ROMP of Norbornene Derivatives - A Possible Route for the Preparations of Helical Polymers by Post-Polymerization Modifications

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Certificate of Examination

This is to certify that the dissertation titled "*ROMP of Norbornene derivatives- A possible route for the preparations of helical polymers by Post-polymerization modifications*" submitted by Ms. Asha Ramesh (Reg. No. MS14149) for the partial fulfillment of BS-MS dual degree program of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report is to be accepted.

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Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Raj Kumar Roy at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussion. This thesis is a bonafide record of original work done by me and all sources listed within has been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Raj Kumar Roy
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List of Schemes

List of Abbreviations

TEA	Triethylamine
DCM	Dichloromethane
ROMP	Ring opening metathesis polymerization
THF	Tetrahydrofuran
DMSO	Dimethyl Sulphoxide
Na_2SO_4	Sodium sulphate
$CDCl_3$	Deuterated chloroform
K_2CO_3	Potassium carbonate
PBr_3	Phosphorus tribromide
TIPS-Cl	Triisopropyl chloride
nBuLi	n-Butyllithium
HPLC	High performance liquid chromatography
NMR	Nuclear magnetic resonance
^{1}H-NMR	Proton NMR
^{13}C-NMR	Carbon-13 NMR
GPC	Gel permeation chromatography
RB	Round bottom flask
mM	Milli molar

Abstract

Fascinating helical polymers in biological systems like DNA and protein performing different functions always inspired scientists. Synthetic helical polymers have wide variety of applications in material science. We tried to synthesize a Norbornene based helical polymer with the help of ring opening metathesis polymerization (ROMP) and post polymerization functionalization. ROMP using Grubbs catalysts is one of the most used functional group tolerant living polymerization known. Since organic azides are not tolerated by ruthenium carbine initiators and non-protected alkynes can slow down the propagation reaction and lead to broad molecular weight distibutions. Here we report the polymerization of Norbornene based monomer carrying a trialkylsilyl-protected alkyne by ROMP. The polymer was obtained in good yield with a low polydispersity index and high molecular weight. The findings of this studies will contribute to the development of functional and responsive polymeric systems.

CHAPTER-1

Introduction

1.1 Polymer

Polymers are macromolecules composed of many repeating units called monomers, which have been covalently or non-covalently bonded to form three dimensional structures as depicted in **Figure 1**. Depending on the sources polymers can be classified into two major categories such as biopolymers for example DNA, proteins, Polysaccharide etc. and synthetic polymers such as Polyethylene, Poly styrene, polyvinyl chloride. Protein polymers like Spider silk, hair, and horn, and polysaccharides like starch and cellulose are all other fantastic polymers the nature produce.[1] The first synthetic polymer Bakelite, was invented in 1909 and first polymeric fiber Rayon was synthesized from cellulose in the following year.[2]

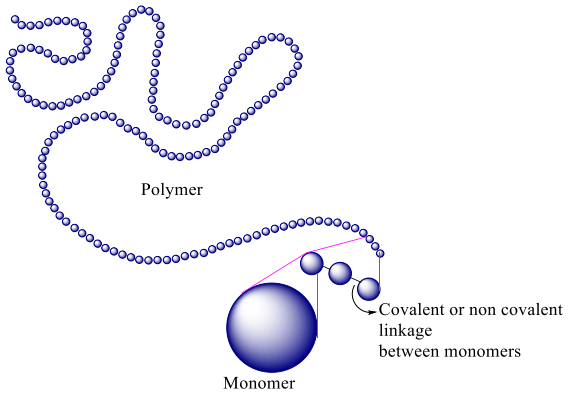


Figure 1. Schematic depiction of a polymer chain.

Many commercially important polymers are synthesized by chemically modifying naturally occurring polymers for example Rubber tree latex and cellulose have been used as raw materials to manufacture polymeric rubber and plastics. Vulcanized rubber is prepared by heating natural rubber in the presence of sulphur because of that the rubber become stronger, and more resistant to heat and other environmental conditions.

Polymers are having many advantages like light weight, strength, optical clarity, resistivity to chemicals, stability for long time which makes it desirable for wide range of applications and became an integral part of our day today life. Importance of polymers has been highlighted because of their applications in different dominions of sciences, technologies and industry from basic uses to biopolymers and therapeutic polymers.[3]

1.2 Different structural architectures polymer can form

Depending on their architecture, they can be classified into linear, branched and cross-linked or network polymers as depicted in **Figure 2**.When monomer molecules link in one continuous length, they form a linear polymer. Linear chain can be decorated with pendent groups. But depending upon the reaction conditions and kind of monomers used polymer can deviate from the linear structure to form different architectures.

When side branches of linked monomers arise from polymer backbone it forms branched polymer. There are different kinds of branching forming comb like structure with long or short branches or with extensive branching they form dendritic or hyperbranch structure in which branches are arising from branches. The presence of branching effects the polymer properties. Branched polymers do not pack easily into crystalline lattices as linear polymers do thus branching decreases crystallinity.

When polymer molecules are linked to each other at points other than ends they are called cross-linked polymer. Cross linking can be achieved by employing different methods. Low crosslinking is used to impart elasticity to the polymer and high crosslinking is used to impart rigidity and stability to the polymer under conditions of heat and stress.

Architecture of the polymer determines many of its physical properties including solution viscosity, melt viscosity, solubility in various solvents, glass transition temperature and the size of individual polymer coils in solution.

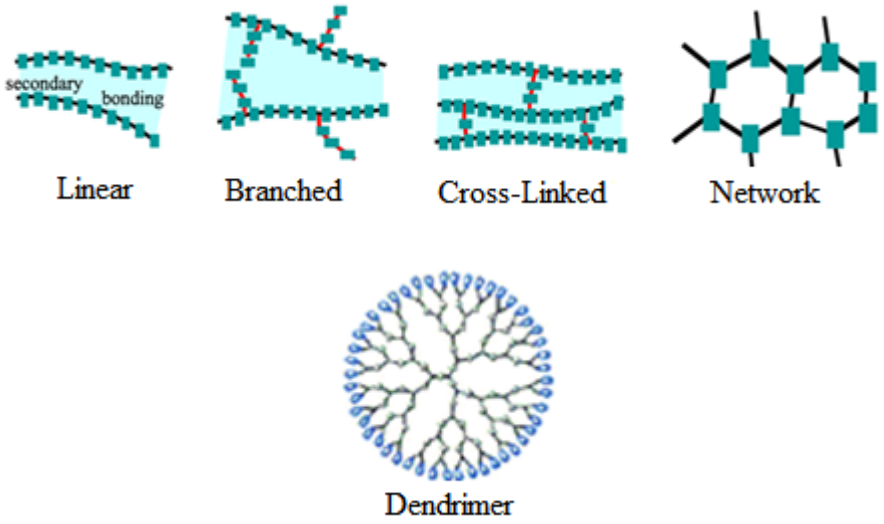


Figure 2. Different polymer architectures.[4]

1.3 Helical Polymer

In the biological system macromolecules such as DNA and Protein are performing many functions that are arising from there higher order structure. Helix is key secondary structure for several biological process.[5,6] Most importantly helix is chiral architecture, can be left and right handed helixes as depicted in **Figure 3**, which are non-superimposable mirror images of each other. Inspired from the biological helical polymers such as DNA, Protein etc. as shown in **Figure 4**, scientist always tried to develop synthetic helical polymers with desired properties considering its potential applications in material sciences, molecular separation recognition and assymmetric catalysis.

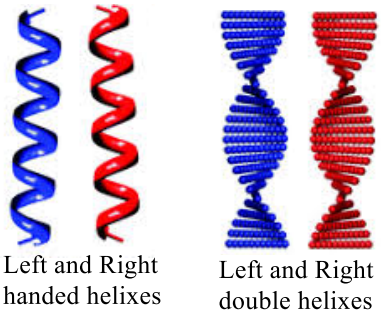


Figure 3. Chirality in single and double helixes.[7]

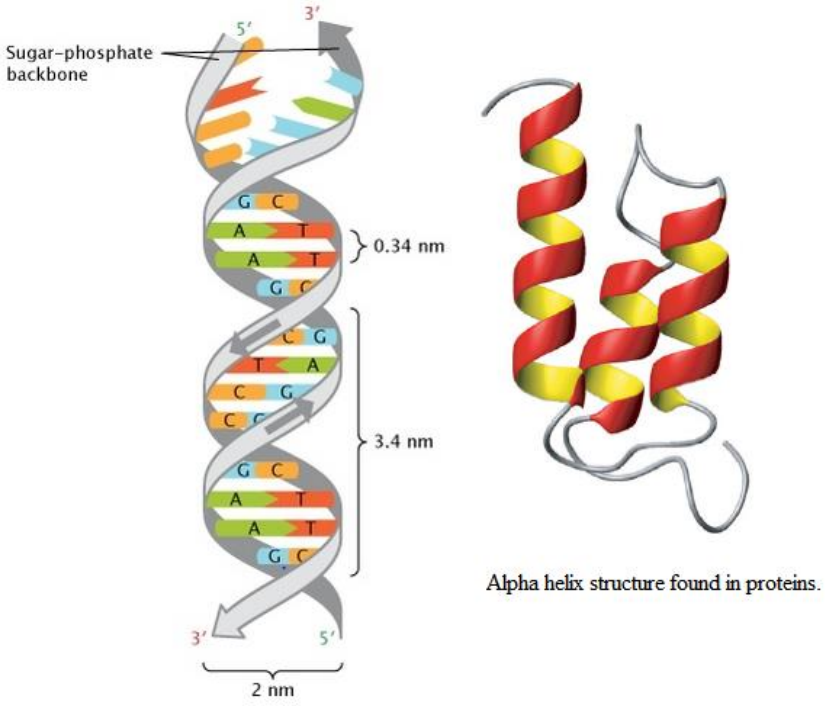


Figure 4. Biological macromolecules with double (DNA) and single helixes (Protein).[8]

There are two types of helical structures, static and dynamic helixes as shown in **Figure 5**. Static helical polymers are with high helix inversion barriers and they are stable at room temperature, whereas dynamic helical polymer is with low helix inversion barriers and helix reversal can take place through the polymer chain. Examples for each type of polymer is shown in **Figure 6**. If a particular handedness can be predominantly synthesized in a polymerization, it is called helix sense selective polymerization. The first helix-sense selective polymerization to achieve a 100% one-handed helix was from the monomer triphenylmethyl methacrylate via a chiral anionic initiator as shown in **Figure 7**.[9] If the energy barrier for the helix inversion is low then a small amount of chiral residue or stimulant can be used to stabilize helix at room temperature. This kind of polymerization has been demonstrated in alkyl isocyanate based polymers.[10, 11]

Figure 5. Different types of helical polymers based on their inversion barrier. (A) Dynamic helical polymer (B) Static helical polymer.[12]

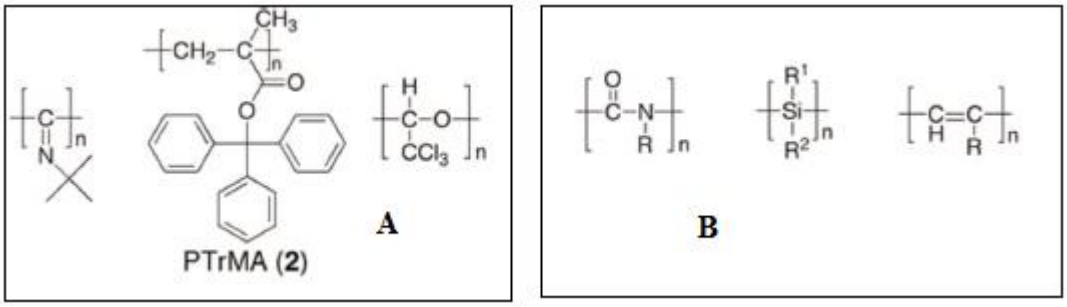


Figure 6. (A) Examples of dynamic helical polymers (B) Examples of static helical polymers.[12]

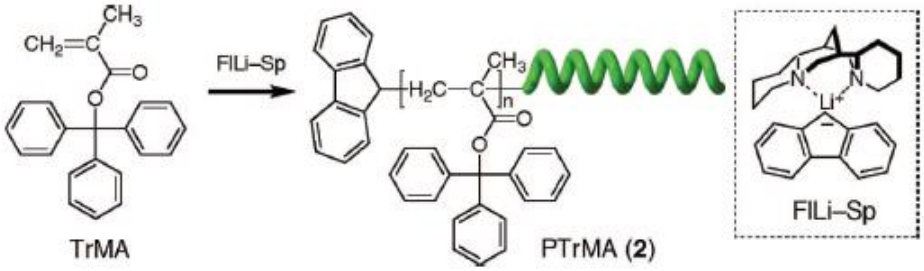


Figure 7. Helix-Sense-Selective Anionic Polymerization of TrMA.[12]

1.3.1 Chirality induction in synthetic helical polymers

Several synthetic helical polymers have already been prepared, including poly(acetylene)s,[13] oligo(m-phenylene ethynylene)s[12], oxazoline functionalized polythiophenes[14] etc. A single bond can have all kind of rotations that alone will not form a specific secondary structure. Double bond is more rigid and due to the restricted rotation, it can only choose those conformations in which it has a minimized steric hindrance. When they try to do that they have some secondary structures which is some sort of ordered structure as well as stable. If no chiral inducing agents are used then the helical polymer can have both right and left handed helixes.

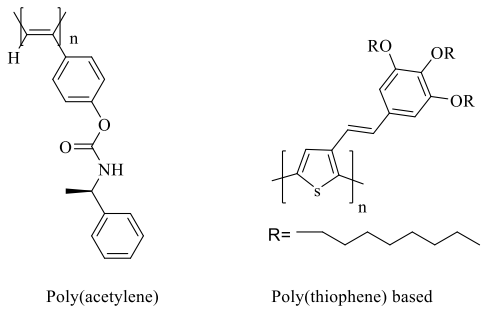


Figure 8. Examples of synthetic helical polymers having predominantly one handed helixes.[15]

1.4 Ring Opening Metathesis Polymerization (ROMP)

ROMP, is a polymerization technique in which release of ring-strain of the monomer duing the polymerization acts as a driving motivation for the process. ROMP using well-defined ruthenium initiators, is tolerant to many functional groups. In this regard Grubbs catalyst is highly used for ROMP.[16]There are three generations (First, Second and Third) of Grubbs catalyst as shown in **Figure 9**. Second and third generation catalysts are quite stable in comparison to first generation. The second generation catalyst is the most used catalyst among them.

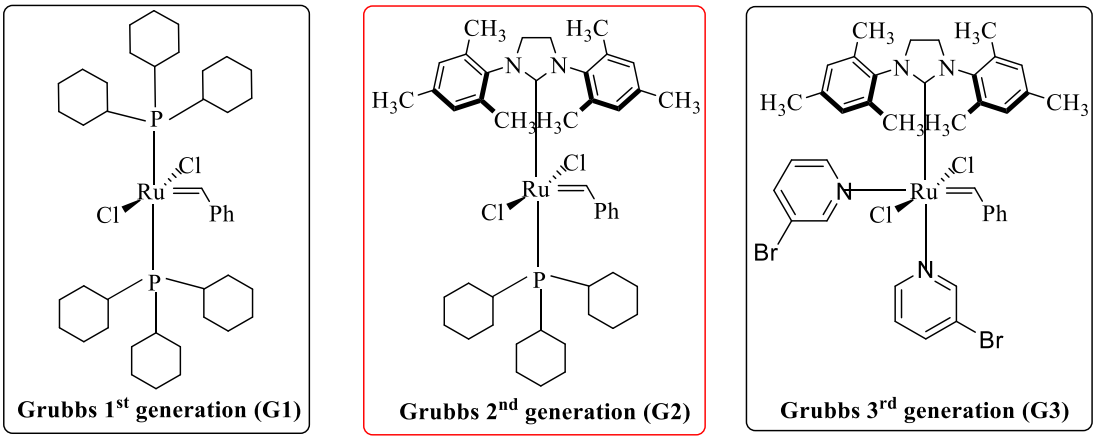


Figure 9. Generations of Grubbs Catalyst.[17]

1.5 Click chemistry

The 1, 3-dipolar cycloaddition reaction between a 1, 3-dipole and a dipolarophile to form a five-membered ring was known from the late 19th century. Mechanistic investigation and synthetic application were established in the 1960s, primarily by Rolf Huisgen, [18] hence the reaction was called Huisgen cycloaddition. High temperature was required to perform the reaction and two regioisomers were equally possible as shown in **Figure 10.** Later in 2001 Sharpless showed that copper catalyst can improve these reactions. Additional advantages are high yield, regiospecificity, mild reaction conditions, least side products etc., after that these reactions were called Sharpless click reactions.[19] Mechanism of Sharpless click reaction between alkyne and azide is shown in **Figure 11**.

Functionalized Polymer can be made by two different approaches (a) either by modifying the monomer before the polymerization or (b) by post-polymerization modification with the help of click reaction. Reaction between azides to terminal alkynes is most common among these type of reactions. They give high efficiency usually above 95% with a high tolerance of functional groups and solvents, as well as require only moderate reaction temperatures.[20,21] These characteristics of azide-alkyne addition click reaction makes it very much applicable in material science and polymer chemistry.[22]

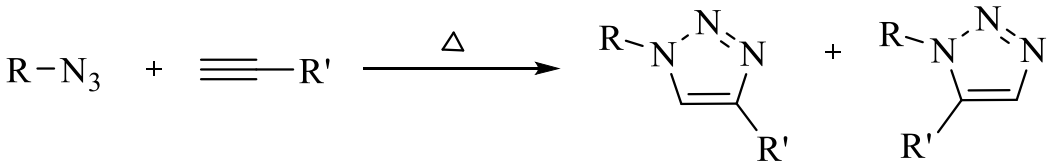


Figure 10. Huisgen 1, 3-Dipolar Cycloaddition of alkynes to azides.[23]

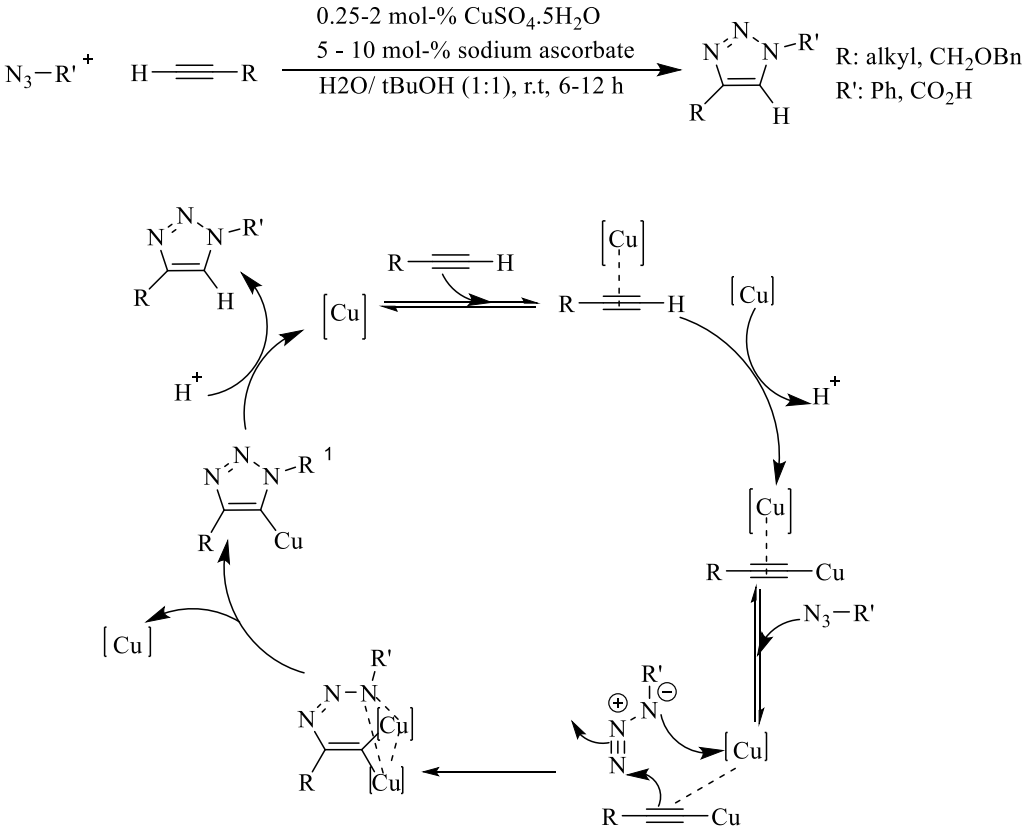


Figure 11. Mechanism of Sharpless click reaction between alkyne and azide.[24]

1.5 Norbornene and Derivatives

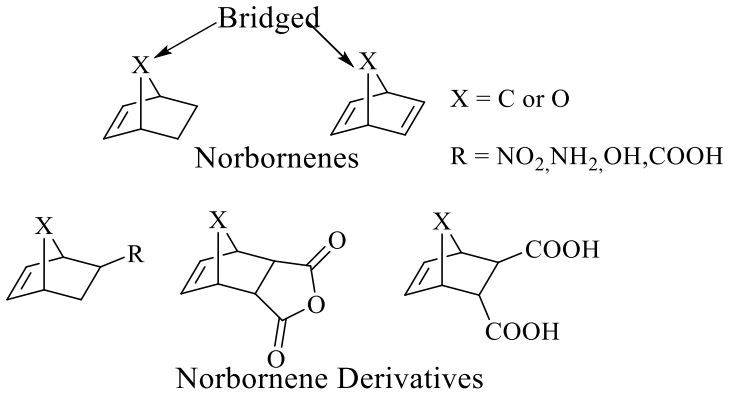


Figure 12. Norbornene and Norbornene derivatives.

Bicyclo [2.2.1] hept-2-ene, better known by its trivial name Norbornene is versatile bridged, unsaturated cyclic molecule. Norbornenes and its derivatives as shown in **Figure 12** are having high ring strain, the release of the ring strain is the driving motivation for ROMP. Polynorbornene system has double bond across the backbone as shown in **Figure 13**.

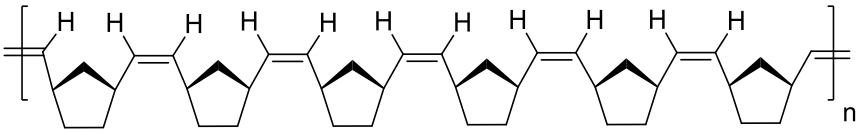


Figure 13. Schematic representation of Polynorbornene.

Norbornene and its Derivatives can be polymerized in three different ways as shown in **Figure 14.** Which include ROMP, radical or cationic polymerization, and vinyl or addition polymerization. The best known polymerization of norbornene is the ROMP. The polymer thus obtained contains double bonds in the polymer backbone giving it enough rigidity. Polynorbornenes exhibit high glass transition temperatures and high optical clarity.

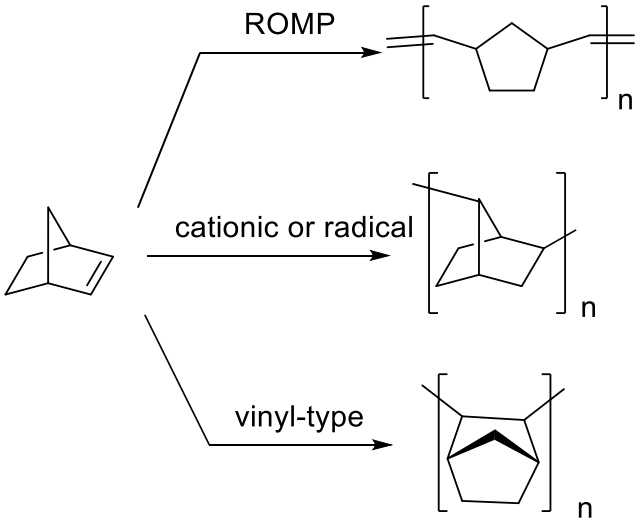


Figure 14. Three different types of polymerization for Norbornene.[25]

1.6 Objective

In this work our focus is to synthesize a helical polymer and control its helicity by incorporating a chiral moeity. Inorder to do that, a protected propargyl group functionalized poly(Norbornene) was targeted wherein the functionalization can be carried out with the help of a suitable azide group and click chemistry to transform the polymer into a predominantly one-handed helical structure. Objective is schematically represented in **Figure 15.**

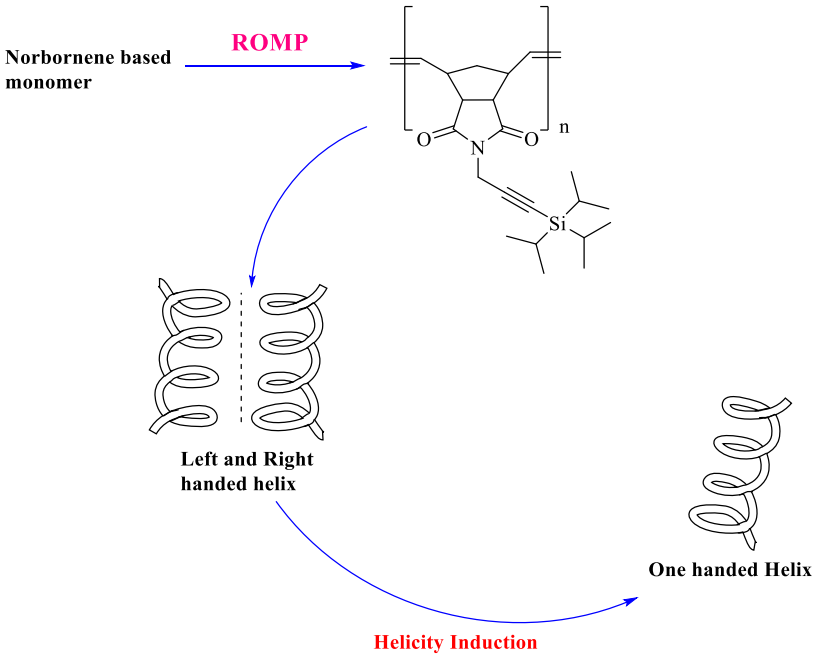
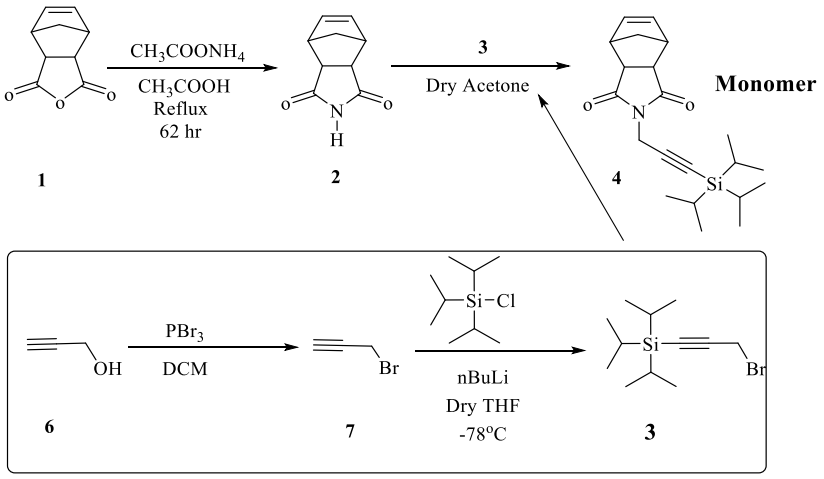


Figure 15. Schematic representation of objective

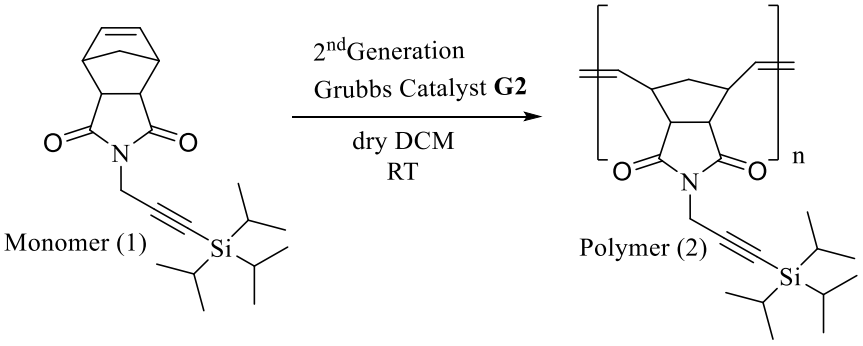
CHAPTER-2

2.1 Results and Discussion

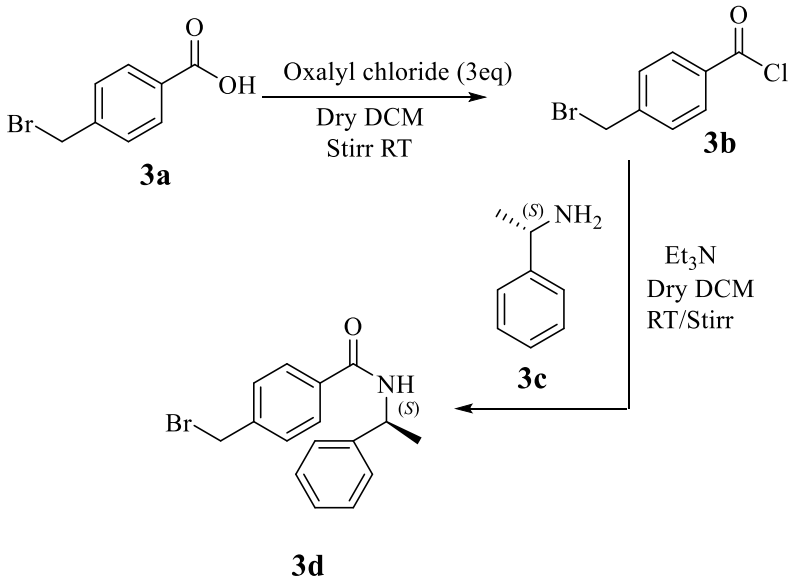
A norbornene carrying, maleimide and a silyl protected alkyne as monomer was designed and synthesized with a yield of 72% following **Scheme 1**. The polymerization of the monomer using **G2** as catalyst via ROMP was achieved by following the experimental schematic shown in **scheme 2** in dry DCM at room temperature for the desired reaction time. Resulted reaction mixture was poured into MeOH under stirring, affording the polymer as an off white powder in almost a yield of 86%. Polymer was characterized by ^{1}H and ^{13}C NMR and Gel Permeation Chromatography (GPC). A chiral group (*R*)-4-(bromomethyl)-N-(1-phenylethyl)benzamide was synthesized to attach to the polymer with a yield of 15% following the **Scheme 3**.



Scheme 1. Synthesis of Norbornene based monomer



Scheme 2. ROMP Polymerization of Norbornene based monomer using **G2**



Scheme 3. Synthesis of (*R*) -4-(bromomethyl)-N-(1-phenylethyl) benzamide for the attachment to polymer.

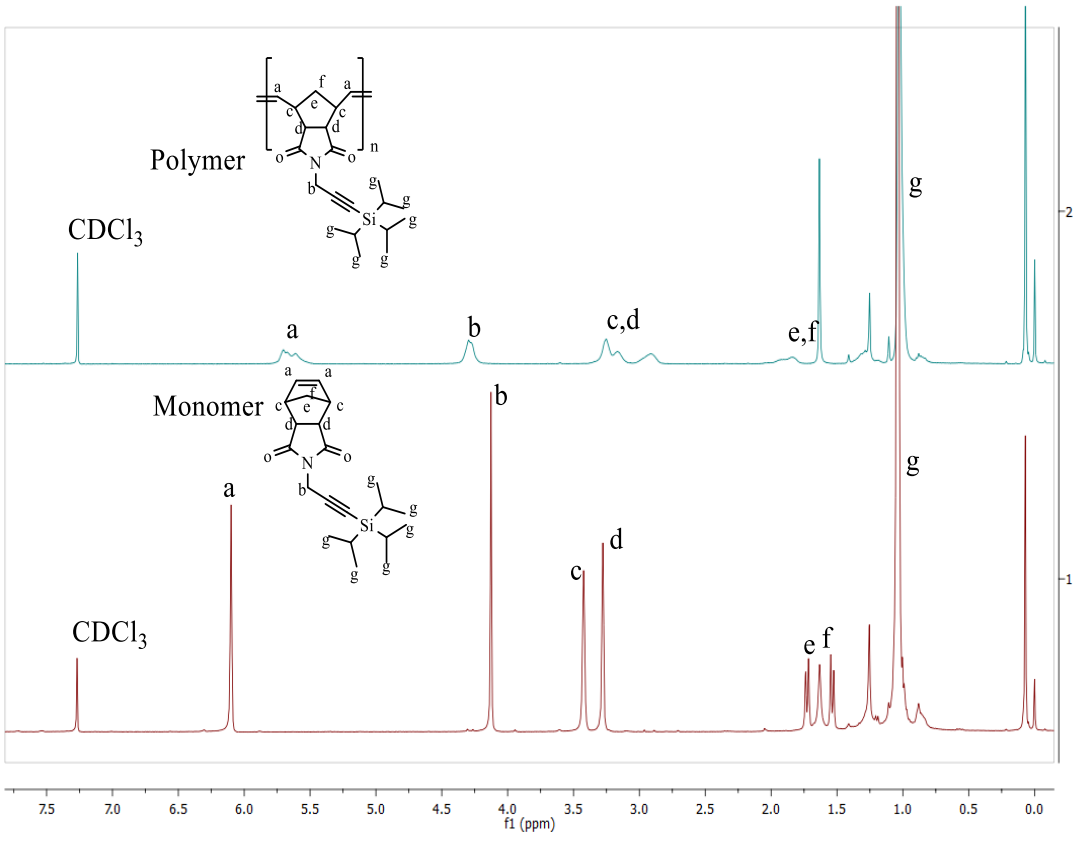


Figure 16. ^{1}H NMR spectra of monomer and polymer combined.

^{1}H NMR stack plot of the monomer and polymer as shown in **Figure 16**, confirmed the formation of the polymer. In the NMR spectra of polymer, protons corresponding to double bond of the monomer shifted towards upfield with respect to the monomer which indicating the release of ring strain in polymer. Proton NMR spectra of polymer get significantly broadened which implies high molecular weight polymer formation.

From GPC, Number averaged and weight average molecular weight of the polymer was obtained as 40,530 and 49,101 g/mol respectively, with a poly dispersity of 1.211.

2.2 Summary and Outlook

Main objective of our work was to synthesize a norbornene based helical polymer and control its helicity. We designed a monomer 4 in scheme 1 and carried out the ROMP via grubbs second generation catalyst and obtained a high molecular weight polymer. Chiral (*R*)-4-(bromomethyl)-N-(1-phenylethyl) benzamide was synthesized to functionalize the polymer and thereby control the helicity. After functionalizing the polymer via click reaction, helicity of the polymer will be monitored with the help of circular dichroism very soon.

Once we can control the helicity it can be used for several applications like molecular recognition, enantiomeric separation and asymmetric catalysis.

2.3 Experimental section

General information:

2.3.1 Materials

The chemicals Grubbs catalyst 2nd generation, Propargyl alcohol (99%), nBuLi (2M solution in cyclohexane) triethyl amine (98%), Oxalyl chloride (99%), $CDCl_3$, Acetic acid (98%), Sodium Acetate (98%), were purchased from Sigma Aldrich. Ethyl vinyl ether (98%), TIPS-Cl (97%), 4-bromomethyl benzoic acid (97%), Ammonium chloride,

Sodium bicarbonate were purchased from AVRA. 5-Norbornene-2,3-dicarboxylic anhydride (97%) and *(R)*-(+)-1-phenylethyl amine (99%) were purchased from TCI and PBr_3 was purchased from Spectro Chem, Anhydrous Na_2SO_4 was purchased from HiMedia Laboratories Pvt. Ltd and Na metal was purchased from Central Drug House. Every solvent (HPLC grade) used during the experiment were purchased from Rankem and Merk.

2.3.2 Measurements

^1H and ^{13}C NMR spectra were recorded in Avance-III, Brucker Biospin at 400 MHz and 100 MHz spectrometers, respectively with TMS as standard at room temperature. All the coupling constants were reported in Hz. Buchi Rotavapor and vacuum pump from HHV pumps were used. The solvents used for the same were $CDCl_3$. Column chromatography was done using silica gel (100-200, 60-120 mesh). Kugelrohr distillation was done in Buchi Rotavapor R-100, Molecular weight of the polymer was determined using GPC (Malvern).

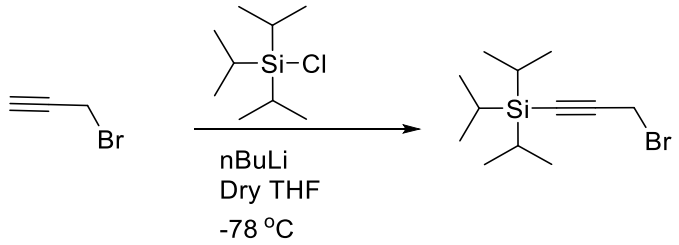
2.3.3 General procedure for the preparation of propargyl bromide[26]

Propargyl alcohol (5 g, 89.2 mmol) was dissolved in 30 ml dry DCM under N_2 atmosphere in a RB flask at -5 ^oC. PBr_3 (10 ml, 26 g, 96.05 mmol) was added drop wise into the flask at 0 ^oC and stirred at that temperature for 1hr. Further the reaction mixture was stirred at room temperature for 3 hr and quenched by adding ice cold water to the reaction mixture in an ice bath. The product was then extracted with DCM and washed with Na_2SO_4 and dried over anhydrous $NaSO_4$. The solvent was evaporated and final product was obtained as colourless oil (4.77 g, 45% yield). Final product was distilled using kugelrohr to obtain the pure product.

2.3.4 Procedure for the Preparation of TIPS protected propargyl bromide[27]

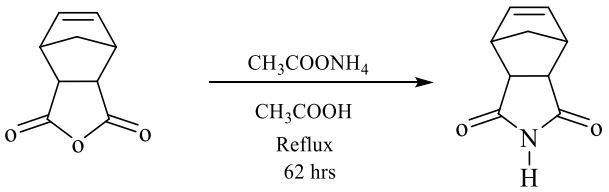
Propargyl bromide (3 g, 25.21 mmol, 1eq.) was dissolved in 20 ml of dry THF. Reaction mixture was cooled to -78 ^oC then 13 ml nBuLi (2M solution in hexane, 1 eq.) was

added drop wise. Then allowed the reaction mixture to stir for 10 min. Then solution of TIPS-Cl (5.01 g, 1eq.) in dry THF was added drop wise in resulting reaction mixture. Allowed the reaction mixture to come on the room temperature then stirred for 2 hr and then quenched the reaction mixture with ammonium chloride then extracted with DCM then dried over anhydrous Na_2SO_4. After the column the yield of the pure compound was 3.33 g (50%).



2.3.5 Synthesis of Norbornenimide [28]

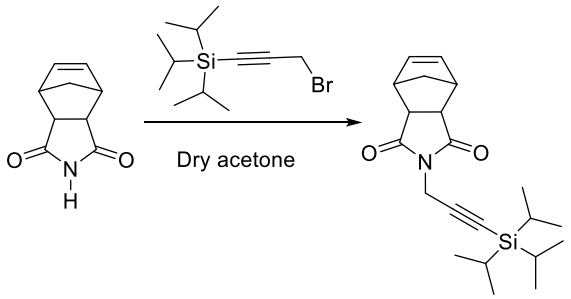
22 g of 5-Norbornene-2, 3-dicarboxylic anhydride (0.13 mol, 1eq.) was dissolved in 400 ml acetic acid. The reaction mixture was stirred at room temperature to make a clear solution. 32 g (0.42 mol, 3eq.) ammonium acetate was added in 10 min duration time the resulting reaction mixture was refluxed for 62 hrs. After the reaction solvent was removed under reduced pressure. Obtained solid compound was dissolved in ethyl acetate and washed with water, brine and then passed through anhydrous sodium sulphate. Obtained yield was 21.8 g (100%)



2.3.6 Functionalization of norbornenimide with TIPS protected Propargyl bromide.[29]

K_2CO_3 (250 mg, 1.8089 mmol) in acetone then added 178 mg (1.09 mmol) Norbornenimide in the solution and allowed to dissolved on the stirrer. Reaction mixture was allowed to stirr for 10 min at 55 °C and then added the drop wise solution of TIPS protected propargyl bromide (271.129 mg, 0.9848 mmol) in dry acetone. Then

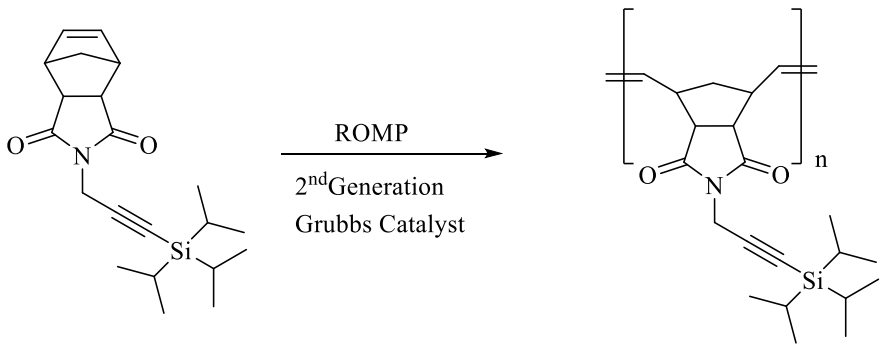
allowed the reaction mixture to reflux at 55 ^{o}C for 48 hrs. Then filtered the solid precipitate and washed with hexane. After the column obtained yield was 233 mg (72%).



2.3.7 Procedure for Polymerization[29]

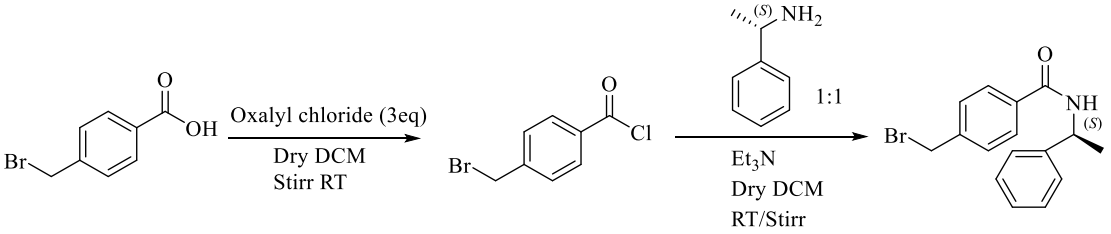
560 mg (1.720 mmol) monomer was transferred in 10 ml RB flask and then under the glove box condition desired amount of the catalyst (100:1, monomer-catalyst ratio) was added into the same RB. Then the degassed dry DCM (liquid N_2 freeze-Pumb-Thaw method) 6 ml was added into the RB (1 ml/100 mg) then allowed to stir the reaction mixture at room temperature.

After the 5 hr, 3 ml of the reaction mixture was removed from the RB and remaining mixture was allowed to stir for 12 hrs. Both reaction mixtures were quenched with ethyl vinyl ether (200 mL). Both reaction mixtures after quenching were precipitated out in methanol. Then the precipitate was again dissolved in chloroform and reprecipitated in methanol. Yield for 5 hr reaction was 256 mg and for 12 hr reaction was 224 mg. Overall yield for the reaction was 85.71%.



2.3.8 Synthesis of (*R*)-4-(bromomethyl)-N-(1-phenylethyl)benzamide [30]

Under the N_2 atmosphere, 1.5 g bromomethyl benzoic acid was dissolved in 10 ml dry DCM and then the excess of the oxalyl chloride (2.36 ml, 4 eq.) was added followed by 2-3 drops of dry DMF. Reaction mixture was allowed to stir for 1 hr at room temperature. The solvent and the excess of the oxalyl chloride was removed under high vacuum and remaining compound was again dissolved in dry DCM. This solution was added drop wise into the RB already containing the solution of dry DCM (*R*)-(+)-1-phenylethylamine (840 mg, 1 eq.), dry TEA into dry DCM. Overall yield of the reaction was 15%.



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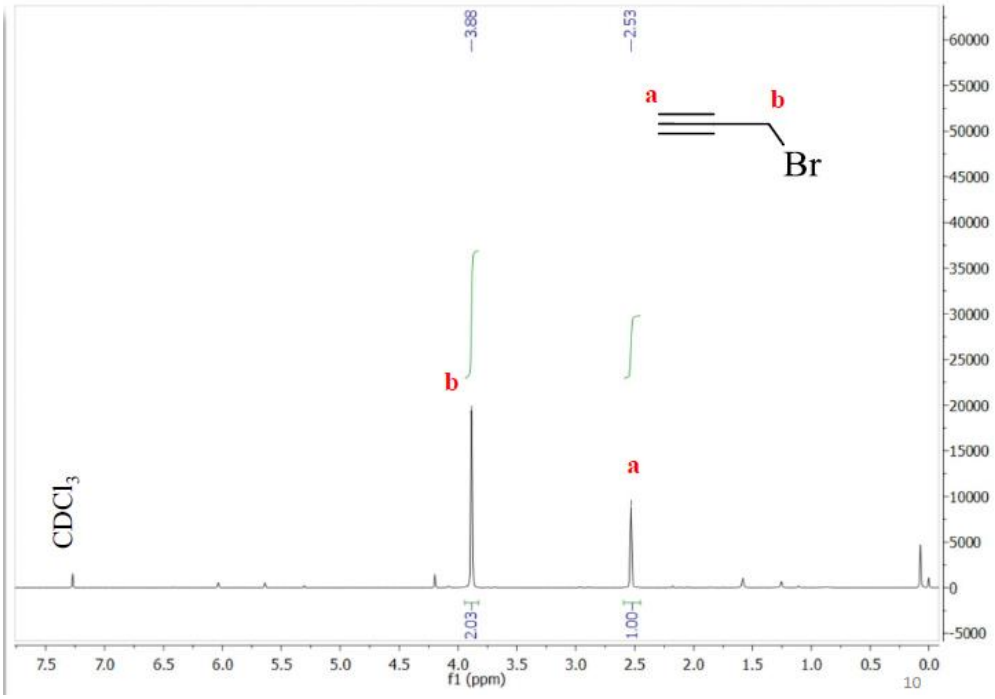
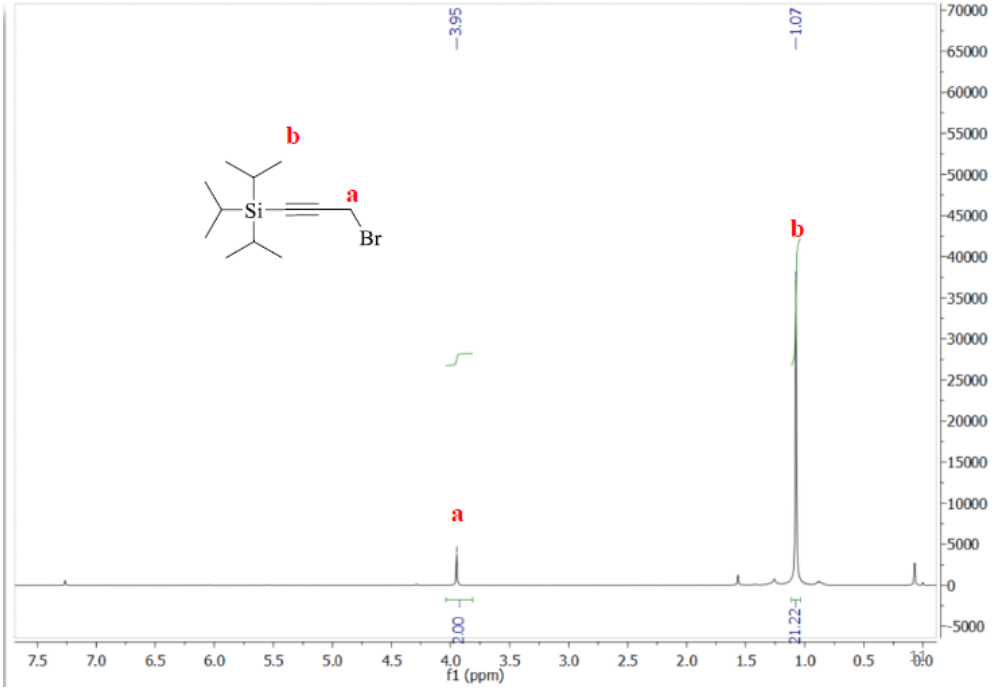
Appendix

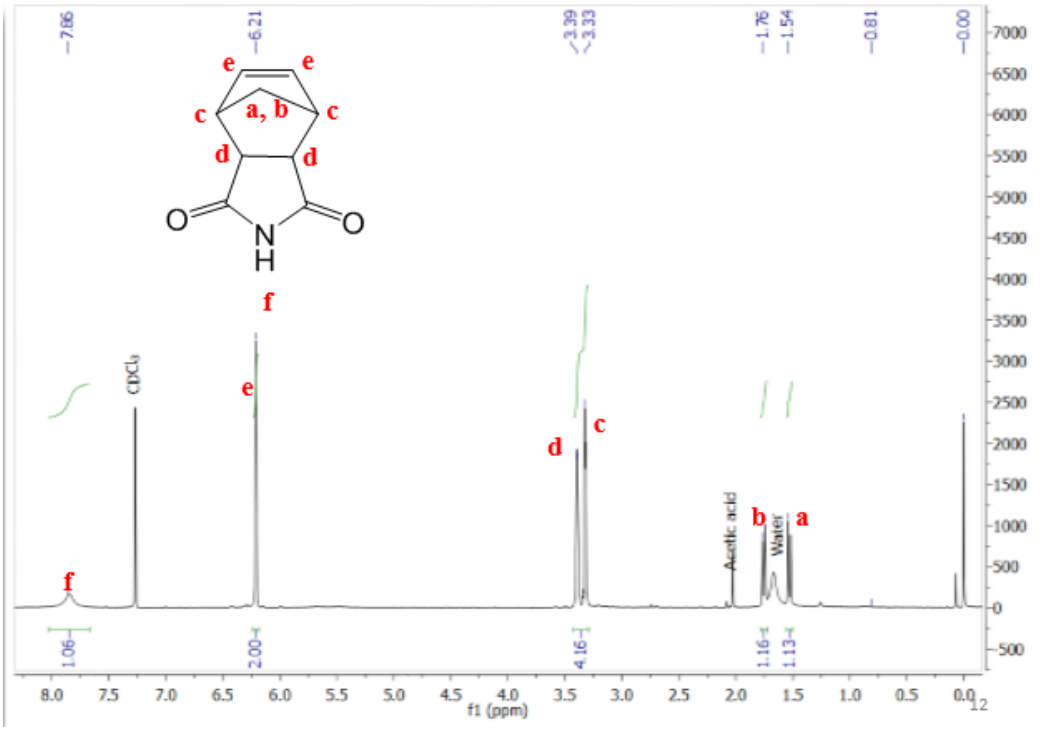
^{1}H NMR for Propargyl bromide (carried out in $CDCl_3$)



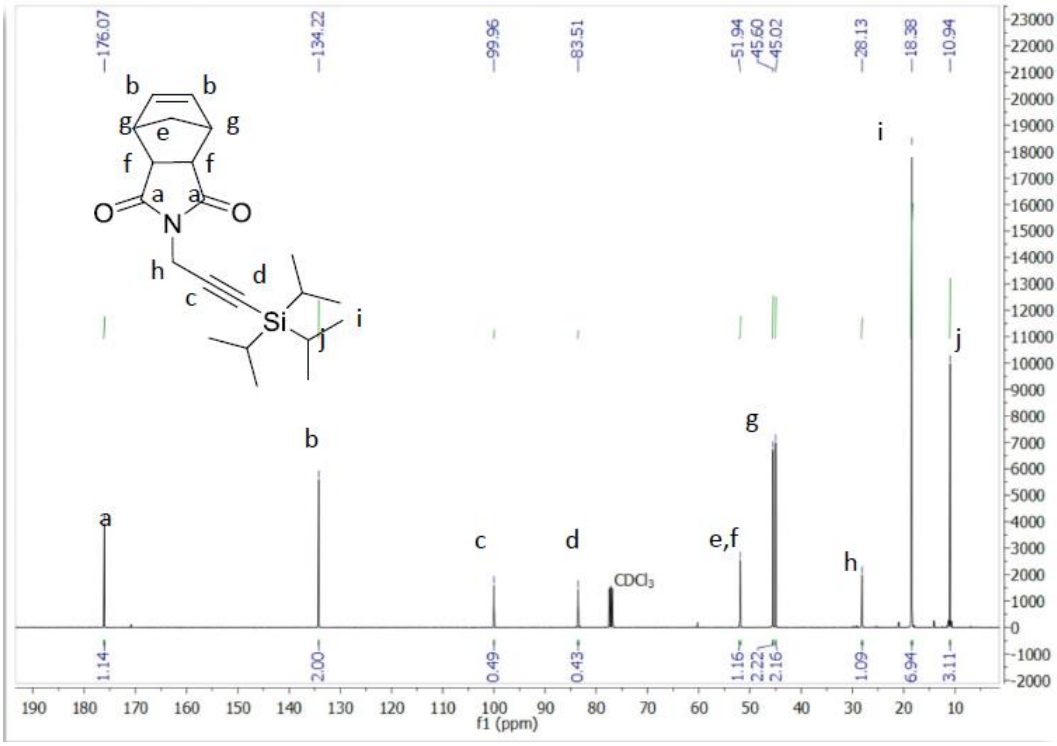
^{1}H NMR for TIPS protected Propargyl bromide (carried out in $CDCl_3$)



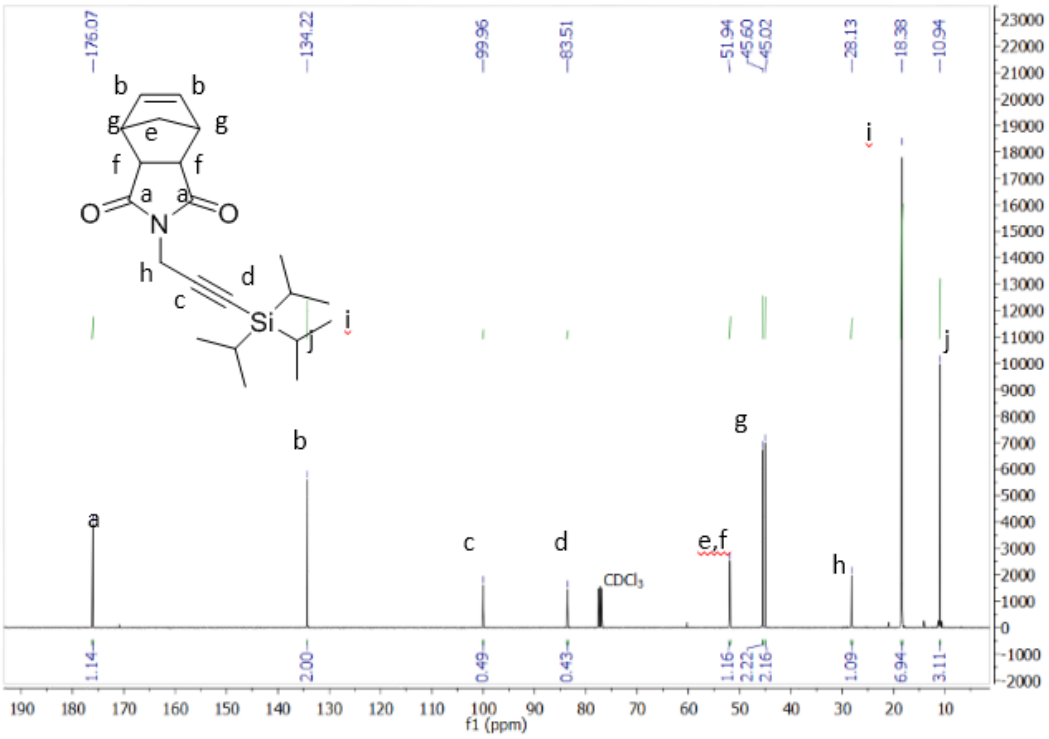
^{1}H NMR for Norbornenimide (carried out in $CDCl_3$)



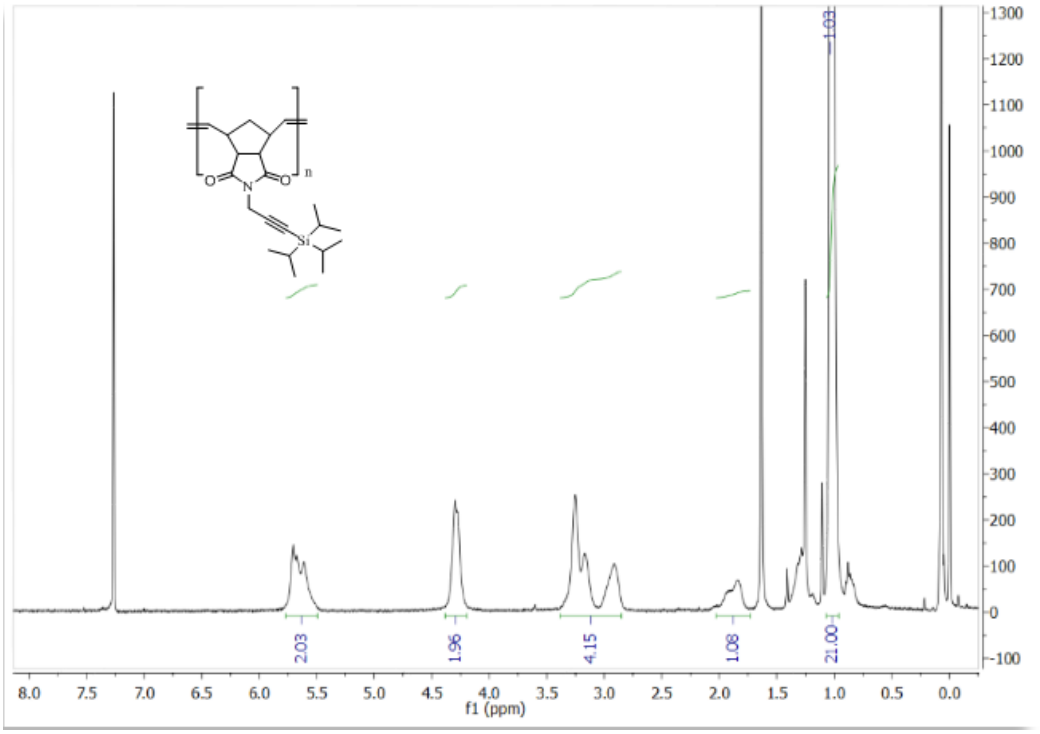
^{1}H NMR for Monomer (carried out in $CDCl_3$)



^{13}C NMR for Monomer (carried out in $CDCl_3$)



1H NMR for polymer (carried out in $CDCl_3$)



Synthesis of (*R*)-4-(bromomethyl)-N-(1-phenylethyl)benzamide (carried out in $CDCl_3$)