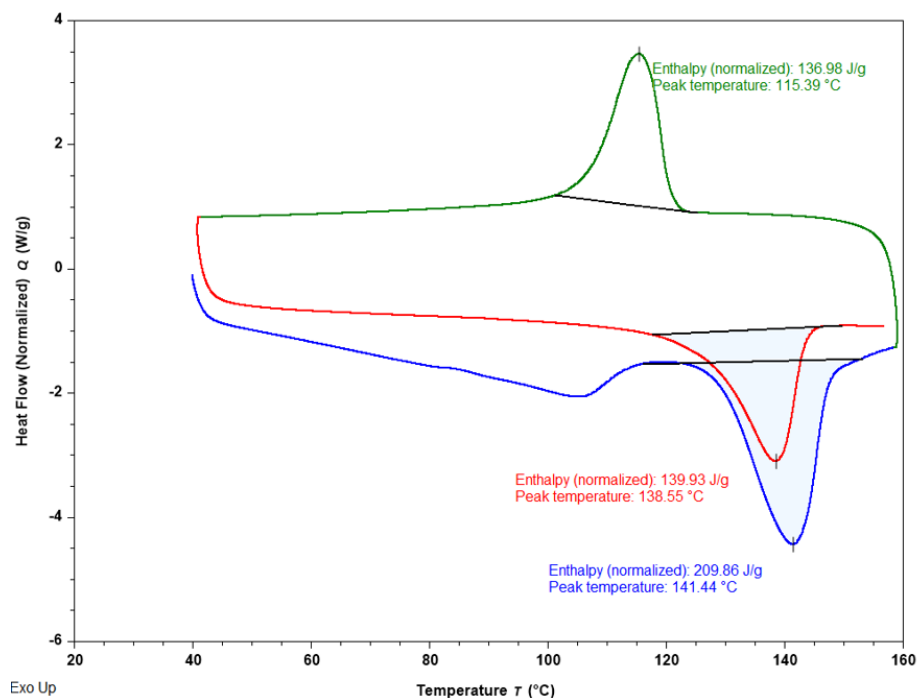


Figure 4.75: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 19).

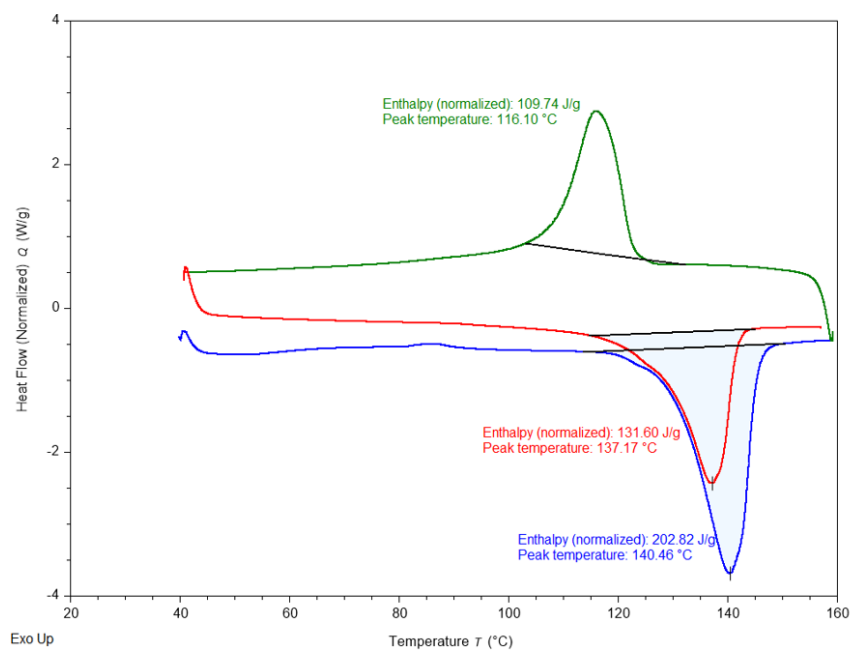


Figure 4.76: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 20).

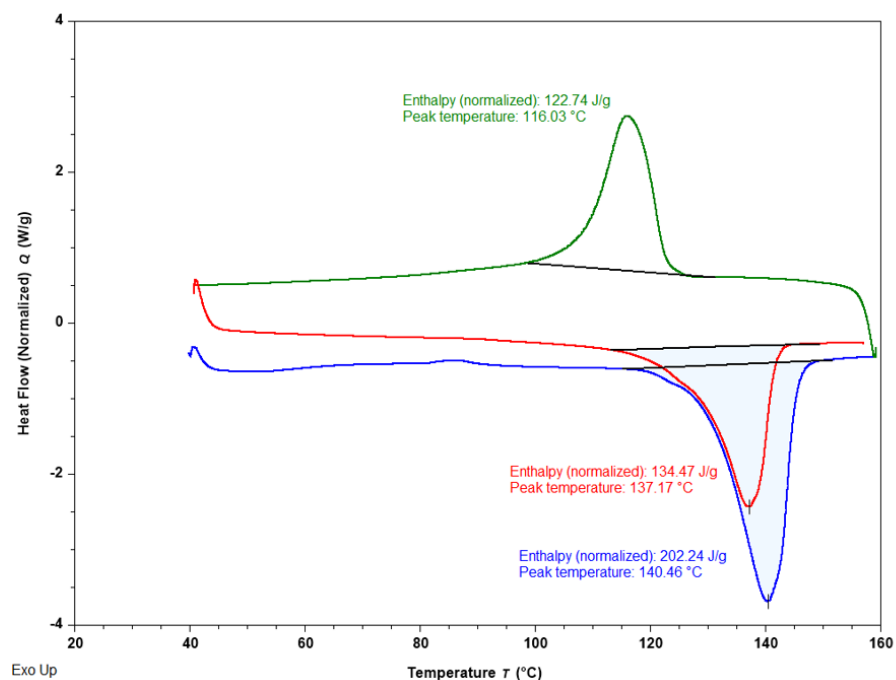


Figure 4.77: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 21).

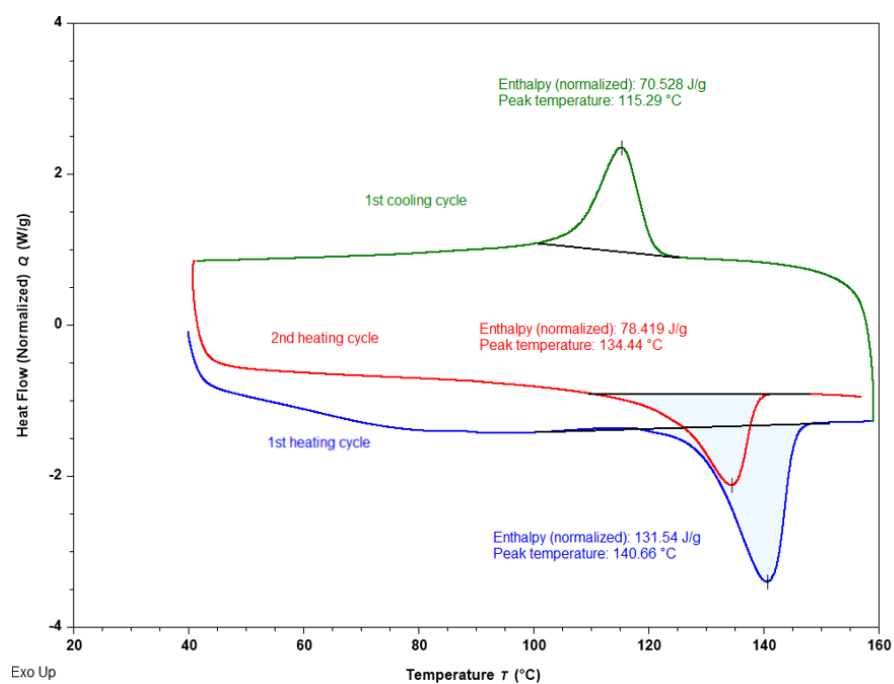


Figure 4.78: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 22).

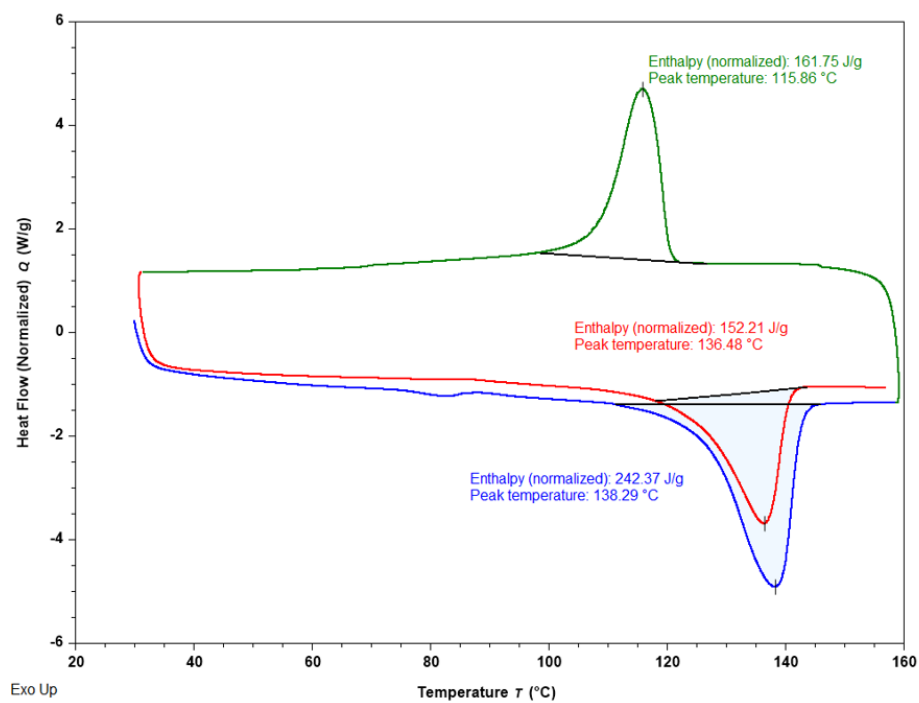


Figure 4.79: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 23).

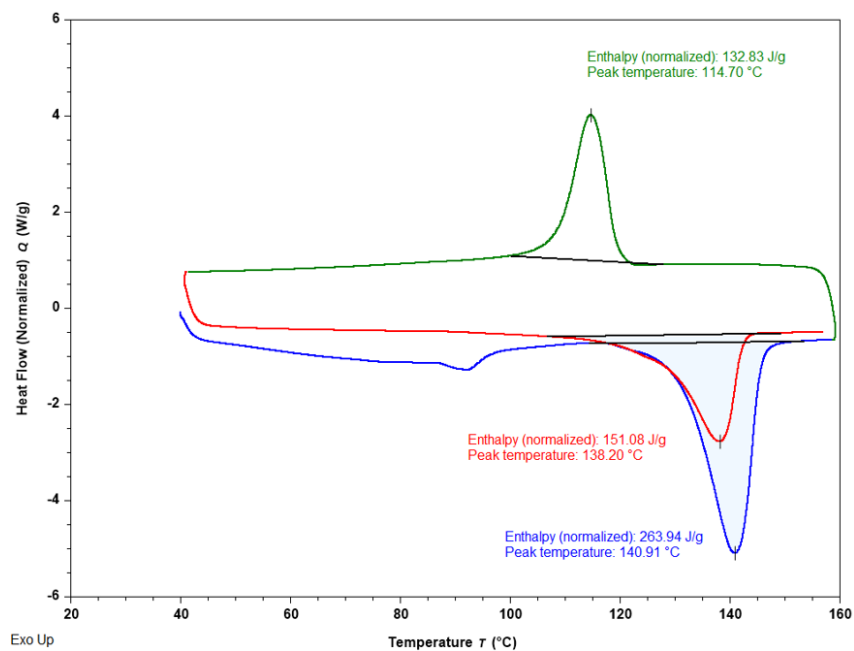


Figure 4.80: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 24).

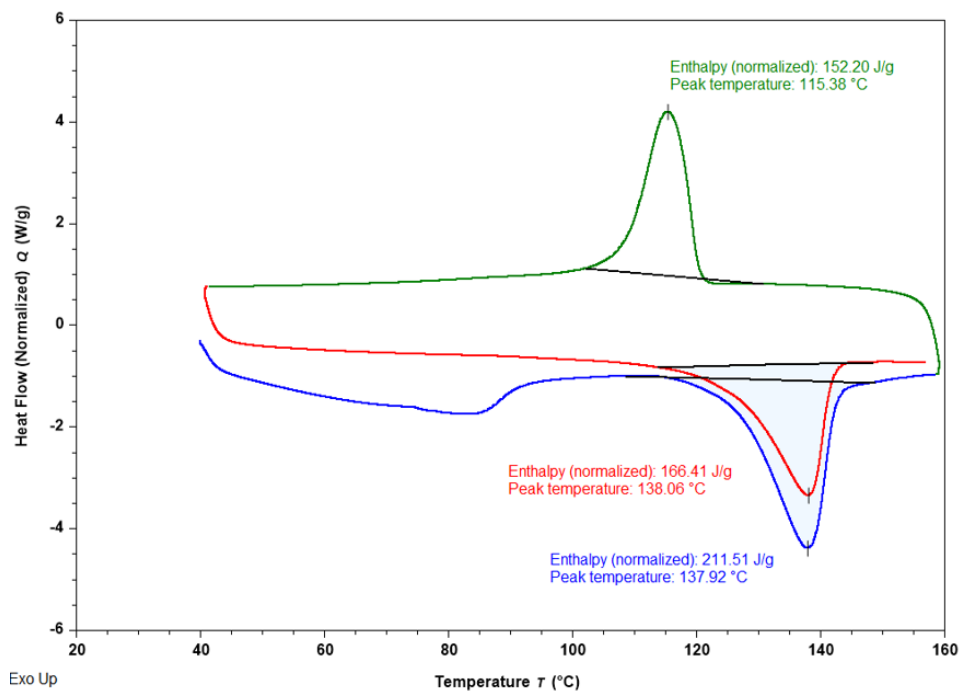


Figure 4.81: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 25).

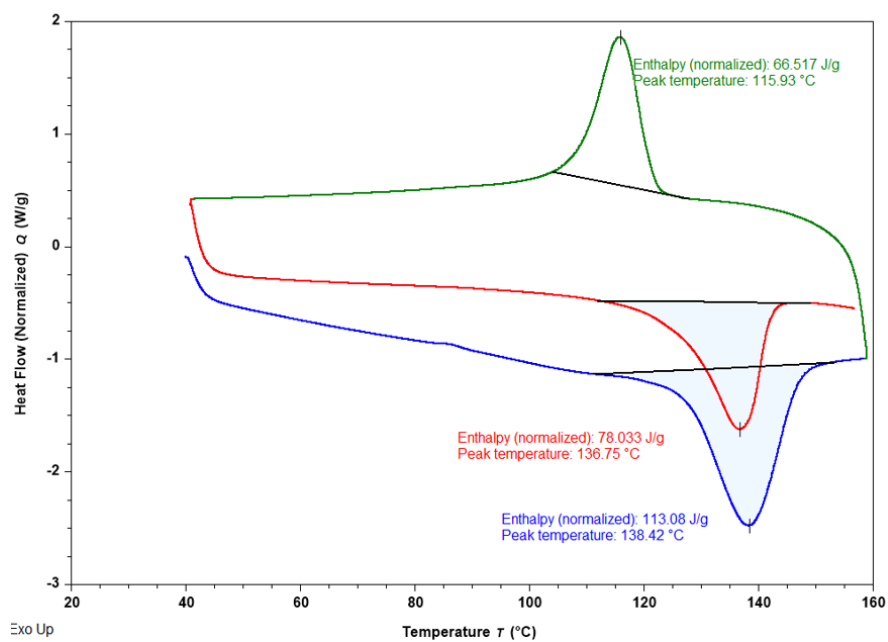


Figure 4.82: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 26).

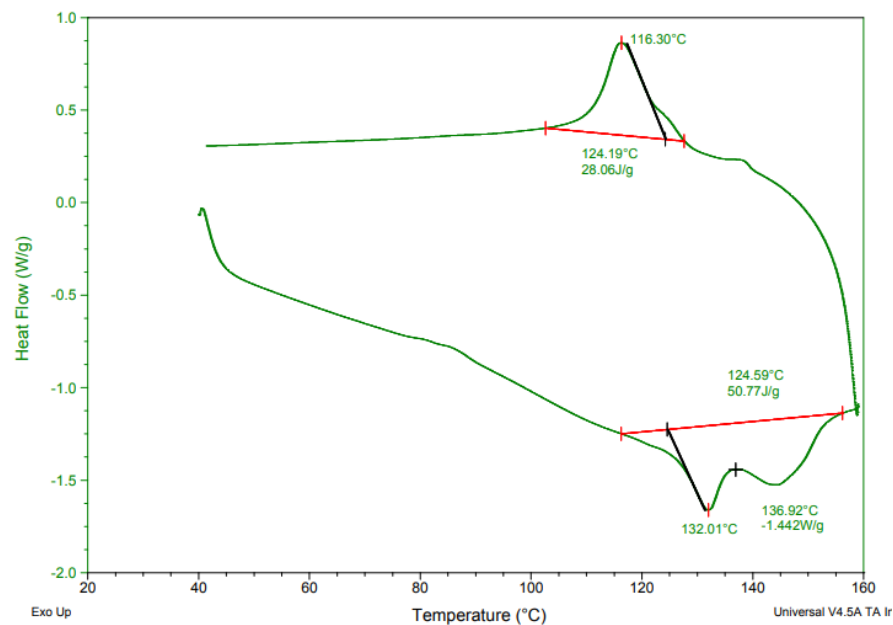


Figure 4.83: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 27).

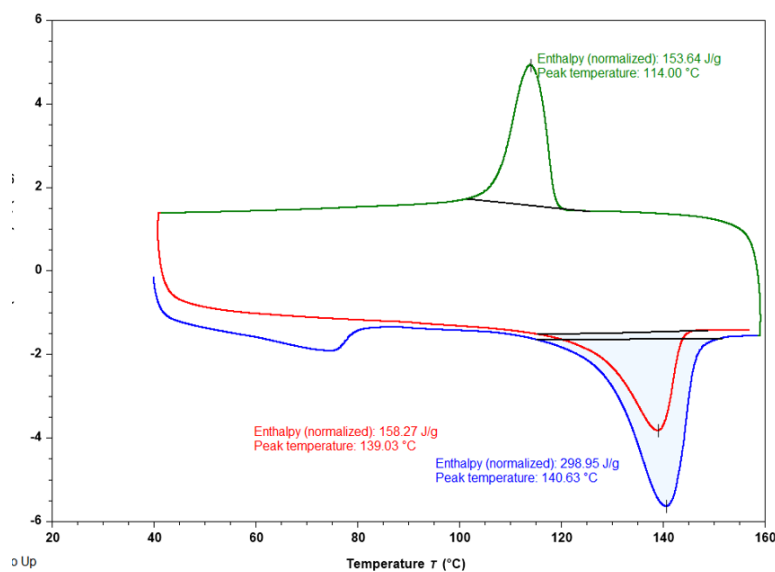


Figure 4.84: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 28).

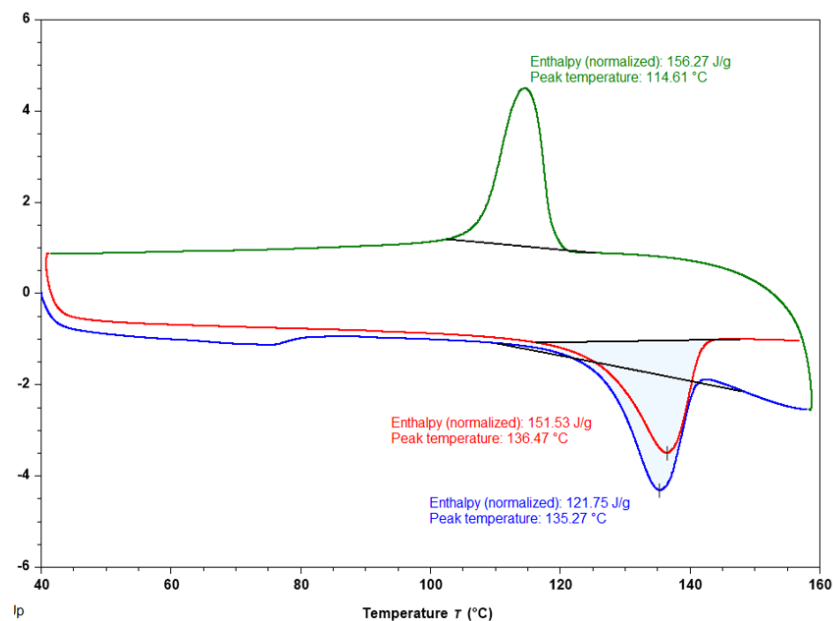


Figure 4.85: DSC curves for the first heating, cooling and second heating cycle (Table 4.4, entry 29).

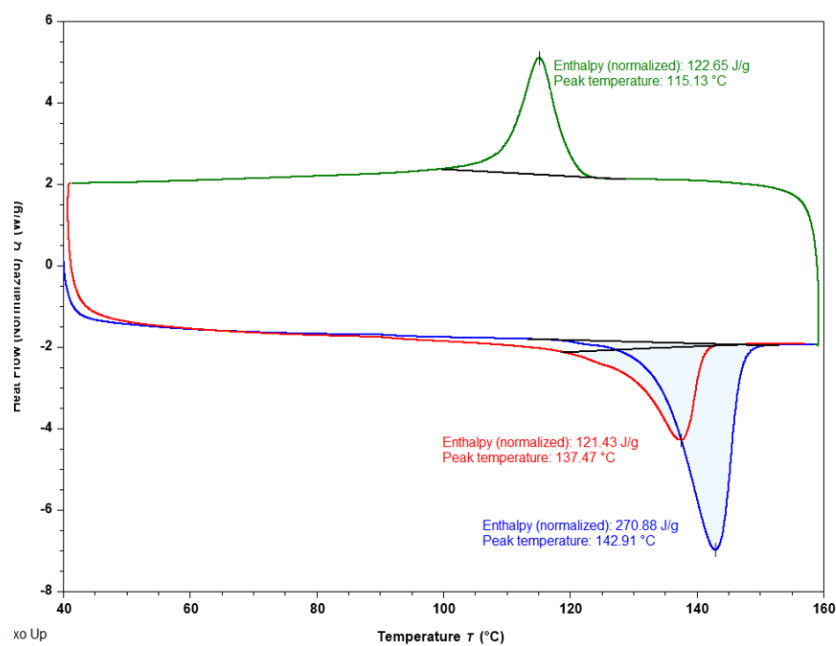


Figure 4.86: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 1).

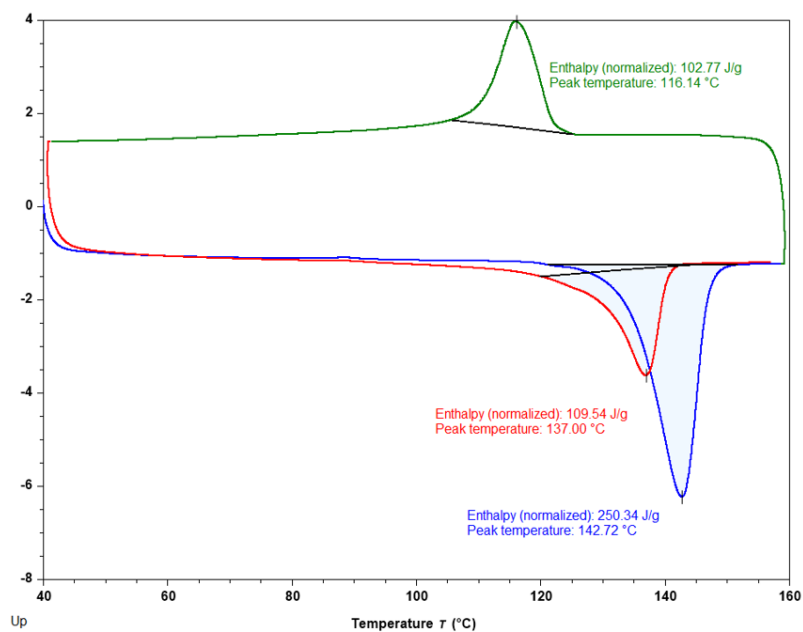


Figure 4.87: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 2).

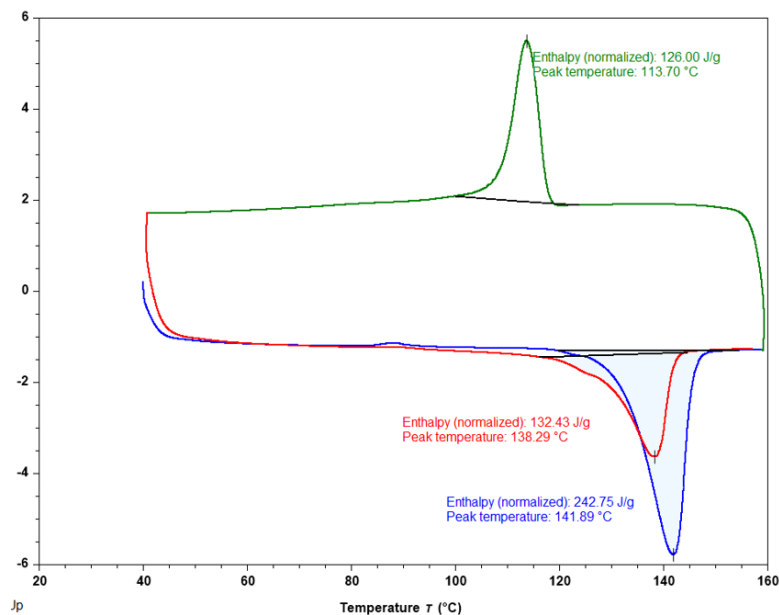


Figure 4.88: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 3).

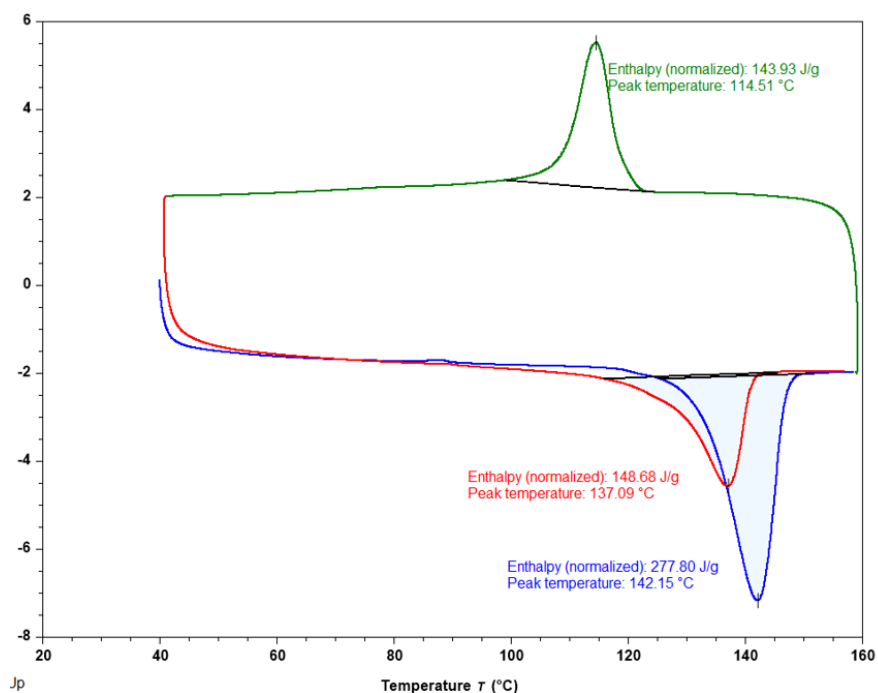


Figure 4.89: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 4).

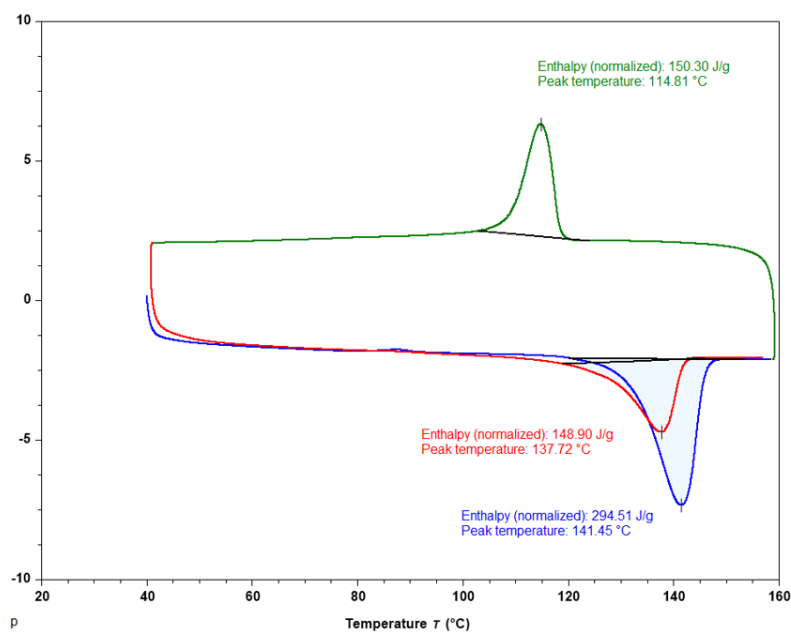


Figure 4.90: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 5).

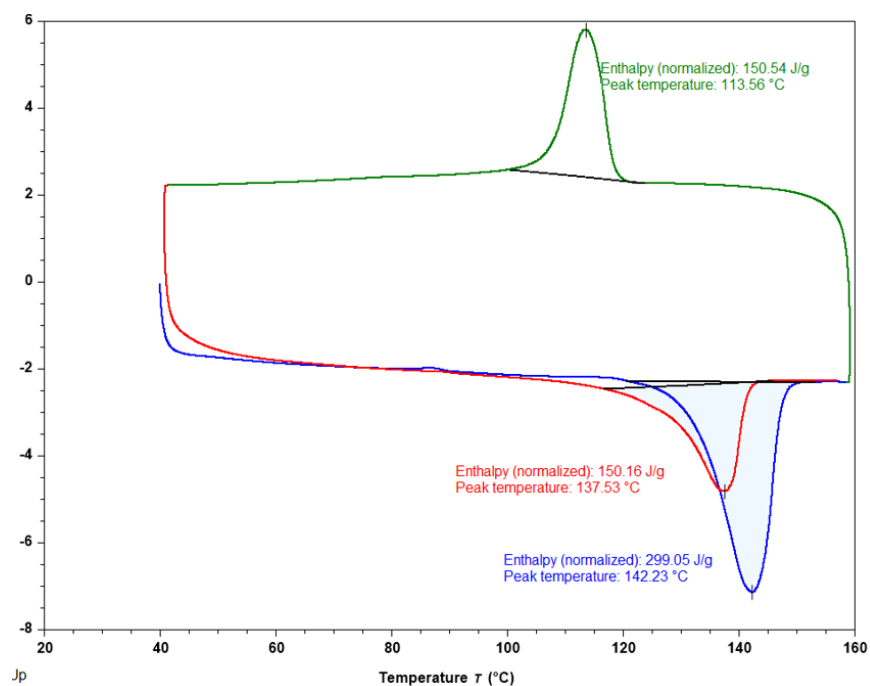


Figure 4.91: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 6).

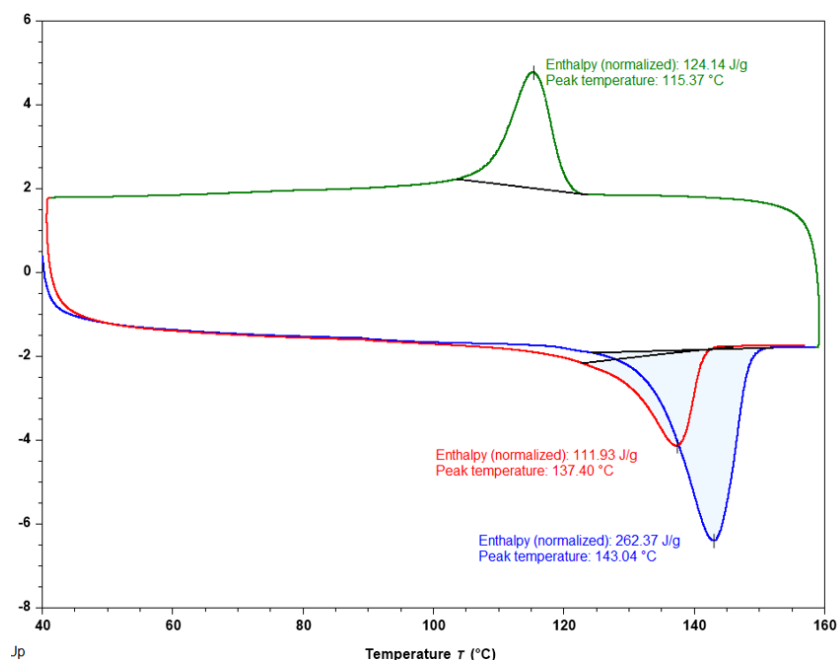


Figure 4.92: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 7).

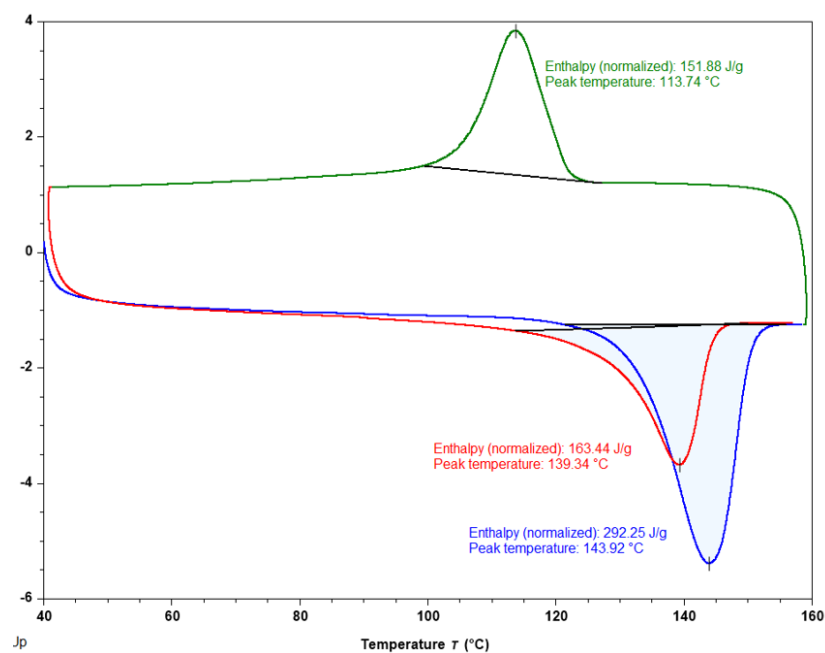


Figure 4.93: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 9).

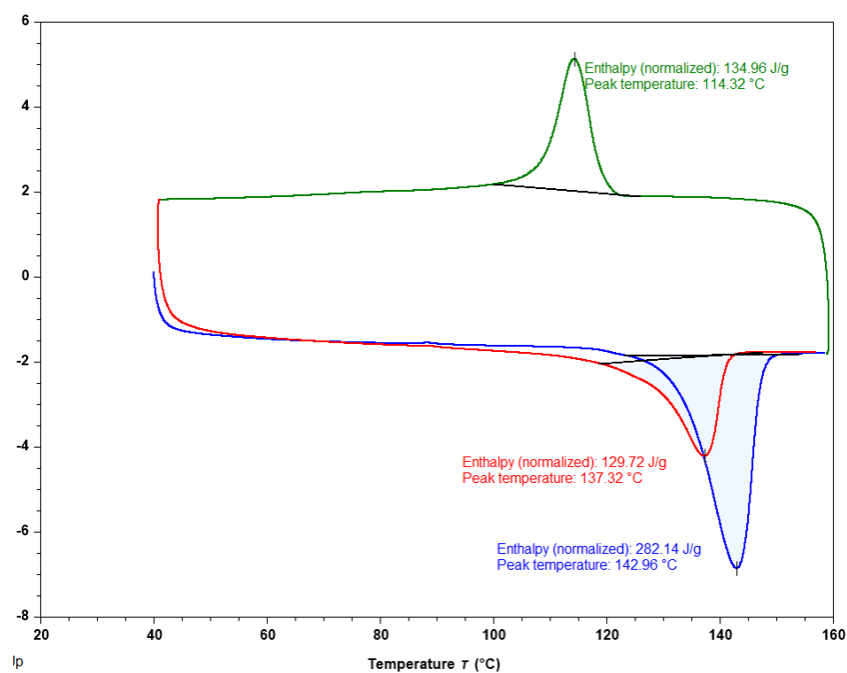


Figure 4.94: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 10).

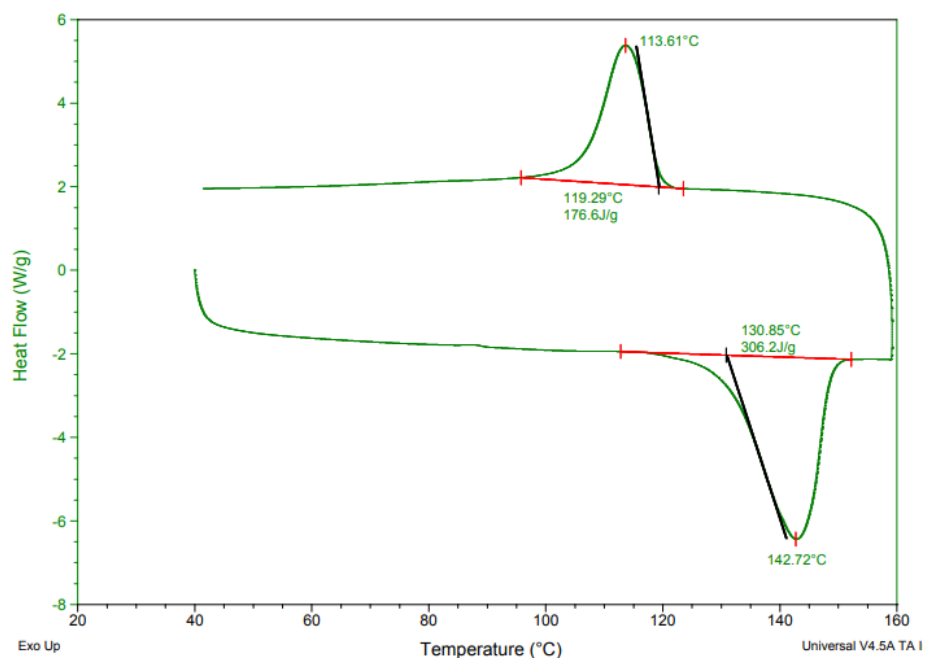


Figure 4.95: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 11).

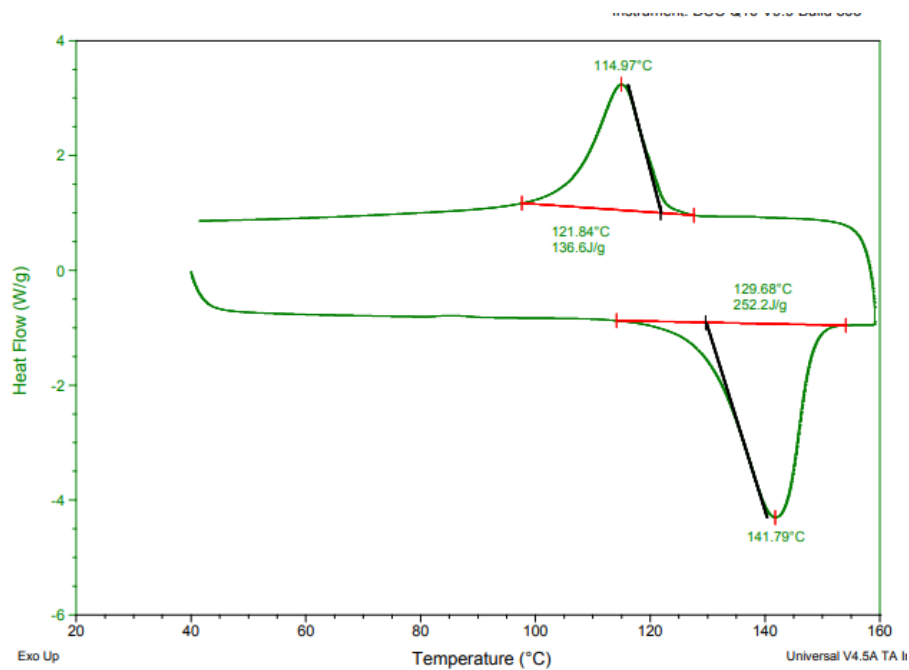


Figure 4.96: DSC curves for the first heating, cooling and second heating cycle (Table 4.5, entry 12).

4.11. Determination of percentage crystallinity and disentanglement in UHMWPE

4.11.1. % Crystallinity (x)

Based on the melting enthalpy determined by DSC and in relation to the theoretical value of 293.6 J/g for 100 % crystalline polyethylene, the crystallinity of the resulting polyethylene was determined (Table 4.6).

The heat of melting, if the polymer were 100% crystalline, is denoted by the reference value ΔH_m° . Table 4.6 below lists some of the frequently used polymers for which this reference heat of melting has been determined.

Table 4.6 Melting enthalpy for 100% crystalline polymers

Polymer	ΔH_m° (J/g)
Nylon 6	230.1
PET	140
Nylon 6, 6	255.8
Polypropylene	207.1
Polyethylene	293.6

The DSC program directly offers melting enthalpy data to facilitate the assessment of the % crystallinity more easy and easier. The following procedure is used to ascertain the crystallinity of one of the polyethylene samples (Table 4.6, entry 12).

$$(J/g) \times 100 = \Delta H_m / \Delta H_m^\circ = \% \text{ Crystallinity}$$

Consequently, $H_m = 252.2 \text{ J/g}$ and $H_m^\circ = 293.6 \text{ J/g}$ % Crystallinity is equal to $252.2 / 293.6 \times 100 = 85.8\%$.

4.11.2. Disentanglement studies by DSC

Melting temperatures (T_m) and accompanying melt enthalpies were measured using a TA device, the Q-10 Differential Scanning Calorimeter (DSC). The weight of each sample is maintained within $6 \text{ mg} \pm 0.1 \text{ mg}$ to reduce the thermal lag that the samples create. Nitrogen was continuously purged at a rate of 50 mL/min throughout the measurement. As shown in Figure 4.97, a DSC

method has been developed to obtain various entanglement densities by adhering to a procedure given in the literature. At a rate of 10 °C per minute, the sample was heated from 50 °C to 160 °C, which is greater than PE's equilibrium temperature of 145 °C. The sample was annealed for a predetermined amount of time (5 and 30 minutes) at this temperature. To change the entanglement density in the melt, two distinct annealing times were selected. The sample was then cooled at a rate of 10 °C per minute to an isothermal crystallization temperature of 128 °C. For a predetermined period of 180 minutes, the sample was maintained at the isothermal crystallization temperature. The sample was then cooled to 50 °C at a rate of 10 °C per minute, and then it was heated again from 50 to 160 °C at a rate of 10 °C per minute. This second heating ramp produced the DSC graphs.¹⁹

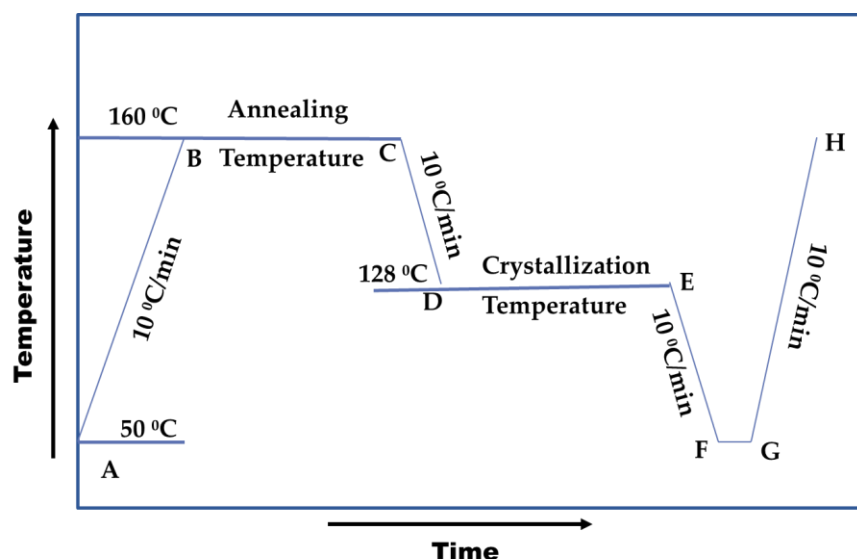
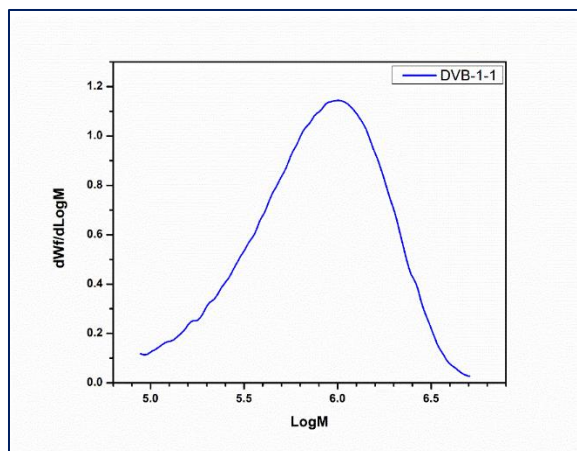


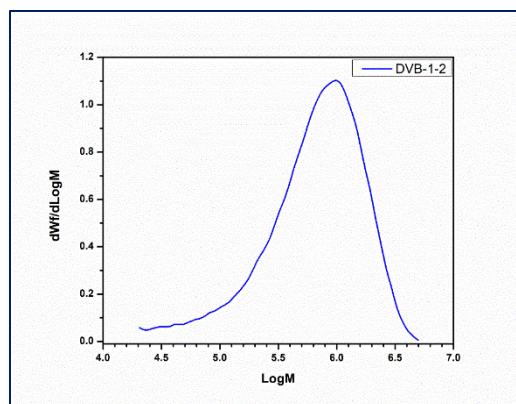
Figure 4.97: Thermal protocol followed to demonstrate disentangled nature of UHMWPE.

4.12. Determination of Mw by HT-GPC



Mw	1016000	g/mol
Mn	539800	g/mol
Mw / Mn	1.88	

Figure 4.98: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 1).



Mw	915900	g/mol
Mn	336700	g/mol
Mw / Mn	2.72	

Figure 4.99: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 2).

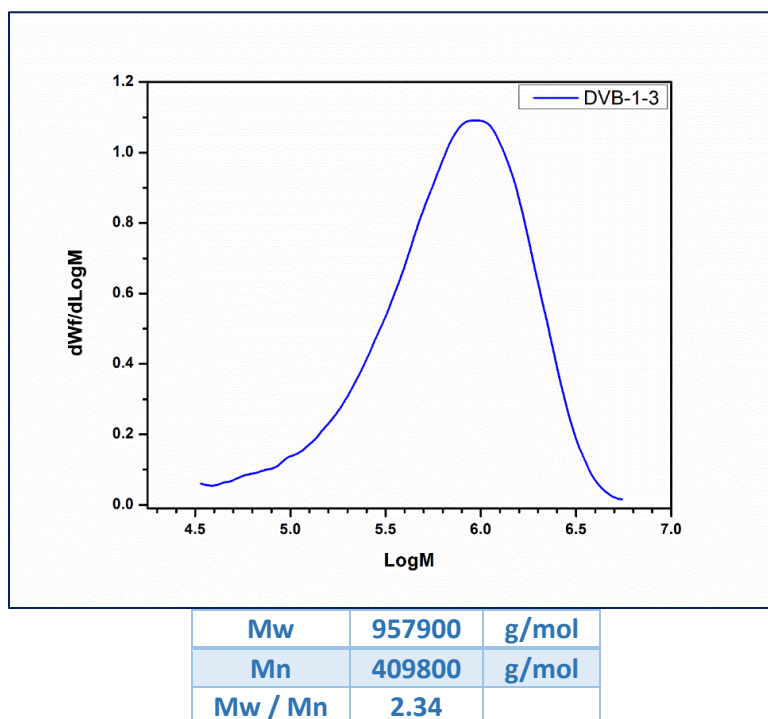


Figure 4.100: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 3).

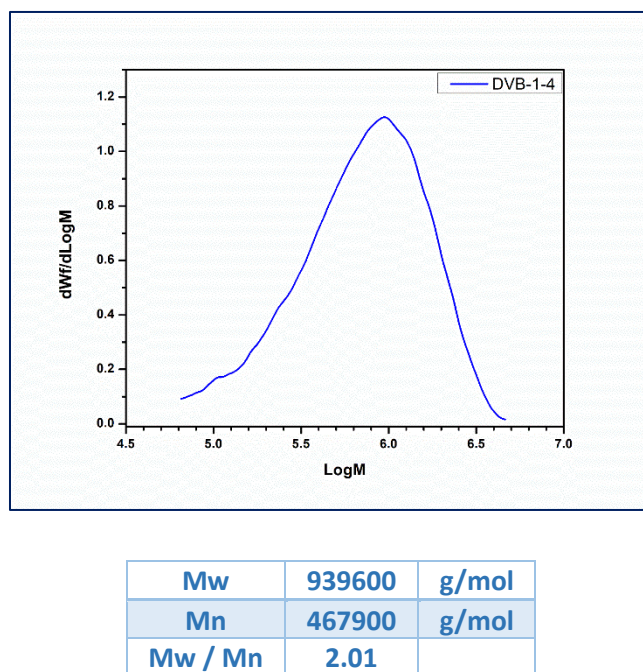
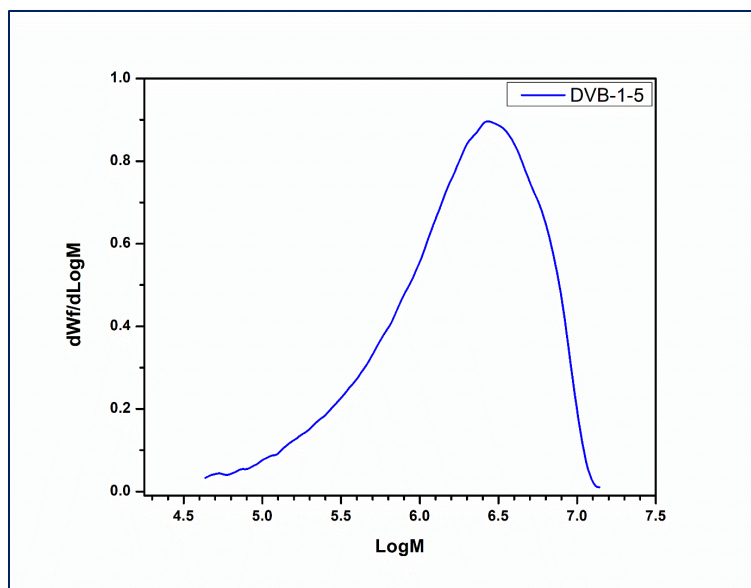
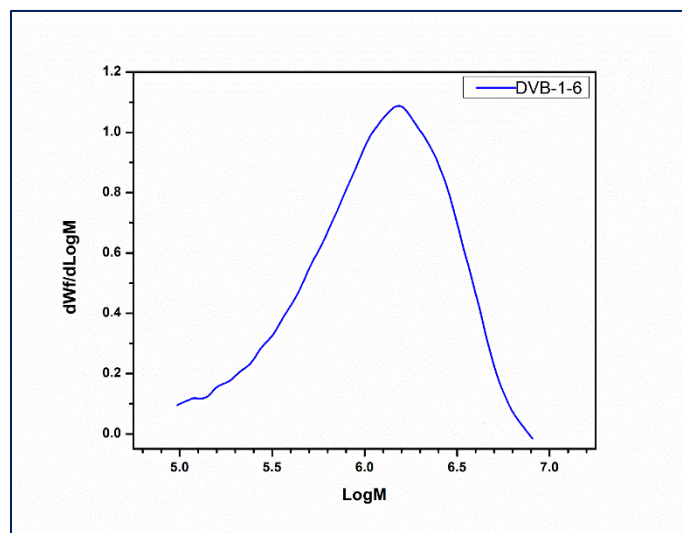


Figure 4.101: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 4).



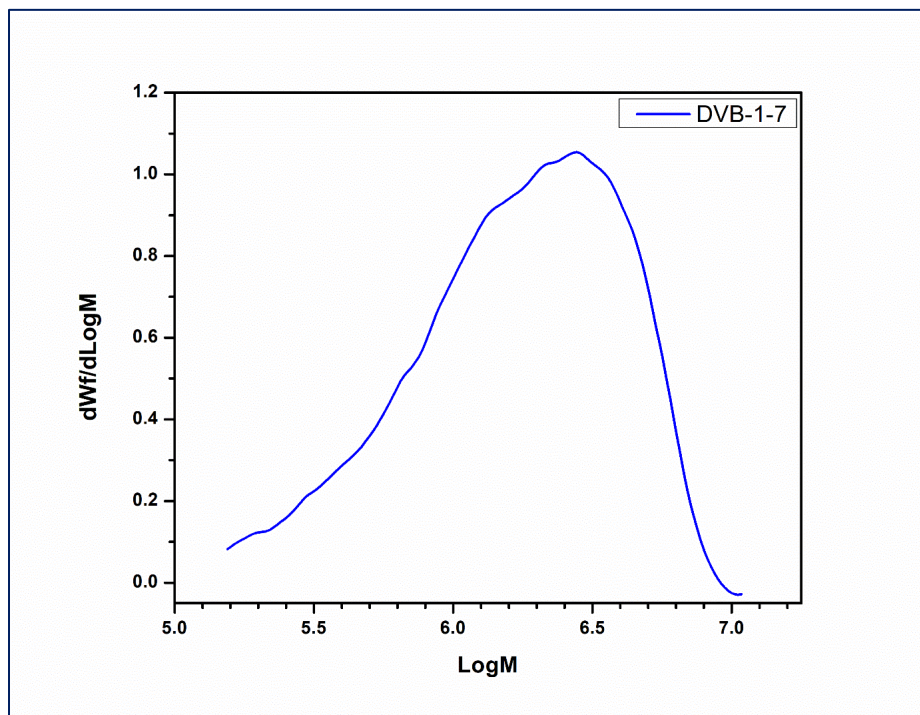
Mw	2758900	g/mol
Mn	793300	g/mol
Mw / Mn	3.48	

Figure 4.102: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 5).



Mw	1565800	g/mol
Mn	740300	g/mol
Mw / Mn	2.12	

Figure 4.103: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 6).



Mw	2252400	g/mol
Mn	1113500	g/mol
Mw / Mn	2.02	

Figure 4.104: HT-GPC chromatogram of UHMWPE (for Table 1, run 7).

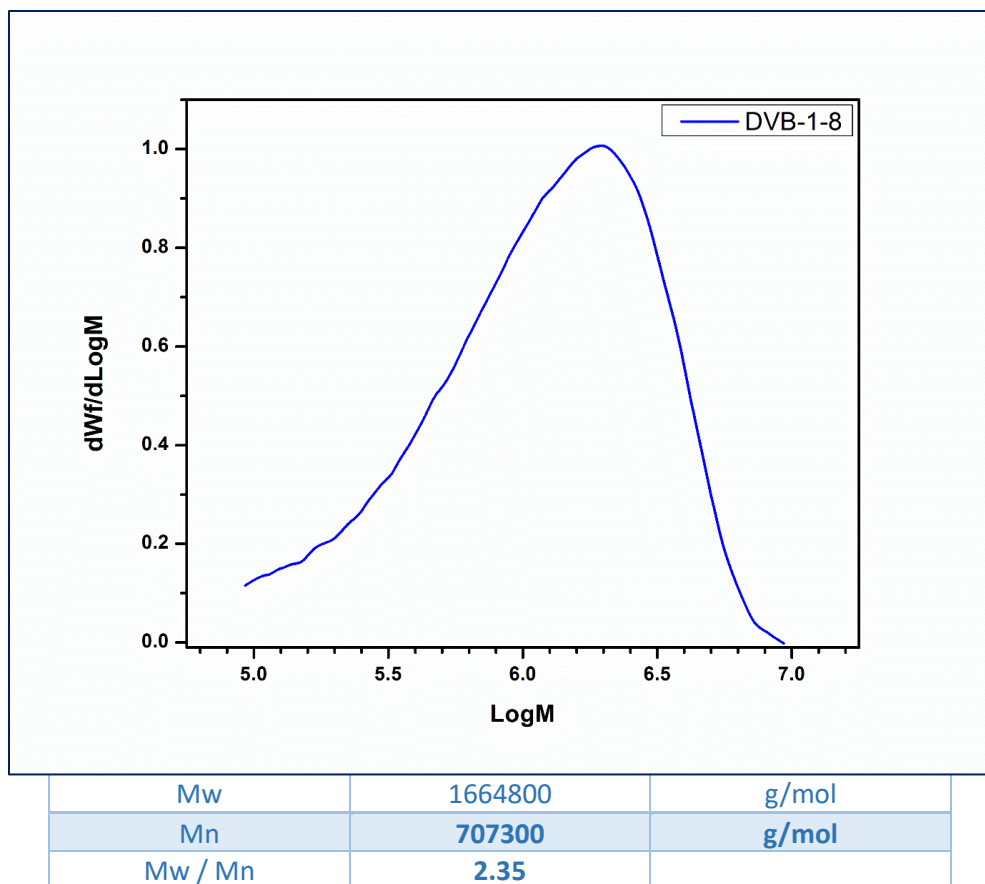


Figure 4.105: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 8).

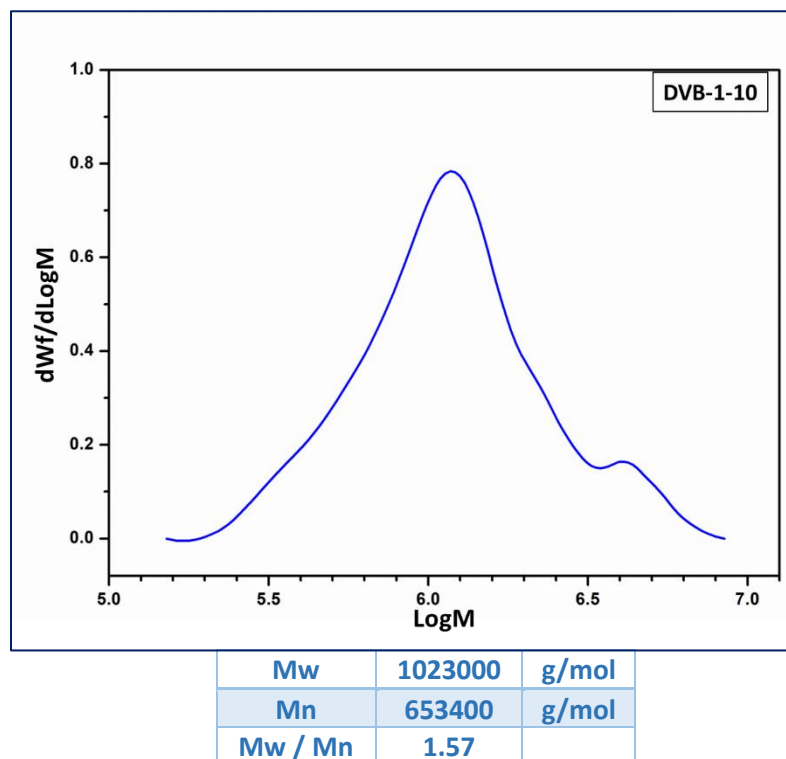
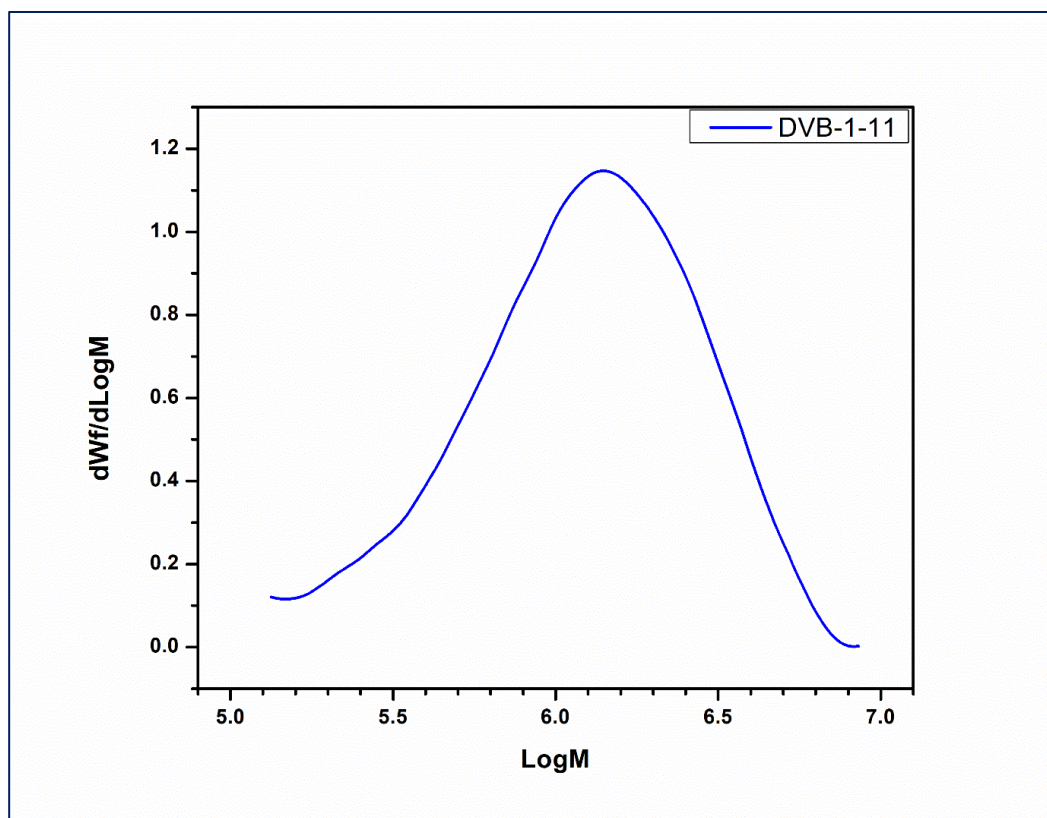
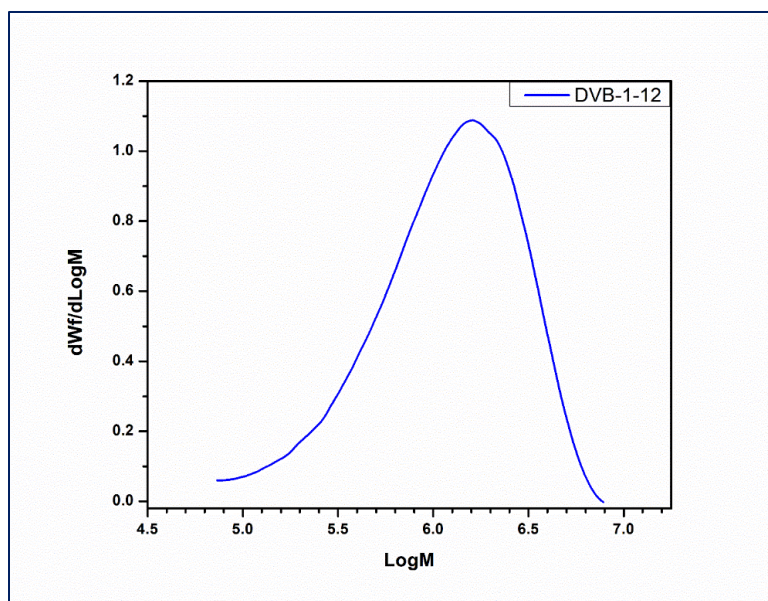


Figure 4.106: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 10).



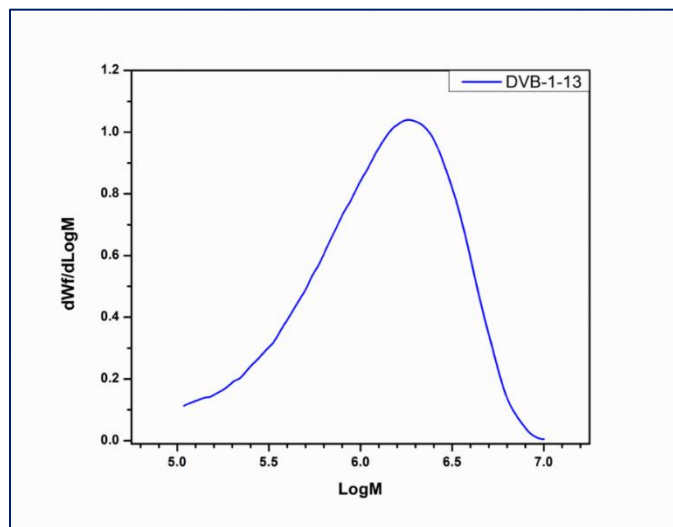
Mw	2199900	g/mol
Mn	1258000	g/mol
Mw / Mn	1.75	

Figure 4.107: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 11).



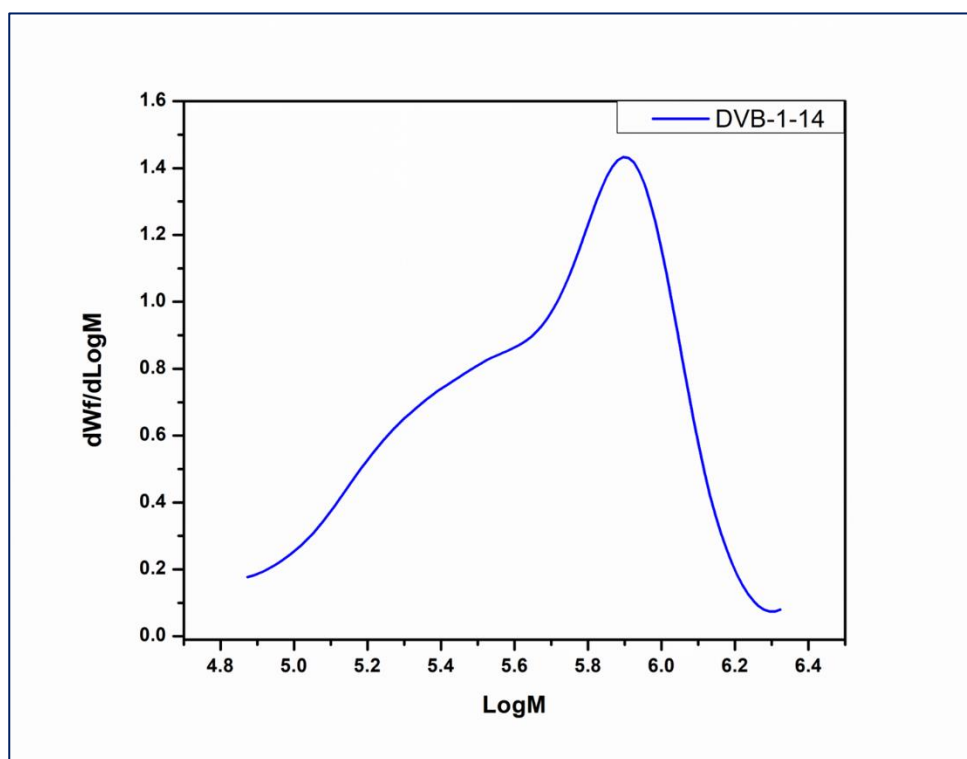
Mw	1598000	g/mol
Mn	742900	g/mol
Mw / Mn	2.15	

Figure 4.108: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 12).



Mw	1765600	g/mol
Mn	800800	g/mol
Mw / Mn	2.2	

Figure 4.109: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 13).



Mw	669400	g/mol
Mn	383300	g/mol
Mw / Mn	1.75	

Figure 4.110: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 14).

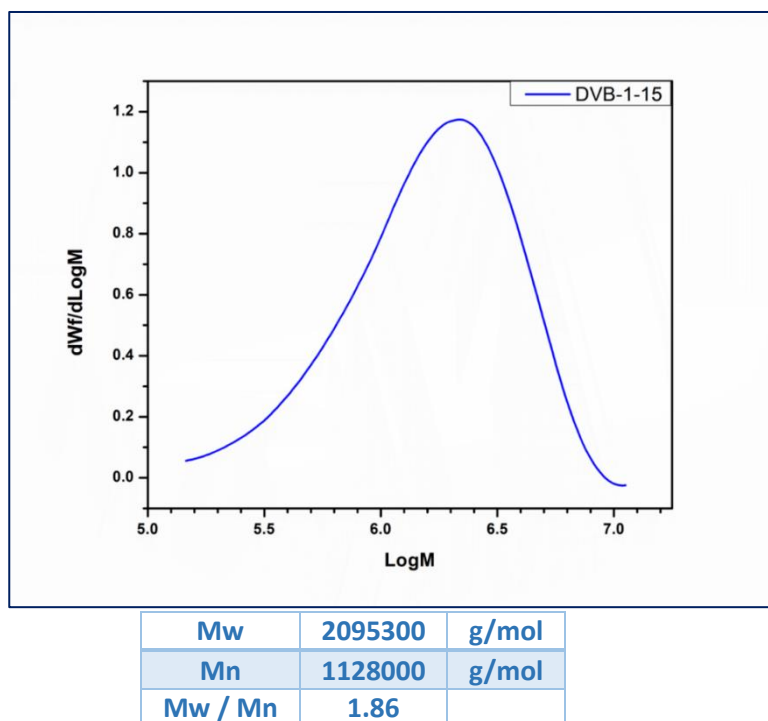


Figure 4.111: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 15).

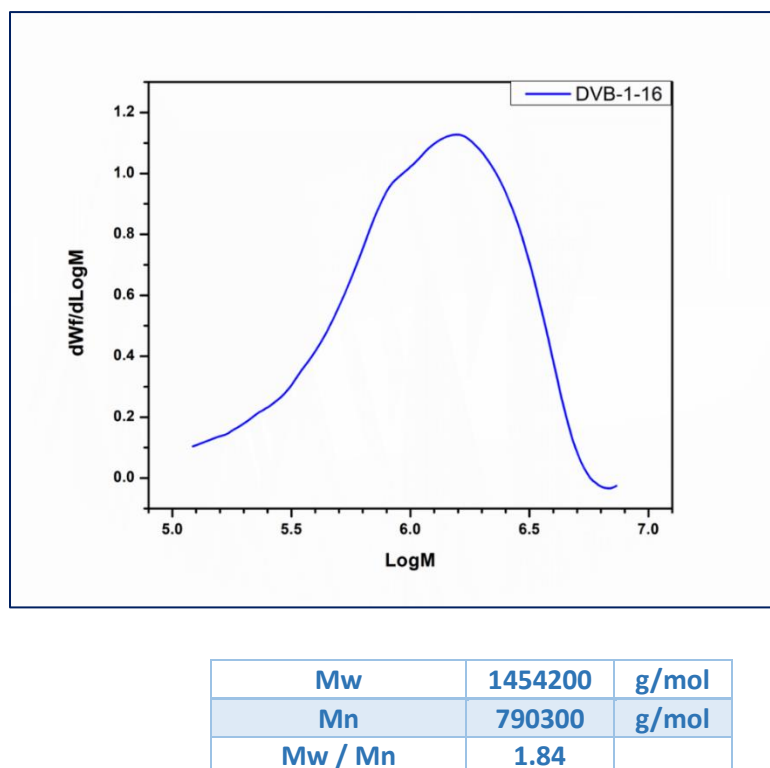


Figure 4.112: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 16).

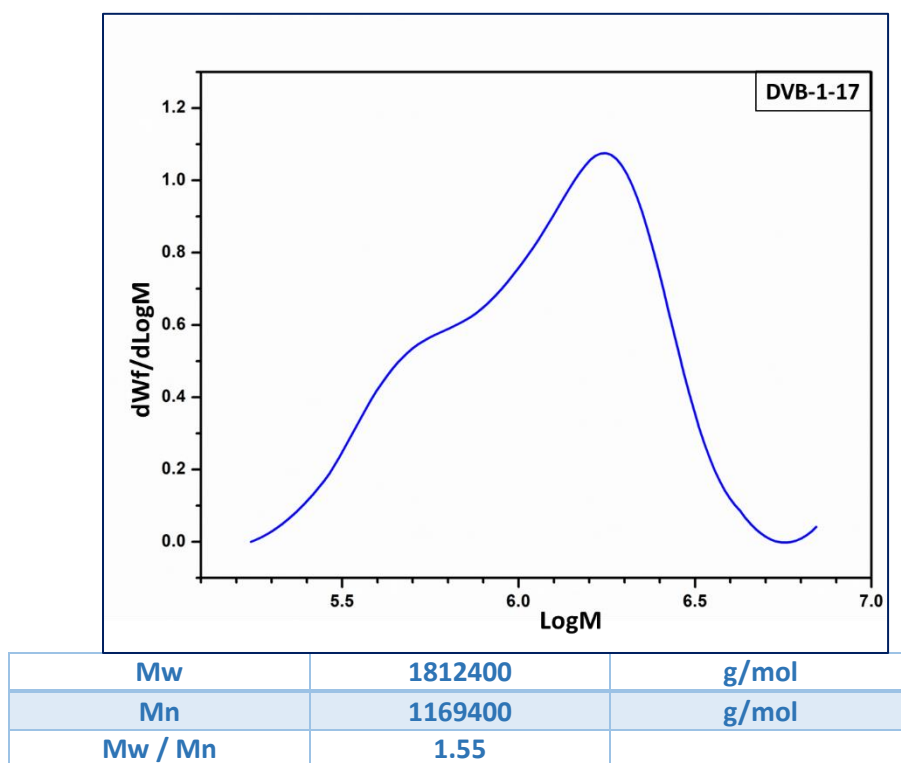
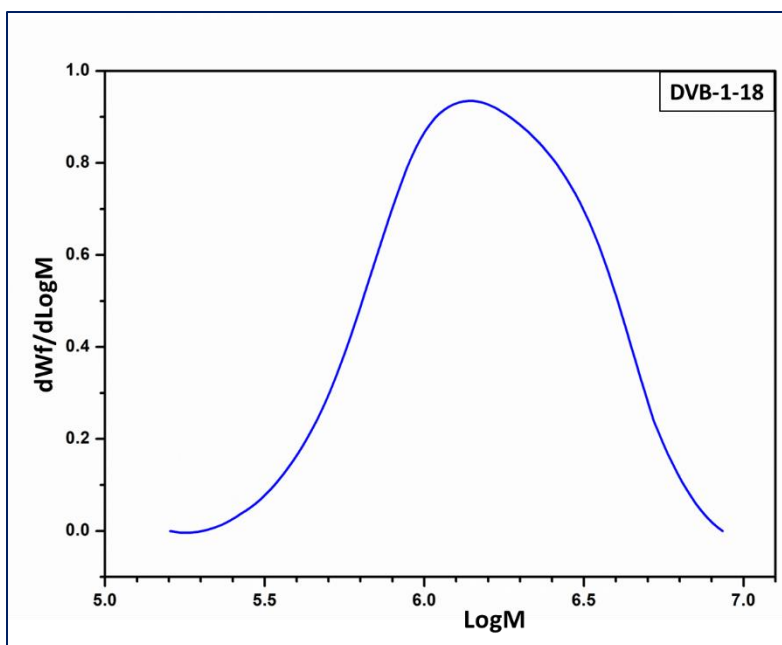
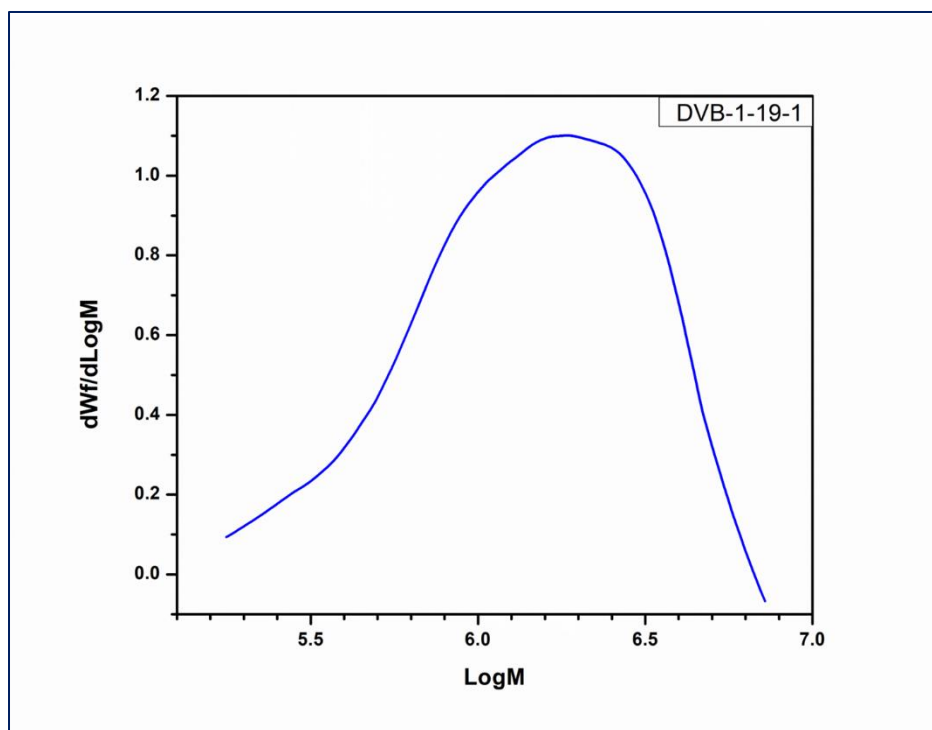


Figure 4.113: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 17).



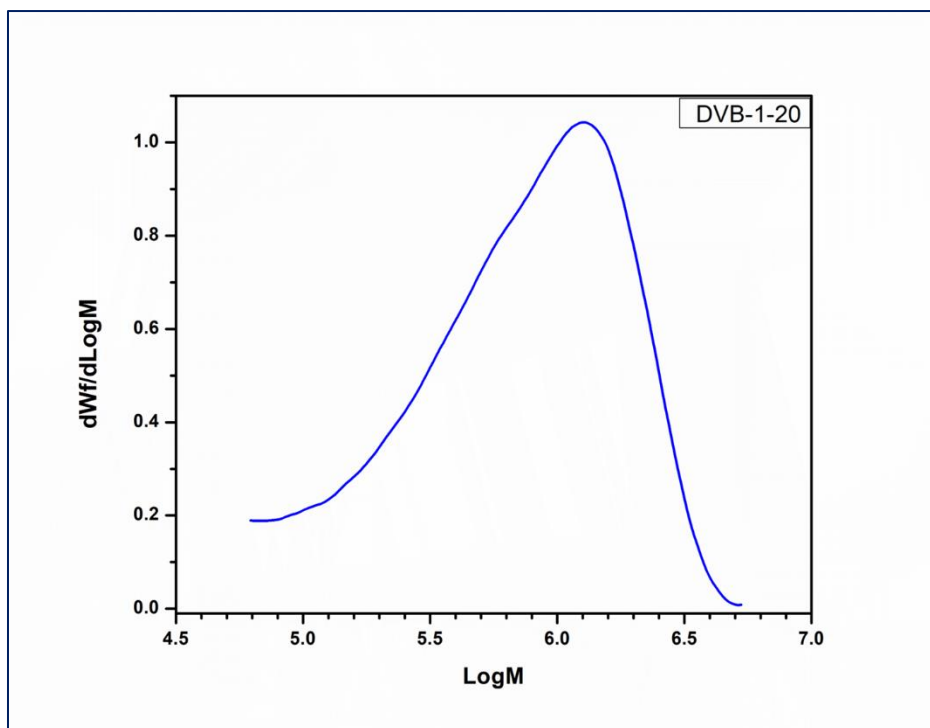
Mw	2255900	g/mol
Mn	1351400	g/mol
Mw / Mn	1.67	

Figure 4.114: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 18).



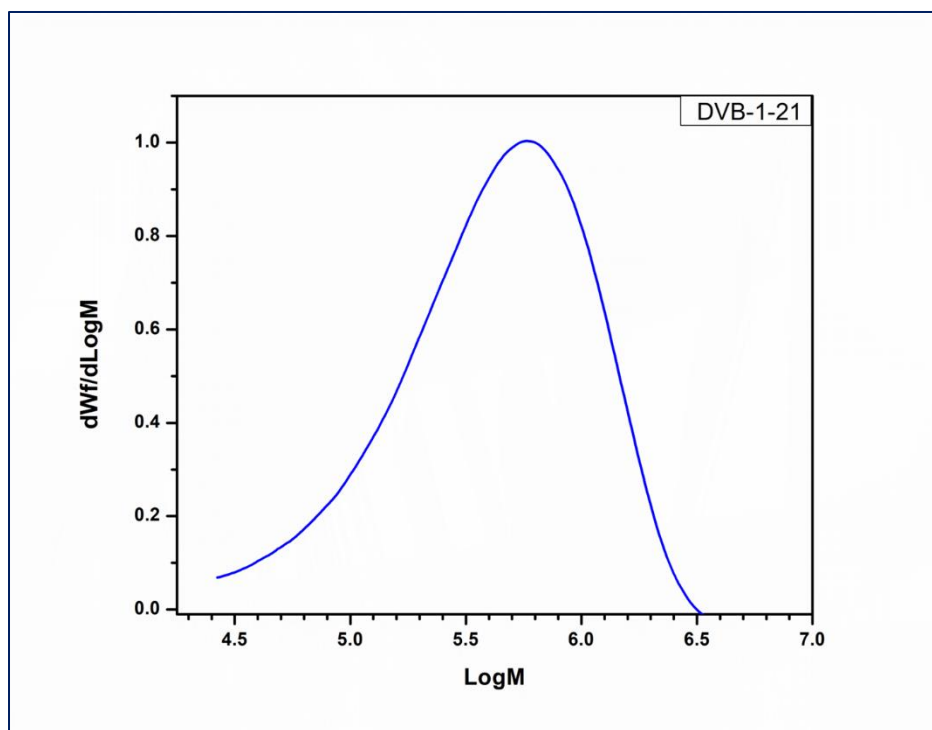
Mw	1793700	g/mol
Mn	1019700	g/mol
Mw / Mn	1.76	

Figure 4.115: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 19).



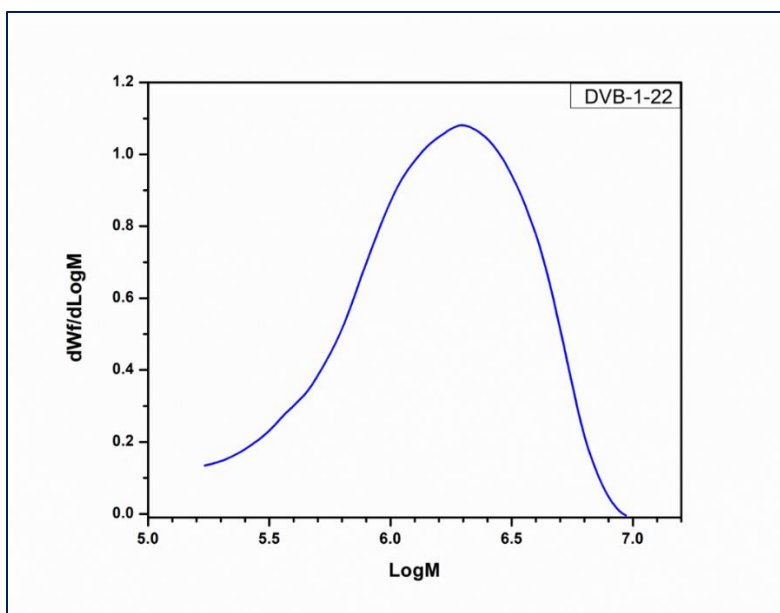
Mw	1004400	g/mol
Mn	424000	g/mol
Mw / Mn	2.37	

Figure 4.116: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 20).



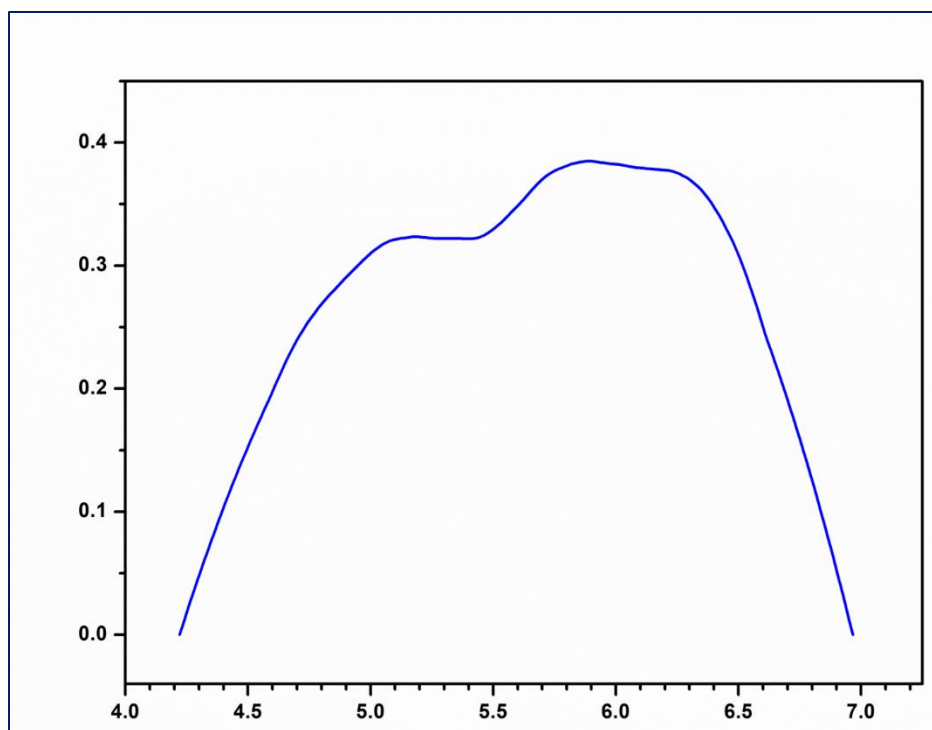
Mw	588600	g/mol
Mn	249900	g/mol
Mw / Mn	2.36	

Figure 4.117: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 21).



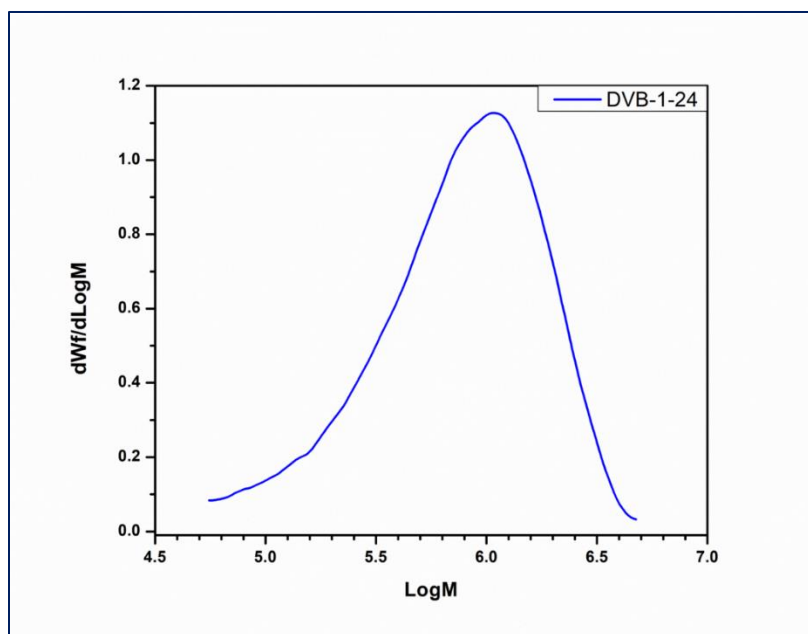
Mw	2631400	g/mol
Mn	1452900	g/mol
Mw / Mn	1.81	

Figure 4.118: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 22).



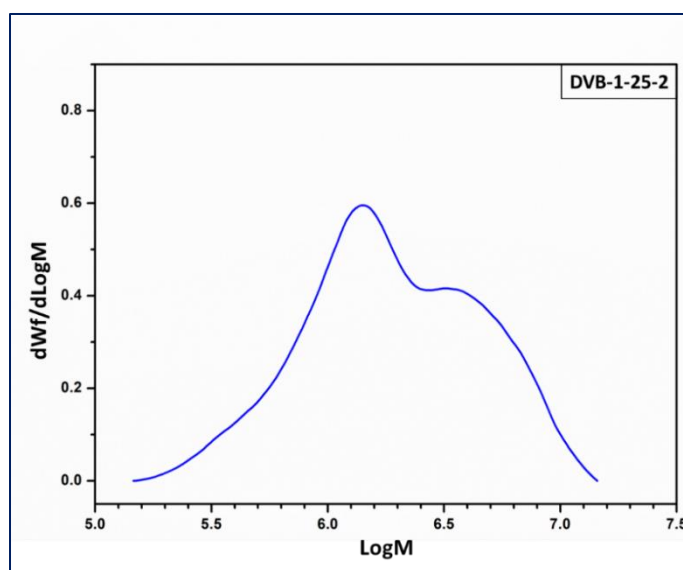
Mw	1104800	g/mol
Mn	71300	g/mol
Mw / Mn	15.49	

Figure 4.119: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 23).



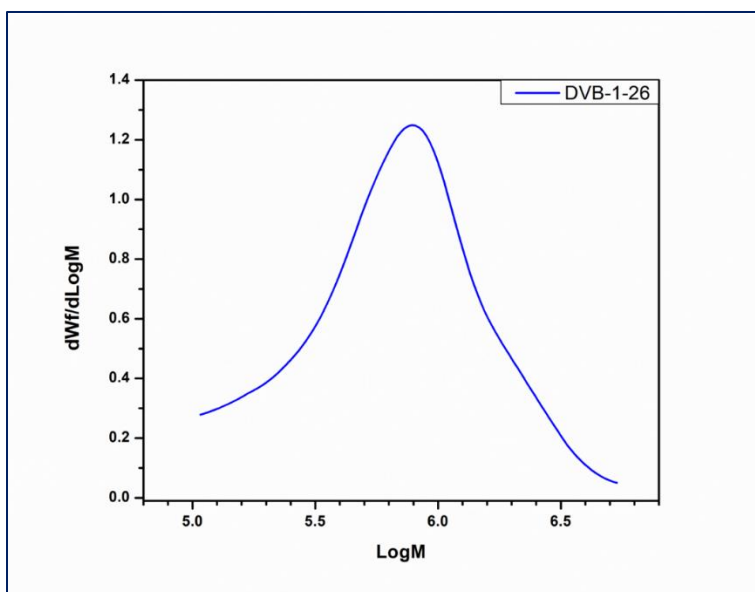
Mw	1018000	g/mol
Mn	478500	g/mol
Mw / Mn	2.13	

Figure 4.120: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 24).



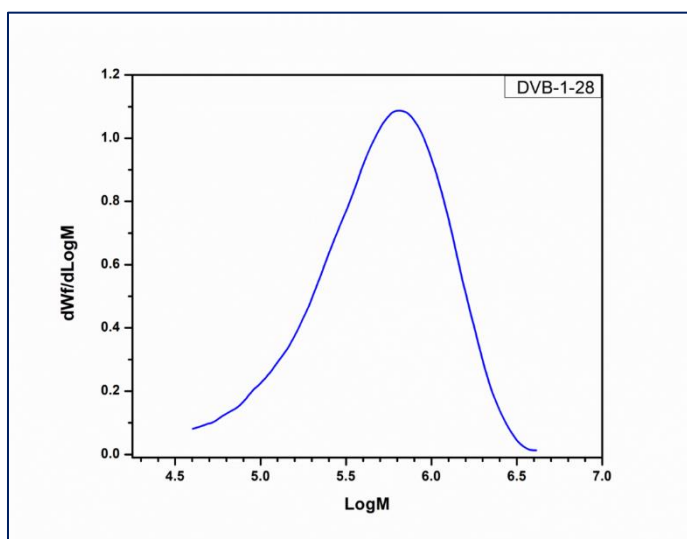
Mw	2000700	g/mol
Mn	656600	g/mol
Mw / Mn	3.05	

Figure 4.121: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 25).



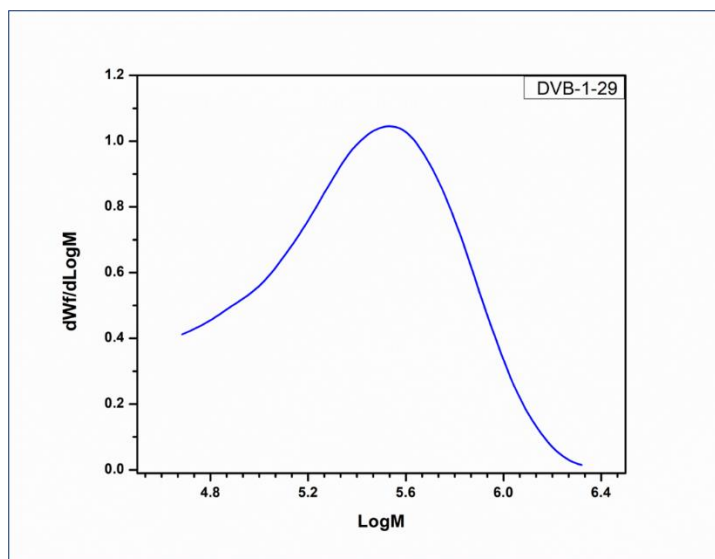
Mw	924900	g/mol
Mn	485100	g/mol
Mw / Mn	1.91	

Figure 4.122: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 26).



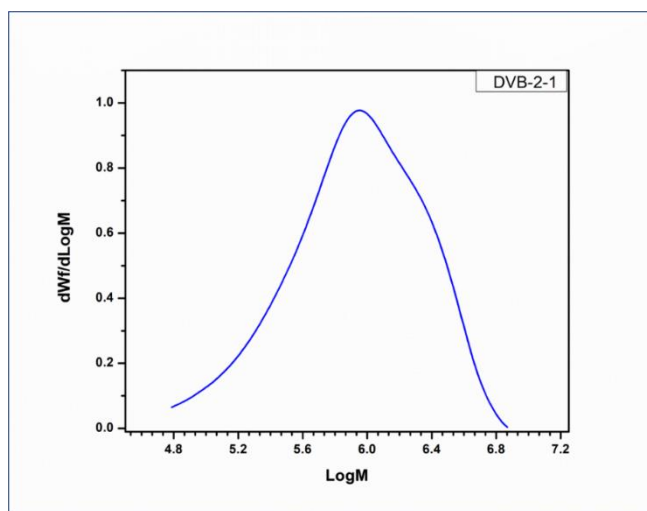
Mw	685600
Mn	322200
Mw / Mn	2.13

Figure 4.123: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 28).



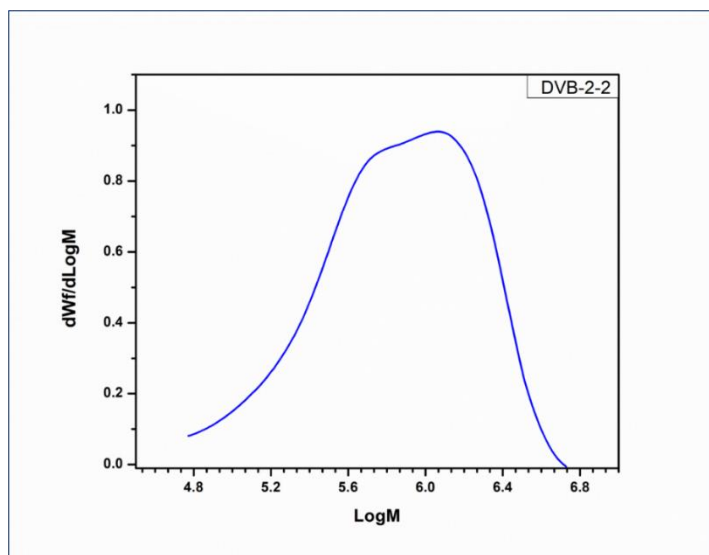
Mw	357700
Mn	186700
Mw / Mn	1.92

Figure 4.124: HT-GPC chromatogram of UHMWPE (for Table 4.4, run 29).



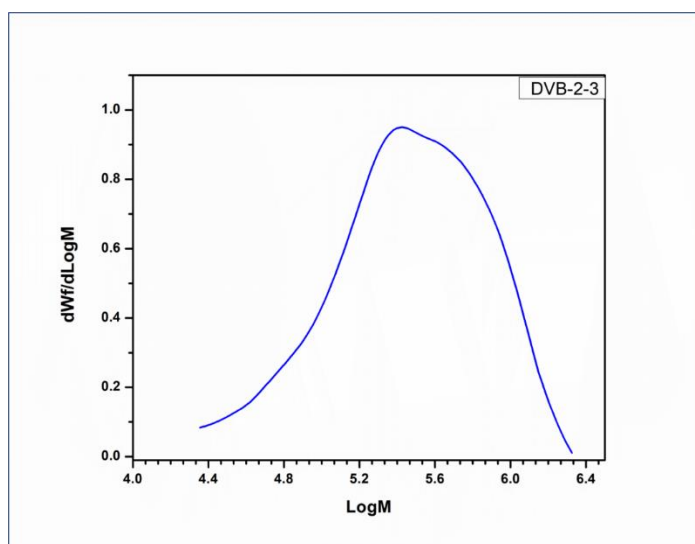
Mw	1003900
Mn	457700
Mw / Mn	2.19

Figure 4.125: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 1).



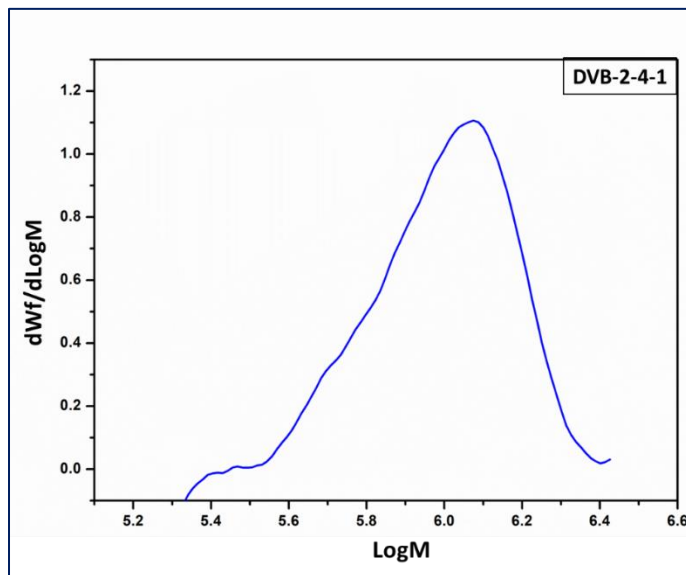
Mw	1253400
Mn	525600
Mw / Mn	2.38

Figure 4.126: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 2).



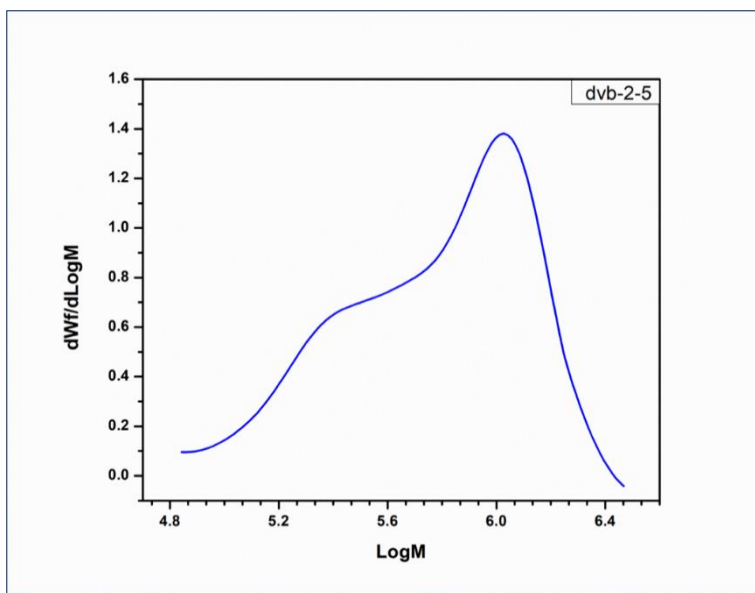
Mw	415000
Mn	181200
Mw / Mn	2.29

Figure 4.127: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 3).



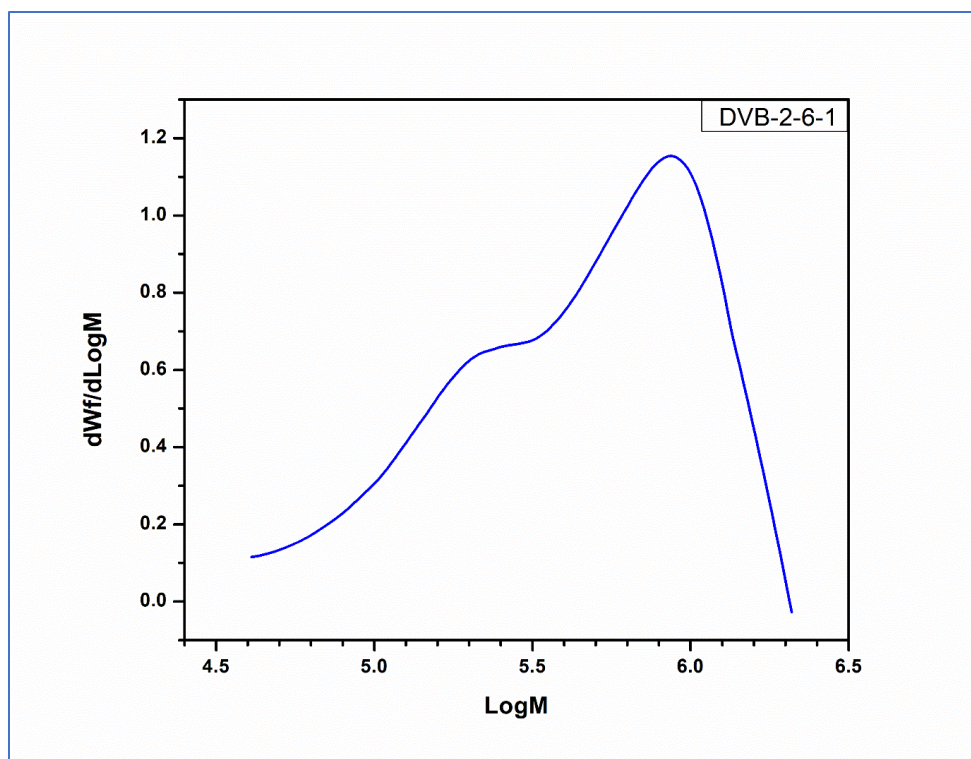
Mw	804300
Mn	529700
Mw / Mn	1.52

Figure 4.128: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 4).



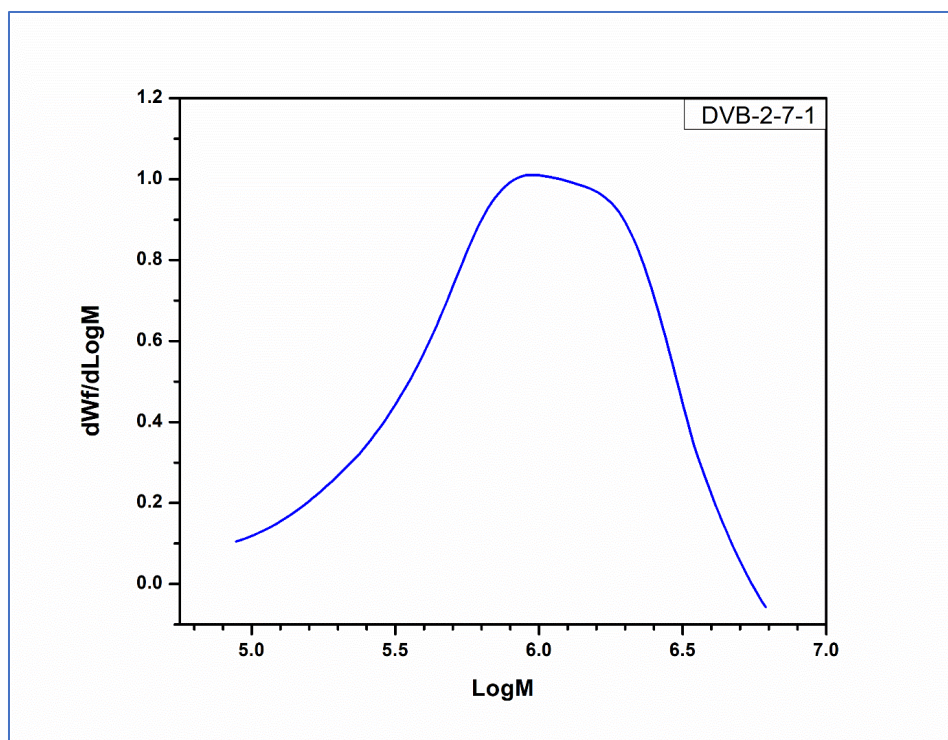
Mw	753500
Mn	419100
Mw / Mn	1.8

Figure 4.129: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 5).



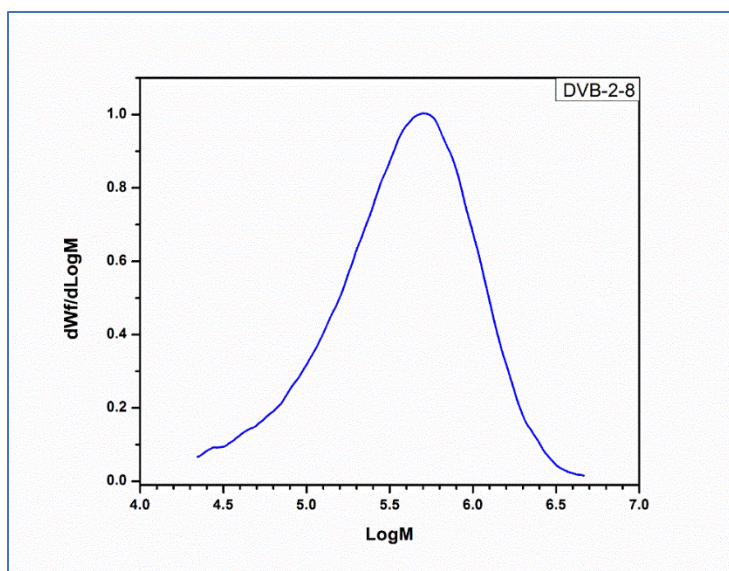
Mw	594500	g/mol
Mn	279600	g/mol
Mw / Mn	2.13	

Figure 4.130: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 6).



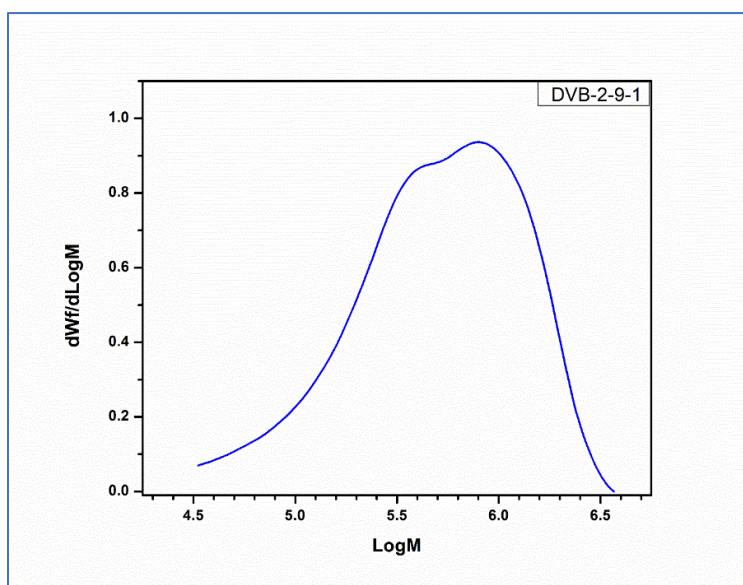
Mw	1203600	g/mol
Mn	593600	g/mol
Mw / Mn	2.03	

Figure 4.131: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 7).



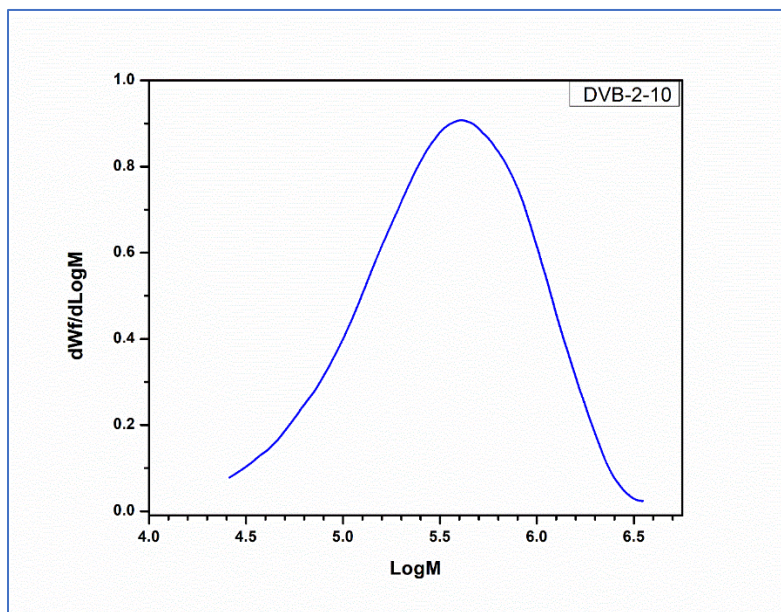
Mw	563100	g/mol
Mn	217900	g/mol
Mw / Mn	2.58	

Figure 4.132: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 8).



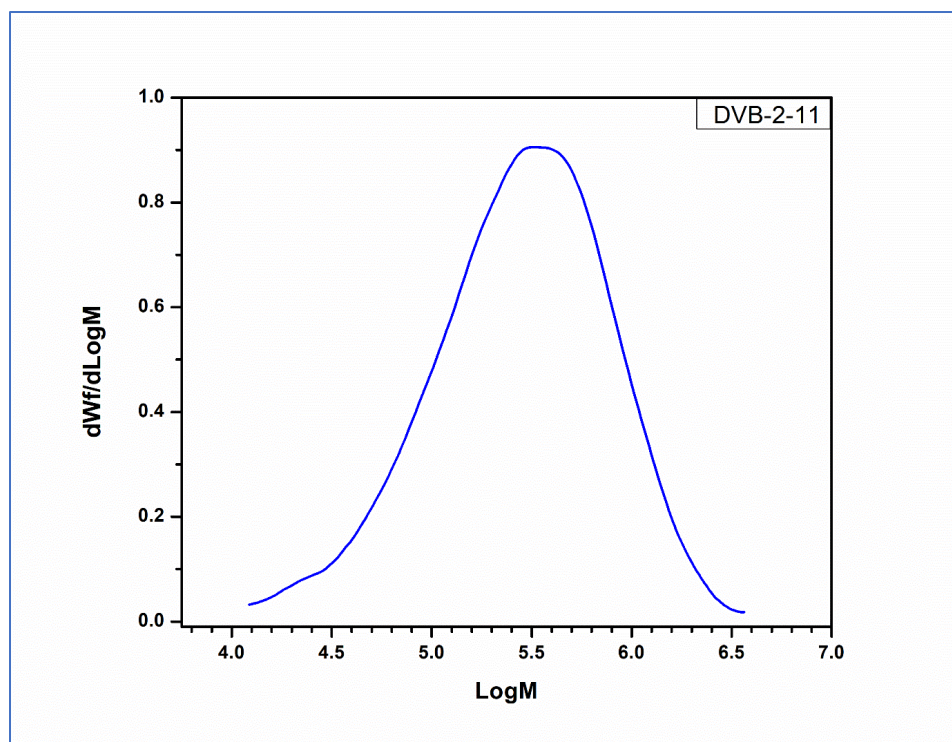
Mw	713400	g/mol
Mn	304000	g/mol
Mw / Mn	2.35	

Figure 4.133: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 9).



Mw	514400	g/mol
Mn	205300	g/mol
Mw / Mn	2.51	

Figure 4.134: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 10).



Mw	433100	g/mol
Mn	156600	g/mol
Mw / Mn	2.77	

Figure 4.135: HT-GPC chromatogram of UHMWPE (for Table 4.5, run 11).

4.13. Conclusion

One step synthesis of three phenoxy-imine ligands with increasing steric bulk in excellent yield is reported. Using a mix of spectroscopic and analytical tools, such as single crystal X-ray diffraction, the ligands' identities were definitively determined. These three different substituted phenyl cyclohexylimine ligands were treated with Ti-precursor and corresponding titanium complexes were prepared. Upon activation with methyl aluminoxane (MMAO), triisobutylaluminum (TIBA), and tetrakis (pentafluoro phenyl) borate (BT), the complexes (Cat.1 to Cat.3) were methodically evaluated for their catalytic activity. The insertion of steric bulk around the active site typically enhanced catalytic activity, except for cat. 3. In cat. 3, substantial steric hindrance led to diminished activity, perhaps due to obstructed monomer access to the active site or disruption of polymer chain

elongation. MMAO was notably successful among several activators in the synthesis of ultrahigh molecular weight polyethylene (UHMWPE). Optimal polymerization conditions were attained with an Al/Ti ratio of 2000 equivalents, ethylene pressure of 2 bar, a temperature of 40 °C, and a polymerization duration of 10 minutes. Under these optimized conditions, cat. 2 yielded UHMWPE with a Mw of 2.75×10^6 g/mol, demonstrating high crystallinity (95 %) and a melting temperature ranging from 140 to 143 °C, indicative of disentangled UHMWPE (d-UHMWPE). These findings yield significant insights into the correlation between steric effects and catalytic efficacy, presenting crucial considerations for the systematic design of effective catalysts in ethylene polymerization.

4.14. References

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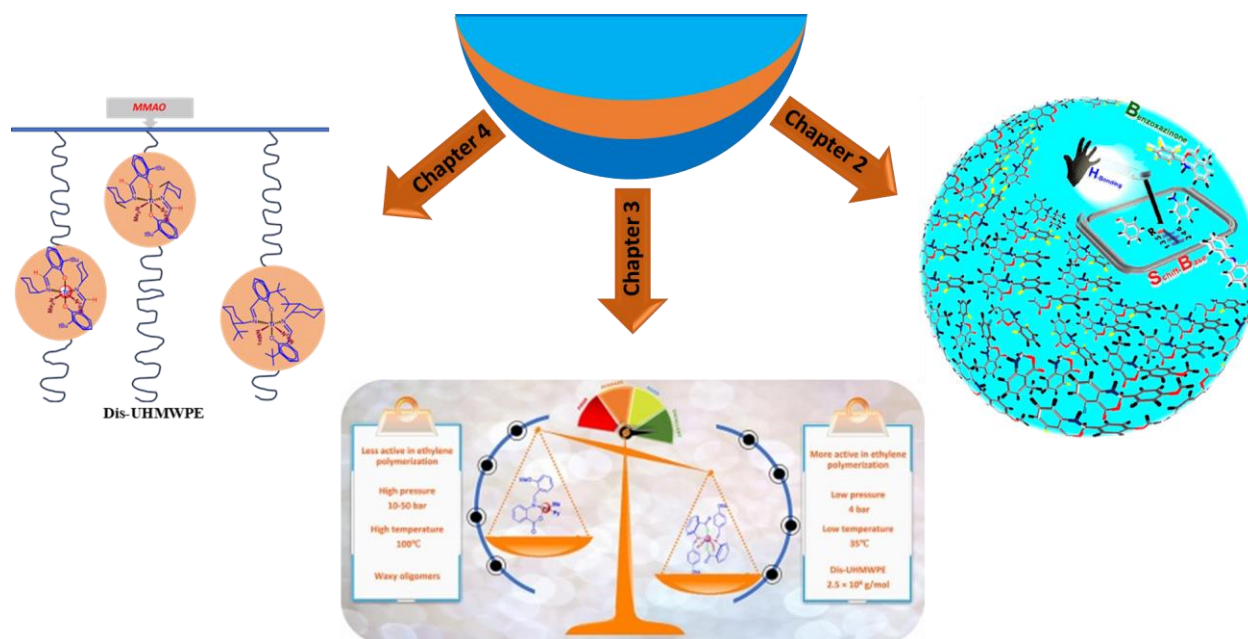
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Chapter 5



Summary and Outlook



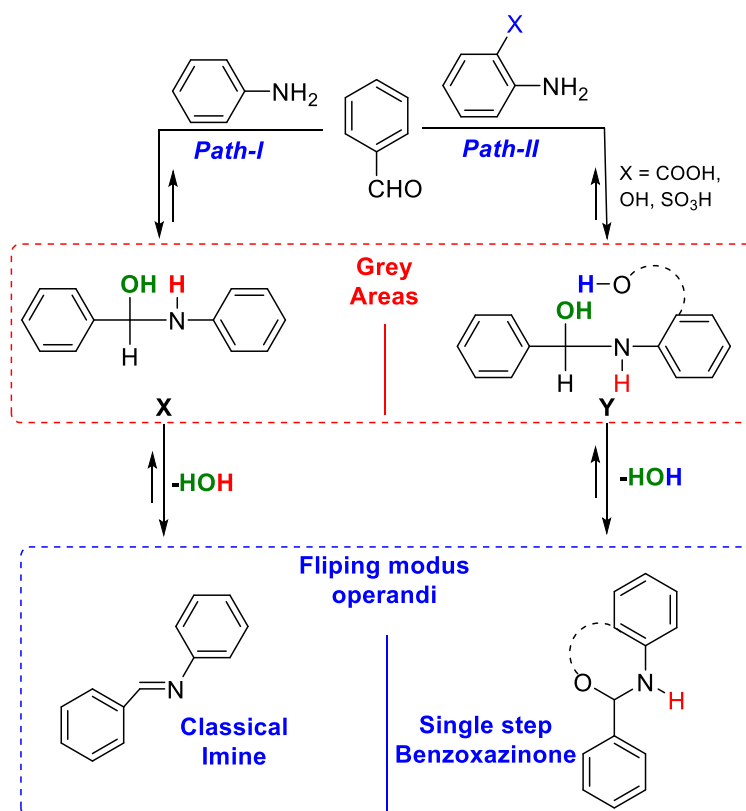
5.1. Summary

The Ph.D. thesis, titled “**A Catalyst Desing for Preparation of Ultrahigh Molecular Weight Polyethylene**” contains five chapters. Efforts have been made to provide a systematic study on the influence of catalytic systems utilizing early transition metal complexes, and reaction parameters on the chain growth mechanism to produce UHMWPE. Additionally, the characterization of UHMWPE has been explored in order to understand molecular architecture and morphology during synthesis. The two states of UHMWPE, tailored during the polymerization by varying catalysts and co-catalysts, combined with the polymerization reaction parameters have been explained. Our intension behind this work is to provide in-depth insights how a chain is forming and entangling during the polymerization, which can affect processing of UHMWPE. The work also explains role of metal catalysts in olefin polymerization. Role of ligand backbone (with controlled steric and electronics) becomes decisive parameter in controlling kinetics of olefin polymerization. **Chapter 2** presents our efforts in preparing imine ligands. While synthesizing the desired imine ligand, we encountered an unexpected result. Our observations indicated that the traditional reaction between amines and aldehydes could be influenced by secondary interactions. By strategically placing an ortho-substituent, we were able to selectively inhibit the formation of Schiff bases and instead promote the production of benzoxazinones, which are a class of prodrug compounds. Specifically, treating electrophilic pentafluoro benzaldehyde with 2-amino-6-methylbenzoic acid resulted in nearly quantitative yields of 5-methyl-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d] [1,3] oxazin-4-one. The effectiveness of our strategy was demonstrated by developing a library of 30 compounds. A comprehensive mechanistic investigation was conducted to elucidate the reaction pathway, employing advanced techniques such as low-temperature NMR spectroscopy, UV–vis spectroscopy, and isotopic labeling using ^{18}O . These studies revealed that the reaction proceeds exclusively through Pathway B (Scheme 5.1), as the formation of intermediate species characteristic of Pathways A and C was not observed. The exclusion of Pathways A and C was further supported by the absence of their corresponding spectral signatures and product profiles.

To reinforce these experimental findings, Density Functional Theory (DFT) calculations were performed to evaluate the energy landscapes of the three proposed pathways. The results conclusively indicated that Pathway B represents the lowest-energy pathway, with an energy

barrier approximately 20 kcal/mol lower than Pathway A and 35 kcal/mol lower than Pathway C. This significant energy difference underscores the thermodynamic and kinetic preference for Pathway B, aligning seamlessly with the experimental observations.

The synergy between experimental data and computational insights provides a robust understanding of the reaction mechanism, offering valuable predictive power for related transformations and guiding further optimizations in reaction design.

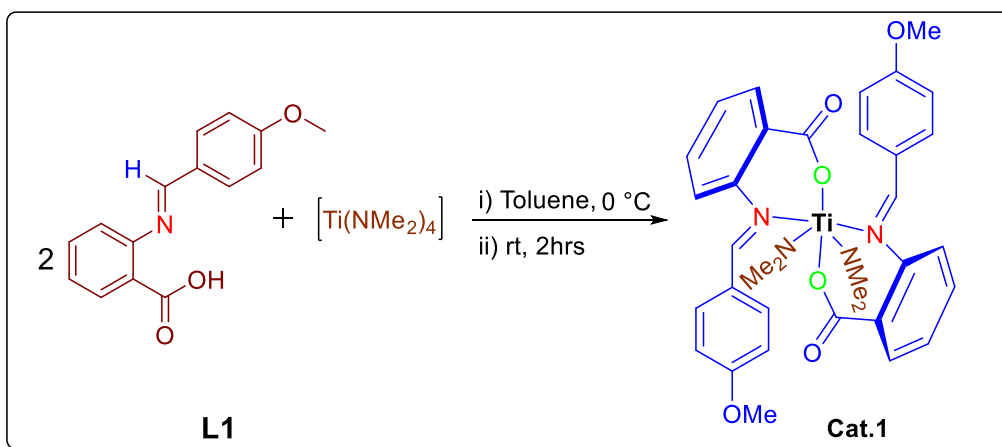


Scheme 5.1: Benzoxazinone synthesis by Schiff base reaction and reactivity modulation.

While investigating the scope of benzoxazinone formation, we discovered that the presence of an acidic proton plays a crucial role in influencing the outcome of a reaction. Consequently, we aimed to adjust this factor to enhance the reactivity for producing imine compounds. Aldehyde and an amine were treated to obtain imine ligand **L1** (chapter 3). An iminocarboxylate ligand (L1) was combined with tetrakis(dimethylamido-titanium) [Ti (NMe₂)₄], yielding a bis-ligated titanium complex, Cat.1, with a 62 % yield. Characterization was done using ¹H, ¹³C, HSQC, HMBC, NMR, and mass spectrometry. Initial screenings revealed that methylaluminoxane (MMAO) was the most effective cocatalyst. The optimal Al/Ti ratio was determined to be 1000, while the best

polymerization temperature was found to be 35 °C and deviations from this temperature resulted in decreased activity.

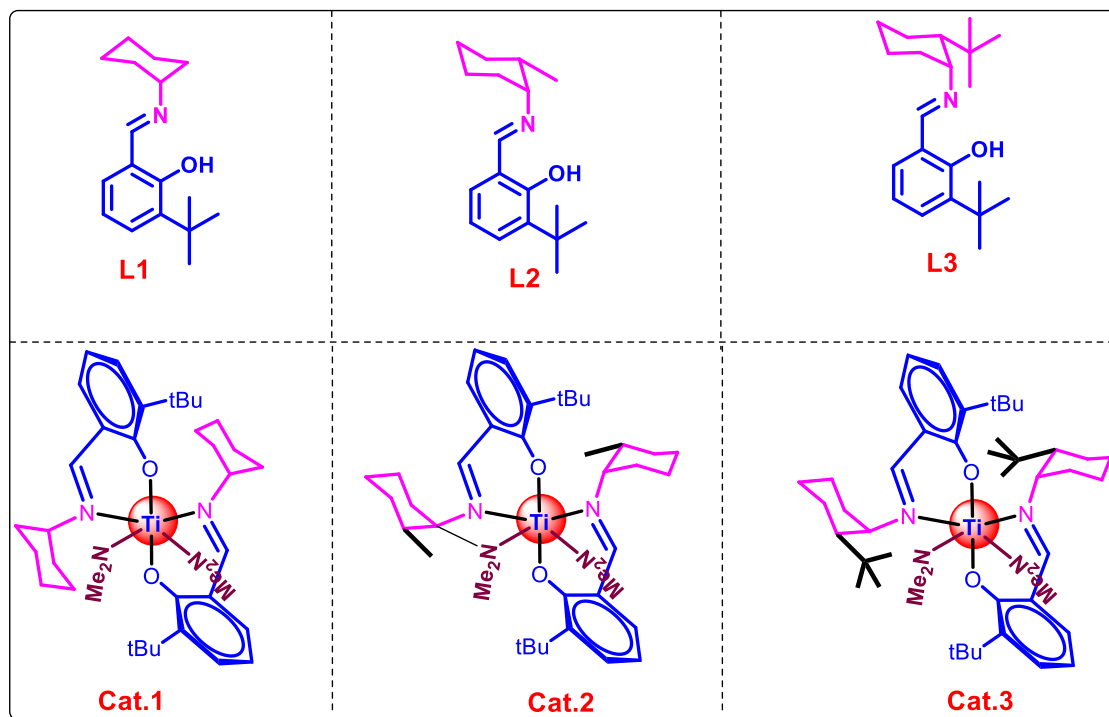
The resulting polyethylene was examined through differential scanning calorimetry (DSC), high-temperature gel permeation chromatography (HT-GPC), and high-temperature NMR spectroscopy.



Scheme 5.2: Synthesis of amido Ti-iminocarboxylate complex **Cat.1**.

This investigation indicated the formation of linear polyethylene with a molecular weight of 2.5 million g/mol, classifying it as UHMWPE according to ASTM-D4020, and confirming a high crystallinity of 96 %. Furthermore, a specially designed DSC method demonstrated that the UHMWPE exists in a "disentangled" state. This study highlights the effectiveness of the [bis-dimethylamido-Ti-(bis-iminocarboxylate)] complex in catalyzing ethylene polymerization to produce d-UHMWPE. The ongoing investigations are aimed at enhancing catalyst performance through modifications to the ligand structure. In **Chapter 4**, β -hydride elimination is identified as a critical challenge during ethylene polymerization, as it can interfere with the formation of UHMWPE. This undesired process disrupts chain propagation by facilitating premature chain termination. To address this issue, the ligand backbone was strategically modified by introducing increasing steric hindrance, aiming to suppress β -hydride interaction with the metal center. This approach ensures that the growing polymer chain remains intact, thereby enabling the synthesis of UHMWPE with high molecular weight. The study focuses on the one-step synthesis of three phenoxy-imine ligands (**L1–L3**) featuring progressively enhanced steric bulk. These ligands were synthesized in notable yields, providing a robust platform to evaluate the steric effects on polymerization efficiency and suppressing β -hydride elimination.

The ligands were characterized using a variety of spectroscopic and analytical techniques, including single crystal X-ray diffraction, which confirmed their structures. Following their synthesis, the ligands were reacted with a titanium precursor to form titanium complexes. These complexes were activated with different cocatalysts methyl aluminoxane (MMAO), triisobutylaluminum (TIBA), and tetrakis (pentafluoro phenyl) borate (BT) to assess their catalytic activity, denoted as **Cat. 1 to Cat. 3** (Scheme 5.3).



Scheme 5.3: Structure of Phenoxycycloalkylidene ligands and their Ti-phenoxycycloalkylidene complexes Cat.1- Cat.3.

The findings reveal that the introduction of steric bulk generally enhances catalytic activity, with the exception of Cat. 3, where increased steric hindrance negatively impacted performance. This decline in activity is likely due to restricted monomer access to the active site or interference with polymer chain growth. MMAO was identified as the most effective activator for producing ultrahigh molecular weight polyethylene (UHMWPE). The optimal polymerization conditions were established as an Al/Ti ratio of 2000 equivalents, an ethylene pressure of 2 bar, a temperature of 40 °C, and a polymerization duration of 10 minutes. Under these conditions, Cat. 2 achieved a weight average molecular weight (M_w) of 2.75×10^6 g/mol, with a remarkable crystallinity of 95 % and melting temperatures between 140 and 143 °C, indicative of d-UHMWPE. Overall, this

study emphasizes the critical relationship between steric effects and catalytic efficiency, providing valuable insights for designing of advanced catalysts in ethylene polymerization.

5.2. Outlook

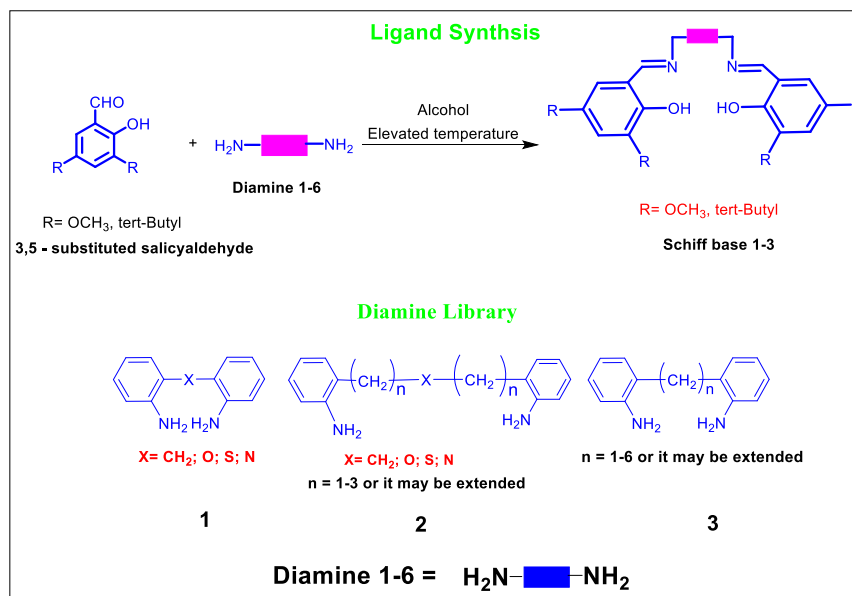
Historically, the development of catalysts for olefin polymerization relied heavily on trial-and-error approaches, which, while effective in some cases, lacked a deep mechanistic understanding. Over the past two decades, however, there has been a transformative shift toward rational and systematic strategies for catalyst design. This evolution has enabled researchers to move beyond conventional empirical methodologies and explore non-canonical approaches, including innovative modifications to ligand frameworks. These advances have facilitated the development of highly efficient and selective catalytic systems, offering superior control over polymerization processes.¹ For UHMWPE, these advancements are particularly significant, as achieving the desired molecular weight, crystallinity, and morphology remains a challenge. Traditional methods, often limited by issues such as β -hydride elimination and steric hindrance, have been complemented by modern approaches that incorporate tailored ligand architectures, computational modeling, and mechanistic insights. Non-canonical ligand modifications, which go beyond standard electronic and steric tuning, have proven effective in creating catalysts with enhanced activity and precision, thereby addressing critical barriers in UHMWPE synthesis.²

Looking forward, the synthesis of UHMWPE can greatly benefit from a deeper integration of these rational design principles. Computational tools, such as density functional theory (DFT), can aid in predicting reaction pathways and optimizing catalyst structures, minimizing experimental trial-and-error. Additionally, advanced characterization techniques, like low-temperature NMR and isotopic labeling, can provide mechanistic clarity, enabling the fine-tuning of catalysts for specific polymerization conditions.

5.2.1 Synthesis of flexible tetradentate Schiff base ligand and its complexes

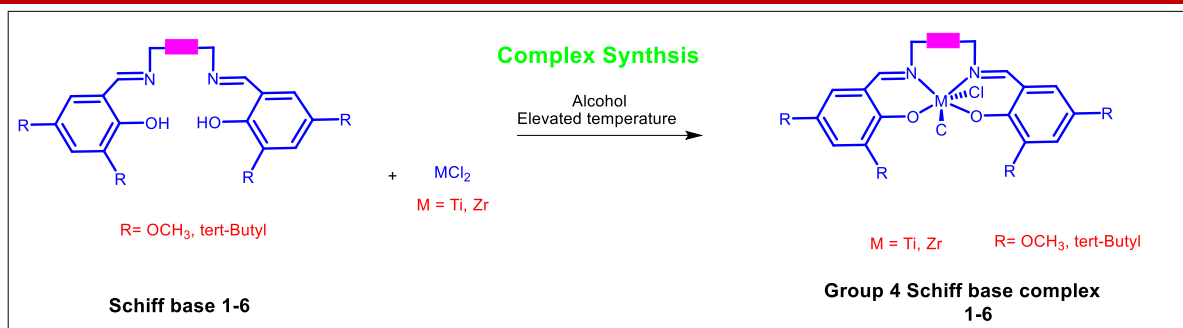
In the overall thesis, we have focused on the development of bidentate monoanionic ligand backbone systems for the production of UHMWPE. Building on this approach, a potential

direction for future work involves the use of tetradentate ligand frameworks, where the stoichiometry of the catalyst system can be carefully balanced to ensure optimal catalytic performance (Scheme 5.4). By utilizing tetradentate ligands, we can achieve enhanced stability and better control over the metal center, which could significantly improve polymerization efficiency.³



Scheme 5.4: Synthetic route of tetradentate Schiff base ligand

Furthermore, tetradentate ligands provide the unique ability to fine tune both steric and electronic properties through the strategic placement of substituents. This level of flexibility enables the suppression of undesirable side reactions, such as β -hydride elimination, which is a significant challenge in the synthesis of UHMWPE. Additionally, these ligands can be employed with early transition metals, which are more acidic in nature, allowing for better tuning of the reaction conditions to achieve the desired molecular weight and polymer properties (Scheme 5.5).



Scheme 5.5: Synthesis of Group 4 complexes (1-6)

The introduction of specific steric bulk and the careful selection of electron-donating or electron-withdrawing groups can further enhance the control over the chain growth mechanism. This can ultimately improve the production of high molecular weight polyethylene, ensuring that the polymer exhibits the desired crystallinity and morphology. By optimizing these factors, tetradentate ligands can play a crucial role in overcoming existing challenges in UHMWPE synthesis, leading to more efficient, scalable processes for the production of advanced polyethylene materials with tailored properties. Incorporating these tetradentate ligand systems could address existing challenges in UHMWPE synthesis, such as improving polymerization efficiency, controlling molecular weight distribution, and enhancing the processability of the polymer. This approach holds promise for advancing the field of polyethylene production, opening the door to more sustainable, scalable, and high-performance materials for a variety of applications.⁴

Moreover, the scalability of UHMWPE production will require a balance between achieving high molecular weights and maintaining processability. This can be addressed through innovations in catalyst design that allow precise control over chain growth mechanisms while suppressing undesired side reactions. By tailoring molecular architectures and influencing morphology during synthesis, researchers can optimize the physical and mechanical properties of UHMWPE, paving the way for its enhanced performance in demanding applications such as medical implants, industrial equipment, and high-strength fibers.⁵

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ABSTRACT

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Year of Submission: 2024

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Dr. H. V. Pol

Title of the thesis: A Catalyst Design for Preparation of Ultrahigh Molecular Weight Polyethylene

This study explores the impact of catalytic systems, early transition metal complexes, and reaction parameters on the synthesis of ultra-high molecular weight polyethylene (UHMWPE). It focuses on modifying molecular architecture and polymer morphology to optimize product properties. The research examines the disentangled state of UHMWPE, analyzing polymerization parameters, catalysts, and co-catalysts. Emphasis is placed on the role of ligand backbones in controlling polymerization kinetics, providing insights for advancing high-performance polyethylene production. To address the need for simplified synthetic pathways in ligand design and catalysis, we developed imine-based ligands and their titanium complexes. These systems demonstrate significant potential for advancing the efficiency and tunability of UHMWPE synthesis. **Chapter-1** provides a literature review on significant advancements in catalysts for UHMWPE production, addressing challenges to be overcome for successful UHMWPE synthesis. It also explores methods to specifically produce disentangled UHMWPE rather than its entangled counterpart. **Chapter-2** this study outlines our efforts in synthesizing imine ligands and explores an unexpected outcome encountered during the preparation of the imine carboxylate ligand backbone, leading to detailed investigations into the formation of benzoxazinone. **Chapter-3** details the synthesis of a neutral titanium (Cat.1) complex, synthesized by treating $[\text{Ti}(\text{NMe}_2)_4]$ with 2-((4-methoxybenzylidene) amino) benzoic acid, yielding [bis-dimethylamido-Ti-(bis-iminocarboxylate)]. The identity of **Cat.1** was confirmed through a combination of 1D and 2D NMR spectroscopy and mass spectrometry. Various cocatalysts were tested for activation, with MMAO (modified methylaluminoxane) proving most effective.⁴ **Chapter-4** discusses sterically tuned three different cyclohexylphenoxyimine ligands and their corresponding titanium complexes. These complexes were characterized using multiple spectroscopic techniques. The steric bulk was calculated using DFT, and its effects on ethylene polymerization were studied for the production of disentangled UHMWPE. **Chapter-5** summarizes the findings and outlines potential directions for future research.

List of Publications and Patents Emanating from the Thesis Work

1. **Bodkhe, D.V.**; Chikkali, S. H. Ti-Iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene, *Eur. Polym. J.* **2023**, *182*, 111725/1-8.
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 3. Patel, K. P.; Deshmukh, S. S.; **Bodkhe, D.V.**; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanan, P.; Nandi, S.; Vaidhyanath, R.; Chikkali, S. H. Secondary Interactions Arrest the Hemiaminal Intermediate to Invert the Modus Operandi of Schiff Base Reaction: A Route to Benzoxazinones, *J. Org. Chem.* **2017**, *82*, 4342 – 4351.
 4. Chikkali, S. H.; Patel, K. P.; Deshmukh, S.; **Bodkhe, D. V.** Metal free single step synthesis of substituted benzoxazinones, *IPA: IN201611002384* (2016).
 5. **Bodkhe, D. V.**; Patel, K. P.; Shaikh, M. H.; Shivaram, S.; Chikkali, S. H. Sterically Tailored Phenoxy-imine Titanium Complexes as a Catalysts for the Preparation of Ultra-High Molecular Weight Polyethylene. (*Manuscript under preparation*).
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List of Publications Non-Emanating from the Thesis Work

1. Rajput, B. S.; Pawal, S. B.; **Bodkhe, D. V.**; Rao, I. N.; Sainath, A. V. S.; Chikkali, S. H. Renewing Polyethylene: Insertion Copolymerization of Sugar Derived Hydrophilic Monomers with Ethylene. *Eur. Polym. J.* **2020**, *134*, 109775/1-6. DOI: 10.1016/j.eurpolymj.2020.109775.

List of Oral/Poster Presented with Details

1. Presented poster in National Science Day, NCL Research Foundation at CSIR-NCL, Pune held on 25-26 Feb. 2017. Patel, K. P.; Deshmukh, S. S.; **Bodkhe, D.V.**; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanan, P.; Nandi, S.; Vaidhyathan, R.; Chikkali, S. H. *Secondary Interactions Arrest the Hemiaminal Intermediate to Invert the Modus Operandi of Schiff Base Reaction: A Route to Benzoxazinones*, *J. Org. Chem.* **2017**, *82*, 4342 – 4351.
 2. Presented poster in 16th International Conference on Science and Technology of Polymers and Advanced Materials, **SPSI-MACRO-2022**, in CSIR-NCL, Pune. “*Ti-Iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene.*” **Bodkhe, D.V.**; Chikkali, S. H.
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Ti-iminocarboxylate catalyzed polymerization of ethylene to highly crystalline, disentangled, ultrahigh molecular weight polyethylene

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ABSTRACT

Disentangled ultrahigh molecular weight polyethylene (d-UHMWPE) is a niche, highly sought-after, and an emerging class of polyethylene. However, the synthesis of d-UHMWPE is uncommon and is equally challenging. Here, we report a Ti-iminocarboxylate complex that produces d-UHMWPE under ambient polymerization conditions. Treatment of tetrakis(dimethylamido-titanium) $[Ti(NMe_2)_4]$ with 2-((4-methoxybenzylidene)amino)benzoic acid produced a novel titanium complex Cat.1 [bis-dimethylamido-Ti(bis-iminocarboxylate)]. The identity of Cat.1 was unambiguously ascertained using a combination of 1-2D NMR spectroscopy and mass analysis. Cat.1 was activated using various cocatalysts, and MMAO (modified methylaluminoxane) outperformed the others. Screening of polymerization parameters suggested an Al/Ti ratio of 1000, 4 bar ethylene pressure, 35 °C temperature, and a polymerization time of 30 min as the optimal condition. Under the optimized polymerization conditions, Cat.1 polymerizes ethylene to ultrahigh molecular weight polyethylene with a weight average molecular weight (Mw) of 2.5×10^6 g/mol. The thermal behavior of the thus prepared material disclosed a highly crystalline [crystallinity χ (DSC) 96 %], strictly linear polyethylene. Detailed thermal analysis of the nascent polyethylene using a specifically designed DSC method revealed the existence of a high melting peak at 139–140 °C, which is a hallmark of disentangled UHMWPE. Thus, a homogeneous, single-site ethylene polymerization catalyst has been developed, which upon activation with MMAO produced highly crystalline d-UHMWPE.

1. Introduction

Within a span of 100 years, polymers have reached every corner of the planet earth. The global annual production of polymers stands at about 380 million tons [1,2]. Among these, the largest volume polymer is polyethylene (PE) [3,4], and it is produced mainly using “Mülheim atmospheric polyethylene process” or “low pressure process” [5,6]. Since the pathbreaking discovery of transition metal-catalyzed olefin polymerization by Ziegler, many academic and industrial centers have pursued olefin polymerization, and today PE is the largest volume polymer in the world. A key to the discovery of “low pressure process” was a catalyst. Thus, a large volume of literature on olefin polymerization deals with the synthesis of metal catalysts. A heterogeneous Ziegler catalyst is used to produce PE, and these catalysts are made of $TiCl_4$ epitaxially adsorbed on a substrate made of anhydrous $MgCl_2$ [7]. As the problems associated with investigations of heterogeneous catalysts started surfacing, the community moved to the homogeneous catalysts, and in the process, MAO and metallocenes were discovered by Sinn and Kaminsky [8]. Metallocenes have slowly entered into the market and about 5–8 % of the total PE is now produced using metallocene catalysts [9]. Catalysts which were discovered after metallocenes and which do

not meet the criteria of being metallocenes are generally called “Post-metallocenes” or “Non-metallocenes” [10]. Thus, olefin polymerization has evolved over the years, and slowly, the focus has been shifting to more specialty polyolefins. Among the specialty polyolefins, functional polyethylene [11–18], telechelic polyethylene [19], PE dispersions [20], ultrahigh molecular weight polyethylene [21–24], and polyethylene vitrimers are emerging as a new class of high-end materials [25,26].

As defined in ASTM D4020, a polyethylene with viscosity average molecular weight of 2.5 million g/mol is considered as UHMWPE [27]. Due to inherent outstanding physical properties, UHMWPE is used in prostheses, body armors, sport wears, battery separators, siding for ships at harbors, etc. However, synthesis of UHMWPE is not trivial and requires careful catalyst tweaking. Control over the rate of propagation (k_p), rate of transfer (k_{tr}) or rate of termination (k_t) is crucial to obtain such high molecular weight polyethylene. The three rates (k_p , k_{tr} , k_t) can be altered by suitable catalyst design that consists of an appropriate metal cation and ligand framework with a correct balance of the electronic and steric environment. The current understanding of the field allows us to draw the following guidelines to design a catalyst for UHMWPE. The rate of propagation should be much higher than the k_{tr} and k_t . Therefore, the metal centre should be very acidic (oxophilic),

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which will allow the chain to grow faster. The ligand should force the β -H out of the metal-plan and thus suppress the two rates (k_{tr} , k_p). Thus, a suitable catalyst combined with correct choice of reaction parameters may enable the synthesis of ultrahigh molecular weight PE [28].

There are two states of ultrahigh molecular weight polyethylene. The traditional UHMWPE is “entangled”, while another state called “disentangled” (d-UHMWPE) has been identified in the last decade [29]. Literature reports suggest that the heterogeneous Ziegler-type catalysts generally produce “entangled” UHMWPE. Entangled UHMWPE is difficult to process, and an additional step of gel-spinning is necessary. While, only homogeneous catalysts have been reported to be capable of producing disentangled UHMWPE (d-UHMWPE). Chikkali and co-workers have reported a recent exception to the rule [30]. A heterogeneous catalyst was subjected to controlled reduction of Ti (IV) to Ti(III), which enabled the synthesis of d-UHMWPE. Among the homogeneous catalysts, the titanium bis(phenoxy imine) or the FI-catalysts have been extensively investigated (Fig. 1, 1) [31–33]. Under optimized conditions, the FI catalyst can produce d-UHMWPE. Recently, Enders and co-workers reported a naphthyridine cyclopentadienyl chromium catalyst (Fig. 1, 2). The chromium catalysts, upon activation with a suitable cocatalyst, produced d-UHMWPE [34,35].

The weak coordination of nitrogen to the metal causes the FI catalyst family to experience structural isomerism [36]. Therefore, rational ligands designing approaches have frequently concentrated on creating and altering auxiliary ligands to offer an attractive catalyst [37]. A very frequently used parameter in rational designing is steric and electronic control by changing substituents on the ligand framework. Imine ligands are largely favoured for three main reasons: (1) easy synthesis, (2) relative stability towards moisture/oxygen, and (3) ease of tailoring electronic and steric by choosing different amine and aldehyde. Metal complexes that produce polyethylene from ethylene have been successfully prepared using a variety of nitrogen-containing ligands. We pondered if an imine-based carboxy ligand can deliver bis-ligated titanium complex and if the Ti-complex can initiate ethylene polymerization.

Here in, we describe a single-step synthesis of iminocarboxylate ligated titanium complex [(L1)₂Ti(NMe₂)₂] (Cat.1) (Fig. 1). Spectroscopic and analytical techniques unambiguously ascertained the identity of the Ti-complex. The resultant titanium complex [(L1)₂Ti(NMe₂)₂] was employed as a precatalyst for the polymerization of ethylene. To our delight, under defined polymerization conditions, Cat.1 produced highly crystalline, disentangled, ultrahigh molecular weight polyethylene.

2. Results and discussion

2.1. Synthesis of imine carboxylate ligand (L1) and its titanium complex

The condensation of amine with an aldehyde to produce imine (Schiff base) is well known for decades. However, condensation of *ortho*-

amino acids with aldehydes is highly challenging and has been found to produce benzoxazinones, instead of expected imines [38]. The cyclization to benzoxazinones can be addressed by substituting the acidic proton with a heavy metal cation [39]. Therefore, choosing the amine and aldehyde partners is crucial for condensing the *ortho*-amino acid compounds. Based on our past experience, we envisaged the condensation of anthranilic acid with anisaldehyde [33,34]. Thus, 1 g of anthranilic acid was treated with anisaldehyde to obtain the anticipated 2-((4-methoxybenzylidene) amino) benzoic acid (L1) in an improved isolated yield of 90 % (2.5 g) [40]. The identity of the resultant compound was ascertained using a combination of spectroscopic and analytical methods, including a single crystal X-ray diffraction [35].

After establishing a robust ligand synthesis protocol, we examined the coordinating ability of iminocarboxylate ligand with a transition metal. It is necessary to have both, the ligand and the metal precursor, to create a single component metal complex for ethylene polymerization. Our initial effort to obtain the desired metal complex (Cat.1) by treating L1 with titanium tetrachloride [TiCl₄] as a titanium precursor was not very successful. We could not isolate and characterize the resultant metal complex (Cat.1). The ligand is highly acid sensitive, and one must first prepare ligand-salt before treating it with [TiCl₄]. Thus, after treating the sodium salt of L1 with [TiCl₄], it was found that the imine bond is cleaved. To address this bottleneck, we were in search of a titanium precursor with less acidity. Marks and co-workers recently reported an unexpected behavior of phenoxy-imine ligated zirconium bis(dimethylamine) precursor on ethylene-olefin copolymerization [41]. Based on this, we anticipated that the titanium congener of the reported zirconium complex might suppress cleavage of L1 (imine bond) as the by-product is a base (HNMe₂) and may allow coordination of iminocarboxylate ligand to enable the formation of mononuclear titanium complex. With this hypothesis, two equivalents of iminocarboxylate ligand L1 (1 g, 3.9 mmol) was treated with one equivalent of tetrakis(dimethylamido-titanium) [Ti(NMe₂)₄] (1.9 mmol) at 0 °C. After the addition, the temperature of the reaction mixture was raised to room temperature (~35 °C) and the stirring was continued for 2 h. After two hours, volatiles were evaporated, and the titanium complex Cat.1 was isolated in 62 % yield (see SI for details). The synthesis of the iminocarboxylate-Ti(NMe₂)₂ complex was very straightforward, and the resultant by-product [Me₂NH] was easily evaporated from the reaction mixture. The reddish brown crystalline solid of complex Cat.1 (Scheme 1) was subjected to detailed characterization.

The ¹H NMR spectrum of the above reddish brown solid disclosed a resonance at 8.34 ppm, which can be assigned to the imine proton. Compared to the free ligand L1, the imine proton is shifted slightly up-field (from 8.65 ppm in the free ligands L1 to 8.34 ppm for the Cat.1) in the complex Cat.1. The change in chemical shift suggests coordination of the imine nitrogen to the titanium. Such up-field shifts are not very common but have been observed for other metal complexes [34,42]. Furthermore, the methyl protons in Ti-NMe₂ group could be

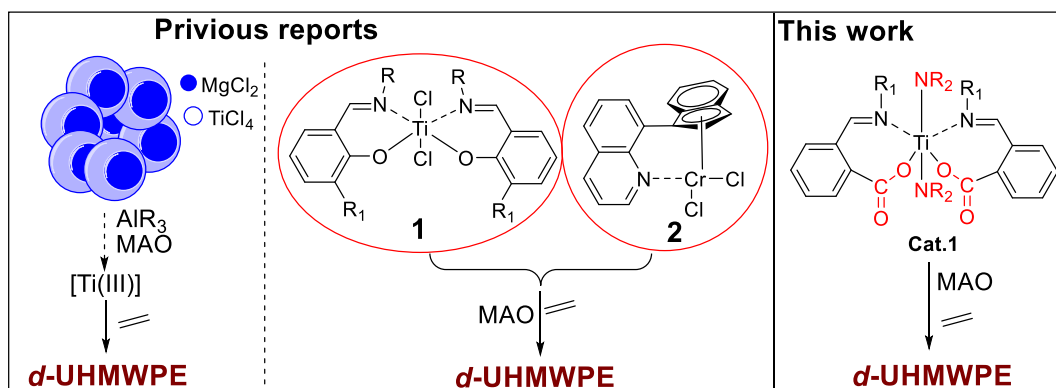
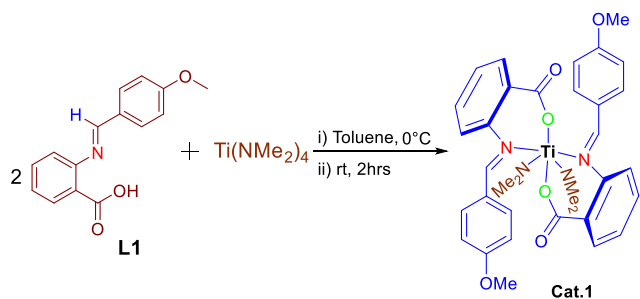


Fig. 1. State-of-the-art catalysts for the synthesis of d-UHMWPE (left) and the present work (right).



Scheme 1. Synthesis of amido Ti-iminocarboxylate complex **Cat.1**.

identified as two sets, one at 3.10 ppm and the other at 2.91 ppm. The ^{13}C NMR spectrum of **Cat.1** revealed a characteristic imine-carbon resonance at 160.4 ppm. The short-range C—H correlation HSQC spectrum displayed cross-peaks to corresponding carbons. Unambiguous evidence of the existence of **Cat.1** was obtained from a long-range C—H correlation HMBC spectrum (Fig. 2). The methyl proton of the TiNMe_2 group displayed a cross-peak to the acid carbon, confirming chelation of **L1** to Ti-precursor. The NMR findings were further corroborated by mass analysis, and a molecular ion peak was observed at $m/z = 610$ [**Cat.1**- $2\text{NMe}_2 + 2\text{H} + \text{HNMe}_2 + \text{Li}$] $^+$ Da. As the titanium complex, **Cat.1**, is highly air and moisture-sensitive, fragments with different masses could be observed in the mass spectrum (see SI, Fig. S12).

2.2. Ethylene polymerization:

After establishing the synthesis, we examined the reactivity of **Cat.1** in ethylene polymerization. The ethylene polymerization was conducted

in a Büchi high-pressure reactor with a heating/cooling jacket, an overhead mechanical stirrer, and gas inlet/outlet facilities. The reactor was continuously fed with ethylene gas to maintain the necessary pressure.

The titanium complex **Cat.1** is just a pre-catalyst and has to be activated to obtain the catalytically active species for ethylene polymerization. Alkyl aluminum or boron compounds are well-known activators and have been commonly used in olefin polymerization [36]. Table 1 summarizes the cocatalyst/activator screening and Fig. 3 depicts the performance of various activators in ethylene polymerization. The cocatalyst was used in two lots, see supporting information for details. Please note that 30 min stirring with about 70 % cocatalyst was required before the addition of **Cat.1**. First, the efficiency of trimethyl aluminum (TMA) in the presence of BT (Trityl Borate) was examined. At a TMA (cocatalyst) to catalyst (**Cat.1**) ratio (Al/Ti) of 40, under 4 bars of ethylene, 250 mg of polyethylene was obtained (Table 1, entry 1). The best polymer yield of 350 mg was obtained at a TMA to catalyst ratio (Al/Ti) of 100. While, the yield was reduced to 150 mg when TMA to catalyst ratio (Al/Ti) was increased to 120. Thus, the highest yield was 350 mg under the given polymerization conditions. The difference in crystallinity (67 vs 91 %) can be ascribed to the existence of more crystalline domains, due to which melting enthalpy (area under the peak) increases, leading to higher crystallinity. Next, di-isobutyl aluminum hydride (DiBAL-H) was screened for ethylene polymerization, but no polymer was produced. Subsequently, MMAO was tested as cocatalyst and was found to produce 700 mg of polyethylene under similar conditions (Table 1, entry 5). As presented in Fig. 3, MMAO outperformed TMA/BT, DiBAL-H, and DiBAL-H/MMAO, and disclosed the highest activity.

Thus, MMAO was finalized as the best cocatalyst and further studies

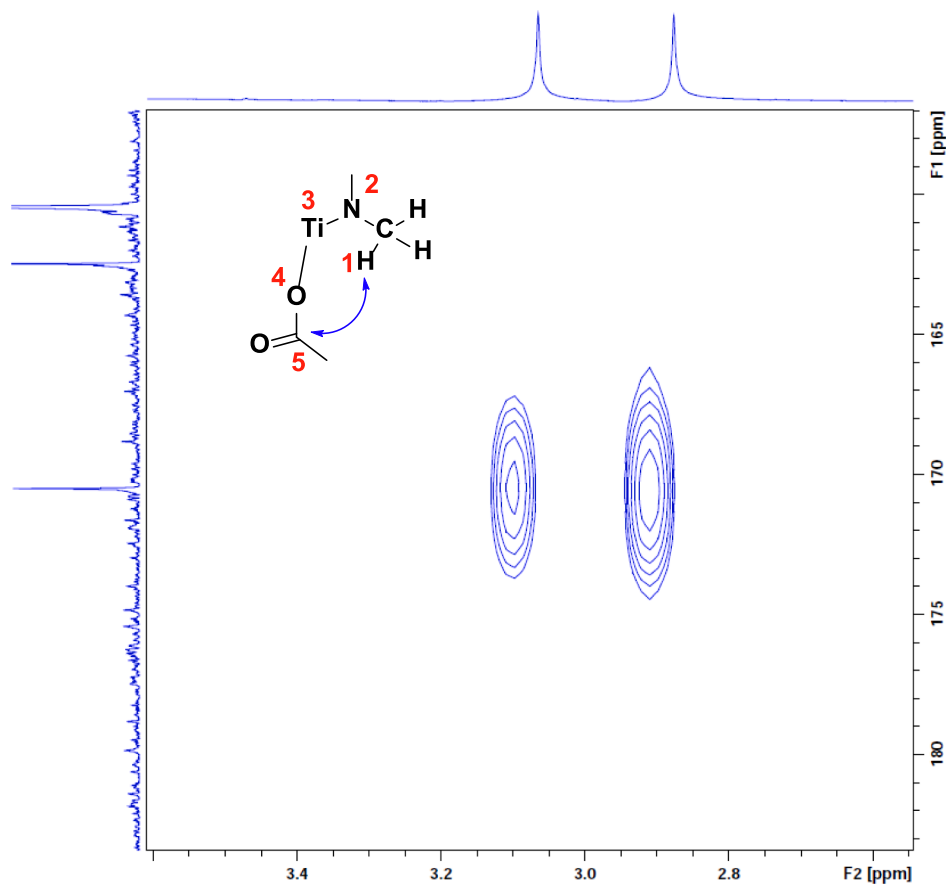
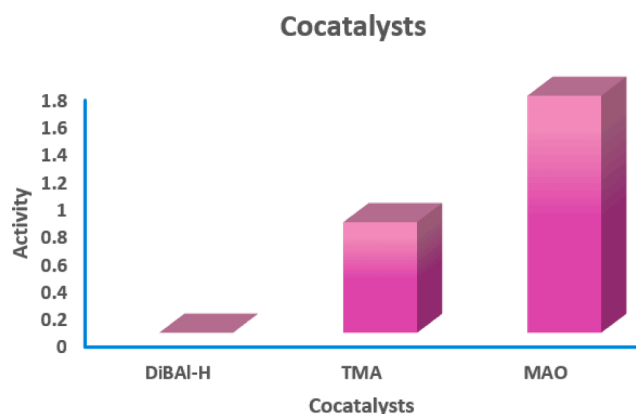


Fig. 2. Expanded view of a long-range C—H correlation (HMBC) spectrum of **Cat.1** displaying cross peak between the methyl protons ($-\text{TiNMe}_2$) and the carboxylate carbon (in CDCl_3).

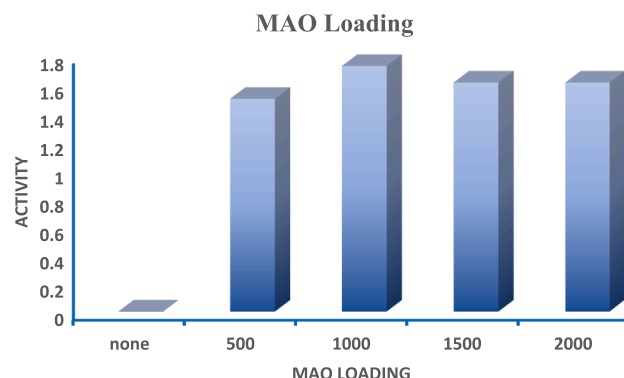
Table 1Ethylene polymerization catalyzed by Cat.1 in the presence of various cocatalysts.^a

Entry	TMA (equiv.)	BT (equiv.)	MMAO (equiv.)	Yield (g)	Activity ^f	^b M _w	^c D	^d Tm	^e Cryst. (%)
1	40	1.2	–	0.250	16.1	1.49×10^5	6.4	141.8	67.4
2	100	1.2	–	0.350	22.5	1.12×10^5	3.5	141.3	86.8
3	120	1.2	–	0.150	9.6	2×10^5	4.4	139.9	91.9
4	40	–	–	0.106	6.8	–	–	136.8	62.7
5	–	1	1000	0.700	–	–	–	–	–

^a Conditions: Cat.1–31 μmol of Ti (20 mg), Solvent-Toluene (100 mL), Ethylene-4 bars, Temperature-40 °C, Time-30 min, equiv.-equivalent. ND-Not detected. ^{b,c}As obtained from HT-GPC at 160 °C in 1,2,4-Trichlorobenzene (TCB) against polystyrene standards. ^dObtained from DSC, heating and cooling curves of first heating, cooling, and second heating; ^eCrystallinity was calculated from the melting enthalpy measured by DSC and relative to the theoretical melting enthalpy of 293 J/g for 100 % crystalline polyethylene; ^fActivity in Kg of PE/mol Ti/h.

**Fig. 3.** Screening of cocatalysts and activity in ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

were undertaken (Table 2). The effect of Al/Ti ratio on the polymerization activity was investigated (Table 2, entries 1–4). At a Al/Ti ratio of 500 under 4 bar ethylene pressure, 650 mg of polyethylene was obtained (Table 2, entry 1). The melting temperature was found to be 138.7 °C, suggesting high molecular weight, crystalline polyethylene. The Al/Ti ratio was further increased to 1000, 1500, and 2000 (Table 2, entries 2–4). The highest TOF and yield of 750 mg was obtained at an Al/Ti ratio of 1000. Increasing the Al/Ti ratio further to 2000, deteriorated the polyethylene yield to 700 mg. Fig. 4 presents the comparative performance of Al/Ti ratio on polyethylene activity. In our attempts to estimate the life time of the catalyst, ethylene polymerization was carried out for different time period (5, 30, 60 min) and the activity was determined. As can be seen in the Fig. 6, the highest activity was obtained after 30 min, suggesting existence of active catalyst. While increasing the polymerization time to 60 min revealed lower activity, suggesting catalyst decomposition. Thus, the optimized polymerization condition is 20 mg Cat.1, Al/Ti ratio of 1000, 4 bar ethylene pressure, 35

**Fig. 4.** Screening of Al/Ti ratio and activity in ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

°C temperature, and a polymerization time of 30 min.

One of the crucial parameters that influence the activity, molecular weight, polydispersity and entanglement of polyethylene, is the polymerization temperature. Therefore, we investigated the effect of temperature on polymerization, and Fig. 5 summarizes the results. As compared to the optimized temperature of 35 °C, ethylene polymerization at 25 °C disclosed a slight drop in the catalyst activity (1.56×10^3 , 680 mg PE). While increasing the polymerization temperature to 50 °C significantly decreased the catalyst activity (Table 2, entry 7, 360 mg PE). Further increasing the polymerization temperature to 60 °C led to a colossal drop in catalyst activity (Table 2, entry 8). Thus, polymerization temperature significantly influenced catalyst activity, and 35 °C remained the optimal reaction temperature.

2.3. Highly crystalline, disentangled ultrahigh molecular weight polyethylene (d-UHMWPE)

The polyethylene produced under the optimized polymerization conditions was subjected to detailed characterization. The molecular

Table 2Ethylene polymerization catalyzed by Cat.1 and MMAO.^a

Entry	Precatalyst	Al/Ti	Temp (°C)	^d Poly. (g)	Activity ^b	^e TOF(10 ³)	^j M _v	^f M _w × 10 ⁶	^g D	^h Tm	ⁱ Cryst. (%)
1	Cat.1	500	35	0.650	41.9	1.497	4.90×10^5	2.5	2.4	138.7	62.1
2	Cat.1	1000	35	0.750	48.3	1.728				137.2	87.9
3	Cat.1	1500	35	0.750	48.3	1.612	1.6×10^5			139.5	60.8
4	Cat.1	2000	35	0.700	45.1	1.612	1.94×10^5			136.5	53.5
5 ^c	Cat.1 + Al ⁱ BuH + MAO	40 + 1000	35	NO	–	–	–	–	–	NO	–
6	Cat.1	1000	25	0.680	43.8	1.566	7.4×10^5	–	–	139	96.4
7	Cat.1	1000	50	0.360	23.2	0.829	1.93×10^5			138.3	80
8	Cat.1	1000	60	0.297	19.1	0.684	0.54×10^5			134	48.6

^a Conditions: Catalyst = 31 μmol of Ti (20 mg of catalyst); Solvent = 100 mL of toluene, Time-30 min, ^bActivity in Kg of PE/mol Ti/h; ^cAl ⁱBuH 1 Equiv. + MAO 1000, 4 bar ethylene pressure, time 30 min; ^dWeight of produced polyethylene (in gm); ^eTOF = mol of polyethylene/mol of Ti/h; ^{f,g}As obtained from HT-GPC at 160 °C in 1,2,4-Trichlorobenzene (TCB) against polystyrene standards, in 10⁶ g/mol. ^hObtained from DSC, heating and cooling curves of first heating, cooling, and second heating; ⁱCrystallinity was calculated from the melting enthalpy measured by DSC and relative to the theoretical melting enthalpy of 293 J/g for 100 % crystalline polyethylene. ^jViscosity average molecular weight was determined at 135 °C in TCB using Ubbelohde viscometer. NO- Not obtained.

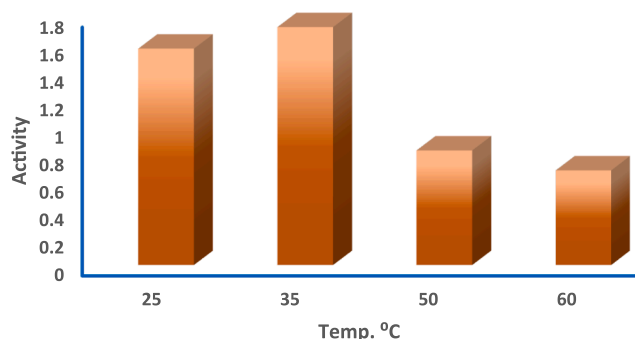


Fig. 5. Effect of temperature on ethylene polymerization (Activity = mol of polyethylene/mol of Ti/h).

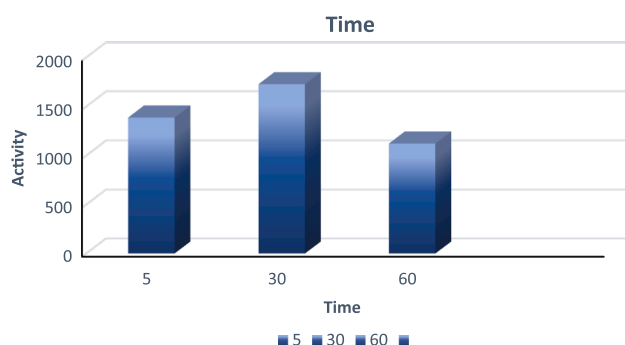


Fig. 6. Ethylene polymerization at 5, 30 and 60 min (Activity = mol of polyethylene/mol of Ti/h).

weight of the thus prepared PE was determined using a High-Temperature Gel Permeation Chromatography (HT-GPC). To our delight, HT-GPC analysis of this polyethylene in trichlorobenzene (TCB) at 160 °C disclosed the formation of ultrahigh molecular weight polyethylene (UHMWPE) with a whopping molecular weight of 2.5 million g/mol (Table 2, entry 2). Interestingly, the polydispersity index was found to be narrow (2.4), which suggests single-site behavior of the catalyst (Cat.1). Our attempts to record the molecular weight for other entries were not very successful as the PE was only partially soluble and produced a gel even at 160 °C with 1 mg per 10 mL TCB.

The melting temperature of the resultant PE and crystallization data were obtained from differential scanning calorimetry. The melting temperature obtained during the first heating is considered. As compared to regular commodity PE grades (such as LDPE, HDPE), the melting temperature (T_m) of the polyethylene produced using Cat.1 was high (137–140 °C), suggesting a high degree of order or crystallinity. As a representative case, the sample with Mw of 2.5 million g/mol (Table 2, entry 2) disclosed a very high crystallinity of 88 % (Table 2, entry 2). While, the highest crystallinity of 96 % was observed for polyethylene produced at 25 °C (Table 2, entry 6). Such highly crystalline PE is a result of highly active catalyst and polymerization conditions that enable crystallization of the growing polymer chain. If the PE is crystallizing while the chain is growing, there should not be any time for entanglement, and one should expect disentangled ultrahigh molecular weight polyethylene (d-UHMWPE).

Therefore, we anticipated that the resultant UHMWPE would be disentangled in nature. The first melting peak of the reactor PE can be attributed to the melting of single crystal lamellae, which is the signature of the “disentangled” state of UHMWPE. To demonstrate the disentangled nature of UHMWPE prepared using Cat.1, this material was subjected to thermal analysis protocols developed by Rastogi and co-workers [43]. A special DSC method was developed, and Fig. 7 presents various steps involved in this protocol.

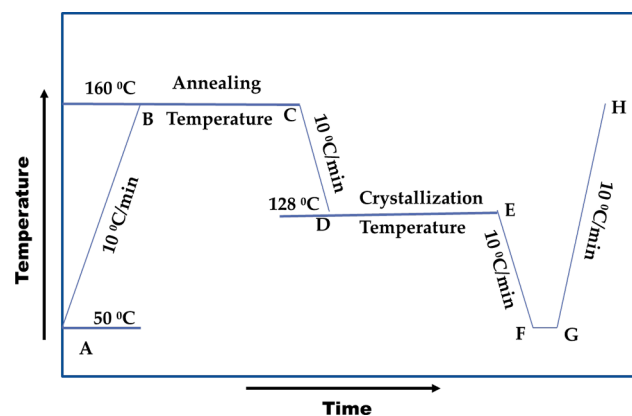


Fig. 7. Thermal protocol developed to demonstrate disentangled nature of UHMWPE. Thermal protocol: Ramp 1: 50 °C to 160 °C (A-B) @ 10 °C/min. hold @ 160 °C for 5 min. (B-C). Ramp 2: Cooling to 128 °C @ 10 °C/min. (C-D) and hold at 128 °C for 180 min. (D-E). Ramp 3: Cooling to 50 °C at 10 °C/min. (E-F) and hold at 50 °C for 1 min. (F-G). Ramp 4: Heating from 50 to 160 °C at 10 °C/min. (G-H). The DSC plot shown in Fig. 8 was obtained during ramp 4 (G-H).

To examine the melt behavior of UHMWPE, Rastogi and co-workers designed a DSC method that can distinguish “entangled” and “disentangled” domains. The method involves heating the UHMWPE from 50 °C to 160 °C (@10 °C per minute) (a and b) (Fig. 7) and annealing the sample at 160 °C for a predetermined amount of time (b and c). When the UHMWPE sample is kept at 160 °C, the polymer chains can move to achieve the thermodynamically stable “entangled” state (b and c). Therefore, depending upon the annealing time in step b-c, the polymer sample may show various degrees of “entangled” and “disentangled” domains (heterogeneity in the sample). After that, the sample was cooled to 128 °C (c and d), and was allowed to isothermally crystallize for 180 min (d and e), then it was cooled to 50 °C (e and f). Finally, the sample was heated from 50 °C to 160 °C (g-h). The information collected during the g-h heating stage is displayed in Fig. 8. Fig. 8 (blue line) disclosed two distinct melting domains, the initial high melting peak around 139–140 °C is believed to originate from a crystalline domain, representing the “disentangled” state of the UHMWPE. The high melting disentangled domain disappears at 30 min of annealing time, and a single melting peak was observed (Fig. 8, orange line). UHMWPE entangled domains are responsible for the second melting peak, which occurred at about 133–134 °C. The above observations are in line with previous reports on “entangled” and “disentangled” UHMWPE.[44,45] Thus, the DSC experiment confirms that catalyst Cat.1 polymerizes ethylene to disentangled UHMWPE. A comparative DSC thermogram of a commercial entangled UHMWPE and our disentangled UHMWPE is presented in SI (see SI Fig. S31).

3. Conclusions

In summary, an iminocarboxylate ligand L1 was treated with a [Ti(NMe₂)₄] to produce [bis-dimethylamido-Ti-(bis-iminocarboxylate)] in good yield (62 %). ¹H, ¹³C, HSQC, HMBC NMR and mass analysis conclusively proved the existence of a bis-ligated Titanium complex Cat.1. Preliminary screening of cocatalysts suggested MMAO to be the best activator. The effect of Al/Ti ratio on the activity of Cat.1 was investigated and an Al/Ti ratio of 1000 was found to be the optimal ratio. Temperature screening suggested 35 °C as the optimal temperature, while, either lowering the temperature to 25 °C or increasing it to 50 and 60 °C displayed reduced activity. The resultant polyethylene was examined by using DSC, high temperature GPC, high temperature NMR (HT NMR) spectroscopy. High temperature proton (¹H) and carbon (¹³C) NMR of the polymer suggested the formation of linear polyethylene. High temperature gel permeation chromatography revealed a molecular weight of 2.5 million g/mol, which can be classified as UHMWPE as per

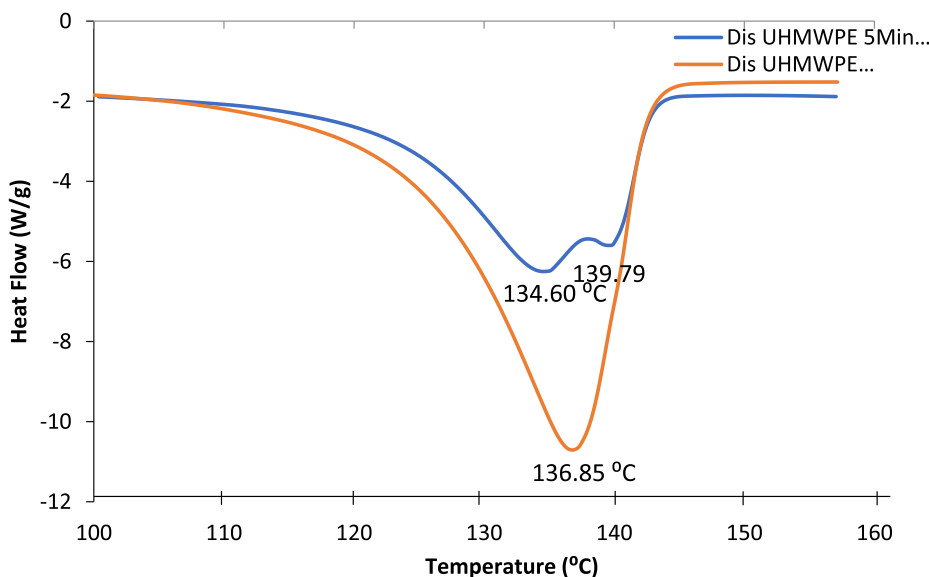


Fig. 8. DSC plot of the d-UHMWPE sample (Table 2, entry 6) annealed for 5 (blue line) and 30 (orange line) min.

ASTM-D4020. DSC analysis of the resultant PE revealed a very high degree of crystallinity (96 %). A specially designed DSC method disclosed that the thus formed UHMWPE exists in a “disentangled” state. Thus, [bis-dimethylamido-Ti-(bis-iminocarboxylate)] complex catalyzed polymerization of ethylene in the presence of MMAO to disentangled ultrahigh molecular weight polyethylene (d-UHMWPE). Further investigations to improve the activity by tweaking the ligand structure are in progress.

4. Materials and methods

All manipulations involving moisture sensitive compounds were carried out under an inert gas atmosphere using standard Schlenk or glove box techniques. Toluene was distilled from sodium/benzophenone under an argon atmosphere. Chloroform or CDCl_3 , ethanol, dichloromethane, etc. were dried and distilled as per reported procedures [46]. Ethylene (purity; 99.95 %, 3.5 grade) was supplied by Ms. Vadilal Chemicals Ltd, Pune, India. 2-aminobenzoic acid, 4-methoxy benzaldehyde, $[\text{Ti}(\text{NMe}_2)_4]$, TiCl_4 , Trityl tetrakis (pentafluoro phenyl) borate, MMAO-12 (7 wt% Aluminum in Toluene), Diisobutyl aluminum hydride (DIBAL-H), deuterated 1,1,2,2-tetrachloroethane were procured from sigma-aldrich and used without further purification. Ethanol was purchased from Spectrochem Pvt. Ltd. Trimethyl aluminum (TMA) was supplied by Schering AG, Germany and was used as received. Commercial entangled UHMWPE (CAS 9002-88-4) with M_w 3,000,000–6,000,000 g/mol was procured from Sigma-Aldrich. NMR spectra were recorded on a Bruker Avance 200, 400, 500 and JEOL 600 MHz instruments. The polymerization was run in a Büchi picoclave mini pressure reactor equipped with overhead mechanical stirrer, heating/cooling jacket and pressure regulators. High temperature NMR (HT NMR) of the polymers was recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ solvent at 130 °C. Chemical shifts are referenced to external reference TMS (^1H and ^{13}C). Mass spectra were recorded on Agilent Q-ToF mass spectrometer. FT-IR spectra were recorded on a Bruker α -T spectrophotometer in the range of 4000–400 cm^{-1} . Differential scanning calorimeter (DSC) was carried out on DSC Q-10 equipment from TA instruments with a heating and cooling rate of 10 K min^{-1} , unless mentioned otherwise. High temperature Gel Permeation Chromatography (HT-GPC) of the PE was recorded in 1,2,4-trichlorobenzene at 160 °C on a Viscotek GPC (HT-GPC module 350A) instrument equipped with triple detector system. The columns were calibrated with linear polystyrene standards and the reported molecular weights are with respect to polystyrene standards. Weight-

average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) of the synthesized UHMWPE was recorded using HT-GPC.

4.1. Synthesis of [bis-dimethylamido-Ti-(bis-iminocarboxylate)] (Cat.1):

Improved synthesis of 2-((4-methoxybenzylidene) amino) benzoic acid (L1) is described in supporting information. A 250 mL oven-dried Schlenk flask was vacuum-cooled and argon gas-purged. The Schlenk flask was heated and cooled three times under vacuum to reduce the moisture content. Under the positive flow of argon, 1 g (3.9 mmol.) of L1 was added to the above Schlenk flask. Subsequently, toluene (40 mL) was added, the mixture was stirred for 5 min. The Schlenk was cooled to 0 °C and $\text{Ti}(\text{NMe}_2)_4$ (0.4 mL, 1.9 mmol) was added gradually over a period of 5 min. A turbid yellow solution turned to a clear reddish brown one. Subsequently, the ice bath was then replaced with a water bath and the temperature of the reaction mixture was raised from 0 °C to about 30 °C. The mixture was then stirred for a further two hours at room temperature. After another 30 min of stirring, volatiles were evaporated under vacuum. A reddish brown residue was obtained. This crude complex was further purified by washing with dried, freshly distilled hexane (20 mL $\times$ 3). The content was stirred for 5 min to let the solid settle, and the supernatant liquid was separated. The solid was then vacuum-dried and stored in the glove box for future use.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 8.35 (s, 2H, $\text{HC}=\text{N}$), 7.80 (d, J = 8.58 Hz, Ar, 4H), 7.36 (t, J = 6.38, 7.50, Ar, 5H), 7.06 (d, J = 7.88, Ar, 3H), 6.97 (d, J = 8.75, Ar, 4H), 3.86 (s, 6H), 3.07 (s, 6H) and 2.88 (s, 6H, $-\text{NMe}_2$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ = 170.4 ($-\text{COOH}$), 162.4, 160.4 ($-\text{C}=\text{N}$), 148.5, 131.3, 129.8, 127.4, 125.6, 118.7, 114.7, 55.4 (OCH_3), 38.2 and 34.7 ($-\text{N}(\text{CH}_3)_2$).

ESI-MS (+ve) m/z for $\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_6 \text{ Ti}$ [$M + \text{H}$] + Calculated: 644.21 Da, observed: m/z = 610.18 [$\text{Cat.1-2NMe}_2 + 2\text{H} + \text{HNMe}_2 + \text{Li}$] $^+$ Da.

4.2. General procedure for ethylene polymerization

The ethylene polymerization reaction was carried out in a Büchi glasuster cyclone 075 high pressure reactor, equipped with overhead mechanical stirrer, heating/cooling jacket and pressure regulators. A pre-dried 250 mL Büchi reactor was kept under vacuum at 90 °C for 30 min before usage. After cooling down, the reactor was filled with argon and after 3 cycles of vacuum/argon, the reactor was filled with ethylene gas (20 bar) and flushed 3 times. It was charged with 100 mL of freshly

distilled toluene at room temperature under the positive flow of ethylene gas. The reaction temperature was set to the desired value using Julabo temperature controller and after the thermal equilibrium is reached, 70 % of total amount of cocatalyst (MMAO-12) was added and the mixture was stirred for about 30 min. Simultaneously, in a separate Schlenk tube, 10 mL of freshly distilled toluene was taken and the remaining amount of cocatalyst (MMAO-12) (30 %) was added and the content was stirred for 30 min. After 30 min. suitable amount of catalyst was injected in to the reactor along with 10 mL of dry toluene containing cocatalyst (MMAO-12), and the polymerization was initiated by pressuring the reactor with ethylene. The polymerization was carried out for the required time under vigorous stirring and a constant feed of ethylene and then terminated by the addition of acidified methanol. The polymer was filtered out, washed with a copious amount of methanol/acetone, and dried overnight under vacuum at 60 °C to obtain free-flowing powder. The polymerization results have been summarized in [tables 1 and 2](#).

¹H NMR (500 MHz, C₂D₂Cl₄, 130 °C): δ = 1.37 (broad, s, CH₂); ¹³C NMR (125 MHz, C₂D₂Cl₄, 130 °C): δ = 29.3 (s, CH₂).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The raw data required to reproduce these findings are available to download from supporting material files. The processed data required to reproduce these findings are available to download from supporting material files.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2022.111725>.

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Update

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Corrigendum



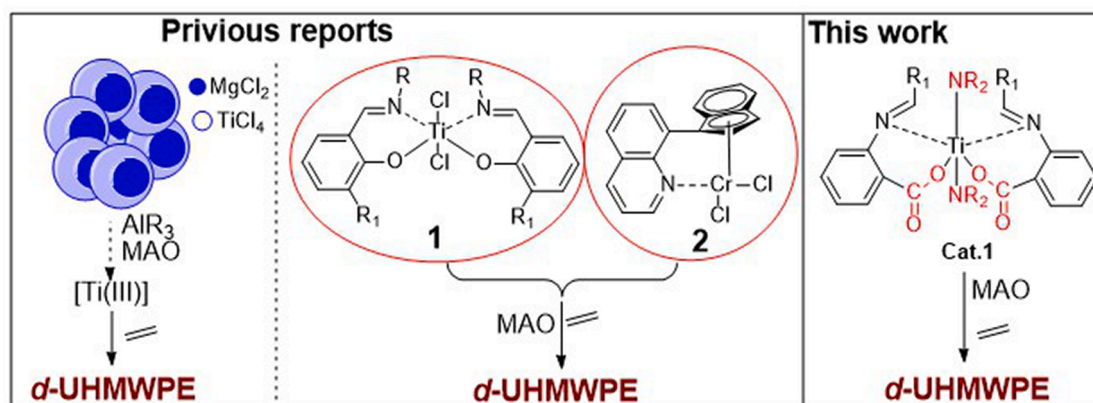
Corrigendum to “Ti-iminocarboxylate catalyzed polymerization of ethylene to highly crystalline, disentangled, ultrahigh molecular weight polyethylene” [Eur. Polym. J. 182 (2023) 111725]

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There was a small error in one of the structures in the introductory Fig. 1 of the published article. We have corrected the structure and have deleted 1 extra carbon. The authors would like to apologise for any

inconvenience caused. The correct Fig. 1 is shown below:



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Emerging trends in olefin polymerization: a perspective

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ABSTRACT

The seemingly matured field of olefin polymerization still poses several challenges and holds enormous potential to meet contemporary material requirements. In this feature article, we examine the progress of olefin polymerization in the last two decades. Among the several emerging trends, we identify four most impactful discoveries, namely, (i) disentangled ultra-high molecular weight polyethylene (dUHMWPE), (ii) disubstituted functional olefin copolymerization, (iii) incorporation of bioderived comonomers in polyolefins, and (iv) application of above (ii, iii) functional polyolefins as compatibilizers. The dUHMWPE has attracted significant attention and heterogeneous Ziegler-type catalysts, homogenous metallocene, and post-metallocene catalysts have been reported to produce disentangled ultrahigh molecular weight polyethylene. Insertion copolymerization of difunctional disubstituted olefins has been reported only recently and ortho-phosphinobenzene sulfonate palladium catalyst outperforms the other catalysts. Interestingly, insertion copolymerization of bioderived olefins has witnessed a surge in the number of reports. Sugar and plant oil-derived olefins have been copolymerized with ethylene to obtain relatively hydrophilic polyethylene. The functional polyethylene is finding a new application as compatibilizer or displays better adhesion to surfaces. Thus, the feature article offers a succinct account of emerging trends in polyolefins, identifies the most impactful contributions, and debates the application potential of these new materials.

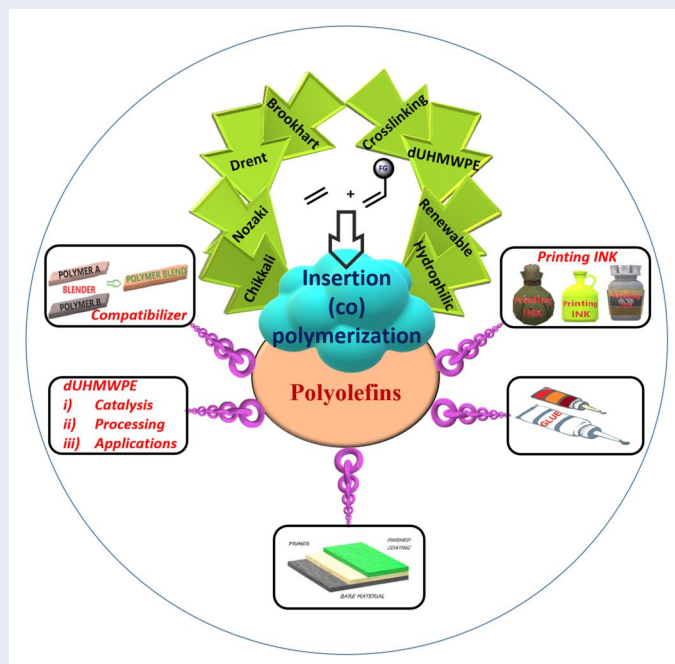
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Insertion (co)polymerization; uHMWPE; functional polyethylene; renewable monomers; compatibilizer

GRAPHICAL ABSTRACT



1. Introduction

1.1. Early years in olefin polymerization

Olefin polymerization is known for several decades.^[1] Among various polymers, polyethylene (PE) and polypropylene (PP) are two of the most widely used polymers in the world.^[2] These versatile materials have revolutionized various industries, including packaging, automotive, construction, and textiles. Polyethylene and polypropylene offer exceptional properties and therefore are widely used.^[3] These polymers possess a unique combination of strength, flexibility, chemical resistance, and thermal stability, making them ideal for a wide range of applications. Their low cost, lightweight, and ease of processing further contribute to their popularity. Polyethylene is widely used for packaging materials, including plastic bags, films, and bottles. It is also employed in the manufacturing of pipes, wire insulation, and automotive components. Polypropylene, on the other hand, finds applications in food packaging, textiles, medical devices, and automotive parts. The demand for these polymers continues to grow as industries seek lightweight, durable, and sustainable materials. The global production of polyolefins is close to 200 million tons per annum and it is bound to increase in the near future.

Moving back in time, we may follow the history of the synthesis of polyethylene and polypropylene, which has an intriguing tale before we take stock of the most recent advancements in olefin polymerization. Around the end of the nineteenth century, for the first time, traces of polyethylene were observed during a thermal decomposition reaction of diazomethane, which was named “polymethylene.”^[1] During that period, the field of polymer science was underdeveloped and was not accepted by the community. German chemist Hermann Staudinger proposed that polymers consist of long chains, connected through covalent bonds.^[1] This theory was initially met with skepticism, but it was eventually widely accepted and laid the foundation of rational polymer science. In 1933, Fawcett and Gibson at the Imperial Chemical Industry (ICI) found a white powdery material on the reactor wall while performing a high-pressure condensation reaction of ethylene and benzaldehyde (Figure 1, top).^[1] When they were repeating the experiment without benzaldehyde, the reactor exploded and the project was halted. It took a couple of years to understand this and develop radical polymerization of ethylene to polyethylene.^[1] The ICI process operates at high pressure (1000–4000 bars) and high temperature (200–300 °C).^[1] After this discovery, several academic groups initiated research programs on ethylene polymerization to make polyethylene.

The major breakthroughs were reported in the early 1950s. The first one was by Hogan and Banks at the Phillips Petroleum Company who reported low molecular weight oligomer from gaseous olefin using nickel oxide supported on silica or alumina.^[1] In 1951, while studying the effect of nickel oxide and chromium oxide supported on silica or alumina they found solid HDPE in their reactor.^[1] In the 1950s, Ziegler, at the Max Planck Institute in Mülheim,

Germany, made a significant breakthrough in ethylene polymerization. Before embarking on the journey of polyethylene, he was investigating the reactivity of alkyl lithium/alkyl aluminum compounds with ethylene.^[1] These organometallic reagents formed the foundation for his development of the “Aufbaureaktion,” a process enabling the synthesis of 1-olefins, aliphatic alcohols (known as alfol synthesis), and high-purity alumina through the oxidation of alkyl aluminum compounds. By a stroke of luck, Ziegler discovered that the presence of nickel had a profound effect on the “Aufbaureaktion” by favoring chain termination, leading to the formation of 1-butene. This unexpected phenomenon, known as “the nickel effect,” was attributed to the presence of nickel in the autoclave resulting from previous hydrogenation reactions. This discovery marked the beginning of significant metal screening conducted by Ziegler’s students to investigate the behavior of different metal precursors when associated with alkyl aluminum compounds.^[1] In 1953, Ziegler’s team evaluated the combination of triethyl aluminum with various transition metal compounds, including chromium, vanadium, manganese, and platinum. The most notable result was achieved by combining zirconium acetylacetonate with triethyl aluminum, resulting in a conversion rate of over 90% for the introduced ethylene. The patent application claimed “a process for the production of a high molar mass polyethylene” which involved the association of triethyl aluminum with complexes containing metals from group 4 (Ti, Zr, Hf), 5 (V, Nb, Ta), and 6 (Cr, Mo).^[1] This process operates at lower temperatures and with ethylene pressure below 55 bars and is widely known as the “Mülheim Atmospheric Process.”^[1] In March 1954, Natta, an Italian chemist, successfully achieved the stereospecific polymerization of propylene using a Ziegler catalyst composed of titanium trichloride and triethyl aluminum.^[1] For this groundbreaking discovery, Ziegler and Natta were bestowed with the Nobel Prize in 1963. Subsequent to this discovery, several developments, such as metallocene, MAO, post-metallocenes, etc. have been reported.^[4,5]

1.2. State-of-the-art and scope

The preparation of polyethylene and polypropylene involves a complex and fascinating journey, starting from the discovery of the raw materials to the development of an efficient manufacturing process. In the ever-evolving landscape of polymer science, researchers are continuously pushing the boundaries of material engineering to develop innovative solutions with enhanced properties and sustainability in mind. Among the several frontiers in polyolefins, the most impactful discoveries in the last two decades have been in the realm of (i) ultra-high molecular weight polyethylene (UHMWPE),^[6] (ii) incorporation of bioderived comonomers in polyolefins, (iii) functional olefin copolymerization, and (iv) application of some of i–iii as compatibilizers.^[7,8] A polyethylene with a viscosity average molecular weight of 2.5 million g/mol is considered as UHMWPE (ultra-high molecular weight polyethylene).^[9] UHMWPE is known for its exceptional mechanical properties, chemical resistance,

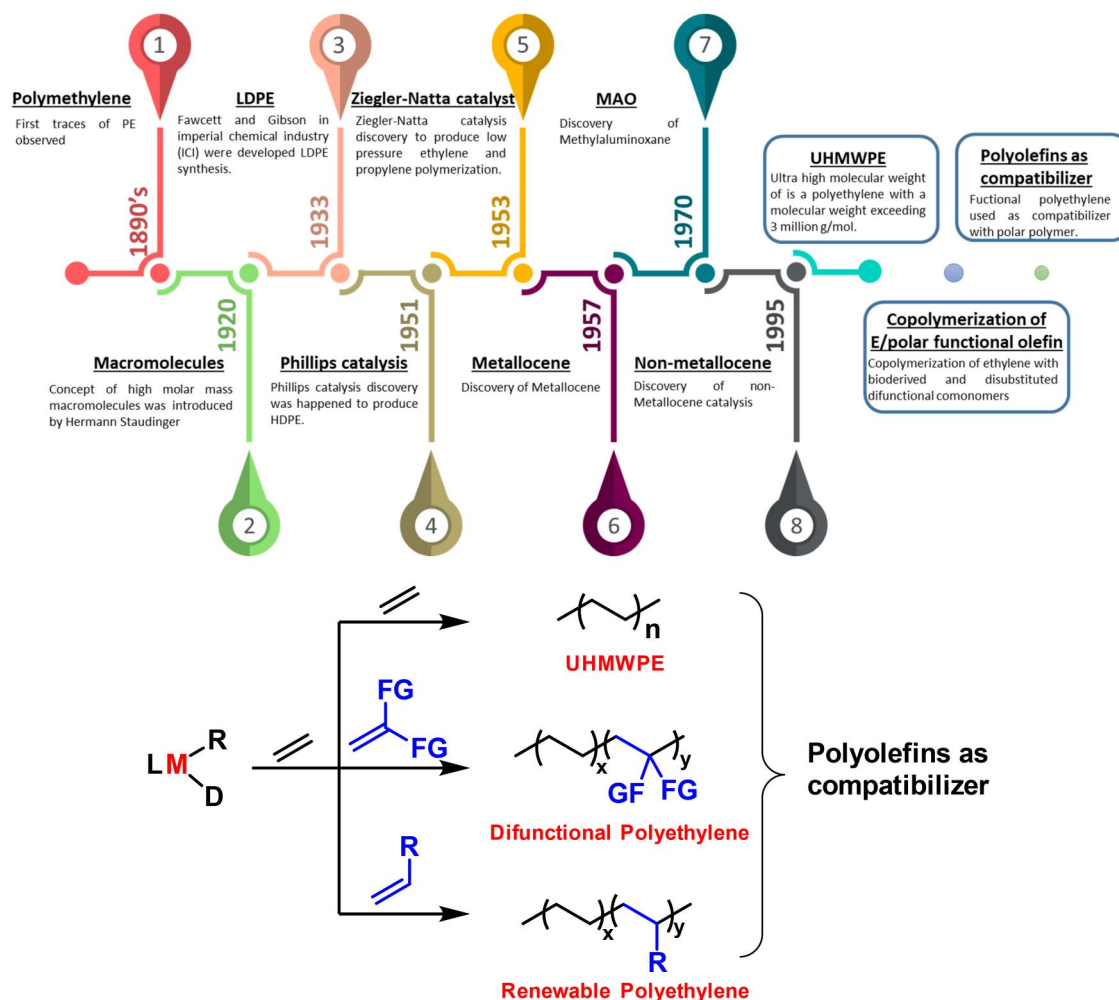


Figure 1. Significant advancements in the development of polyolefins (top) and emerging polyolefins (bottom).

and low coefficient of friction. This material has established itself as a key player in various industries, including automotive, medical, bulletproof vests, industrial parts, and sports equipment.^[6,10,11] Ziegler catalyst can be suitably modified to produce UHMWPE. Synthesis and processing present significant challenges due to its unique characteristics and requirements.

Polyethylene or UHMWPE is made up of ethylene repeating units, which are hydrophobic in nature. It does not contain any functional group in its backbone. The lack of functional groups leads to certain limitations in the application of polyethylene. For example, polyethylene cannot be used in printing inks, adhesives, binders, paints, dyeing, flame retardancy, barrier, etc.^[12] Incorporating a small amount of functional groups in the polymer backbone can open up a new application window for polyethylene.^[13–15] One promising approach involves the insertion copolymerization of bioderived and substituted difunctional comonomers with ethylene.^[7] However, the insertion copolymerization of ethylene and functional olefin remains a highly challenging area of research even today. The metal catalysts are readily poisoned in the presence of polar functional groups and form a stable σ -complex or chelate, or there is no incorporation of functional comonomer into the polyethylene backbone. Considering these challenges,

late transition metal complexes-based catalysts have been developed for functional olefin copolymerization.^[5] Comonomers derived from renewable resources, such as plant-based feedstocks, present an eco-friendly alternative to traditional petrochemical-based comonomers. Their incorporation into polyethylene not only imparts improved properties but also enables the development of relatively sustainable polyolefins with a reduced environmental footprint.

Two functional groups per insertion can be built into the polyethylene backbone by copolymerization of disubstituted polar olefins with ethylene. These polar olefins, characterized by their distinct dipolar and functional groups, introduce additional functionalities and tune the copolymer's chemical, thermal, and mechanical attributes. This strategic incorporation can fine-tune polyethylene surface energy, adhesion, and overall performance, expanding its applications into previously unexplored domains. The introduction of a polar functional group will enhance the polar nature and hydrophilicity of the resultant polyethylene. The hydrophilic polyethylene opens up new opportunities to use this material with polar polymer (Nylon-6, PLA, etc.). These polymers can be used as additives to promote miscibility and blend uniformity between two different polyolefins. By judiciously selecting and optimizing compatibilizer formulations, researchers can

effectively overcome the immiscibility barrier and enhance the mechanical and thermal properties of the resulting copolymer materials.

In this feature article, we delve into the emerging areas of olefin polymerization. This feature article aims to identify successful strategies in olefin polymerization that allow access to polyolefins with significantly different properties than traditional polyolefins. To do so, we focus on four frontiers of olefin polymerization, (i) UHMWPE, (ii) disubstituted difunctional olefin copolymerization, (iii) renewable/bioderived functional olefin copolymerization, and (iv) functional PE as a compatibilizing material (Figure 1, bottom). The perspective debates these concepts that might drive further scientific explorations and presents an overview of exciting advancements in these chosen areas. The other areas in olefin polymerization, such as (mono)functional olefin copolymerization, olefin polymerization, etc. have been reviewed elsewhere and are beyond the scope of this feature article.^[5–7,16–21]

2. UHMWPE (ultra-high molecular weight polyethylene)

As defined in ASTM D4020, a polyethylene with a viscosity average molecular weight of 2.5 million g/mol or higher is considered as ultrahigh molecular weight polyethylene (UHMWPE).^[9] The synthesis of UHMWPE is highly challenging and the following 4 key aspects have to be addressed. (i) Designing appropriate metal catalysts and co-catalysts is crucial to achieve high molecular weights. (ii) Identifying suitable reaction conditions is essential to enhance the rate of propagation while minimizing the rate of chain transfer reactions. (iii) Manipulating the steric and electronic properties of the metal center is crucial in minimizing transfer and termination reactions. (iv) Moderating the Lewis acidity of the metal catalyst is important to reduce β -hydride elimination, which can lead to chain termination and the production of lower molecular weight polymers. Despite these difficulties, researchers have made significant progress in developing catalytic systems capable of producing UHMWPE. The two commercial grades of UHMWPE, Spectra, and Dyneema, are produced using Ziegler-type catalysts. However, the UHMWPE reactor powder cannot be processed using standard melt processing techniques and requires a special gel-spinning facility. To address this bottleneck, Rastogi et al. attempted to understand the processing challenge and introduced a new state of the same material and named it “disentangled” ultrahigh molecular weight polyethylene (dUHMWPE).^[22]

There are three main classes of catalysts used for UHMWPE production: (i) heterogeneous Mg-Ti catalysts, (ii) homogeneous metallocene complexes, and (iii) homogeneous/heterogeneous post-metallocene catalysts. The following section gets into details of each of the above three broad types of catalysts and covers the recent advances in the dUHMWPE synthesis.

2.1. Heterogeneous Mg-Ti catalysts

Heterogeneous Ziegler-type catalysts are known to produce entangled UHMWPE. It is believed that the multiple sites available in Ziegler-type catalysts are responsible for entanglement. In a recent advancement, Chikkali et al. attempted to prepare a single-site heterogeneous Ziegler-type catalyst and tested it in ethylene polymerization. The authors reported a one-pot two-step synthesis of a MgCl_2 supported $[\text{Ti}(\text{OEt})_4]$ derived catalyst and controlled reduction of Ti center to +3 (Ti^{3+}) as a single oxidation state. This Ziegler-type, heterogeneous catalyst, with a two-stage activation strategy produced disentangled ultrahigh molecular weight polyethylene (Figure 2, top).^[23] The catalyst demonstrated quasi-living behavior and allowed the synthesis of dUHMWPE with a molecular weight range of $1.0\text{--}13.0 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ and a polydispersity index (PDI) of ~ 3 . The catalyst disclosed moderate activity, and the polymer had a storage modulus of up to 1.82 MPa. The resultant dUHMWPE displayed the first melting temperature at $141.3\text{--}144.1^\circ\text{C}$. The entangled vs. disentangled nature of UHMWPE was probed using two techniques, namely, DSC and rheology. Rastogi et al. have developed a DSC method that allows access to the two states of UHMWPE.^[24] This method was employed and the melting temperature was recorded at a time interval of 5, 15, 30, and 60 min (Figure 2, center). As depicted in Figure 2 bottom, the 5-min DSC thermogram disclosed two melting temperatures, one at 134 and another at 139.5°C . These two curves indicate the T_m of the entangled and the disentangled domain, respectively. As the hold time (Figure 2, center, step B–C) increases, the disentangled domain starts to convert to an entangled domain, which is a thermally stable state. In line with the DSC findings, the rheological measurements revealed that an equilibrium storage modulus of 1.82 MPa is attained after 37 h.

2.2. Homogeneous metallocene catalysts

In 2021, O'Hare et al. reported permethylindenyl-phenoxide (PHENI*) ligated ansa-metallocene complexes as catalysts in ethylene polymerization (Figure 3, top).^[25] Catalyst **1** (Figure 3) was found to exhibit high activity and produced disentangled ultrahigh molecular weight polyethylene (dUHMWPE) with excellent strength and wear resistance. The PHENI* catalyst **1** was activated using polymethylaluminumoxane. The thus activated catalyst **1** displayed an excellent activity of $3.7 \times 10^6 \text{ g}_{\text{PE}} \text{ mol}_{\text{Ti}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ in ethylene polymerization and produced dUHMWPE (Mw: 3.4 million g/mol). Additionally, these PHENI* complexes are more active than indenyl-PHENICS analogs in the polymerization of ethylene. Overall, the use of PHENI* ansa-metallocene titanium complexes as catalysts has shown a great potential for producing high-quality dUHMWPE.

Cui et al. reported binuclear half-sandwich scandium complexes to polymerize ethylene under high temperatures and pressures, producing disentangled ultra-high molecular weight polyethylene (dUHMWPE) with excellent mechanical properties, including high tensile strength and modulus (Figure 3, bottom).^[26] The **C1-Sc₂** complex was particularly effective in

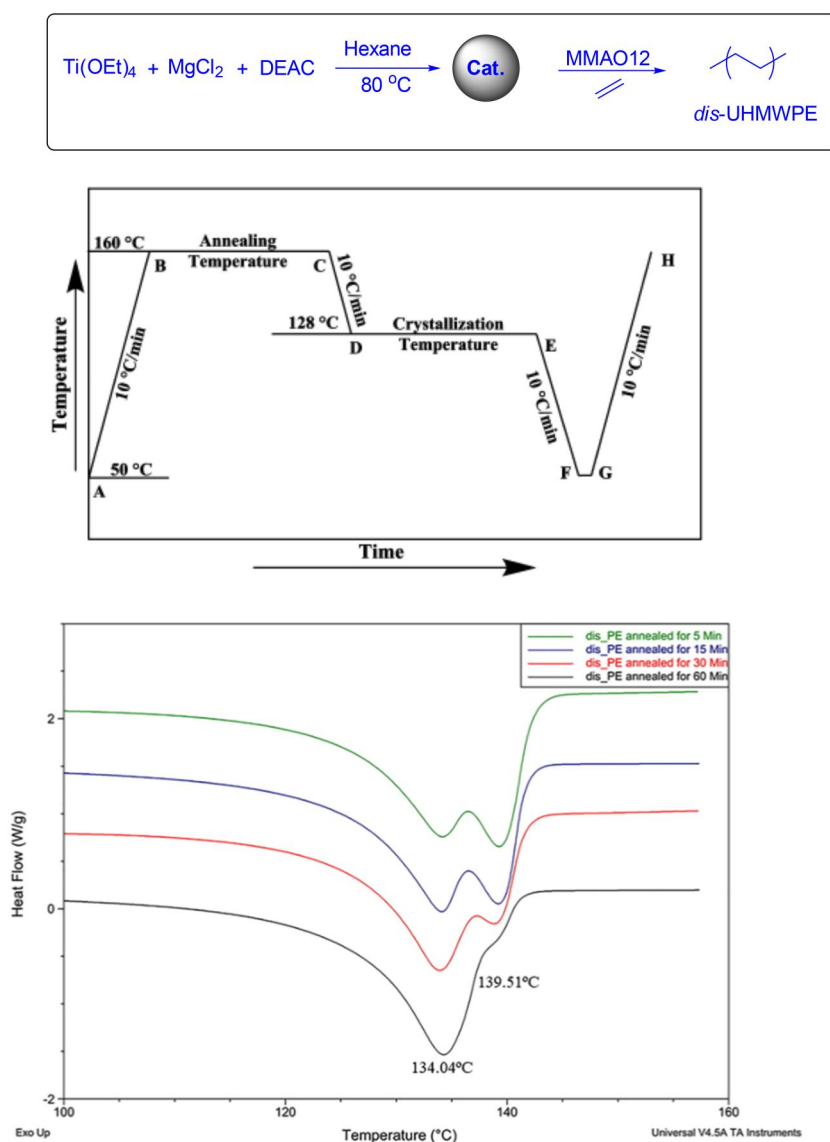


Figure 2. Synthesis of MgCl_2 supported $[\text{Ti}(\text{OEt})_4]$ catalyst and its application in the preparation of UHMWPE (top), DSC method employed to study entangled vs. disentangled UHMWPE (center) and DSC plots of the dUHMWPE samples (bottom) (obtained during final G–H stage). Reproduced with permission from Gote et al.^[23] Copyright 2018 American Chemical Society.

producing dUHMWPE. While the mononuclear Sc_1 and the relatively flexible binuclear C2-Sc_2 could not meet the performance of C1-Sc_2 . Based on the DFT inputs, the success of C1-Sc_2 complex is believed to be due to the binuclear synergistic effect and agostic interaction between the active center and the growing polymer chain. Another contributing factor is the conformational ordering of the polymer chains due to the steric effect. The existence of dUHMWPE was proved using DSC and rheology, which displayed tensile strength and modulus of up to 149.2 MPa and 1.5 GPa, respectively. This study represents an important advancement in the production of dUHMWPE and has the potential to lead to new and improved materials for a variety of applications.

2.3. Homogenous/heterogeneous post-metallocenes catalysts

In 2001, Fujita et al. reported a substituted phenoxy-imine (which they named as “FI” catalyst) ligated titanium

complex **3** (Figure 4).^[27,28] The authors demonstrated that complex **3** catalyzes the living polymerization of ethylene upon activation with methyl aluminoxane (MAO). Although the catalyst displayed living behavior, high molecular weight, etc., the ability of the catalyst to produce dUHMWPE was overlooked. The potential of the FI system to produce dUHMWPE was recognized by Rastogi et al. almost a decade later.^[24,29] The performance of FI catalyst **3** in ethylene polymerization was investigated in great detail and the resultant polymer was meticulously characterized. Optimized polymerization conditions allowed the authors to prepare UHMWPE and DSC, solid-state NMR and rheological measurements allowed the authors to demonstrate the disentangled nature of UHMWPE. This study is considered the early breakthrough in the field of disentangled ultrahigh molecular weight polyethylene and is a current “benchmark” for dUHMWPE. The tensile properties of dUHMWPE produced by catalyst **3**, were compared with those of entangled UHMWPE produced using a standard heterogeneous Ziegler

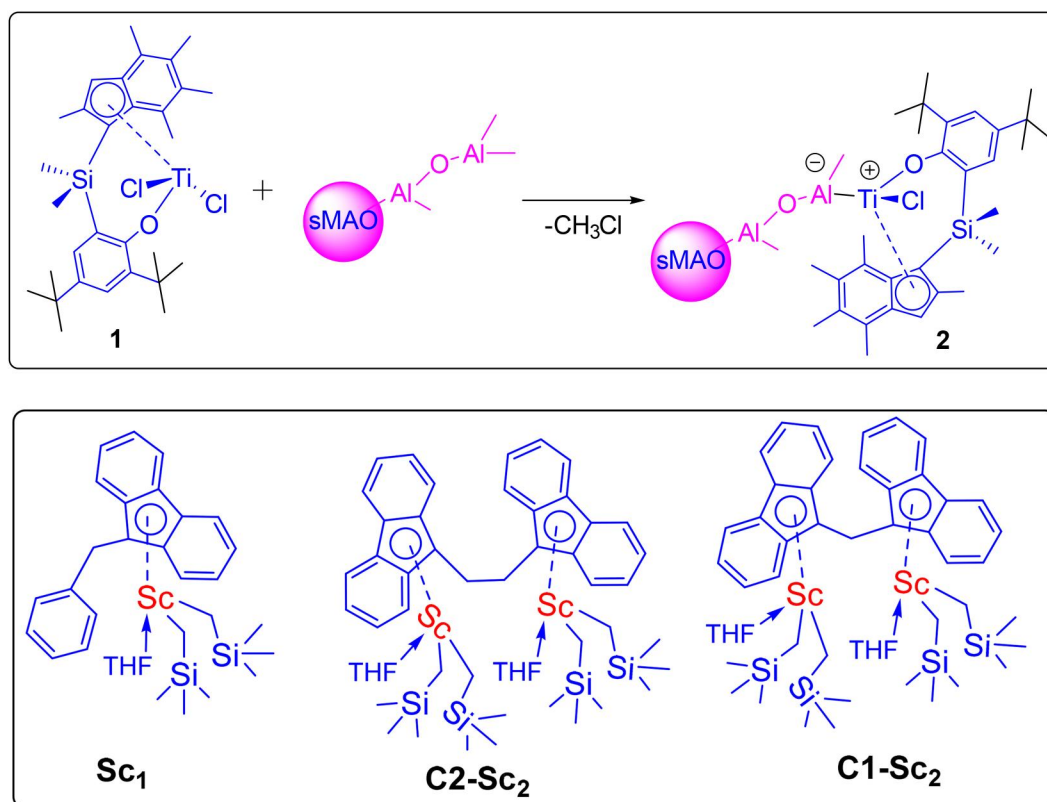


Figure 3. Permethylindenyl-phenoxide and binuclear scandium complexes for UHMWPE.

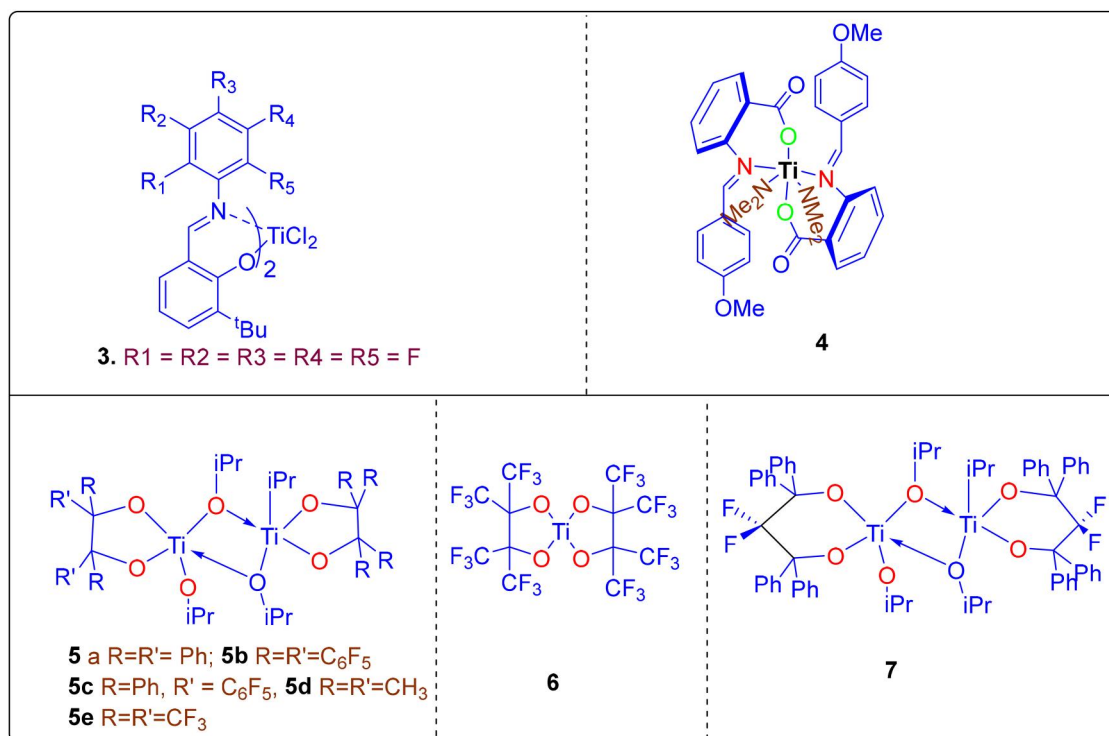


Figure 4. Ti-based catalysts for ethylene polymerization to UHMWPE.

catalyst. Rastogi, Romano, et al. have described the development of dUHMWPE in several reports.^[30] The impact of the co-catalyst modification on the catalytic performance and material properties was investigated.^[31] A similar investigation was carried out by employing catalyst 3 and other

co-catalysts made of aluminoxane, modified methyl aluminoxane (MMAO12, MMAO3), and polymethyl aluminoxane (PMAO).^[32] However, no discernible improvements in the properties of UHMWPE were observed. Using 3/MAO to improve the polymerization conditions Ivanchev et al. and

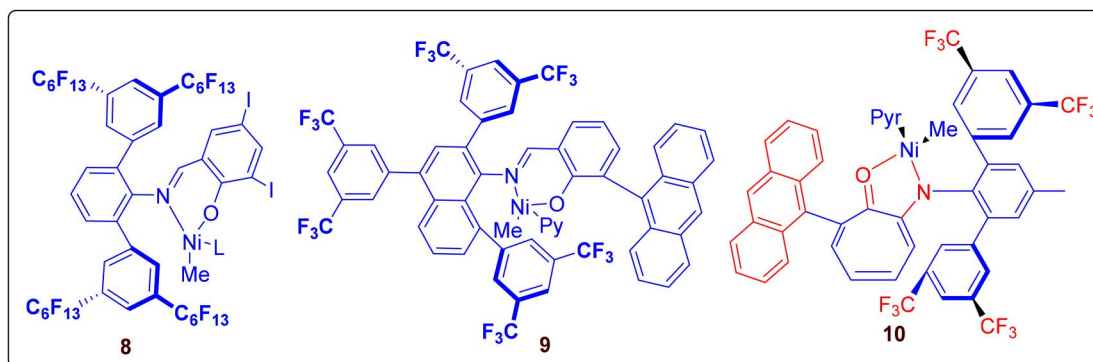


Figure 5. Ni-based catalysts 8–10 employed in ethylene polymerization to produce UHMWPE.

Forte et al. both reported the same information.^[33,34] The effects of catalyst concentration and solvent type (toluene), on the catalytic activity, molecular weight, and shape of the resulting UHMWPE were meticulously examined.

Disentangled UHMWPE offers several advantages over entangled UHMWPE. This includes the ability of dUHMWPE to be treated and pulled with ease throughout a large temperature range below the equilibrium melting point. Disentangled UHMWPE showed better tensile strength, higher tensile modulus, and the ability to draw biaxially without any solvent.^[35] The polymerization of ethylene with 3/MAO (1100 equiv. of MAO) in toluene was carefully controlled by Rastogi et al. in an additional effort to reduce the number of entanglements. The authors thoroughly investigated the effect of experimental parameters, including temperature, time, and solvent volume, on the final entanglement number and molecular weight. The molecular weight and number of entanglements per unit chain revealed an increase/decrease as polymerization time increased. Consequently, it is opined that the majority of the entanglements are generated in the early stages of the polymerization process. The catalyst activity spanned from 620 to 10,330 kg of PE (mol Ti).h⁻¹. Along the same line, Rastogi et al. made an effort to stabilize the disentangled state of UHMWPE by adding linear low-density polyethylene (LLDPE) to the reaction mixture to prevent UHMWPE aggregation/entanglement.^[36] It was demonstrated that the LLDPE can prevent entanglements and stabilize UHMWPE in a disentangled state.

Tuskaev et al. synthesized [OOOO]⁴⁻ ligated titanium complexes 5, 6, 7 (Figure 4) for ethylene polymerization using cheaper co-catalysts (Et₂AlCl/Bu₂Mg or Et₃Al₂Cl₃/Bu₂Mg).^[37] The resulting dUHMWPE exhibited Mn of (0.34–7.73) × 10⁶ g · mol⁻¹, a melting temperature of 136–144 °C, and crystallinity of 59–80%. The catalysts demonstrated high activity of (0.24–4.05) × 10⁶ g PE · mol⁻¹Ti · h⁻¹ · bar⁻¹. The synthesized UHMWPE showed a broad PDI range of 3.3–11.5, highlighting the multi-center nature of these catalysts. Catalysts 6 and 7 maintained stable catalytic activity and polymer molecular weight increased with increasing temperature from 30 to 80 °C, indicating high thermal stability. The titanium concentration in the solvent was considerably higher (1.66–10.00 μmol Ti/100 mL toluene) compared to previous studies. The synthesized UHMWPE exhibited excellent solid-phase processing performance, with draw ratios of 20–44,

tensile strength of 1.83–2.81 GPa, tensile modulus of 85–145 GPa, and breaking elongation of 1.96–3.09%. However, it still fell short compared to solid-phase processed dUHMWPE obtained from “living” FI catalysts.

Recently, Chikkali et al. reported Ti-iminocarboxylate complex 4 and its performance in ethylene polymerization (Figure 4).^[38] The titanium precursor tetrakis (dimethyl amido-titanium) [Ti(NMe₂)₄] was treated with 2 equivalents of 2-((4-methoxybenzylidene) amino) benzoic acid to give the new titanium complex 4 [bis-dimethyl amido-Ti-(bis-mono-carboxylate)] in good yield. Complex 4 was activated using various cocatalysts and MMAO (modified methyl aluminoxane) outperformed the others. The best polymerization conditions were determined by screening the polymerization parameters. Thus, the optimal conditions were found to be an Al/Ti ratio of 1000, 4 bar ethylene pressure, 35 °C temperature, and a polymerization period of 30 min. Catalyst 4 polymerizes ethylene to ultrahigh molecular weight polyethylene with a weight average molecular weight (Mw) of 2.5 × 10⁶ g/mol under the optimal polymerization conditions. The thus prepared UHMWPE revealed a high crystallinity of 96% and the existence of strictly linear polyethylene. A specially created DSC method unambiguously ascertained the existence of a disentangled state of UHMWPE. Sun et al. reported aroylhydrazine-arylates ligated vanadium(V) complexes as catalysts for the synthesis of ultra-high molecular weight polyethylene (UHMWPE).^[39] When the vanadium complex was activated with MAO, the resultant polymer revealed a molecular weight (Mw) of 3300 kg/mol and qualifies to be considered as UHMWPE.

There has been a substantial increase in the number of reports on nickel-catalyzed synthesis of high molecular weight and ultra-high molecular weight polyethylene (UHMWPE).^[40–43] In 2019, Mecking et al. employed water-soluble catalysts (8) (Figure 5) in the mini emulsion coordination polymerization of ethylene to UHMWPE.^[44] This approach enabled the synthesis of UHMWPE within oil droplets dispersed in an aqueous phase. The catalysts exhibited remarkable “living” characteristics, including a narrow molecular weight distribution ($M_w/M_n < 1.4$), minimal branching (up to 1.0 branch/1000C), and nearly one nickel center per chain. Interestingly, the nascent UHMWPE formed aggregates consisting of lozenge-shaped single crystals with a size distribution of <100 nm. This finding

challenges the conventional notion that polyethylene aggregates primarily consist of spherulites or lamellae. The nascent UHMWPEs demonstrated typical disentangled UHMWPE properties, such as a higher melting point (140–143 °C) and higher crystallinity (64–73%) as compared to the melt crystallized component (melting point of 133–136 °C and crystallinity of 41–48%). Along the same line, **Cat.9** (Figure 5) was found to have a low propensity for β -H elimination, as a result, **Cat.9** produced a highly linear polymer even at high temperatures (60 °C).^[45] The UHMWPE was produced in polar organic solvents (THF and diethyl ether), the molecular weight was around 1.1×10^6 g/mol, and $M_w/M_n = 1.2$. Wang et al. reported a neutral, sandwich-like, salicylaldiminato nickel catalyst consisting of 8-arylnaphthyl and dibenzosilyl groups.^[46] It was found that the above catalyst, in polar solvents, at a high temperature of 90 °C, enables controlled, living ethylene polymerization and produces nearly linear UHMWPE ($M_w = 6020$ kDa, $M_w/M_n = 1.10$). A UHMWPE with a molecular weight of 1002 kDa was obtained. To increase TOF and Mw in olefin polymerization, suppressing chain transfer and stimulating chain propagation is a crucial yet challenging task. The key to regulating these essential steps is designing a transition-metal catalyst, such as **10** (Figure 5).^[47] Jian et al. employed **Cat.10** in ethylene polymerization, which produced a highly linear UHMWPE with a molecular weight of 212.4×10^4 g/mol and having 2 branches per thousand carbon atoms.

Thus, synthesis of entangled and disentangled UHMWPE is a challenging task and the field is being revived after the initial commendable contributions from Rastogi et al. The entangled UHMWPE is well explored and there are two commercial grades produced by DSM (Dyneema) and Honeywell (Spectra). While the disentangled UHMWPE is a new kid on the block with great potential. The disentangled UHMWPE has attracted significant attention in the recent past. The commercial exploitation of dUHMWPE has begun and the first announcement to introduce dUHMWPE in the market was made by “Teijin Aramid” around 2015. The company offers a dUHMWPE grade named “Endumax®.” Thus, the field of dUHMWPE is witnessing revived interest in the academic and industrial world and is bound to grow in the coming years.

3. Copolymerization of ethylene with disubstituted difunctional olefins

Commodity polyethylenes, such as LDPE, LLDPE, and HDPE are made up of ethylene repeating units which are highly hydrophobic in nature. It does not contain any functional group in its backbone. The lack of functional groups in the PE backbone limits its application in printing inks, adhesives, paints, binders, dyeing, etc.^[12] While catalyst development is crucial, it is equally important to explore the insertion copolymerization of “novel monomers” with added features, functionality, and purpose.^[7] Incorporating a small amount of functional groups in the polymer backbone can open up new avenues for polyethylene applications.

Insertion copolymerization of disubstituted olefins with ethylene offers an opportunity to double the functional group density in the polymer backbone while incorporating the same number of olefins. This increased functional group density can result in enhanced adhesion, even with the same incorporation. However, compared to mono-substituted olefins, 1,1- and 1,2-disubstituted olefins pose significant challenges for metal-catalyzed insertion copolymerization. The additional substitution in disubstituted olefin increases steric hindrance around the double bond, thereby reducing the coordination ability of the olefin.

The classical Ziegler-Natta type catalysts use early transition metals which are highly oxophilic in nature. Due to the high oxophilicity of early transition metals (such as Ti, Zr), the functional group on polar monomer coordinates to the vacant site on metal which poisons the catalyst. Various strategies, such as post-functionalization of PE,^[48] OMRP of polar vinyl monomers with ethylene,^[49] or ADMET polymerization of functionalized dienes have been developed.^[50] Nevertheless, these methods have their own advantages and limitations. Therefore, it has been a dream for organometallic chemists to incorporate functional groups in the PE backbone in a single step. There are three features associated with this transformation that hinder the insertion of polar monomer and makes it a challenging task.^[7] (i) One of the main obstacles is the coordination of the functional group on the polar monomer with the metal to form an σ -complex. This coordination often results in catalyst poisoning and decreases the overall activity of the catalyst. (ii) The electron-deficient nature of functional olefin leads to the formation of a weak π -complex compared to ethylene, resulting in lower or no incorporation of polar monomer into the polymer backbone. (iii) The formation of a stable chelate complex after the insertion of polar monomer or β -X elimination represents the final bottleneck. The late transition metals are less oxophilic in nature and more tolerant to the polar groups. Late transition metals, such as Pd and Ni have been widely employed in ethylene, functional olefin copolymerization. A breakthrough was reported in the early 90s when Brookhart et al. copolymerized ethylene and methyl acrylate.^[51] The rationally designed α -diimine ligated Pd-complex (Figure 6(A)) successfully achieved the insertion copolymerization of ethylene with methyl acrylate for the first time. Along with variation in late transition metal, ligand and designing to tolerate functional groups was explored. The major catalytic systems that have been tested in ethylene-functional-olefin copolymerization are depicted in Figure 6. Out of these, the most successful system is *ortho*-phosphinobenzenesulfonate or Drent catalyst C. The ligand consists of a neutral phosphine donor and an anionic sulfonate group that coordinates with the metal. This unique ligand structure makes the palladium complex tolerate a wide range of functional groups.^[52]

As compared to mono-functional olefin, the use of disubstituted difunctional olefin increases the complexity by one order of magnitude. Due to this uphill task, only a handful of research groups have taken on the cumulative challenge posed by disubstituted difunctional olefins and have made

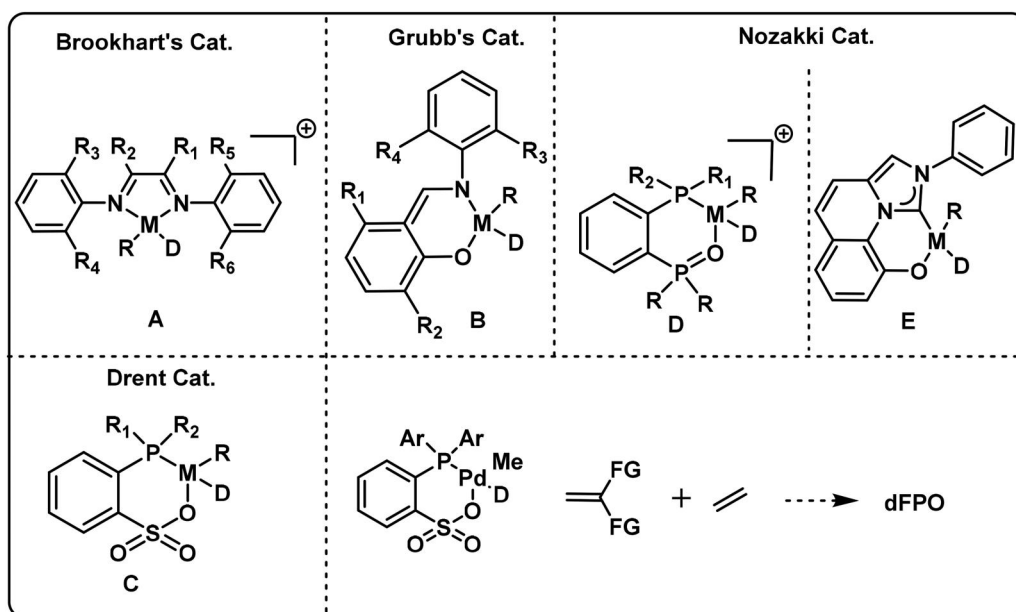


Figure 6. Typical catalysts for polar functional olefin insertion copolymerization.

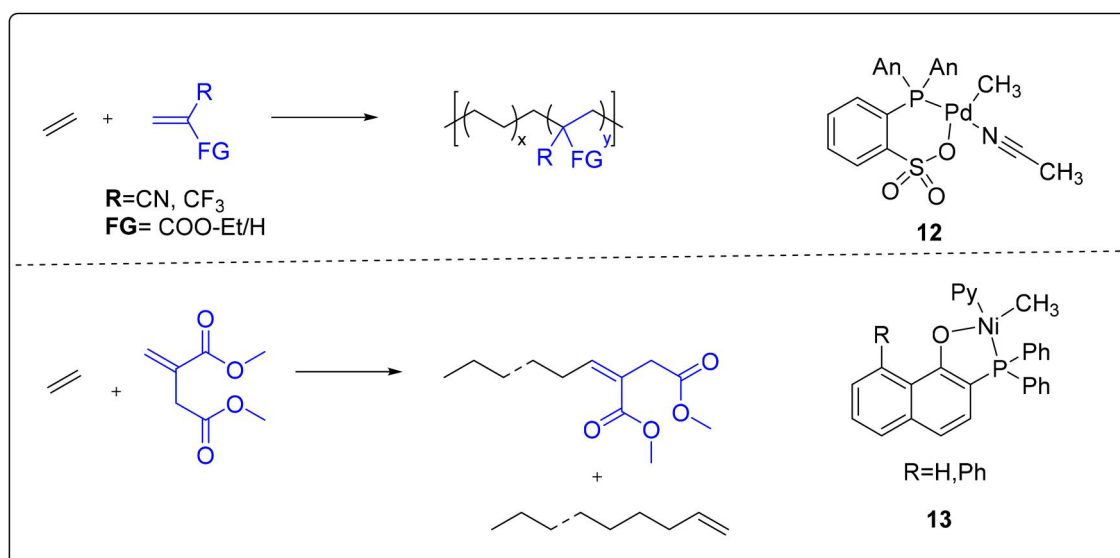


Figure 7. Insertion copolymerization of ethylene with 1,1-disubstituted difunctional olefin.

progress in this area. Among all the catalysts, the phosphine sulfonate system's exceptional performance further raised scientific hopes, and the following research concentrated on the catalyst's structural fine-tuning. Three major sites were identified, and substantial research has been done on the impact of the donor group "D" in each of them.^[53] 1,1-disubstituted olefins can be further divided into two groups based on the number of functional groups: (i) di-substituted monofunctional olefins, and (ii) di-substituted difunctional olefins. The first report on the insertion copolymerization of 1,1-disubstituted difunctional olefins appeared in 2015.^[12] The authors reported the synthesis of Pd-phosphinobenzene sulfonate acetonitrile complex (**12**) (Figure 7) and its implications in the insertion copolymerization of ethylene with 1,1-disubstituted difunctional vinyl monomers (see Figure 6; dFPO-difunctional polyolefin). The effectiveness of catalyst

12 in the copolymerization of ethylene with difunctional olefin was examined. The commonly known "Krazy glue" contains a monomer called ethyl-2-cyanoacrylate (ECA), has cyano- and acrylate- groups, and was chosen as a model 1,1-disubstituted difunctional olefin. It should be noted that cyanoacrylates are frequently marketed under the name "Super Glue" and their polymers are commercial adhesives. It is one of the most widely made adhesives worldwide. At 95 °C, the Pd-catalyst **12** (Figure 7) catalyzed the copolymerization of ethylene with ECA and disclosed the highest incorporation of 6.5%. The existence of the copoly(ethylene-ECA) was unambiguously ascertained using a combination of 1-2D NMR, GPC, and MALDI-TOF-MS.

Insertion copolymerization of another 1,1-disubstituted difunctional monomer, trifluoromethyl acrylic acid (TFMAA) was investigated and an incorporation of 3% was achieved.

The resultant copolymer was fully characterized using spectroscopic and analytical methods. After the initial success, Chikkali et al. investigated the insertion mechanism of 1,1-disubstituted functional olefins, and a comprehensive understanding of the mode of insertion of the disubstituted difunctional olefin was reported in 2017 (Figures 8(A,B)).^[54] The methyl 2-acetamidoacrylate (MAAA) can undergo 1,2 insertion to produce **15** and **15'**, while 2,1 insertion can yield **16** and **16'**. The authors observed 1,2 and 2,1-insertion products **15** and **16**, respectively. Product **15** was isolated and fully characterized, including single-crystal X-ray diffraction. A similar study for TFMAA insertion produced only 2,1-insertion product **18**. The way polar vinyl monomers are inserted into a metal-carbon bond involves striking the right balance between electronic effects and steric constraints. Careful tuning of these parameters can allow access to 1,2-insertion products or the insertion can be reversed to 2,1-insertion.^[55]

The above investigation provides direct evidence for the insertion of MAAA and TFMAA, which allowed the authors to install these into the polymer backbone without difficulty. The researchers also examined the polymerization of ethylene with several difunctional olefins, including MAAA and

TFMAA, and discovered that dimethyl allyl malonate (DMAM) had the highest incorporation (11.8%). By monitoring the water contact angle, the researchers assessed how the surface characteristics of the copolymers changed after the incorporation of difunctional olefins into the polyethylene backbone. With a reduced water contact angle of 76°, the copolymer containing maximum DMAM incorporation was found to be the most hydrophilic.

In 2018, Nozaki et al. examined the insertion copolymerization of disubstituted functional olefins with ethylene (Figure 9).^[56] The authors designed a new ligand named imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) and prepared the corresponding palladium complex **20** (Figure 9). The complex **20** was found to be active in ethylene, 1,1-disubstituted functional olefin copolymerization, and produced statistical copolymers of ethylene and methyl methacrylate (MMA). The resultant copolymers were thoroughly characterized and the incorporation was determined. Further, the authors investigated the insertion mechanism and successfully isolated the MMA-inserted complex. Isolation of MMA inserted product suggests that complex **20** is amenable to the insertion of 1,1-disubstituted olefins. The isolated complex was exposed to ethylene and polyethylene with MMA chain-end was obtained. These investigations reaffirm that the insertion of 1,1-disubstituted difunctional olefin is feasible and holds great potential.

Later in 2020, the insertion copolymerization of various 1,1-disubstituted difunctional monomers was reported using

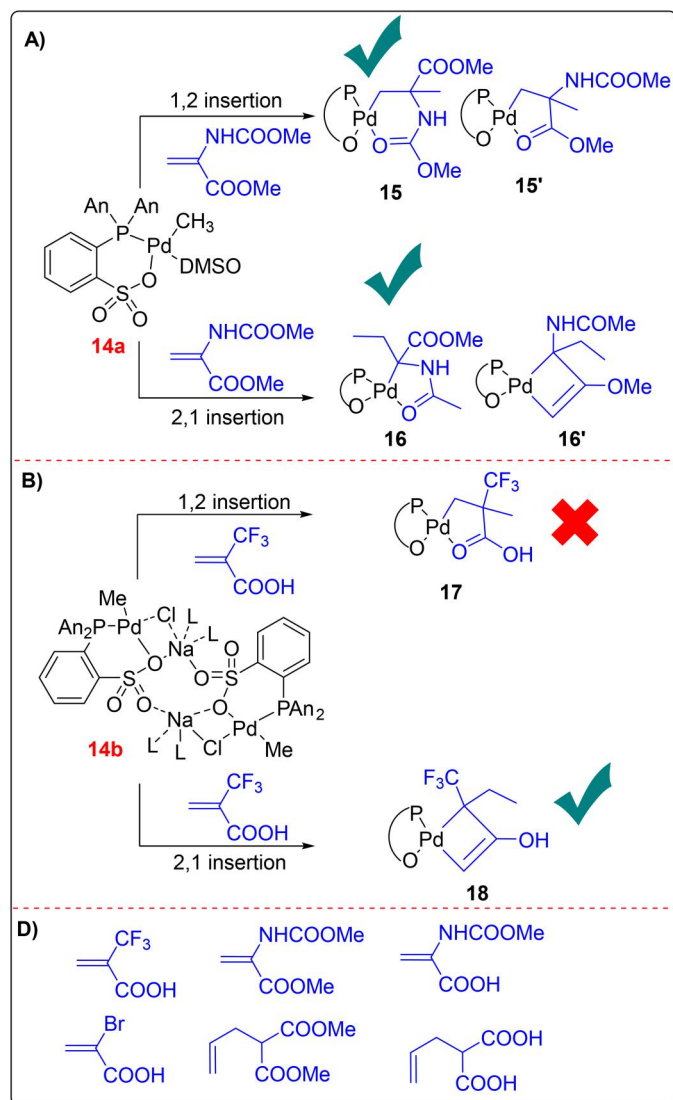


Figure 8. Possible insertion products of MAAA and TFMAA.

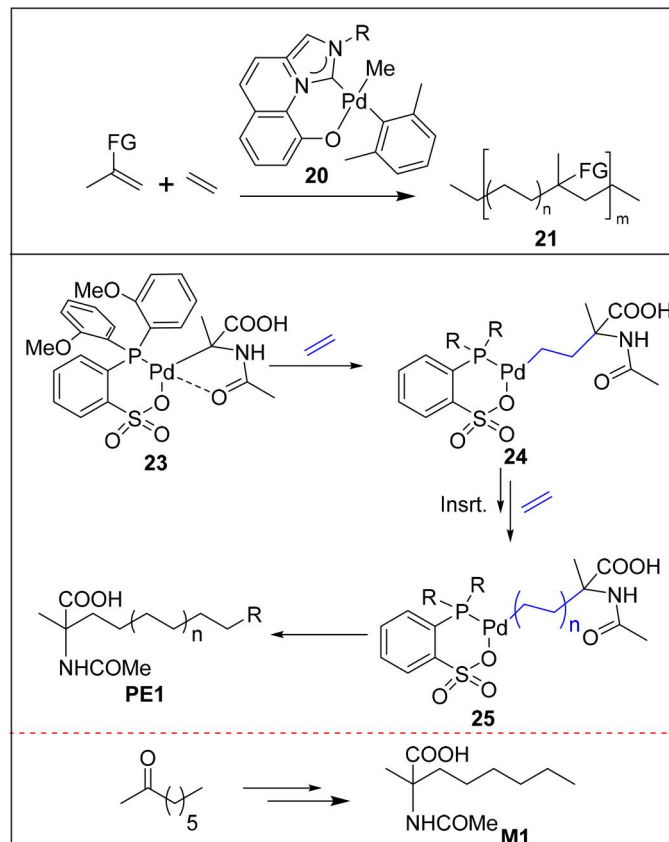


Figure 9. Insertion copolymerization of ethylene with methyl methacrylate catalyzed by imidazo[1,5-*a*]quinolin-9-olate-1-ylidene ligated Pd complex **20** (top) and insertion of 2-acetamidoacrylic acid and corresponding AAA functionalized PE1 (bottom).

phosphine sulfonate complex.^[57] The article presents the challenges associated with the copolymerization of ethylene and disubstituted olefins through insertion or coordination mechanisms. Specifically, the researchers focused on difunctional olefins, such as 2-acetamido acrylic acid, methyl 2-acetamidocrylate, and ethyl 2-cyanoacrylate. They demonstrated that these difunctional olefins can undergo ethylene insertion and polymerization when treated with a palladium complex called $[P^O]PdMe$ (L). The researchers were able to establish the presence of insertion intermediates (Figure 9 bottom) with moderate yields (up to 37%) and were successful in isolating and characterizing the corresponding products **23/24** (Figure 9 bottom). When **23** was exposed to ethylene, **PE1** was produced with 2-acetamido acrylic acid (AAA). This observation demonstrates that the AAA-inserted species is amenable to ethylene insertion and copolymerization. The existence of **PE1** was authenticated by preparing model compound M1 and comparing the NMR data. The research team combined experimental investigations with computational studies and presented a comprehensive understanding of the insertion of 1,1-disubstituted difunctional olefin copolymerization.

In 2021, Li et al. reported the design, synthesis, and characterization of a series of methyl nickel(II) complexes with phosphino-naphtholate chelate ligands (Figure 7, **13**).^[58] These complexes exhibited high activity in ethylene polymerization and copolymerization with unsaturated acid ester and challenging 1,1-disubstituted difunctional polar monomers. The diphenylphosphino-8-phenylnaphtholate ligated nickel catalyst was optimized and displayed unprecedented activity for ethylene polymerization (3.0×10^7 g PE mol Ni⁻¹ h⁻¹). The copolymers produced through this process consist of functional groups incorporated within the polymer chain as well as at the chain ends. Remarkably, end-functionalized polyethylene was directly obtained. The copolymerization of ethylene and 1,1-disubstituted difunctional dimethyl itaconate (Figure 7) was successfully conducted and up to 1.8 mol % incorporation was achieved. The ¹³C NMR spectrum disclosed a signal at 145.6 and 125.9 ppm, which can be assigned to a carbon-carbon double bond (Figure 7), which is formed by the 2,1 insertion of dimethyl itaconate and subsequent β -hydride elimination.

Similar to 1,1 disubstituted olefin, 1,2-disubstituted olefins are equally challenging. In 2020, Chen et al. studied the copolymerization of ethylene with 1,2 di-substituted difunctional olefins (dimethyl fumarate and dimethyl maleate).^[59] It was found that the trans isomer (dimethyl fumarate), could not be enchaind but the cis isomer, or dimethyl maleate, was successfully inserted (1.1 mol%) into the polyethylene chain. Also, in recent study, copolymerization of difunctional olefins long spacers (5,6-disubstituted norbornenes) revealed high polymerization activity, copolymer molecular weight, and comonomer incorporation.^[60]

4. Copolymerization of ethylene with bioderived/renewable functional comonomer

Renewable resource-derived functional olefins are of current interest and are important for the sustainable future of the planet.^[61] Therefore, in this section, we examine the recent

developments in the area of insertion copolymerization of ethylene and bioderived/renewable functional monomers.

Miri et al. reported the copolymerization of ethylene with two bioderived comonomers, eugenol, and 4-penten-1-ol, using a palladium aryl phosphine sulfonate (**27**) catalyst in a toluene solution (Figure 10, top).^[62] The co-polymerizations were carried out at 80 °C for 1 h, and the reactions were quenched with methanol. To characterize the resulting copolymers, various analytical techniques were employed. The ¹H and ¹³C NMR analysis revealed that eugenol exhibited higher tolerance as compared to 4-penten-1-ol. Both co-monomers were predominantly inserted into the polymer chains rather than added as end groups. Despite the fact that the lengths between the terminal alkene group and the hydroxyl group are comparable in both monomers, the aromatic group works as a more effective spacer group. Eugenol is incorporated extensively into the copolymer chains by both 2,1 and 1,2 insertion mechanisms, whereas 4-penten-1-ol was mainly polymerized by 2,1-insertion and contributes significantly to end groups. Furthermore, the antibacterial efficiency of the copolymers was studied and it was observed that copolymers containing more than 3.1% eugenol exhibited a significant reduction in bacterial growth, surpassing 90%. These findings provide a new twist to known material and demonstrate the untapped potential functional polyolefins. Later in 2020 Chen et al. reported the synthesis of polymeric materials from renewable monomers, by using a phosphine-sulfonate palladium catalyst (**28**) (Figure 10).^[63] Apart from copolymers of ethylene (E) with eugenol (Eug), terpolymers of E, Eug with other biore-sourced comonomers were investigated. The copolymerization activity was found to decrease with the direct use of Eug-OH, but the use of protected comonomer, Eug-Si, improved copolymerization activity. Terpolymerization of ethylene with Eugenol and 1-hexene (Hex) displayed reduced molecular weight, while, E/Eug-Si/Hex terpolymer disclosed increased comonomer incorporation. The resulting terpolymer could be fully hydrolyzed to E/Eug-Si/Hex-HCl. Copolymers E/Eug (0.5) and E/Eug-Si(0.5) showed ductile behavior, while hydrolyzed E/Eug-Si(0.5)-HCl revealed improved stress-at-break. In addition, the introduction of Fe³⁺ ions enhanced mechanical properties, especially in Fe³⁺ functionalized E/Eug-Si(0.1)/Hex-HCl-Fe³⁺ terpolymer. Chain flexibility and Fe³⁺ catechol interactions played vital roles in improving polymer properties. By incorporating eugenol and catechol functionality, the researchers observed improvements in the mechanical properties of the resulting polyolefin materials. The influence of metal ions on these materials was investigated which led the authors to discover the self-healing properties of these co/ter-polymers. Additionally, the incorporation of catechol functionality allowed the authors to modulate the surface properties, adhesion, and compatibilizing capabilities in immiscible polyolefin blends. These findings highlight the potential of these bioresourced polymers in biomedical applications. Such an application of polyolefins was probably unthought of a few decades ago. Along the same line, Liu et al. synthesized functionalized isotactic poly(1-butene) (iPB)

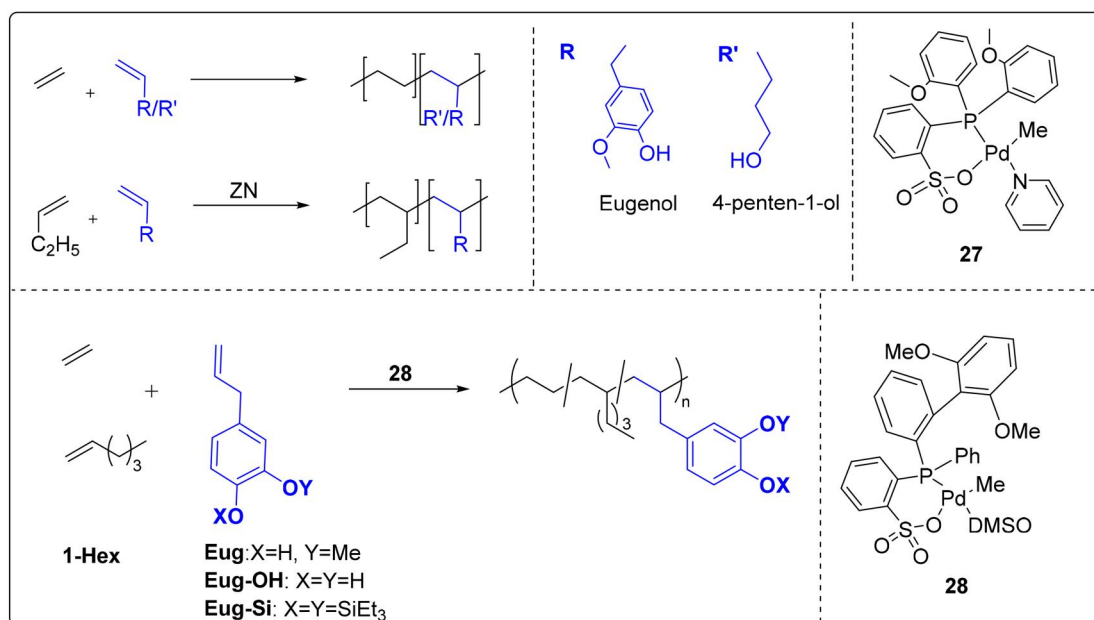


Figure 10. Ethylene copolymerization with eugenol and 4-penten-1-ol (top) terpolymerization of ethylene with 1-hexene and eugenol derivatives (bottom).

copolymers bearing natural antioxidant eugenol (Eug) using a Ziegler-type catalytic system.^[64] By carefully adjusting comonomer concentration and reaction parameters, authors could successfully incorporate Eug units into the *i*PB chain, although the maximum incorporation was limited to only 0.62 mol%. The Eug-functionalized *i*PB copolymers show enhanced thermal-oxidative stability. This improvement in thermal stability is of great interest in various applications where heat and oxidation resistance are crucial factors. Remarkably, *i*PB copolymers with 0.62 mol% Eug units displayed an oxidation induction time (OIT) that was 25 times longer than that of copolymers without Eug. This substantial increase in OIT demonstrates the effectiveness of Eug units in retarding the oxidation process, effectively prolonging the lifespan of the copolymer.

Gao et al. reported the insertion copolymerization of petroleum-based ethylene and bio-based polar monomers.^[65] The authors introduced a series of dibenzobarrelene-derived α -diimine palladium complexes (30) for the (co)polymerization of ethylene and bio-based furfuryl acrylate (FA) (Figure 11, top). Increasing the steric bulk on the ligand backbone enhanced the tolerance of palladium catalysts toward the polar monomer FA. This finding indicated that the structural modifications in the catalyst can improve its ability to accommodate polar monomers. Furthermore, the authors focused on the living (co)polymerizations of ethylene and furfuryl acrylate using the dibenzobarrelene-derived α -diimine palladium catalysts. A mechanistic study revealed that furfuryl acrylate inserts into a Pd–Me bond in a 2,1-mode, without any significant interactions between the furyl ring and the palladium center. The primary product undergoes rapid isomerization, leading to the formation of a six-membered chelate palladium complex. The incorporation of furan-based monomers in a polyethylene backbone offers the advantage of post-functionalization through thermoreversible Diels-Alder reactions.

Chikkali et al. investigated the insertion copolymerization of ethylene with various sugar-derived functional olefins (Figure 11, bottom).^[66] The copolymerization reactions were carried out using a Pd-phosphinesulfonate acetonitrile catalyst (Figure 11, 31). The renewable functional monomers, such as isomannide mono-ene (SDa), isosorbide mono-ene (SDb), isoidide mono-ene (SDc), and methacryl-2,3,4,6-tetra-O-acetyl-D glucopyranoside (SDd) were copolymerized with ethylene resulting into functional polyethylene. The copolymerization of ethylene with isosorbide mono-ene (SDb) and isoidide mono-ene (SDc), was performed at a high temperature of 95 °C which showed improved incorporations of 0.44 and 1.45%, respectively. The results indicate that the stereochemistry of the isohexide monomers influences their incorporation. The exo-endo and exo-exo configurations revealed better incorporation. Copolymerization of a 1,1-disubstituted functional olefin (SDd) and a tri-functional allyl monomer (SDe) resulted in relatively low incorporations of 0.48 and 0.41%, respectively. The copolymers exhibited melting temperatures ranging from 117 to 126 °C. The water contact angle of the copolymer derived from SDc with the maximum incorporation was 104°, indicating improved hydrophilicity.

Jian et al. successfully synthesized bio-based monomers through a carefully designed telomerization process (Figure 12).^[67] By employing 1,3-butadiene and three renewable alcohols, namely furfuryl alcohol, tetrahydrofurfuryl alcohol, and solketal, the team was able to produce three distinct 2,7-octadienyl ether monomers, namely OC8-FUR, OC8-THF, and OC8-SOL (Figure 12). These novel monomers possessed intriguing structural features, consisting of a terminal double bond, an internal double bond, and a terminal polar cyclic group in a linear molecule. After preparing the renewable polar monomers, the authors examined the insertion copolymerization of OC8 with ethylene in the presence of phosphine-sulfonate palladium catalysts (27, 28, 32). This strategic choice enabled the successful creation of polar-

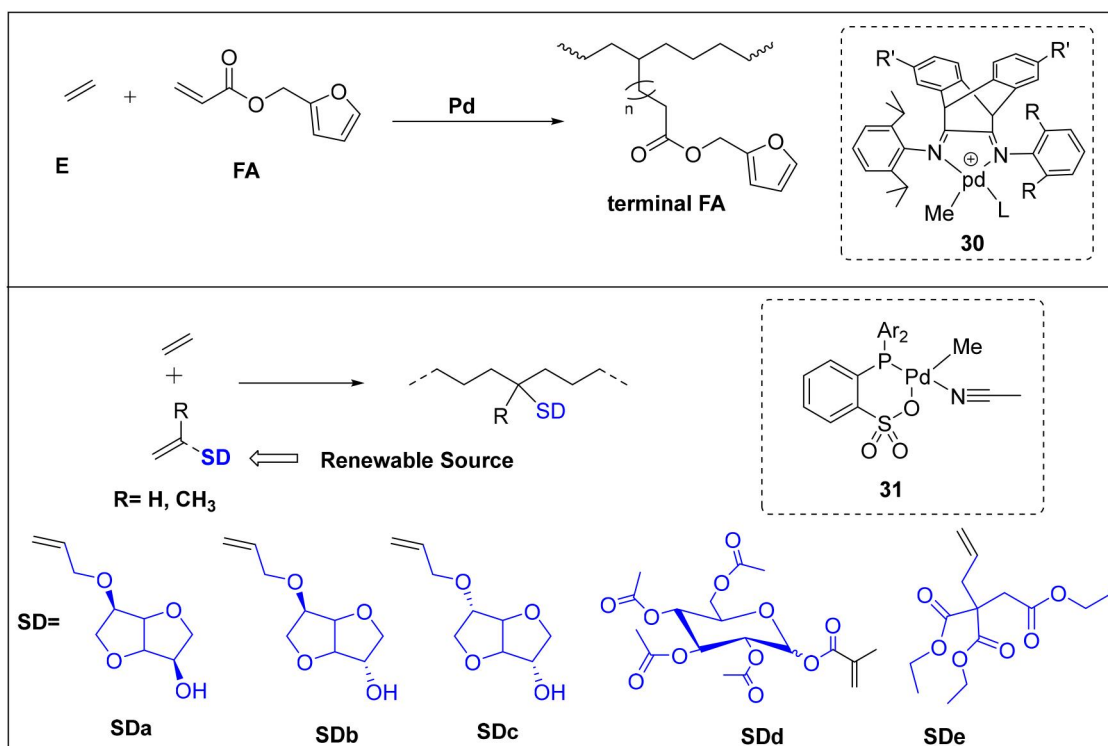


Figure 11. Copolymerization with ethylene and furfuryl acrylate (FA) with α -diimine palladium catalyst (30) (top) and insertion copolymerization of sugar-derived functional olefins with ethylene (bottom).

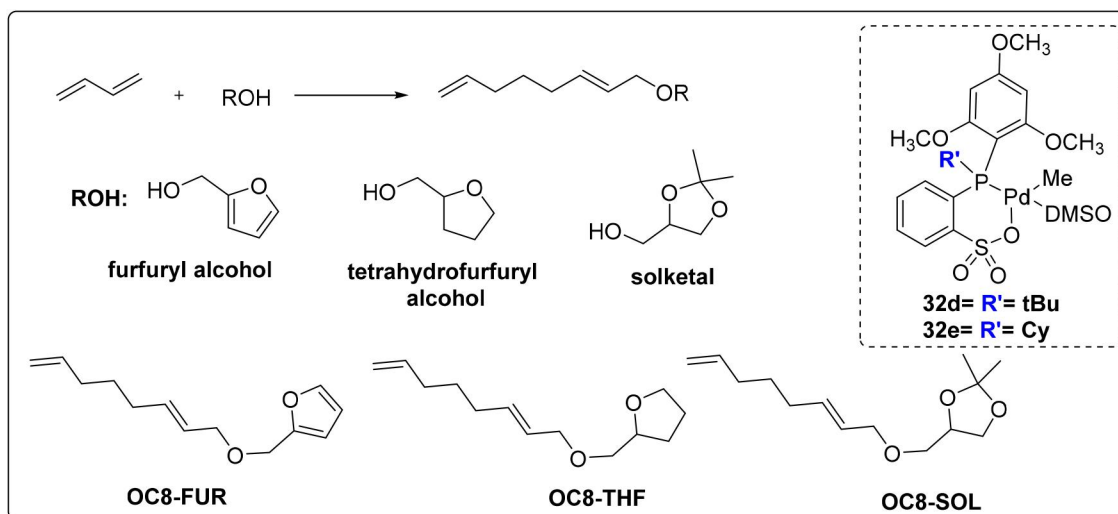


Figure 12. Synthesis of bio-derived 2,7-octadienyl ether monomers and copolymerization with ethylene.

functionalized polyethylenes with improved properties. Analysis of the resultant copolymers using NMR revealed linear structures with the incorporation of long-side chains. These side chains exhibited a unique combination of allyl ether units and polar cyclic groups, conferring the copolymers with enhanced functional motifs. These copolymers displayed superior strain-at-break as compared to non-polar polyethylene. Among the various copolymers synthesized, the one with the incorporation of 0.3 mol% OC8-FUR monomers, revealed exceptional performance. It exhibited the highest strain-at-break of 940% and a remarkable stress-at-break of 35.9 MPa.

Chen et al. reported the synthesis of polar functionalized polyolefins with high biomass content through insertion

copolymerization reactions.^[68] Two bioresourced oleyl and cinnamyl groups were installed on a norbornyl ring and were incorporated into polyolefins using phosphine-sulfonate palladium catalysts (33 and 34) (Figure 13). The use of a norbornene-based comonomer in the reaction allows efficient copolymerization with ethylene, resulting in high catalytic activities, polymer molecular weights, and comonomer incorporations. Additionally, the presence of internal carbon-carbon double bonds in the biomass groups provides reactive sites for vulcanization, which can enhance the tensile strength of the copolymers. The carbon-carbon double bonds also enable the creation of reversible dynamic cross-linked networks, for remodeling applications. The copolymerization results show that the choice of catalyst (33 and

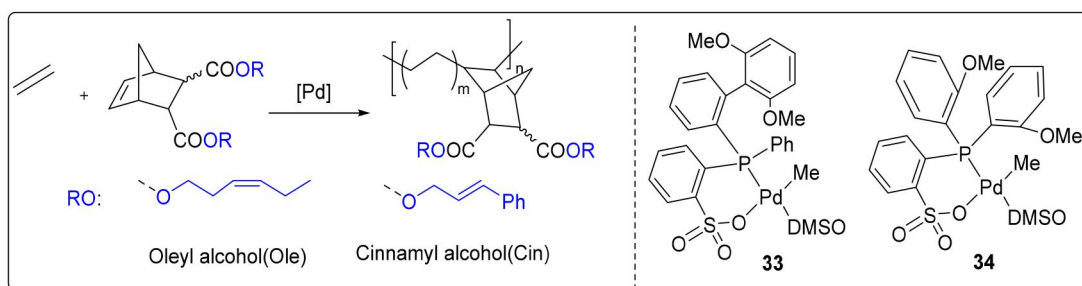


Figure 13. Copolymerization of ethylene with bioresourced disubstituted norbornene-based comonomers using phosphine-sulfonate palladium-catalysts.

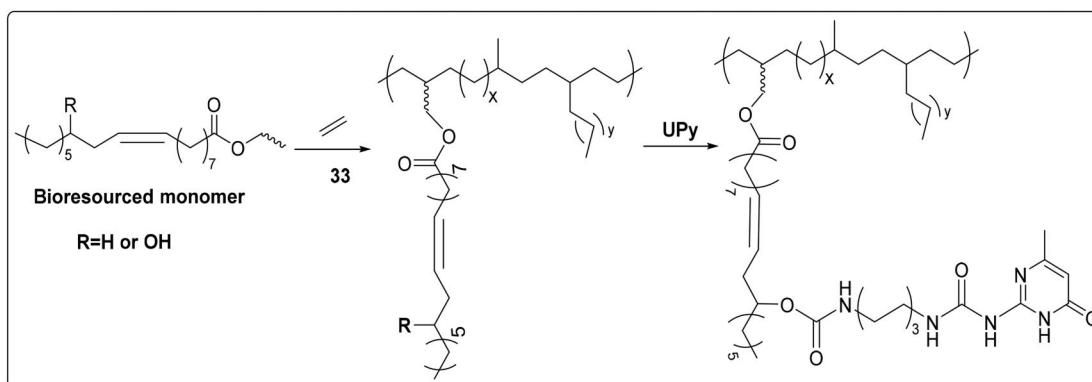


Figure 14. The bioresourced comonomers copolymerization with ethylene with phosphine-sulfonate palladium catalyst 33.

34) and comonomer configuration (endo or trans) influences the copolymerization outcome. The trans-configurations of the comonomers lead to higher activities, comonomer incorporations, and copolymer molecular weights as compared to the endo-configurations. The sterically less bulky catalyst, 34 exhibits higher polymerization activities and comonomer incorporations.

Chen et al. reported direct insertion copolymerization of plant oils derived monomers with ethylene using a palladium catalyst (33) (Figure 14).^[69] The researchers also examined the possibility of ureido-pyrimidinone (UPy) functionalization by leveraging the hydroxyl group in the polymer structure. The researchers could successfully tailor the surface and mechanical properties of the developed materials. These polymers effectively served as tougheners for gutter oil, addressing waste management and environmental sustainability challenges. The UPy functionalization enabled a self-complementary hydrogen bonding network, allowing applications in multifunctional smart materials. The polar nature and exceptional elastic properties, render them highly suitable as toughening components in polymer blends. One of the standout features of UPy is its dynamic equilibrium nature, which engenders a polymer network with unconventional mechanical properties, such as strain rate dependence and remarkable mechanical damping. The diverse combinations and interactions of these properties hold immense potential for the development of novel applications. Furthermore, the optimization of the dynamic exchange of UPy promises to expand the horizons of polymer applications, unlocking greater possibilities and offering extensive application potential in various industries.

5. Functional polyolefins as compatibilizer

Polymer compatibilization refers to the process of improving the compatibility between two or more polymers that are immiscible or exhibit poor interfacial adhesion. The importance of polymer compatibilizer lies in its ability to enhance the performance and properties of polymer blends or composites. When two or more polymers are blended together, their individual properties can be combined to create a material with enhanced polymer characteristics. However, if the polymers are immiscible, phase separation and weak interfacial adhesion can occur, leading to a reduction in mechanical strength, toughness, and other properties. By introducing a compatibilizer, which is a third polymer or a reactive agent, the interfacial adhesion between the polymers can be improved, resulting in a homogeneous blend with enhanced properties. Polymer blends often face challenges during processing due to the differences in melt viscosity and melt temperature of the constituent polymers. Incompatibility can lead to phase separation, melt fracture, or poor dispersion of fillers, additives, or reinforcements. Compatibilization can help to overcome these issues by improving the melt flow, reducing melt viscosity mismatch, and promoting uniform dispersion, leading to better processability and stability of the blend.

The third application of compatibilizers is in plastic recycling. Compatibilizers can be added to different types of post-consumer polymers, such as polyethylene and polypropylene, to blend them together and create a recycled material with improved properties. This promotes the reuse of polymer waste and reduces the amount of plastic going to

landfills, contributing to a more sustainable and environmentally friendly approach to plastics. Overall, polymer compatibilization is essential for improving the processability, properties, and versatility of polymer blends.

Chen et al. reported the compatibilization of two immiscible polymers, such as polyethylene-isotactic polypropylene (PE-iPP) and polyethylene-polystyrene (PE-PS) using bis(phenylsulfonyl)ethylene (BPSE) (Figure 15).^[70] The modified polyethylene samples (PE-gBPSE) were examined as a compatibilizer with polystyrene. The PE-PS ratio of 80/20 was used to obtain a binary blend, and PE/PE-g-BPSE/PS ratio of 78/8/18 was used to create a ternary blend (Figure 16). As evidenced in Figures 16(A,B), the PE/PS binary blend displayed significant voids (about 20–30 μm) that result from phase separation. Figure 16(B) shows a large cavity that may arise when small volumes of PS merge. The area outside of these cavities has a smooth and homogenous morphology indicating that they were formed from relatively pure PE. While, Figures 16(C,D) (PE/PE-g-BPSE/PS ternary blend) displayed a surface consisting of spherulites surrounded by amorphous regions, with no sizeable cavities. Thus, a significant enhancement in the blend's properties was achieved by the addition of the modified polymer.

Tang et al. reported the ethylene/styrene interpolymer (E-SI) as a compatibilizer for the LDPE/PS blends.^[71] Polystyrene (PS) is a typical brittle polymer that exhibits high strength, high modulus, and excellent dimensional stability. It was highlighted that by fine-tuning the molecular structure of the compatibilizers, it is possible to produce PS/LDPE blends with finer phase structure and better mechanical properties. As a result of the compatibilization of PS/E-SI, LDPE/E-SI binary, and PS/LDPE/E-SI ternary blends the Izod impact strength and elongation at break were greatly improved. Adding 10 wt % E-SI improved the ductility and hardness of all blends. Along similar lines, Xie et al. reported the compatibilization of immiscible polypropylene/polystyrene and polypropylene/polyamide-6.^[72,73] A multi-phase compatibilizer (PP-g-(MAH-co-St) prepared from maleic anhydride (MAH) and styrene (St) monomers melt grafted on polypropylene(PP), was utilized. It is well known that a maleic anhydride (MAH) functional group can readily react with an amine end group of a polyamide, which leads to a significant improvement in the state of PA6 phase dispersion and particle size. The compatibilized blends exhibit very fine particle sizes and appear to have good interfacial adhesion between the phases.

Chen et al. reported the synthesis of high-molecular-weight polar-polyolefins using eugenol and related comonomers through the utilization of a sterically bulky phosphine-sulfonate palladium catalyst (Cat.28).^[63] Because of the polar nature and good adhesion, these catechol-functionalized polyolefins can be a great candidate to serve as compatibilizers. E/Eug-Si(0.5)/Hex-HCl represents a polar counterpart of the widely used LLDPE material. Therefore, commercially available LLDPE ($M_n = 7.8 \times 10^4$) and PLA ($M_w = 1.0 \times 10^5$) were blended together using an internal mixer at a set temperature of 180 °C and with a rotor speed of 80 rpm, for 10 min. Clear phase separation was observed for this sample. The addition of 5 wt% E/Eug-Si(0.5)/Hex-HCl led to a more homogeneous distribution of the LLDPE and PLA. It was observed that the un-compatibilized LLDPE and PLA blend show reduced tensile strength and strain at break, but the addition of 5 wt% E/Eug-Si(0.5)/Hex-HCl improved the mechanical properties. Recently, Chen et al. reported polar functionalized polyethylenes containing ionic clusters and their composites.^[74,75] The addition of these polyethylene composites with polar functional groups to the recycled waste HDPE/PET led to a significant enhancement in mechanical properties (Tensile-strength: from 17 ± 2 to 42 ± 2 MPa; Elongation at break: from 9 ± 2 to $17 \pm 3\%$).

In 2023 Chikkali et al. reported the synthesis of hyper-branched functional ethylene oligomer (HBFO) as a compatibilizer for linear low density polyethylene (LLDPE) and Nylon-6.^[76] As the HBFO contains a polar functional group (OH) and non-polar hydrophobic unit (methylene backbone), they can lend themselves to compatibilize two immiscible polymers (one polar and the other non-polar). The hydroxyl group in HBFO forms a hydrogen-bonding interaction with Nylon-6 (Figure 17(b)) and the alkyl chain mixes with LLDPE, leading to a compatible blend. The tensile test data shows that, while the un-compatibilized blend formulation displays a higher tensile strength, the compatibilized blend formulation displays equivalent Young's modulus and, more importantly, higher strain to failure vis-à-vis that for un-compatibilized blend formulation (Figure 17(a)). The toughness of the blends increases upon increasing the compatibilizer content and reaches an optimum at 5 wt%. The functionalized ethylene oligomer as a compatibilizer played an important role in creating a tough yet flexible blend formulation. The potential applications could be in the packaging sector requiring a good oxygen barrier property in addition to the water vapor barrier. SEM images

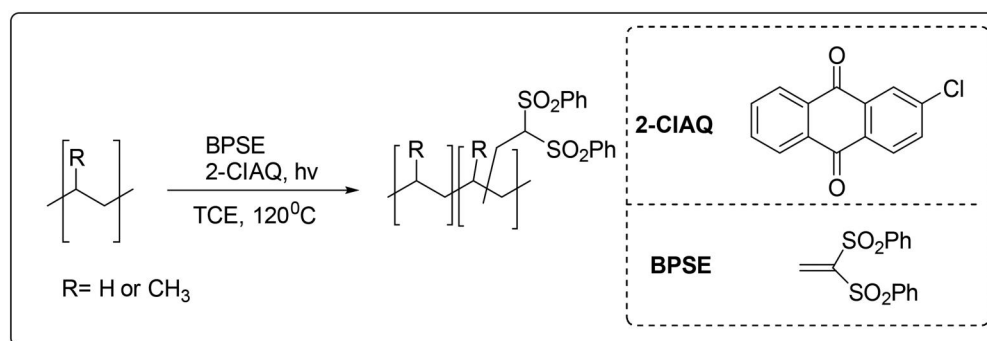


Figure 15. The preparation of modified polyethylene (HBPE/PE-g-BPSE) and isotactic polypropylene (iPP-g-BPSE).

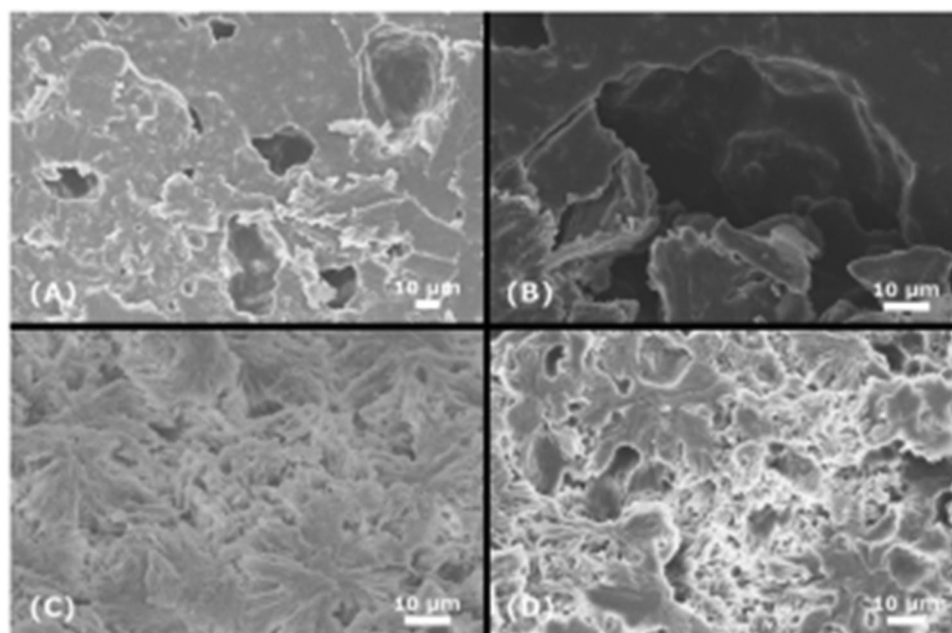


Figure 16. SEM Micrographs of fractured surfaces etched by acetone. (A,B) PE/PS (80/20), (C,D) PE/PE-g-BPSE/PS (74/8/18). Reproduced from Ref.^[59] with permission from the Royal Society of Chemistry.

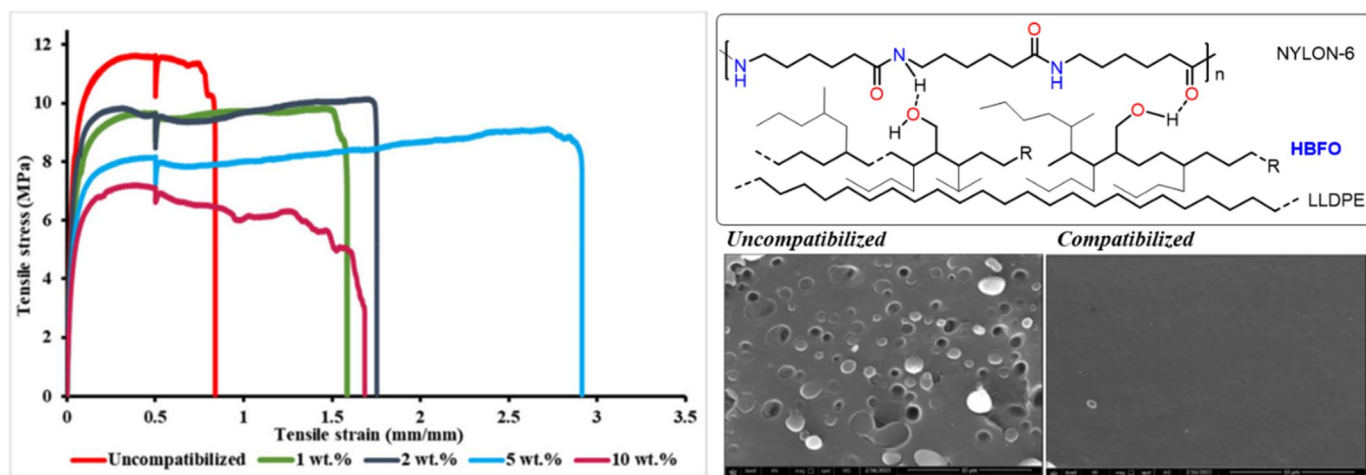


Figure 17. (a) Tensile plot for uncompatibilized and compatibilized blends. (b) Proposed hydrogen-bonding interaction between Nylon-6 and the HBFO F4. (c) SEM images of the uncompatibilized and compatibilized polymer blend.

(Figure 17(c)) clearly display a dispersed phase for compatibilized blends compared to the uncompatibilized blends.

Kumaraswamy et al. reported nanocomposites comprising polyethylene covalently grafted onto sheet-like silsesquioxanes by ring-opening metathesis polymerization (ROMP) of cyclooctene using the second-generation Grubbs catalyst.^[77] This catalyst was covalently tethered to a sheet-like norbornenyl-Mg-silsesquioxane. The ROMP reaction led to the formation of poly(cyclooctene) chains. Subsequently, the poly(cyclooctene) chains were subjected to catalytic hydrogenation. The obtained polyethylene nano-composite shows extraordinary adhesion to metals and glass (Figure 18). The adhesion observed in this nanocomposite is ~ 100 times greater than that found in pure polyethylene and 10 times

higher than what is typically observed in polyethylene copolymers or surfaces treated with corona treatment.

6. Conclusion and outlook

The feature article provides an overview of the recent developments in the area of olefin polymerization and pins down the four most impactful trends. These include (a) disentangled ultra-high molecular weight polyethylene (dUHMWPE), (b) disubstituted difunctional olefin copolymerization, (c) incorporation of bioderived comonomers in polyolefins, and (d) application of above (b, c) functional polyolefins as compatibilizers. The remaining challenges in

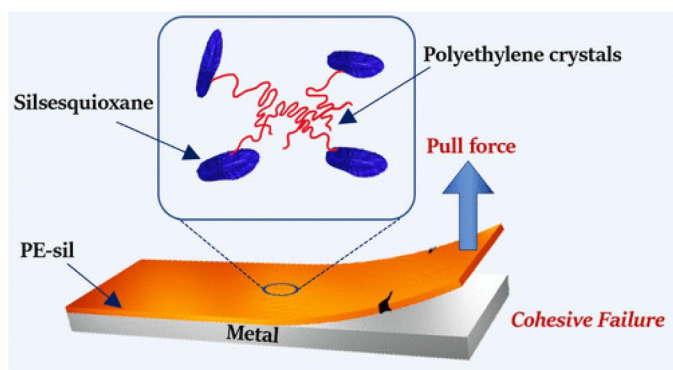


Figure 18. Adhesion property of polyethylene nanocomposite to metal. Reproduced with permission from Sharma et al.^[77] Copyright 2023 American Chemical Society.

the insertion polymerization of ethylene to disentangled ultra-high molecular weight polyethylene (dUHMWPE) and the most successful catalytic systems to produce dUHMWPE have been discussed in detail. It turns out that, with suitable modification, even the Ziegler-type catalyst can produce dUHMWPE. While, homogeneous metallocene and post-metallocene catalysts produce dUHMWPE with much better activity, molecular weight, and polydispersity index (PDI). Characterization of dUHMWPE has been streamlined and rheology, DSC methods, and solid-state NMR can be employed to prove the existence of entangled vs. disentangled states of UHMWPE.

Insertion copolymerization of 1,1-disubstituted difunctional olefins offers a direct route to prepare hydrophilic polyethylene but remained a distant dream until 2015. The first report demonstrated that 1,1-disubstituted difunctional olefin, such as 2-ethyl cyanoacrylate can be inserted and incorporated into the PE chain. Subsequently, detailed mechanistic investigations have been reported by Chikkali and Nozaki groups, and access to functional polyethylene has been secured. The authors were able to isolate 1,2-inserted intermediates of MAAA and AAA. These intermediates were exposed to ethylene and produced end-functionalized (AAA) polyethylene. The scope has been expanded and about 10–12 disubstituted difunctional olefins have been incorporated in a polyethylene chain. Although the percentage incorporation is limited, the functional group density doubles and produces a hydrophilic polyethylene. Insertion copolymerization of bioresourced olefins with ethylene was almost missing from the scene until 2017. Several reports started surfacing in the recent past and insertion copolymerization of bioresourced olefins has been examined. Plant-derived molecules, such as catechol, isohexides, furfural, eugenol, oleic acid derivatives, etc. have been suitably modified and incorporated in polyethylene chains using late transition metal catalysts. Incorporation of these monomers increases the bio-content (green content) of the polyethylene and improves several properties, such as hydrophilicity, degradability, etc., and opens up new application avenues. The last part of the feature article delved into developing new applications for functional polyethylene. In this section, the use of functional polyethylene as a compatibilizer

for two immiscible polymers was examined. As the reports suggest, the functional polyethylene can serve as a compatibilizer between a hydrophobic and a hydrophilic polymer. A polyethylene grafted on a sheet-like clay shows extraordinary adhesion to metals. The adhesion observed in this nanocomposite is ~ 100 times greater than that found in pure polyethylene.

Thus, the feature article captures the most significant developments in the area of polyolefins and debates the progress and future. As witnessed throughout the article, catalyst development has been at the core of the progress and it is anybody's guess that it will play a pivotal role in the coming years. The development of disentangled ultra-high molecular weight polyethylene has been driven by the catalyst discovery and tailoring of polymerization conditions. Teijin has already launched a grade "Endumax" that covers certain applications. It is anticipated that new applications will be developed and dUHMWPE will see spectacular growth in the years to come. A proof of concept for the insertion copolymerization of disubstituted difunctional olefins has been demonstrated. However, the activity and incorporations are still low. Therefore, focused efforts to increase the catalyst activity, incorporation of functional olefin, and molecular weight are necessary to meet the minimum threshold for any commercialization effort. It is reasonable to assume that new catalyst developments will drive this area and exploit the potential. The tried and tested recipe of ligand modification, steric and electronic tuning, etc. may not be sufficient and one may have to resort to a precise catalyst designing feature, such as hydrogen bonding, secondary interactions, etc. Insertion copolymerization of renewable monomers with ethylene opens up a completely new area of research. This does not merely incorporate the bioresourced monomers but also meets the growing demand to shift to sustainable polymers. These bioderived functional polyolefins disclose several properties, such as degradability that are uncommon for a regular polyolefin. The untapped potential of these bioresourced polyolefins will catalyze further research across academic and industrial laboratories. Application development for functional polyolefins has been on the back burner for decades. This could be due to the small volume of these functional polyolefins. However, with increasing demand for specialty polyolefins, there will be a renewed emphasis on application development and functional polyolefins will see the light of the day. Thus, this several decade-old field offers enough opportunities even today and is full of potential to meet future material demands.

Disclosure statement

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Secondary Interactions Arrest the Hemiaminal Intermediate To Invert the *Modus Operandi* of Schiff Base Reaction: A Route to Benzoxazinones

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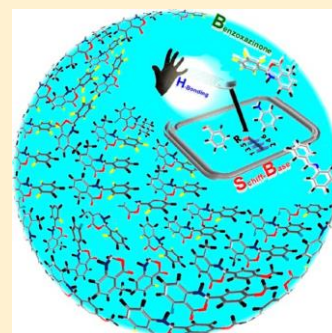
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ABSTRACT: Discovered by Hugo Schiff, condensation between amine and aldehyde represents one of the most ubiquitous reactions in chemistry. This classical reaction is widely used to manufacture pharmaceuticals and fine chemicals. However, the rapid and reversible formation of Schiff base prohibits formation of alternative products, of which benzoxazinones are an important class. Therefore, manipulating the reactivity of two partners to invert the course of this reaction is an elusive target. Presented here is a synthetic strategy that regulates the sequence of Schiff base reaction via weak secondary interactions. Guided by the computational models, reaction between 2,3,4,5,6-pentafluoro-benzaldehyde with 2-amino-6-methylbenzoic acid revealed quantitative (99%) formation of 5-methyl-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (15). Electron donating and electron withdrawing *ortho*-substituents on 2-aminobenzoic acid resulted in the production of benzoxazinones 9–36. The mode of action was tracked using low temperature NMR, UV–vis spectroscopy, and isotopic (¹⁸O) labeling experiments. These spectroscopic mechanistic investigations revealed that the hemiaminal intermediate is arrested by the hydrogen-bonding motif to yield benzoxazinone. Thus, the mechanistic investigations and DFT calculations categorically rule out the possibility of *in situ* imine formation followed by ring-closing, but support instead hydrogen-bond assisted ring-closing to prodrugs. This unprecedented reaction represents an interesting and competitive alternative to metal catalyzed and classical methods of preparing benzoxazinone.



INTRODUCTION

Reversible condensation of an aldehyde with an amine, to construct a carbon–nitrogen double bond, represents one of the most ubiquitous reaction steps in chemistry.^{1,2} The seminal work of Hugo Schiff laid the foundation of this reaction and his contribution has been rightly recognized by the naming of this reaction after him.^{3,4} Tremendous progress has been made and mechanistic details of this reaction have been well established.⁵ Depending on the substitution, the condensation products are called imines or Schiff bases or Salen's. Schiff bases are widely used as synthetic intermediates (such as the cycloaddition reaction in Penicillin synthesis),^{6,7} ligands,⁸ and catalysts,⁹ in molecular recognition and nanoscience,¹⁰ and they play a crucial role in deciding the activity of enzymes and proteins.^{11–13} The synthetic applications of imines include, but are not limited to, imine umpolung reactions,¹⁴ imine multicomponent reactions,¹⁵ the formation of MOF,¹⁶ and COF.¹⁷

In spite of a plethora of applications of Schiff bases, the structure–reactivity relationship between aldehyde and amine is difficult to establish. The intrinsic reactivity of the reaction partners is an interplay between various effects and is usually dominated by the inductive effect, conjugative effects, steric effects, and innate strains. The structural changes (such as substitutions on the reactants) can sometimes completely shut down the desired reaction and enforce a completely different course of reactivity. Therefore, altering the reactivity of an amine and aldehyde in a condensation reaction requires judicious tailoring of the reaction partners. It is known that the amine–aldehyde condensation reaction proceeds via hemiaminal X (Figure 1), which is intermediate to imine (Im).¹⁸ The hemiaminal is highly unstable and NH, H–C–OH fragments condense to liberate water and imine formation

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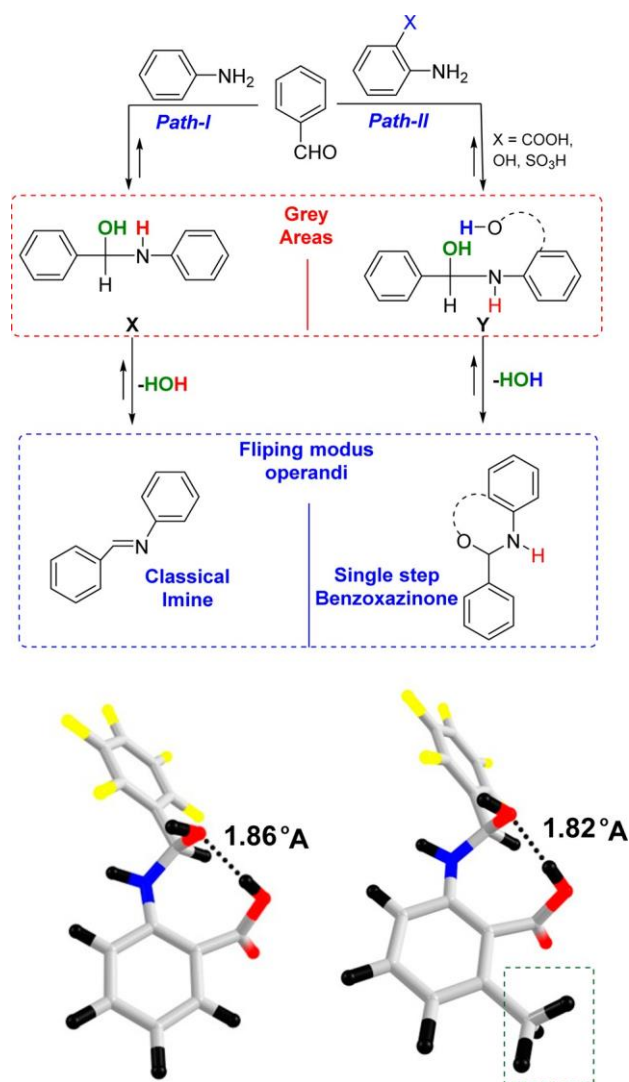


Figure 1. Condensation of an amine and aldehyde to imine (Schiff base: path-I) and H-bonding assisted condensation (path-II). Energy optimized structures of hemiaminal intermediates; 2-aminobenzoic acid (bottom left-A), and 2-amino-6-methylbenzoic acid (bottom right-B).

with sp^2 -carbon is realized. Since altering the amine group or the aldehyde functionality would completely shut down the reaction, we realized that the best way to manipulate their reactivities would be to offer a competitive proton in close proximity to the hydroxy group to construct benzoxazinone (Bz) product with a sp^3 -carbon.

Benzoxazinones have long medical history as biologically active compounds and are being currently used as drug intermediates.¹⁹ Classical synthetic methods involve multistep synthesis,²⁰ but the most recent methods provide direct access to benzoxazinones (Figure 2 top). Among various approaches, Yoshida et al. reported a straightforward access to benzoxazinones via aryne chemistry.²¹ In 2007 Nikpour and co-workers reported synthesis of benzoxazinones. The authors noted that a reaction between anthranilic acid and benzaldehyde proceeds to imine, which was found to be stable up to 3 h under reflux conditions. Further, it was found that the direct-cyclization between amine and aldehyde to benzoxazinones is disfavored and only in the presence of acetic anhydride the reaction yields benzoxazinones.²² In a recent C–H activation

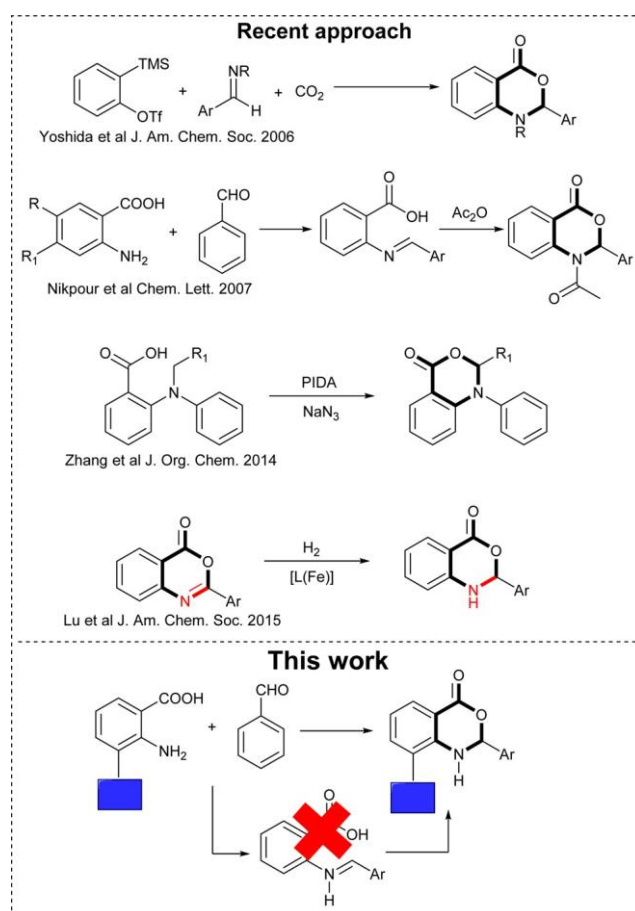


Figure 2. Recent synthetic methods for the synthesis of benzoxazinones (top) and this work (bottom).

strategy, Zhang et al. utilized hypervalent iodine compounds to access benzoxazinones in a single step.²³ Beller and co-workers adopted iron catalyzed asymmetric hydrogenation reaction to prepare benzoxazinones.²⁴ We postulated that the reaction between amine-aldehyde could be turned around via a H-bonding²⁵ assisted ring closing strategy (Figure 1, path-II), in which the hemiaminal C–OH bond is selectively weakened through a relatively acidic proton (compared to the NH proton) located in close proximity. Thus, proposing a simple, straightforward, selective, and versatile synthetic strategy to modulate the Schiff base reaction would represent significant advancement in existing knowledge of Schiff base chemistry and create substantial interest in this area.

Herein, we present a synthetic strategy that regulates the reactivity of amine and aldehyde partners in a condensation reaction via weak secondary interactions. The flipped reaction, which provides a simple selective metal free alternative to the recent metal catalyzed coupling reactions,^{21,23,24} establishes two new carbon-heteroatom bonds bearing medically important benzoxazinones. The generality of the flipped reaction is demonstrated by preparing a library of benzoxazinones in a single step inverted condensation protocol. Mechanistic investigations and density functional theory (DFT) calculations rule out the possibility of *in situ* imine formation followed by ring-closing, but support instead hydrogen-bond-assisted direct ring-closing to produce benzoxazinones.

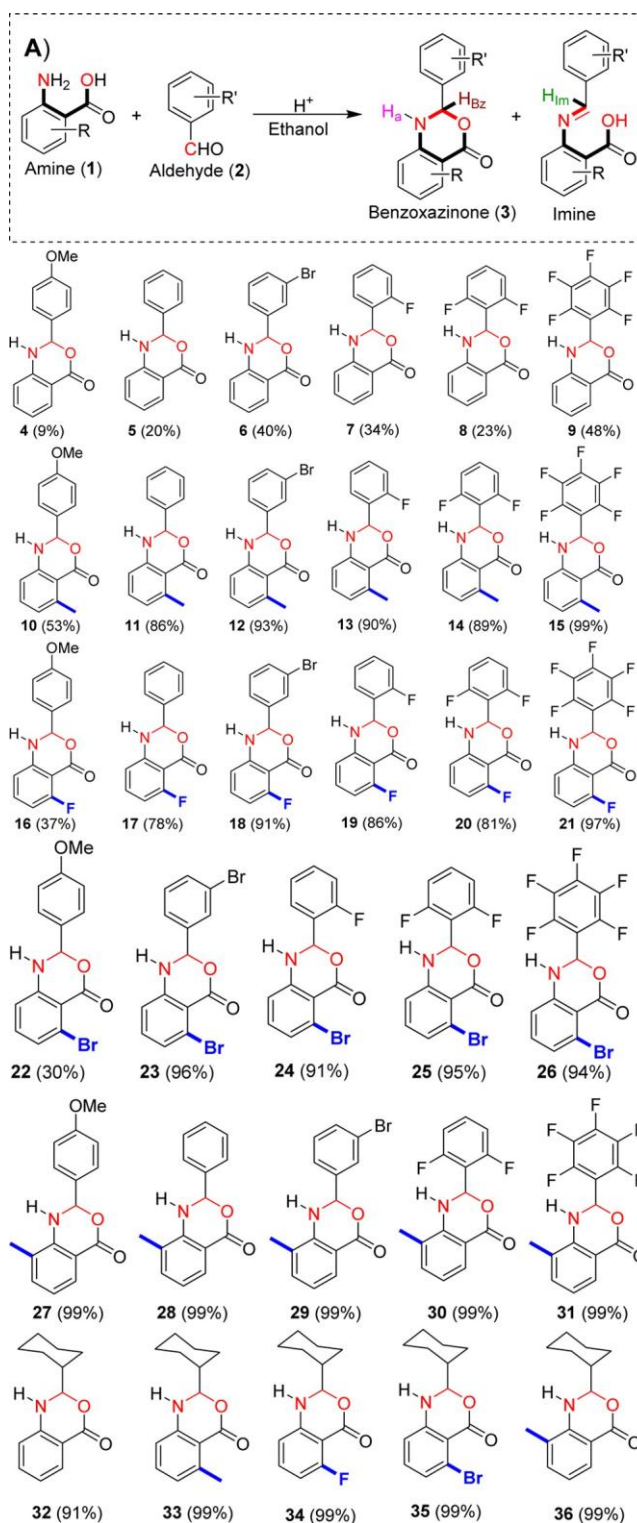
RESULTS AND DISCUSSION

Synthesis of Benzoxazinone. We anticipated that the commercially available amino acid, anthranilic acid, would be the most suitable candidate as it has the suitable acidity and the required directionality to facilitate the condensation reaction. To validate our hypothesis, we selected benzaldehyde as an aldehyde partner with anthranilic acid. The condensation reactions were performed in ethanol under reflux and the substrates were activated using a catalytic amount of acetic acid. Monitoring the progress of the reaction by proton NMR revealed the formation of imine as a major (80%) product. In addition, two new resonances could be observed at 6.19 and 4.84 ppm. To our delight, structural mapping of the condensation products using 2D NMR (COSY, HSQC, HMBC) revealed the presence of a minor (about 20%) amount of cyclized benzoxazinone **5** (Chart 1 and Figure S4–S8). In our endeavor to completely switch over the reactivity to the annulation reaction, more electrophilic benzaldehydes were employed, which led to enhanced formation of benzoxazinones **6–9** (Chart 1). The most electrophilic pentafluoro-benzaldehyde produced 48% of 2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one **9**. Our attempts to further improve the yields of the benzoxazinone, by screening reaction parameters, were not very successful at this stage.

To identify the requirements of the condensation reaction and to understand lower selectivity toward benzoxazinone, we turned our attention to DFT. The energy minimized structures (Figure 1 bottom) revealed that *ortho*-substitution on the 2-aminobenzoic acid orients the carboxylic –OH in close proximity. Intermediate A without any *ortho*-substitution displayed a C–HO–HOOC–Ar distance of 1.86 Å, whereas the methyl substituted analogue B revealed a shorter distance of 1.82 Å. Although these distances are just indicative, the theoretical revelations paved the way for experimental design and we set out to evaluate the reactivity of 2-amino-6-methylbenzoic acid. In fact, treatment of 2-amino-6-methylbenzoic acid with benzaldehyde under identical conditions produced the annulated benzoxazinone product **11** with excellent selectivity (86%) (Chart 1).

Reaction Scope. Condensation of highly electrophilic 2,3,4,5,6-pentafluoro-benzaldehyde with 2-amino-6-methylbenzoic acid led to quantitative (99%) formation of benzoxazinone **15**. Benzoxazinone formation through condensation reaction has been termed as “Benz”, where “Benz” stands for benzoxazinone. 2D C–H correlation NMR spectra revealed cross-peaks that establish the connectivity between various protons and carbons in **15** (Figure 3). The NMR findings were further corroborated by IR and supplemented by electrospray ionization (ESI) mass spectrum that disclosed a pseudomolecular ion peak at $m/z = 330$ [M+H]⁺; 352 [M+Na]⁺ Da. The identity of compound **15** (Chart 1) was unambiguously ascertained from a single crystal X-ray diffraction (Figure 3 bottom). Compound **15** crystallizes in a monoclinic unit cell in space group P1/c. The molecular structure of **15** revealed a distinctly longer C–N bond (N2–C24 = 1.430(5) Å) in comparison to the regular imine (C–N 1.26–1.30)²⁶ bond and thus categorically ruled out the existence of a C=N double bond. Interestingly, the formed six member ring is not planar, but assumes a half-boat conformation with one of the carbon atoms pointing out of the plane. To the best of our knowledge, this is the first example of an amine and aldehyde condensation

Chart 1. Scope of the Reaction with a Library of Benzoxazinones^a



^aSelectivity of benzoxazinone was calculated from ¹H NMR data.

reaction that efficiently produces **15** as the only product.

Similar structural features could be observed for compound **14**. To evaluate the generality of this reaction, we investigated the substrate scope and Chart 1 summarizes the accessible product range. In general, electron poor aldehydes outperformed the electron rich aldehydes. The electron with-

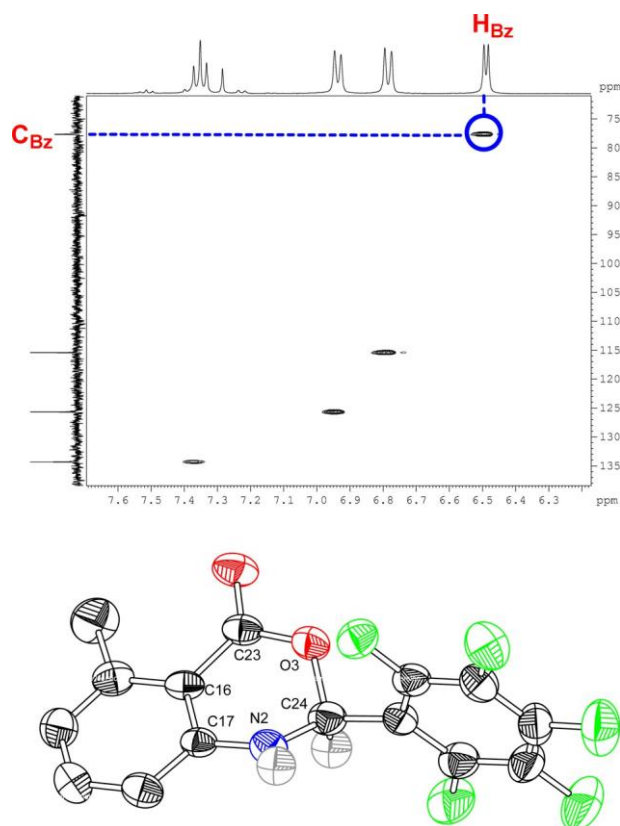


Figure 3. A short-range direct C–H correlation (HSQC) spectrum of compound 15 in CDCl_3 (top) and molecular structure (bottom) (hydrogen atoms except N–H and C–H have been deleted for clarity and thermal ellipsoids are drawn at 50% probability level).

drawing pentafluoro-benzaldehyde furnished excellent selectivity (15, 99%), whereas the electron rich anisaldehyde displayed an inferior selectivity of 53% only (compound 10). In order to investigate the influence of the *ortho*-substituent on the annulation process, the methyl group was replaced with electron withdrawing fluorine. Although counterintuitive, the outcome was largely insensitive to changes in the electronic nature of 2-aminobenzoic acid.

The annulated product yields for 2-amino-6-fluorobenzoic acid (21; 97%) and those obtained with 2-amino-6-methylbenzoic acid (15; 99%) match closely. Thus, the reaction of 2-amino-6-fluorobenzoic acid with electron donating (aldehydes) substituents led to poor performance (16; 37%), whereas electron withdrawing substituents revealed excellent performance (18–21; 80–94%). Encouraged by these findings, we examined the effect of relatively less electronegative bromide in the benzoxazinone reaction. This followed a similar trend as in the case of fluoro-substituted anthranilic acid and benzoxazinones could be obtained with good to excellent selectivity (22–26; 30–96%). After having investigated the effect of substituents *ortho* to the carboxylic group of anthranilic acid, we investigated effect of substitution *ortho* to the amine group. Quite remarkably, the methyl *ortho* to the amine did not pose any problem, but rather surprisingly, an enhanced cyclization was observed. The reaction of various benzaldehydes with 2-amino-3-methylbenzoic acid resulted in quantitative production of benzoxazinones (27–31; 99%). The reaction does not discriminate between the electron donating and electron withdrawing aldehydes and both produced the “Benz” product.

The identity of resultant benzoxazinones 27–31 was established using a combination of spectroscopic and analytical methods. We attribute the enhanced annulation process to the steric crowding around the amine in the hemiaminal intermediate. An sp^3 aldehyde was also tested in this reaction, which produced benzoxazinones in excellent selectivity (32–36; 91–99%). The resultant benzoxazinones were isolated in excellent yields and their identity was fully established using spectroscopic and analytical tools. These observations suggest that steric parameters dominate the annulation process irrespective of the electronic effect of the two reaction partners. This finding is particularly remarkable and is an additional bonus that will aid the extension of the scope of the annulation reaction. To demonstrate the synthetic utility of this reaction, we performed the reaction on gram scale. Treatment of 1 g of 2-methylantranilic acid with two equivalent of pentafluorobenzaldehyde produced 2.03 g of isolated 15 (92% yield). Thus, secondary interactions seem to play a pivotal role and turn around the reactivity of an amine and aldehyde to produce benzoxazinones, an important class of drug intermediates.

Mechanistic Investigations. Unfolding the elementary steps in modulating the textbook condensation reaction will be of great significance for understanding the flipped reactivity and might unlock the synthetic potential of this transformation. In a Schiff base reaction, direct nucleophilic attack of amine on the aldehydic carbocation leads to the generation of the crucial hemiaminal intermediate. The underlying imine mechanism with different rates (K_1 – K_5) has been investigated in depth by Sayer²⁷ and others.²⁸ However, none of these mechanistic proposals touch upon the reactivity reversal and thus fail to explain the observed cyclization (Figure 4). Therefore, a sixth

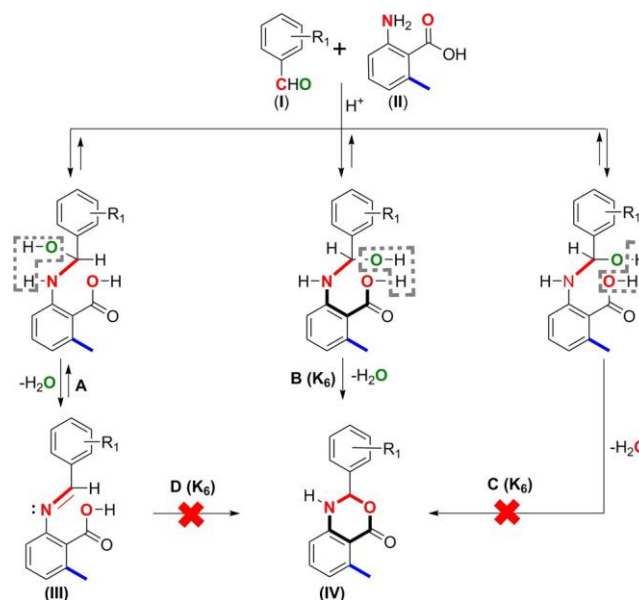


Figure 4. Proposed reaction pathways to benzoxazinone (IV), ($R_1 = \text{F}_5$).

rate constant (K_6) is proposed. The rate constant K_6 can follow, at least theoretically, three different pathways to arrive at benzoxazinone (IV). First, the possibility of rearrangement of imine (III) to benzoxazinone (IV) (proposed by Nikpour,²² Azarifar²⁹ although the starting compounds employed in the proposed mechanism were different) cannot be completely ignored. In our attempts to understand the *modus operandi*, we

investigated this reaction using a set of NMR, UV–vis spectroscopy, and DFT calculations.

To nail down the possible intermediates, NMR tube reaction of 2-amino-6-methylbenzoic acid with pentafluoro-benzaldehyde was attempted and the progress of the reaction was monitored by proton NMR spectroscopy. Even at 0 °C, instantaneous formation of benzoxazinone was observed with traces of imine (Figure 5). As the temperature of the reaction

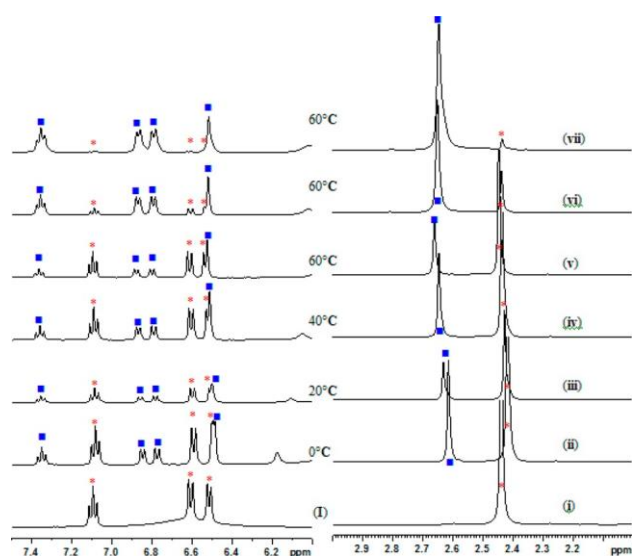


Figure 5. Variable temperature stacked ^1H NMR spectra of a reaction between an aldehyde (I) and amine (*) (II) in CD_3CN ; (ii) addition of 0.75 equiv of II at 0 °C; (iii) NMR recorded at 20 °C; (iv) NMR recorded at 40 °C; (v) NMR recorded at 60 °C; (vi) addition of 0.25 equiv of (II), NMR at 60 °C; (vii) addition of 0.25 equiv of (II), NMR at 60 °C.

mixture was raised from 0 to 60 °C, gradual decrease in the intensity of methyl (2.41 ppm *) resonance in (II) and concomitant increase in the intensity of methyl group in (IV) at 2.60 ppm (■) was observed. Interestingly, only traces of imine (8–9 ppm) could be observed (Figure S130). These findings rule out the possibility of formation of imine (route A) as the first step and subsequent conversion of (III) to (IV) [$D(K_6)$]. The NMR findings were corroborated by UV–vis, which revealed the absence of a $\text{C}=\text{N}$ charge transfer band (at 319 nm) and attested to the formation of benzoxazinone with a characteristic band at 291 nm, which was confirmed by DFT (ESI Figures S136 and S137, respectively). In order to differentiate between route B and C, we labeled the anthranilic acid oxygen (with ^{18}O -isotope). Tracking the progress by ^{13}C NMR revealed a resonance at 77.52 ppm, which clearly indicated retention of labeled oxygen in the benzoxazinone product. The observed isotopic (^{18}O) dependence of ^{13}C chemical shift is in agreement with literature reports.³⁰ The NMR observations were further supplemented by ESI-MS which revealed a pseudomolecular ion peak at $m/z = 332.06$ $[\text{M}+\text{H}]^+$, wherein the mass of oxygen is 18 Da. Therefore, it is very likely that route B is the most preferred mechanistic pathway for the condensation reaction.

Computational Insights. To obtain detailed insights in the benzoxazinone reaction, we sought the assistance of DFT and the energies associated with potential routes A, B, and C were calculated. Figure 6 depicts the energy barriers for hemiaminal formation and the rate determining dehydration reaction for

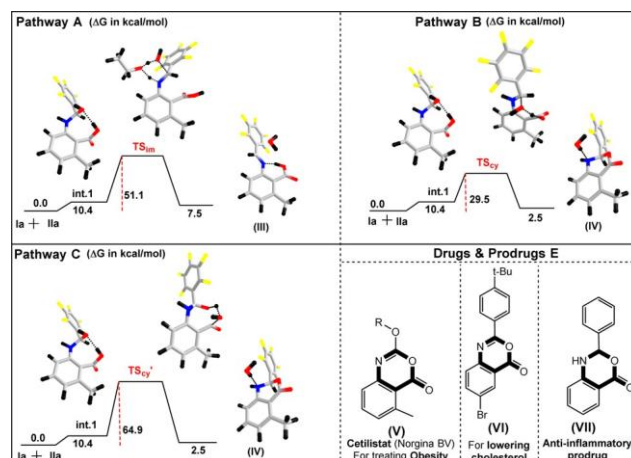


Figure 6. DFT calculated (A, B, C) mechanistic pathways with free energies (kcal mol^{-1}) for various transition states and (E) benzoxazinone as an important building block for drugs and prodrugs.

the three routes. The initial formation of hemiaminal was identical for the three routes with a $\Delta G = 10.4$ kcal/mol. As is evident, route B proved to be the preferred pathway with the lowest barrier of 29.5 kcal/mol, as compared to 51.1 kcal/mol (uphill by +21 kcal/mol) for Pathway A and 64.9 kcal/mol (uphill by +35 kcal/mol) for Pathway C (Figure 6). The lowest barrier for route B is most likely due to the secondary interaction between the acidic proton of the carboxylic acid and the hydroxyl group of the hemiaminal. The *ortho*-(to COOH) substituent likely facilitates the spatial orientation of the acidic proton and brings it to the close proximity of the hydroxyl group, leading to the favored water elimination. The above DFT results therefore complement the experimental findings and reveal the existence of secondary interactions that totally alter the course of the reaction to produce benzoxazinone via a mechanism that changes our perception of Schiff condensation. The thus produced benzoxazinones are pharmaceutically important molecules that are commercially used to treat obesity (V),³¹ to lower cholesterol levels (VI), and as an anti-inflammatory prodrug (VII).³² We anticipate that similar other reactions can be re-engineered using secondary interactions.³³

CONCLUSIONS

In summary, we report on the first synthetic strategy that regulates the reactivity of an amine and aldehyde via secondary interactions. The strategic placement of an *ortho*-substituent selectively suppresses the formation of Schiff base and increase the formation of benzoxazinones, which belongs to a class of prodrugs. Energy optimized models of the hemiaminal intermediate revealed that a *ortho*-substituent correctly orients the hydrogen bonding motif at hemiaminal stage and promotes the condensation reaction via weak secondary interactions. Indeed, reaction of 2-amino-6-methylbenzoic acid with benzaldehyde produced the desired benzoxazinone 11 with 86% selectivity. To our delight, treating electrophilic pentafluoro-benzaldehyde with 2-amino-6-methylbenzoic acid revealed quantitative formation of benzoxazinone 15. The synthetic utility of this strategy was demonstrated by preparing a library of 30 compounds and by scaling up the reaction to gram scale. The benzoxazinone reaction was found to be largely insensitive to the electronic changes and yielded similar results for electron donating methyl-substituent and electron withdrawing substituents. Quite remarkably, a methyl-substituent

ortho to amine yielded benzoxazinones in quantitative yield (27–31). Even the aliphatic aldehyde, such as cyclohexane carboxaldehyde, produced the corresponding benzoxazinones in near quantitative yield (32–36). Detailed mechanistic investigations using low temperature NMR, UV–vis, and isotopic (^{18}O) labeling revealed that the reactions follow Pathway B and the possibility of route A and C was ruled out. These experimental findings were corroborated by DFT calculations, which indicated that Pathway B is the lowest barrier pathway, 20 kcal/mol lower than Pathway A and 35 kcal/mol lower than Pathway C.

EXPERIMENTAL SECTION

General Methods and Material. Starting materials were procured from commercial suppliers and used without further purification. Solvents were dried by standard procedures unless otherwise mentioned.³⁴ 2-Amino benzoic acid was purchased from Loba Chemie Pvt. Ltd. 2-Amino-6-methyl benzoic acid, 2-amino-6-fluorobenzoic acid, 2-amino-3-methylbenzoic acid, benzaldehyde, 4-methoxybenzaldehyde, 3-bromobenzaldehyde, 2-fluorobenzaldehyde, 2,6-difluorobenzaldehyde, 2,3,4,5,6-pentafluorobenzaldehyde, and cyclohexanecarboxaldehyde were received from Sigma-Aldrich. 2-Amino-6-bromobenzoic acid was purchased from Alfa Aesar. ^{18}O labeled water (H_2^{18}O) and solvents (CDCl_3 , CD_3CN) were purchased from Sigma-Aldrich. Ethanol (commercial grade, 99.9%) was obtained from Brampton, Canada. All other solvents were purchased from local suppliers (Spectrochem Pvt. Ltd.; Avra Synthesis Pvt. Ltd.).

Solution NMR spectra were recorded on a Bruker Avance 200, 400, and 500 MHz instruments and internally referenced to residual solvent signals (note: CDCl_3 referenced at δ 7.26 and 77.23 ppm and CD_3CN referenced at δ 1.94 and 1.39 ppm, respectively). Coupling constants are given as absolute values. Multiplicities are given as follows, s: singlet, d: doublet, t: triplet, m: multiplet. Benzoxazinone and imine are denoted as Bz and Im, respectively, in NMR spectra of compounds. Mass spectra were recorded on Thermo scientific Q-Exactive mass spectrometer (Quadrupole analyzer) with Hypersil gold C18 column (150 $\times$ 4.6 mm diameter 8 μm particle size mobile phase used is 90% methanol +10% water +0.1% formic acid). UV–visible spectrum was recorded at ambient temperature on PerkinElmer 35 LAMDA instrument using the 1 cm quartz cell. FT-IR spectra of the samples were recorded using KBr pellet on the PerkinElmer instrument. C, H, and N analyses were carried out using PerkinElmer 2400.

The geometry optimizations were conducted employing density functional theory (DFT) with the Turbomole 7.0 suite of programs.³⁵ The Perdew, Burke, and Ernzerhof (PBE)³⁶ functional was used for the geometry optimization calculations. The triple- ζ basis set augmented by a polarization function (Turbomole basis set TZVP) was used for all the atoms. The resolution of identity (RI)³⁷ along with the multipole accelerated resolution of identity (marij)³⁸ approximations were employed for an accurate and efficient treatment of the electronic Coulomb term. Solvent effects were accounted for as follows: we have done full geometry optimizations of all intermediates and transition state calculations using the COSMO model³⁹ with ethanol as a solvent. Moreover, dispersion corrections (disp-3) were also included through these calculations.⁴⁰ Following this, single point calculations were done with the M06-2X functional⁴¹ on the optimized geometries. With regard to the transition states obtained during the investigations of these reactions, care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode. For compounds (III) and (IV) (HOMO–LUMO calculation), calculations were performed using the Gaussian 09 suite of programs⁴² with the M062X functional and 6-31+G* basis set. The HOMO–LUMO was calculated using the time-dependent (TD-DFT) method based on the optimized ground-state structure at the M062X/6-31+G* level. Isovalue was set to 0.02 to draw orbitals.

Single-crystal data was collected on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) and with a Cu K α radiation (1.5418 Å). The incident X-ray beam was focused and monochromated using Microfocus (μS). The flaky colorless crystals were mounted on nylon Cryo loops with Paratone-N oil. Data was collected at 100(2) K. Full data was integrated using Bruker SAINT Software and absorption correction was done using SADABS. Structure was solved by Intrinsic Phasing module of the direct methods and refined using the SHELXTL 97 software suite. All non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and placed in a riding model.

General Procedure for the Synthesis of Benzoxazinones. One mmol of amine was dissolved in 20 mL ethanol and 2 mmol (2 equiv) aldehyde was added to the above solution. Catalytic amount of acetic acid (0.2 equiv) was added to the reaction mixture and the resulting reaction mixture was refluxed for 6 h. Next, the reaction mixture was concentrated in vacuum to afford a crude semisolid residue. The thus obtained residue was washed with hexane (10 mL $\times$ 2) to yield free-flowing solid.

The identity of the imine and the benzoxazinone (obtained via the proposed condensation) was established from various 1–2D NMR experiments and the NMR spectra have been deposited in [Supporting Information](#). The product (benzoxazinone: imine) distribution was determined from the proton NMR of above residue. Spectrum of respective compounds has been presented in [Supporting Information](#).

Benzoxazinones with more than 90% selectivity were isolated and the yields have been reported.

2-(3-Bromophenyl)-5-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 12). General procedure as above was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 3-bromobenzaldehyde (0.367 g, 2 mmol, 2 equiv) were used as reaction partners. The ratio of the two products was determined from a proton NMR and the respective spectrum is presented in [Figure S32](#). After hexane wash benzoxazinone 12 was isolated as light yellow color solid (0.288 g, 91%) Melting point (m.p.) = 132–134 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.79 (br s, 1H, Ar), 7.57 (d, $J_{\text{H-H}}$ = 8.01 Hz, 1H, Ar), 7.53 (d, $J_{\text{H-H}}$ = 7.63 Hz, 1H, Ar), 7.32–7.27 (m, 2H, Ar), 6.83 (d, $J_{\text{H-H}}$ = 7.63 Hz, Ar), 6.71 (d, $J_{\text{H-H}}$ = 8.39 Hz, 1H, Ar), 6.04 (d, $^3J_{\text{H-H}}$ = 2.29 Hz, 1H, H_{Bz}), 4.88 (br s, 1H, H_{a}), 2.68 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 163.3 (C_{h}), 148.5, 144.5, 138.1, 134.4, 133.3, 131, 130.4, 125.9, 124.7, 122.9, 114.2, 113.0, 85.5 (C_{Bz}), 22.5 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{BrN}$ 318.0124; Found 318.0122, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{BrNNa}$ 339.9944; Found 339.9937.

2-(2-Fluorophenyl)-5-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 13). General procedure as above was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 2-fluorobenzaldehyde (0.248 g, 2 mmol, 2 equiv) were used as reaction partners. The ratio of the two products was determined from a proton NMR and the respective spectrum is presented in [Figure S36](#). After hexane wash the benzoxazinone 13 was isolated as light yellow color solid (0.226 g, 88%). Melting point (m.p.) = 98–100 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.76 (t, $J_{\text{H-H}}$ = 6.87 Hz, 1H, Ar), 7.40 (m, 1H, Ar), 7.24 (m, 2H, Ar), 7.09 (t, $J_{\text{H-H}}$ = 9.16, 1H, Ar), 6.79 (d, $J_{\text{H-H}}$ = 7.63 Hz, 1H, Ar), 6.67 (d, $J_{\text{H-H}}$ = 8.01 Hz, 1H, Ar), 6.39 (s, 1H, H_{Bz}), 4.87 (br s, 1H, H_{a}), 2.66 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 163.8, 161.6, 149.3, 144.7, 134.5, 132.4 (d, $^3J_{\text{C-F}}$ = 8.58), 129.0, 125.0, 124.7, 116.1 (d, $^2J_{\text{C-F}}$ = 20.98), 114.2, 112.9, 80.5 (d, $^3J_{\text{C-F}}$ = 4.77 Hz), 22.6 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{NF}$ 258.0925; Found 258.0922, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{NFNa}$ 280.0744; Found 280.0740.

2-(2,6-Difluorophenyl)-5-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 14). General procedure as above was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 2,6-difluorobenzaldehyde (0.284 g, 2 mmol, 2 equiv) were used as reaction partners. The ratio of the two products was

determined from proton NMR which is presented in Figure S40. The compound was crystallized by slow evaporations from ethanol (Pure crystal, 0.231 g, 84%) and molecular structure is presented in Figure S41. Melting point (m.p.) = 94–96 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.45–7.41 (m, 1H, Ar, H), 7.35–7.28 (m, 1H, Ar, H), 6.97 (t, 2J = 8.45, 2H, Ar, H), 6.88 (m, $J_{\text{H-H}}$ = 7.58, 1H, Ar, H), 6.77 (d, $J_{\text{H-H}}$ = 8.07, 1H, Ar, H), 6.49 (d, $^3J_{\text{H-H}}$ = 5.38, 1H, H_{Bz}), 5.13 (br, s, 1H, H), 2.70 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ = 163.7 (C_{h}), 162.8 (d, $^3J_{\text{C-F}}$ = 6.17 Hz, C), 160.3 (d, $^3J_{\text{C-F}}$ = 6.17 Hz, C), 148.3 (C), 144.5 (C), 134.1 (C), 132.2 (t, $^3J_{\text{C-F}}$ = 10.63 Hz, C), 125.3 (C), 115.7 (C), 114.3 (C), 114.5 (C), 112.2 (d, $^2J_{\text{C-F}}$ = 25.43 Hz, C), 78.3 (t, $^3J_{\text{C-F}}$ = 3.85 Hz, 3J = 4.62 Hz, C_{Bz}), 22.5 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{NF}_2$ 276.0831; Found 276.0826, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{NF}_2\text{Na}$ 298.0650; Found 298.0644.

5-Methyl-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 15). General procedure as above was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 2,3,4,5,6-pentafluorobenzaldehyde (0.392 g, 2 mmol, 2 equiv) were used as reaction partners. Compound 15 was isolated in as pale yellow solid (0.315 g, 96%) after routine hexane wash. The compound was crystallized by slow evaporations from ethanol solution and molecular structure is presented in S56. Melting point (m.p.) = 196–197 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.34 (t, $J_{\text{H-H}}$ = 7.82, 1H, Ar, H_{a}), 6.92 (d, $J_{\text{H-H}}$ = 7.34 Hz, 1H, Ar, H_{c}), 6.77 (d, $J_{\text{H-H}}$ = 8.07 Hz, 1H, Ar, H_{e}), 6.47 (d, $^3J_{\text{H-H}}$ = 5.15 Hz, 1H, H_{Bz}), 5.03 (d, $^3J_{\text{H-H}}$ = 3.42 Hz, 1H, H_{a}), 2.70 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ = 162.8 (C_{h}), 147.9, 146.9, 144.7, 143.7, 139.1, 138.9, 136.9, 134.5, 125.8, 115.5, 115.3, 113.9, 110.7, 77.8 (C_{Bz}), 22.4 (CH_3). ^{19}F NMR (376 MHz, CDCl_3 , 298 K) δ = -139.87 (d, $J_{\text{F-F}}$ = 16.02 Hz, 2F), -149.85 (d, $J_{\text{F-F}}$ = 20.60 Hz, 1F), -160.16 (t, $J_{\text{F-F}}$ = 18.54 Hz, 2F). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_9\text{O}_2\text{F}_5\text{N}$ 330.0548; Found 330.0543. Elemental analysis For $\text{C}_{15}\text{H}_8\text{O}_2\text{F}_5\text{N}$ (FW = 329.05) in %: Calcd: C 54.72, H 2.45, N 4.25; Found: C 54.63, H 2.38, N 4.21. FT-IR (cm $^{-1}$): 1705 (C=O), 1653, 1602, 1504 (N-H (br.)), 1433, 1382, 1338 (C-N), 1274, 1201 (C-O), 1130 (C-O (br.)), 1044, 1003.

2-(3-Bromophenyl)-5-fluoro-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 18). General procedure as above was followed and 2-amino-6-fluorobenzoic acid (0.155 g, 1 mmol, 1 equiv) and 3-bromobenzaldehyde (0.370 g, 2 mmol, 2 equiv) were used as reaction partners. The resultant compound 18 was isolated as light yellow color solid (0.289 g, 90%). Melting point (m.p.) = 146–148 °C. ^1H NMR (200 MHz, CDCl_3 , 298 K): δ = 7.78 (t, $J_{\text{H-H}}$ = 1.77, 1H, Ar), 7.62–7.50 (m, 2H, Ar), 7.46–7.28 (m, 2H, Ar), 6.75–6.64 (m, 2H), 6.11 (d, $^3J_{\text{H-H}}$ = 3.03 Hz, 1H, H_{Bz}), 5.02 (br s, 1H, H_{a}). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 164.0 (C_{h}), 161.0, 159.4, 150.5, 137.8, 135.2 (d, $^3J_{\text{C-F}}$ = 11.45 Hz), 132.5, 130.0, 125.2, 126.0, 121.8, 106.1 (d, $^2J_{\text{C-F}}$ = 20.98 Hz), 126.2, 115.9, 115.3, 114.3, 111.2, 110.3, 84.9 (C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{NFBz}$ 321.9873; Found 321.9876.

5-Fluoro-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 21). General procedure as above was followed and 2-amino-6-fluorobenzoic acid (0.155 g, 1 mmol, 1 equiv) and 2,3,4,5,6-pentafluorobenzaldehyde (0.392 g, 2 mmol, 2 equiv) were used as reaction partners. Workup of reaction mixture produced pure 21 in light yellow color solid (0.306 g, 92%). Melting point (m.p.) = 184–186 °C. ^1H NMR (200 MHz, CDCl_3 , 298 K): δ = 7.53–7.42 (m, 1H, Ar), 6.86–6.72 (m, 2H, Ar), 6.53 (d, $^3J_{\text{H-H}}$ = 4.53 Hz, 1H, H_{Bz}), 5.16 (br, s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ = 164.4 (C_{h}), 161.8, 158.8, 150.0, 135.9 ($^3J_{\text{C-F}}$ = 11.56 Hz), 131.3, 113.3, 111.2 (d, $^4J_{\text{C-F}}$ = 3.85), 109.5, 106.3 (d, $^2J_{\text{C-F}}$ = 20.81), 101.3 (d, $^2J_{\text{C-F}}$ = 11.56), 77.1 (C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_6\text{O}_2\text{NF}_6$ 334.0297; Found 334.0293.

5-Bromo-2-(3-bromophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 23). General procedure as above was followed and 2-amino-6-bromobenzoic acid (0.216 g, 1 mmol, 1 equiv) and 3-bromobenzaldehyde (0.370 g, 2 mmol, 2 equiv) were used as reaction partners. The ratio of the two products was determined from a proton NMR and the respective spectrum is

presented in figure S79. After multiple hexane wash compound 23 was isolated (0.344 g, 90%) as light yellow solid. Melting point (m.p.) = 142–144 °C. ^1H NMR (200 MHz, CDCl_3 , 298 K): δ = 7.79 (br, s, Ar, 1H, H), 7.65–7.52 (m, Ar, 2H), 7.35–7.28 (m, Ar, 2H, H; H), 6.84–6.78 (m, 1H, Ar, H), 7.25–7.20 (m, 1H, Ar, H), 6.03 (d, $^3J_{\text{H-H}}$ = 2.75 Hz, 1H, H_{Bz}), 4.90 (br, s, 1H, H_{a}). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): δ = 160.0 (C_{h}), 148.7, 147.4, 137.2, 136.6, 134.8, 133.0, 131.0, 130.4, 130.04, 129.9, 123.4, 120.7, 117.9, 116.5, 115.0, 114.7, 84.3 (C_{Bz}).

5-Bromo-2-(2-fluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 24). General procedure as above was followed and 2-amino-6-bromobenzoic acid (0.216 g, 1 mmol, 1 equiv) and 2-fluorobenzaldehyde (0.248 g, 2 mmol, 2 equiv) were used as reaction partners. Multiple hexane wash resulted in yellow color solid (0.283 g, 88%). Melting point (m.p.) = 96–98 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.77 (t, $J_{\text{H-H}}$ = 6.71 Hz, Ar, 1H, H), 7.43 (d, $J_{\text{H-H}}$ = 7.34 Hz, Ar, 1H, H), 7.23–7.19 (m, 2H, Ar, H; H), 7.13 (t, $J_{\text{H-H}}$ = 9.24 Hz, Ar, 1H, H), 6.813 (d, $J_{\text{H-H}}$ = 2.75 Hz, Ar, 1H, H), 7.02–6.98 (m, Ar, 1H, H), 6.43 (d, 1H, H_{Bz}), 5.07 (br, s), 1H, H). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ = 161.5 (C), 159.0.8, 150.1, 134.9, 133.2, 132.2 ($^3J_{\text{C-F}}$ = 8.48 Hz, C), 128.7, 127.9, 124.9 (2J = 3.08 Hz), 123.5, 122.6 (d, 2J = 12.33), 116.1 (d, $^2J_{\text{C-F}}$ = 21.58), 115.5, 81.2 ($^3J_{\text{C-F}}$ = 4.62 Hz, C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{NFBz}$ 321.9873; Found 321.9870.

5-Bromo-2-(2,6-difluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 25). General procedure as above was followed and 2-amino-6-bromobenzoic acid (0.216 g, 1 mmol, 1 equiv) and 2,6-difluorobenzaldehyde (0.284 g, 2 mmol, 2 equiv) were used as reaction partners. Hexane washing led to the production of 25 as light yellow color solid (0.312 g, 92%). Melting point (m.p.) = 108–110 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.54–7.44 (m, Ar, 1H), 7.33 (d, $J_{\text{H-H}}$ = 7.63 Hz, Ar, 1H), 7.23 (t, $J_{\text{H-H}}$ = 8.01 Hz, Ar, 1H), 6.98 (t, $J_{\text{H-H}}$ = 8.50 Hz, Ar, 2H), 6.89 (d, $J_{\text{H-H}}$ = 8.01 Hz, Ar, 1H), 6.50 (d, $^3J_{\text{H-H}}$ = 5.34 Hz, 1H, H_{Bz}), 5.34 (d, $^3J_{\text{H-H}}$ = 3.43 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 162.5 (C_{h}), 161.4, 160.5, 149.4, 134.75, 132.6 (t, $^3J_{\text{C-F}}$ = 10.48 Hz), 128.7, 125.7, 117.2, 114.6, 112.5 (d, 2J = 12.33), 112. Five (dd, 2J = 8.26), 77.9 ($^3J_{\text{C-F}}$ = 4.29 Hz, C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_9\text{O}_2\text{NF}_2\text{Br}$ 339.9779, Found 339.9775, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_8\text{O}_2\text{NF}_2\text{BrNa}$ 361.9599, Found 361.9592.

5-Methyl-2-(perfluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 26). General procedure as above was followed and 2-amino-6-bromobenzoic acid (0.216 g, 1 mmol, 1 equiv) and 2,3,4,5,6-pentafluorobenzaldehyde (0.392 g, 2 mmol, 2 equiv) were used as reaction partners. Compound 26 was isolated as pale yellow color solid (0.355 g, 90%). Melting point (m.p.) = 120–122 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.50–7.21 (m, 1H, Ar), 6.82–6.72 (m, 1H, Ar), 6.52 (d, $^3J_{\text{H-H}}$ = 4.27 Hz, 1H, H_{Bz}), 6.48–6.38 (m, 1H, Ar), 5.22 (br, s, 1H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 169.8 (C_{h}), 165.3, 162.8–162.7 (d, J = 7.7 Hz), 159.1, 152.8, 148.4, 136.6–136.5 (d, J = 11.56 Hz), 135.6–135.0 (d, J = 12.33 Hz), 77.5 (C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_6\text{O}_2\text{NF}_5\text{Br}$ 393.9497; Found 393.9495.

2-(4-Methoxyphenyl)-8-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (Compound 27). General procedure as described in Synthesis of Benzoxazinone Section was followed and 2-amino-3-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 4-methoxybenzaldehyde (0.272 g, 2 mmol, 2 equiv) were used as reaction partners. After multiple hexane wash compound 23 was isolated (0.234 g, 87%) as light yellow solid. Melting point (m.p.) = 145–147 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.92–7.86 (m, Ar, 1H), 7.58 (br, s, Ar, 2H), 7.33 (d, $J_{\text{H-H}}$ = 6.10 Hz, 1H), 6.99–6.95 (m, Ar, 3H), 6.14 (br, s, 1H, H_{Bz}), 4.51 (br, s, 1H), 3.86 (OCH_3), 2.20 (CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 165.2 (C_{h}), 161.3, 150.1, 136.3, 132.0, 130.4, 128.9, 128.6, 121.2, 116.1, 114.5, 86.8 (C_{Bz}), 55.6 (OCH_3), 21.2 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}$ 270.1125; Found 270.1123, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{NNa}$ 292.0944; Found 292.0941.

8-Methyl-2-phenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 28). General procedure as described in Synthesis of

Benzoxazinone Section was followed and 2-amino-3-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and benzaldehyde (0.212 g, 2 mmol, 2 equiv) were used as reaction partners. Multiple hexane washing led to pure compound 28, although with about 9% starting 2-amino-3-methylbenzoic acid impurity. Melting point (m.p.): 160–162 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.92–7.86 (m, Ar, 1H), 7.66 (br s, Ar, 2H), 7.48 (br s, 2H), 7.35 (d, $J_{\text{H-H}}$ = 6.87 Hz, Ar, 1H), 6.96 (t, $J_{\text{H-H}}$ = 7.25 Hz, 1H), 6.63 (t, $J_{\text{H-H}}$ = 7.44 Hz, 1H), 6.19 (s, 1H, H_{Bz}), 4.55 (br, s, 1H, H_{a}), 2.20 (CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 164.5 (C_{h}), 149.6, 145.4, 135.8, 130.0, 128.8, 126.9, 124.57, 123.0, 120.9, 115.7, 114.3, 86.6 (C_{Bz}). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}$ 240.1019; Found 240.1016, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{NNa}$ 262.0838; Found 262.0835.

2-(3-Bromophenyl)-8-methyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 29). General procedure as described above was followed and 2-amino-3-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and 3-bromobenzaldehyde (0.370 g, 2 mmol, 2 equiv) were used as reaction partners. Simple hexane wash produced 29 as yellowish white color solid (0.295 g, 93%). Melting point (m.p.): 94–96 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.92 (d, $J_{\text{H-H}}$ = 7.83 Hz, 1H, Ar), 7.84 (s, 1H, Ar), 7.60 (t, $J_{\text{H-H}}$ = 8.62 Hz, 2H, Ar), 7.36 (t, 2H, Ar), 7.00 (t, $J_{\text{H-H}}$ = 7.80 Hz, 1H), 6.18 (d, $J_{\text{H-H}}$ = 4.88 Hz, 1H, H_{Bz}), 4.45 (br, s, 1H, H_{a}), 2.24 (CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 164.1, 144.9, 138.0, 136.0, 133.2, 130.4, 130.1, 128.6, 125.6, 124.9, 122.8, 121.3, 114.6, 85.4 (C_{Bz}), 16.4 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{NBr}$ 318.0124; Found 318.0125, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{NBrNa}$ 339.9944; Found 339.9942.

2-Cyclohexyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 32). General procedure as described in **Synthesis of Benzoxazinone Section** was followed and 2-aminobenzoic acid (0.137 g, 1 mmol, 1 equiv) and cyclohexanecarbaldehyde (0.224 g, 2 mmol, 2 equiv) were used as reaction partners. The ratio of the two products was determined from a proton NMR and the respective spectrum is presented in **Figure S110**. Compound 32 was isolated as yellow color solid (0.203 g, 88%). Melting point (m.p.): 160 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.96 (d, $J_{\text{H-H}}$ = 7.63 Hz, Ar, H), 7.41 (t, $J_{\text{H-H}}$ = 7.25 Hz, Ar, H), 6.95 (t, $J_{\text{H-H}}$ = 7.63 Hz, Ar, H), 6.82 (d, $J_{\text{H-H}}$ = 8.01 Hz, Ar, H), 5.02 (d, $J_{\text{H-H}}$ = 4.58 Hz, H_{Bz}), 4.73 (s, br, H), 1.98 (d, $J_{\text{H-H}}$ = 9.92 Hz, 1H, H), 1.84–1.27 (m, 10H, H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 165.1 (C), 147.6, 135.0, 130.7, 120.6, 116.1, 114.0, 89.2 (C_{Bz}), 40.9, 27.4–25.6. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$ m/z = 232.1332; Found 232.1330, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NNa}$ 254.1152; Found 254.1148.

2-Cyclohexyl-5-methyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 33). General procedure as described above was followed and 2-amino-6-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and cyclohexanecarbaldehyde (0.240 g, 2 mmol, 2 equiv) were used as reaction partners. The resultant compound 33 was isolated in excellent (0.237 g, 97%) isolated yields. Melting point (m.p.) = 122–124 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.23 (t, $J_{\text{H-H}}$ = 7.32, 1H, Ar), 6.75 (d, $J_{\text{H-H}}$ = 7.25 Hz, 1H, Ar), 6.65 (d, $J_{\text{H-H}}$ = 8.01 Hz, 1H, Ar), 4.91 (d, $J_{\text{H-H}}$ = 4.58 Hz, 1H, H_{Bz}), 4.64 (br s, 1H, H_{a}), 2.66 (s, 3H, CH_3), 1.99 (d, $J_{\text{H-H}}$ = 11.06 Hz, 1H), 1.83 (br, d, $J_{\text{H-H}}$ = 8.01 Hz, 4H), 1.73 (d, $J_{\text{H-H}}$ = 11.44 Hz, 1H), 1.29–1.19 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 164.7 (C_{h}), 149.4, 144.5, 134.1, 124.2, 114.3, 113.3, 88.8 (C_{Bz}), 41.3, 27.6–26.1, 22.8 (CH_3).

2-Cyclohexyl-5-fluoro-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 34). General procedure as described above was followed and 2-amino-6-fluorobenzoic acid (0.155 g, 1 mmol, 1 equiv) and cyclohexanecarbaldehyde (0.240 g, 2 mmol, 2 equiv) were used as reaction partners. Pure compound (34) was isolated as light yellow color solid (0.236 g, 95%). Melting point (m.p.) = 132–134 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.37–7.32 (m, 1H, Ar, H), 6.64–6.60 (m, 2H, Ar, H; H), 4.98 (d, $J_{\text{H-H}}$ = 3.43 Hz, 1H, H_{Bz}), 4.85 (br, s, 1H, H), 1.98 (d, $J_{\text{H-H}}$ = 10.68 Hz, 1H, H), 1.84 (br, d, $J_{\text{H-H}}$ = 8.77 Hz, 4H, H), 1.73 (d, $J_{\text{H-H}}$ = 11.44 Hz, 1H, H), 1.32–1.23 (m, 5H, H_{H}). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 164.7 (C_{h}), 162.7, 160.9, 149.6, 135.7 (d, $J_{\text{H-H}}$ = 11.44 Hz, C), 111.5 (d, $J_{\text{H-H}}$ = 3.82 Hz, C), 107.9 (d, $J_{\text{H-H}}$ = 20.98 Hz, C), 88.6 (C_{Bz}), 40.7 (C), 27.57–26.40 (m,

C). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NF}$ m/z = 250.1238, Found 250.1235.

5-Bromo-2-cyclohexyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (Compound 35). General procedure as described above was followed and 2-amino-6-bromobenzoic acid (0.216 g, 1 mmol, 1 equiv) and cyclohexanecarbaldehyde (0.240 g, 2 mmol, 2 equiv) were used as reaction partners. Compound 35 was isolated as light brownish color solid (0.298 g, 96%). Melting point (m.p.) = 131–132 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.21–7.14 (m, 2H, Ar), 6.80 (d, $J_{\text{H-H}}$ = 7.93 Hz, 1H, Ar), 4.93 (d, $J_{\text{H-H}}$ = 4.40 Hz, 2H, H_{Bz} ; H_{a}), 1.98 (d, $J_{\text{H-H}}$ = 10.27 Hz, 1H), 1.84 (d, $J_{\text{H-H}}$ = 6.85 Hz, 4H), 1.74 (d, $J_{\text{H-H}}$ = 10.27 Hz, 1H), 1.34–1.20 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 161.8 (C), 150.0, 134.2, 127.0, 125.1, 115.5, 113.1, 87.9 (C_{Bz}), 40.5, 27.5–26.4 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NBr}$ m/z = 310.0437, Found 310.0436, $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{NBrNa}$ m/z = 332.0257, Found 332.0251. Elemental analysis. For $\text{C}_{14}\text{H}_{16}\text{O}_2\text{NBr}$ (309.10) in %: Calcd C, 54.21; H, 5.20; N, 4.52; Found: C, 54.13; H, 5.14; N, 4.49.

2-Cyclohexyl-8-methyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (compound 36). General procedure as described above was followed and 2-amino-3-methylbenzoic acid (0.151 g, 1 mmol, 1 equiv) and cyclohexanecarbaldehyde (0.224 g, 2 mmol, 2 equiv) were used as reaction partners. Compound 36 was isolated in 96% yield (0.235 g). Melting point (m.p.) = 100–101 °C. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 7.85 (d, $J_{\text{H-H}}$ = 8.01 Hz, 1H, Ar), 7.29 (d, $J_{\text{H-H}}$ = 7.25 Hz, 1H, Ar), 6.90 (t, $J_{\text{H-H}}$ = 7.63 Hz, 1H), 5.00 (d, $J_{\text{H-H}}$ = 4.77 Hz, 1H, H_{Bz}), 4.30 (br, s, 1H, H_{a}), 2.21 (CH_3), 2.03 (d, $J_{\text{H-H}}$ = 9.92 Hz, 1H), 1.86 (m, 4H), 1.74 (d, $J_{\text{H-H}}$ = 11.83 Hz, 1H), 1.35–1.22 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ = 165.3 (C_{h}), 145.6, 135.5, 128.4, 124.6, 120.5, 114.5, 88.9 (C_{Bz}), 40.9, 27.5–25.6 (m), 16.3 (CH_3). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}$ m/z = 246.1489, Found 246.1488.

Mechanistic Investigations. Tracking the Progress by NMR Spectroscopy. In an NMR tube experiment, 1 μmol (15 mg, 1 equiv) of 2-amino-6-methylbenzoic acid was dissolved in 0.6 mL deuterated acetonitrile and the NMR tube was cooled to –5 °C. 0.75 μmol (14 mg, 0.75 equiv) of 2,3,4,5,6-pentafluoroaldehyde was added to the cold NMR tube and a proton NMR was recorded immediately at 0 °C. Imine resonance (in the range of 8–9 ppm) could not be observed at 0 °C, but even at this low temperature a new resonance at 2.60 ppm appeared, which can be easily assigned to methyl group in benzoxazinone (IV). Our attempts to record the NMR at lower temperature (–10 to –25 °C) were not very successful as the amine and the aldehyde start precipitating out and very significant signal broadening was observed. Subsequently, the temperature of the probe was raised from 0 to 20 °C and proton NMR was recorded. Likewise, proton NMR of the same sample was recorded at 40 and 60 °C. To obtain full conversion, another 0.25 equiv of 2,3,4,5,6-pentafluoroaldehyde was added to the NMR tube and proton NMR was recorded at 60 °C. Finally excess (another 0.25 equiv) of 2,3,4,5,6-pentafluoroaldehyde was necessary to fully convert the 2-amino-6-methylbenzoic acid and NMR was recorded at 60 °C. **Figures 5, S130–S131** depict the variable temperature proton NMR spectra.

Isotopic (^{18}O) Labeling Investigation. As depicted in **Figure S132**, 2-amino-6-methylbenzoic acid was first converted to corresponding acid-chloride.⁴³ An oven-dried Schlenk tube was charged with 1 equiv 2-amino-6-methylbenzoic chloride (17 mg, 1 μmol , dark red colored) and 2.5 equiv labeled water (H_2^{18}O) was added. The dark color semisolid chloride immediately turned into light yellow colored precipitate of ^{18}O labeled 2-amino-6-methylbenzoic acid.⁴⁴ The residue was then dissolved in CD_3CN and 2 equiv of 2,3,4,5,6-pentafluorobenzaldehyde (40 mg, 2 μmol) was added. Subsequently, the reaction mixture was refluxed for 6 h and NMR spectra were recorded. Due to the presence of ^{18}O , the C–H carbon adjacent to the labeled oxygen shifts upfield and appears at 77.52 ppm. Similar changes in the chemical shift of ^{18}O labeled C–H carbon have been reported.³⁰ The 2D NMR spectroscopy further confirmed the existence of ^{18}O in the cyclized product (IV) (**Figure S134**). **Figure S133** compares the ^{13}C NMR of ^{16}O benzoxazinone (bottom) and that of ^{18}O labeled benzoxazinone (top). ESI-MS analysis revealed

molecular ion peak at $m/z = 332$ $[M+H]^+$, which can be assigned to ^{18}O labeled benoxazinone (Figure S135).

Monitoring the Reaction by UV–visible Spectroscopy. UV–visible spectroscopy was used as a tool to further investigate the reaction mechanism. Ground state optical absorption of the aqueous solution was measured in a quartz cell (light path 10 mm) on a UV–vis spectrophotometer (PerkinElmer) equipped with a PTC-348WI temperature controller. Stock solution of 2,3,4,5,6-pentafluorobenzaldehyde (I) and 2-amino-6-methyl-benzoic acid (II) (1×10^{-3} M) was prepared in ethanol. Dilute solution of (3.8×10^{-5} M) aldehyde and acid was mixed and the reaction mixture was monitored at different time intervals (Figure S137). In order to interpret the experimental results of UV–visible spectroscopy, the electronic absorption spectra of the cyclized (IV) and imine (III) compounds were theoretically calculated using DFT. The calculation has been carried out at the fixed geometry obtained by the geometry minimization with the help of DFT method. DFT calculation suggested the $\lambda_{max} = 291$ nm for the cyclized structure and 319 nm for the imine (Figure S136). Absence of 319 nm band in the reaction mixture (Figure S137) clearly suggested that the reaction did not follow Pathway A.

Scale Up. In order to demonstrate the synthetic utility of present strategy, a gram scale synthesis was attempted. To a stirred solution of 2-amino-6-methyl-benzoic acid (6.7 mmol, 1.01 g) in ethanol (50 mL), was added 2,3,4,5,6-pentafluoroaldehyde (13.4 mmol, 2.62 g) in the presence of catalytic amount of acetic acid at room temperature. The resulting reaction mixture was refluxed for 6 h with constant stirring and later concentrated in vacuo to afford a crude semisolid material. The residue was further washed with hexane (100 mL $\times$ 3) to produce free-flowing crystalline compound (15) in 92% isolated yield (2.032 g). In addition, excess aldehyde and solvents (ethanol, hexane) were recovered and reused.

ASSOCIATED CONTENT

★ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00352.

Spectroscopic characterization of compounds 4–36, full mechanistic investigation, gram scale experiment, and computational details (PDF)

X-ray crystallographic data for compound 14 (CCDC: 1497807) (CIF)

X-ray crystallographic data for compound 15 (CCDC: 1497808) (CIF)

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Notes

Patent application based on the results presented here is filed (IN 2016/11002384).

The authors declare no competing financial interest.

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OBJECTIVE



To secure a challenging role that allows me to leverage my expertise in organometallic chemistry, polymerization/oligomerization, Z-N Polymerization while contributing to innovative research and development. I aim to bring value through my technical skills, problem-solving abilities, and passion for advancing materials science.

PROFESSIONAL SUMMARY



I am a Ph.D. chemist with extensive expertise in catalysis, ligand design for early transition metals, and advanced polymerization techniques. My doctoral research focused on the synthesis of air- and moisture-sensitive ligands, their metal complexes, and intermediates, as well as their application in polymerization and oligomerization reactions. I have hands-on experience with highly reactive compounds, including trialkyl aluminums, diethyl aluminum chloride, MMAO-12, alkyl lithium, and alkyl magnesium halides. Proficient in producing ultra-high molecular weight polyethylene (UHMWPE) through cutting-edge polymerization methods, I bring strong problem-solving skills for handling air- and moisture-sensitive materials. Additionally, I have demonstrated leadership by mentoring students, managing collaborative projects, and operating and troubleshooting high-throughput analytical tools such as HT-GPC, DSC, GC, HPLC etc.

RESEARCH HIGHLIGHTS



- Metal catalyzed polymerization, Z-N based Polymerization
- Ligand design, synthesis and their transition metal complexes for catalytic reactions
- Design and synthesis of phosphine and nitrogen-based ligands and their early transition metal complexes for organic transformations (insertion ethylene polymerization)

EDUCATION



Doctor of Philosophy, Organometallic Polyolefin Chemistry (2015-2024)

Thesis Title: *"A Catalyst Desing for Preparation of Ultrahigh Molecular Weight Polyethylene"*

Research Guide: Dr. Samir H. Chikkali, Principal Scientist and Associate Professor AcSIR,

Dr. Harshvardhan V. Pol (Research Co-supervisor)

Polymer Science and Engineering Division, CSIR-NCL, Pune, Maharashtra, India-411008.

Master of Science, Analytical Chemistry

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad
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Post Graduate, May 2013
Division I with Distinction

 Bachelor of Science, Chemistry, Botany, Analytical Chemistry

Sarswati Bhuvan Art, Commers, Science, College,
Dr. Babasaheb Ambedkar Marathwada
University, Aurangabad
UGC
Aurangabad, Maharashtra

Graduated, May 2011
Division I

**AWARDS AND
HONORS**



- ✓ **In December 2014, secured 0008/0654 rank & declared successful** in the Examination / Test conducted by Council of Scientific & Industrial Research (CSIR) & UGC **for award of JUNIOR RESEARCH FELLOWSHIP (NET-JRF), also declared successful for Lectureship (LS) (NET).**
 - ✓ **In 2015, rank 296 declared successful in Graduate Aptitude Test in Engineering (GATE) Examination**, conducted jointly by Indian Institute of Science (IISc) & seven Indian Institutes of Technology (IIT's) on behalf of National Coordination Board (NCB)-GATE
 - ✓ **Senior Research Fellowship (July 2017- July 2020):** Awarded by The University Grants Commission (UGC), New Delhi, India in the field of chemical science.
-

**CAREER
HIGHLIGHTS**



- ❖ Presented poster in National Science Day, NCL Research Foundation at CSIR-NCL, Pune held on 25-26 Feb. 2017. "Secondary Interactions Arrest the Hemiaminal Intermediate to Invert the Modus Operandi of Schiff Base Reaction: A Route to Benzoxazinones." Patel, K. S.; Deshmukh, S. S.; Bodkhe, D. V. S.; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanam, P. R.; Nandi, S.; Vaidhyanath, R.; Chikkali, S. H.
 - ❖ Attended and presented poster in 16th International Conference on Science and Technology of Polymers and Advanced Materials, SPSI-MACRO-2022, in CSIR-NCL, Pune. "Ti-Iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene." Bodkhe, D. V.; Chikkali, S. H.
-

**PATENT &
RESEARCH
PUBLICATIONS**



- Samir H Chikkali; Ketan Patel, Satej Deshmukh and **Dnyaneshwar V. Bodkhe**, Metal free single step synthesis of substituted benzoxazinones, [IPA: IN201611002384 \(2016\)](#).
- Birajdar, R. S.; **Bodkhe, D. V.**; Gupta, P.; Shaikh, M. H.; Ramekar, R.; Chikkali, S. H. Emerging trends in olefin polymerization: a perspective. *J. Macromol. Sci. A* **2023**, *60*, 731-750.
- Patel, K. S.; Deshmukh, S. S.; **Bodkhe, D. V.** S.; Mane, M.; Vanka, K.; Shinde, D.; Rajamohanam, P. R.; Nandi, S.; Vaidhyanath, R.; Chikkali, S. H. Secondary Interactions Arrest the Hemiaminal Intermediate to Invert the Modus Operandi of Schiff Base Reaction: A Route to Benzoxazinones. *J. Org. Chem.* **2017**, *82*, 4342-4351. DOI: [10.1021/acs.joc.7b00352](#) (§ = Equal author contribution).
- **Bodkhe, D. V.**; Chikkali, S. H. Ti-Iminocarboxylate Catalyzed Polymerization of Ethylene to Highly Crystalline, Disentangled, Ultrahigh Molecular Weight Polyethylene. *Eur. Polym. J.* **2023**, *182*, 111725/1-8. DOI: [10.1016/j.eurpolymj.2022.111725](#).

- Rajput, B. S.; Pawal, S. B.; **Bodkhe, D. V.**; Rao, I. N.; Sainath, A. V. S.; Chikkali, S. H. Renewing Polyethylene: Insertion Copolymerization of Sugar Derived Hydrophilic Monomers with Ethylene. *Eur. Polym. J.* **2020**, *134*, 109775/1-6. DOI: [10.1016/j.eurpolymj.2020.109775](https://doi.org/10.1016/j.eurpolymj.2020.109775).
- **Bodkhe, D. V.**; Patel, K. P.; Shaikh, M. H.; Shivaram, S.; Chikkali, S. H. Sterically Tailored Phenoxy-imine Titanium Complexes as a Catalysts for the Preparation of Ultra-High Molecular Weight Polyethylene. ([Manuscript under preparation](#)).

TECHNICAL EXPERTIES

- **Organometallic and polymer chemistry:**
- Experience in synthesis of organometallic compounds and their intermediates
- Experience in synthesis of air and moisture sensitive ligands and their early Transition metal complexes
- Polymerization Techniques: Ziegler-Natta catalysis, scale-up experience
- Other Skills: Troubleshooting complex instrument issues, data analysis, and report preparation.
- Skilled in Schlenk techniques and handling of glove box
- Analysis of organic and organometallic compounds using various spectroscopic techniques such as 1-2D NMR, Mass, IR spectroscopy, DSC and single crystal X-ray crystallography
- Mechanistic analysis using NMR, Mass, IR spectroscopy and single crystal X-ray crystallography
- Performed reactions using MMAO-12, dialkyl aluminum chlorides and trimethyl aluminium (TMA)

SOFTWARE TOOL EXPOSURE



- Expertise in Top-spin 3.5, Omnisec, GPC IR Control, GPC One, ACD/NMR processor, Bruker AXS for single crystal XRD, Cambridge Structural Database System (CSD), Mercury 3.7, DSC Q10/Q100, ChemDraw, OriginPro 8, search engines like SciFinder and Web of Science.

OTHER SKILLS

- **Industry-Ready Competencies**
 - ✓ Expertise in scaling polymerization processes from laboratory to pilot plant reactors.
 - ✓ Proficiency in handling moisture-sensitive compounds with stringent protocols.
 - ✓ Ability to independently manage projects and solve technical challenges efficiently.
- **Leadership and Teamwork**
 - ✓ Supervised and trained M.Sc. interns, instilling strong collaboration and mentoring skills.
- **Workshops and Events Management**
 - ✓ **Organizer:** Explore the Polymer Processing/Manufacturing Industries Workshop, Aurangabad, April 28, 2022.
 - ✓ Successfully managed and coordinated a workshop aimed at providing insights into polymer processing and manufacturing industries.

- ✓ Engaged with industry professionals and academia to create a platform for knowledge exchange.
 - ✓ Facilitated participation and logistics for attendees, ensuring the event's smooth execution.
-

LANGUAGES



- English
 - Hindi
 - Marathi
-

INTRESTS

- Traveling
 - Sports (Walking, Exercise, Running & Badminton)
 - Reading
 - Music (Playing, Listening & Singing)
 - Cooking
 - Photography
 - Communicating With People
-

REFERENCES

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 - **Dr. Harshavardhan V. Pol (Ph.D. Co Supervisor)**
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PERSONAL DETAILS

- **Date of Birth:** 8th April 1990
- **Gender:** Male

- **Nationality:** Indian
 - **Marital Status:** Married
-

I hereby declare that all the information given above are true to the best of my knowledge and belief



Dnyaneshwar V. Bodkhe