

## Review Article

# A Review on Olefin Metathesis Reactions as a Green Method for the Synthesis of Organic Compounds

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Received 15 August 2020; Revised 4 February 2021; Accepted 9 July 2021; Published 6 September 2021

Academic Editor: Pasquale Longo

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Olefin metathesis is a metal-mediated C-C bond exchange by which the two fragments within the olefin precursor are redistributed as a result of breaking the double bond to obtain a new product. Currently, most of the synthetic organic compounds, polymers, drugs, plastics, and other synthetic materials are synthesized via the application of olefin metathesis reactions. In this review, different types of olefin metathesis reactions with their plausible mechanisms and their application in synthetic organic chemistry have been discussed.

## 1. Introduction

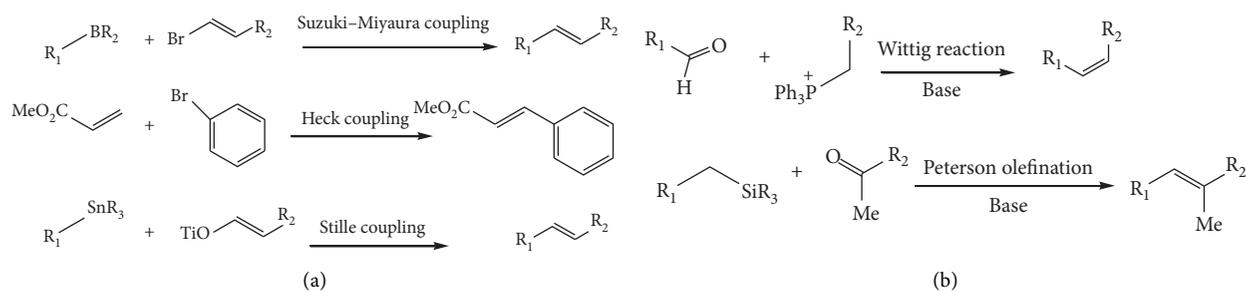
There are many chemical transformation ways that are nonmetal processes that employ reactive functional groups, like aldehydes and ketones, to form carbon-carbon bonds for the synthesis of natural and synthetic organic compounds applicable for different purposes. Once these reactive functionalities are introduced, the subsequent cross-coupling reactions are very reliable double bond-forming processes. In many cases, however, protective groups are required to mask these functional groups prior to their conversion to olefins, such as carbonyl protective groups. Another drawback of these traditional methods is the use of harsh reagents, such as triflic anhydride and brominating reagents to prepare cross-coupling reagents. The most obvious reactions for C-C bond formation which are the Wittig and Grignard reactions require highly basic conditions that are incompatible with many substrates of interest. In the case of Wittig reactions, every mole of the desired carbon-carbon double bond comes along with an equivalent of triphenylphosphine oxide, which is difficult to remove on a large scale as a waste of raw materials [1–3].

The following reactions (Schemes 1(a) and 1(b)) are examples of old methods to form C-C double bonds using different reaction routes.

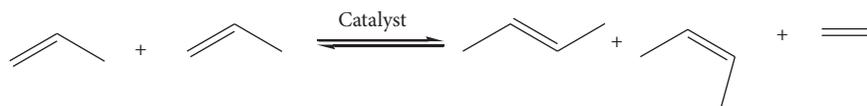
The aforementioned old methods have been proved in a synthesis framework of organic chemistry for C-C double bond formation with their drawbacks. But because of the above overwhelming problems, the effective, environmentally friendly, and elegant method which is the olefin metathesis reaction has been viewed as a synthetic route for the synthesis of target organic compounds. This reaction consists of a metal-catalyzed carbon skeleton redistribution in which a mutual exchange of unsaturated carbon-carbon bonds takes place, as illustrated in the catalyzed self-reaction of propene leading to ethene and but-2-ene shown in Scheme 2 [4, 5].

## 2. Olefin Metathesis

Olefin metathesis is a metal-catalyzed transformation, which acts on carbon-carbon double bonds and rearranges them via cleavage and reassembly [6–10]. This type of reaction is relatively simple and it often creates fewer undesired by-products and hazardous wastes than alternative organic reactions. Most of the olefin metathesis reactions are transition metal alkylidene-catalysed reactions. These constitute a facile and efficient strategy for approaching alkene precursors for the synthesis of various synthetic and natural products through olefin metathesis reactions. Such reaction



SCHEME 1: (a) Metal-catalyzed alkene formation reactions. (b) Alkene formation reactions without metal catalyst.



SCHEME 2: Metathesis reaction of 1-propene to form trans and cis-2-butene.

routes have been emerged in due time in different effortful research studies in different industries and academia [11, 12].

Olefin metathesis is one of the very few fundamentally novel organic reactions which open up new industrial routes to important petrochemicals, polymers, oleochemicals, and specialty chemicals applicable for different purposes [13]. This type of reaction is now being used in drug discovery for the synthesis of anticancer and other antibiotic organic compounds. Mazur et al. discovered a novel drug, the ansa-ferrocene-triazole-uracil conjugate, ( $\pm$ )-9 for the relief of breast cancer through metathesis reactions using 1,1'-diallylferrocene (1) as a starting material through ring-closing metathesis and other consecutive reactions in the presence of Grubbs catalysts (Schemes 3(a)–3(c)) [14].

Development of metathesis catalysts (Figure 1) and improving different metathesis reactions for the synthesis of useful polymers and novel materials have been of interest to many researchers. In fact, the availability of various metathesis catalysts together with research efforts focused on the development of more active complexes helps to improve the economical outcome of industrial processes including those in the pharmaceutical industry [15].

On the other hand, a metal alkylidene catalyst-free metathesis reaction for the construction of the C-C double bond is now taking view and interest in many organic laboratories. Haung et al. (2016) synthesized tetrasubstituted quinolinones using diazo compounds and para-quinone methides via metathesis reactions using TiCl<sub>4</sub> as the Lewis acid and dichloromethane as a solvent (Scheme 4) [16].

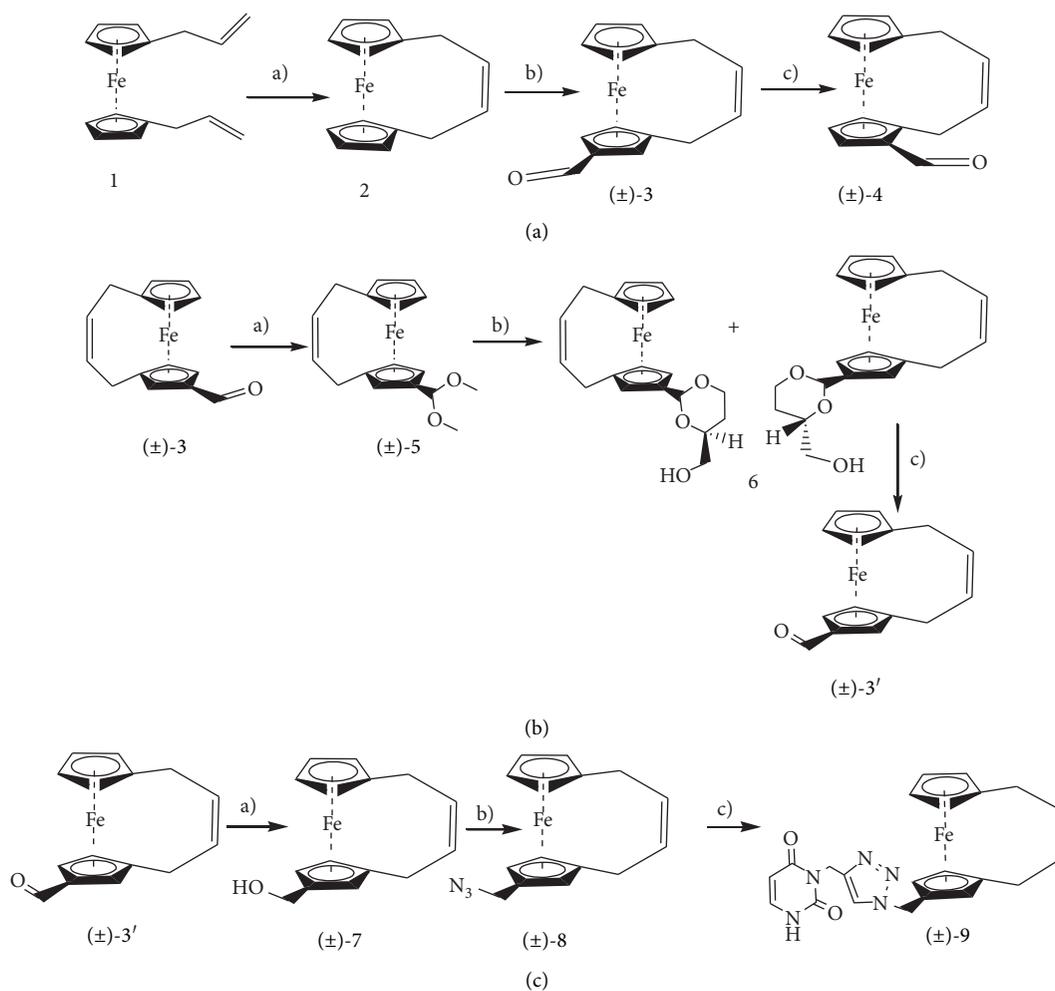
**2.1. General Reaction Mechanism of Transition Metal Alkylidene Olefin Metathesis.** Though the olefin metathesis reaction was discovered in the mid-1950s, its accepted mechanism (Scheme 5) was proposed by Chauvin and Herisson in 1971 which indicated that the reaction is catalyzed by metal carbenes [12].

According to this mechanism (Scheme 5), the coordination of an olefin to a metal-carbene catalytic species leads to the reversible formation of a metallacyclobutane intermediate. The metallacyclobutane can eliminate an olefin from either side of the ring, leading to degenerate metathesis, in which the starting olefin and carbene are reformed (nonproductive path), or productive metathesis, in which new olefins and carbenes are produced. As the catalytic cycle continues, an equilibrium mixture of olefins is produced, and the ultimate product ratio is determined by thermodynamic parameters. For instance, if one of the olefins is volatile, it can be removed from the system to drive the equilibrium towards the desired products [12].

There are two major approaches that are commonly employed to drive the reaction towards the desired products. One tactic is to rely on Le Chatelier's principle by continuously removing one of the products from the reaction system in order to shift the equilibrium in favor of the other product. This method is especially effective in the case of cross-metathesis (CM) reactions involving terminal olefins, ring-closing metathesis (RCM), and acyclic diene metathesis polymerization (ADMET) because the volatile gas by-product (like ethene and propene) formed in these processes can be easily removed [17–25].

The other approach capitalizes on the ring strain of cyclic olefins such as cyclooctenes and norbornenes. The energy released during the ring-opening reaction of these compounds is sufficient to drive reactions such as ring-opening cross metathesis (ROCM) and ring-opening metathesis polymerization (ROMP) forward. In some instances, substrate concentration, which often distinguishes ADMET from RCM or the catalysts' sensitivity to olefin substitution, can also be taken advantage of to influence product selectivity. All of these methods are currently successfully employed in the synthesis of a large variety of small, medium, and polymeric molecules, as well as novel materials [6, 7, 24, 26–35].

Since all of these processes are fully reversible, only statistical mixtures of starting materials as well as all of the



SCHEME 3: (a) Synthesis of the (±)-3 and (±)-4 aldehydes: a)  $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)_2]$ ,  $\text{CH}_2\text{Cl}_2$ , reflux, 3 h; b)  $\text{CH}(\text{OEt})_3$ ,  $\text{AlCl}_3$ , toluene,  $0^\circ\text{C}$  to rt, 1 h or  $\text{DMF}$ ,  $\text{POCl}_3$ ,  $\text{CHCl}_3$ , rt, 20 h. (b) Resolution of (±)-3 into enantiomers: a)  $\text{CH}(\text{OMe})_3$ , *p*-TsOH,  $80\text{--}90^\circ\text{C}$ ; b) (*S*)-(-)-1,2,4-butanetriol, *p*-TsOH,  $\text{CHCl}_3$ ,  $60^\circ\text{C}$ ; then crystallization from hexanes and 2-propanol at  $4^\circ\text{C}$ ; c) *p*-TsOH,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $60^\circ\text{C}$ . (c) Synthesis of (±)-9: a)  $\text{NaBH}_4$ ,  $\text{MeOH}$ ,  $\text{THF}$ , rt, 24 h for 7a; 48 h for (±)-7; b)  $\text{NaN}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $50^\circ\text{C}$ , 3 h; c) 3-propargyluracil,  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , sodium ascorbate,  $\text{EtOH}$ , rt 4 days for (±)-9.

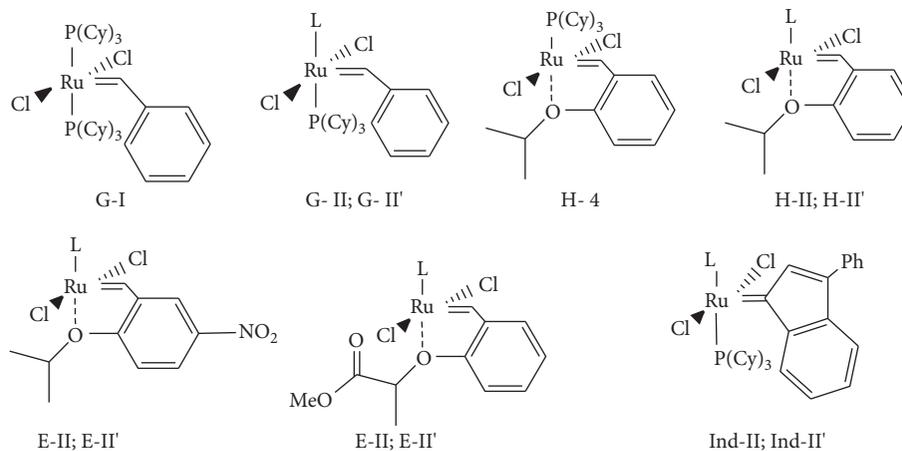
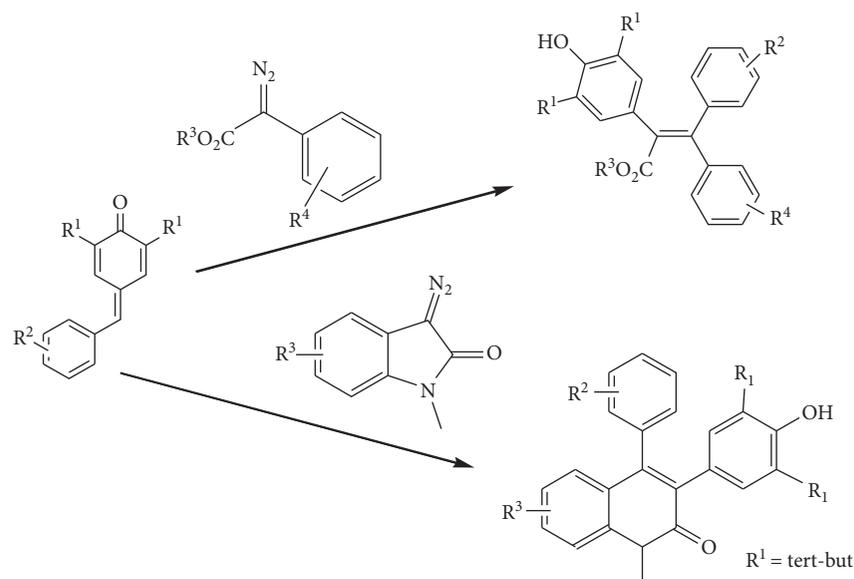
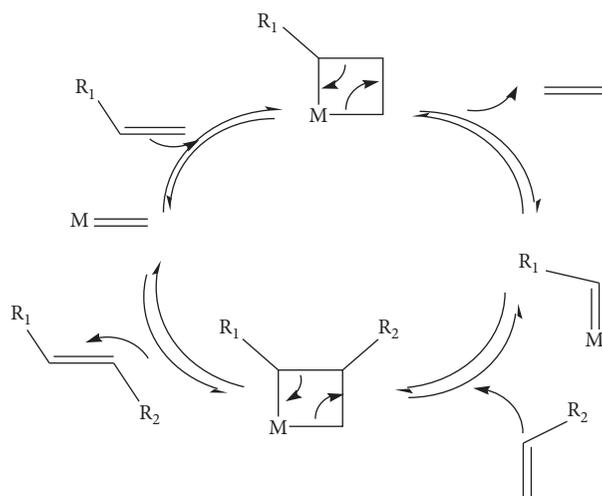


FIGURE 1: Selected modern ruthenium-based olefin metathesis catalysts.



SCHEME 4: Synthesis of tetrasubstituted quinolinones using diazo compounds and para-quinone methides via metathesis reactions using  $\text{TiCl}_4$  as the Lewis acid and dichloromethane as a solvent.



SCHEME 5: General olefin metathesis reaction mechanism.

possible rearrangement products are produced in the absence of thermodynamic driving forces [11, 36].

During the olefin metathesis reactions, many side reactions which may appear like isomerization (especially double bond shift reactions), alkylation, cyclization, and addition across the double bond) are challenging problems. These problems are mostly created due to the residual ruthenium catalyst and can generally be avoided by proper choice of solvent as well as other purification techniques. For example, diethyl ether can leach ruthenium in a reaction with highly polar substrates like alcohols and acids. On the other hand, catalyst I can be removed by  $\text{SiO}_2$  and DMSO at room temperature for 12 hours [37, 38].

### 3. Olefin Metathesis Reaction Types

Olefin cross metathesis (CM) represents an alternative to the olefination methods where olefins themselves are the reactive functional groups (Scheme 6).

Investigations into olefin cross metathesis with several classes of olefins, including substituted and functionalized styrenes, secondary allylic alcohols, tertiary allylic alcohols, and olefins with alpha-quaternary centers, have led to a general model useful for the prediction of product selectivity and stereoselectivity in cross metathesis. As a general ranking of olefin reactivity in CM, olefins can be categorized (Scheme 7) into four by their relative abilities to undergo



SCHEME 6: General reaction for cross olefin metathesis.

homodimerization via cross metathesis and the susceptibility of their homodimers towards secondary metathesis reactions due to steric and electronic influence. By employing a metathesis catalyst with the appropriate activity as well as proper olefinic partners, selective cross-metathesis reactions can be achieved with a wide variety of electron-rich, electron-deficient, and sterically bulky olefins [39, 40]:

Type I: rapid homodimerization, homodimers consumable (i.e., reversible reaction)

Type II: slow homodimerization, sparingly consumable (i.e., somewhat reversible reaction)

Type III: no homodimerization

Type IV: olefins inert to cross metathesis but do not interfere with catalyst activity towards other alkenes

When two type I olefins are paired in a CM reaction, the rates of homodimerization and cross-product formation are similar, and the reactivities of the homodimers and cross products towards secondary metathesis events can be high. In these reactions, the desired cross product will be formed at a rate comparable to the homodimers, and equilibration of the cross products with the various homodimers through secondary metathesis reactions will result in a statistical product mixture [39, 41].

Olefin category is done based on reactivity towards cross-metathesis reactions with Grubbs-II catalyst (the above figure). Therefore, the selective cross-metathesis reaction will occur based on the type of olefinic partner as well as the catalyst reactivity (N-heterocyclic carbene ligand containing catalysts such as the second-generation Grubbs catalyst 1 in Figure 2 are good) [15, 42–44].

Much amount of catalyst and heat should be required to carry out cross olefin metathesis reactions with some challenging olefinic partners such as vinyl ketones [45, 46] acrylic acid [47, 48], and acrylonitrile [49–52]. To make the reaction facile and fast for those substrates, Voigttritter et al. described a new procedure for carrying out CM reactions (Scheme 8) with Grubbs-II catalyst under the assistance of a copper(I) salt, CuI, which not only leads to faster rates of cross couplings but avoids chlorinated solvents as well [53].

As the study indicated that iodine may serve as a stabilizing ligand on ruthenium so that it extends the lifetime of the Grubbs catalyst. Therefore, CuI provides two positive effects. One is the ligand effect of iodide on ruthenium and the second is a phosphine sequestering effect by copper(I) from ruthenium. In this procedure, even very challenging type II and type III olefinic partners listed above (e.g., acrylic acid, acrylonitrile, and isopropylidene derivatives) were involved in cross metathesis (Schemes 8(b) and 8(c)).

**Ring-Closing Metathesis, RCM.** It is the intramolecular metathesis of a diene to form a cyclic olefin which is used for synthesizing both carbocyclic and heterocyclic compounds

[43]. Olefin metathesis, as shown by the mechanism proposed by Chauvin, is a process that is normally fully reversible. This implies that a driving force must be present in order to obtain a single, defined product. For RCM and CM, the equilibrium is usually driven in the desired direction by progressive removal of the by-product from the reaction environment (commonly ethene or propene, liberated as gas). Examples of RCM reactions in which nonvolatile products are produced (e.g., styrene) are known and for specific applications, important results have been obtained [54, 55].

RCM helps to transform linear substrates to cyclic olefins (the following scheme) and therefore is frequently used in the preparation of biologically important compounds containing medium- and large-size rings as well as capsules of varying sizes, properties, and applications. Indeed, RCM targets modification of macrostructure rather than the introduction of new functionality [56, 57].

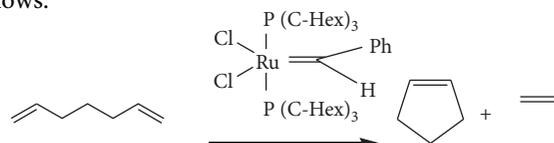
This type of metathesis reaction has also realized the possibility of constructing carbocyclic rings of both small and large sizes with the potential of accessing a variety of heterocyclic systems (Scheme 9) [10, 58].

The most widely used catalysts for olefin ring-closing metathesis are Grubbs's ruthenium alkylidene catalysts (Figure 2) which exhibit high reactivity in a variety of RCM processes and show remarkable tolerance towards many different organic functional groups.

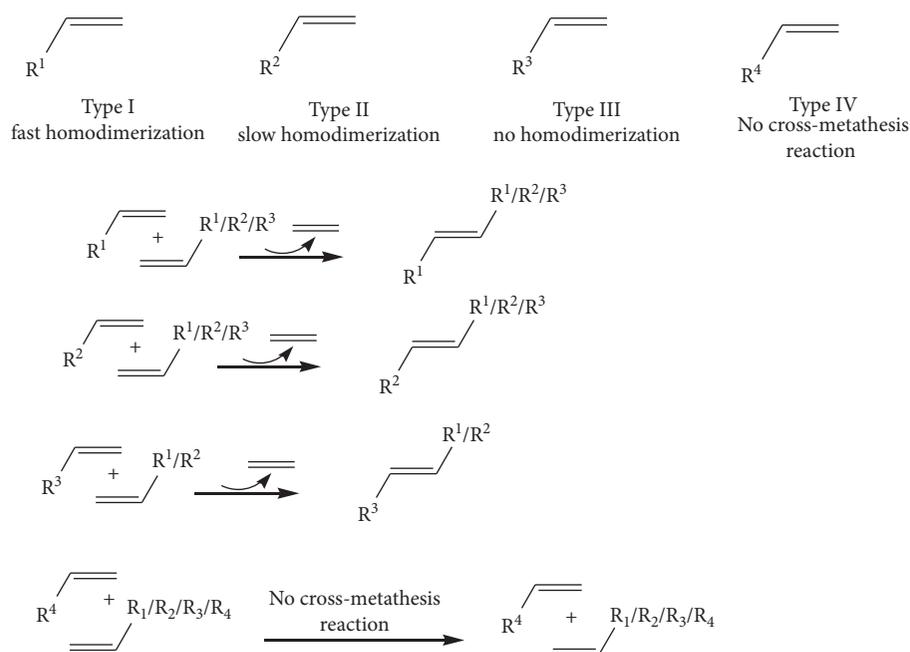
#### 4. Mechanism of Ring-Closing Metathesis (RCM)

RCM reactions like the other olefin metathesis reactions proceed via metallacyclobutane and metal-carbene intermediates (Scheme 10) which involve effectively a series of alternating [2 + 2] cycloadditions and cycloreversions between metal alkylidene and metallacyclobutane species. In the first turn of the catalytic cycle, the alkene by-product depends on the R group in the original catalyst, while in the second and subsequent catalytic cycles, it depends on the substrate. For terminal alkene substrates, the reaction by-product is ethene. Alkene substitution in both substrate and catalyst can dramatically influence the reaction rate and outcome. In particular, several catalysts do not tolerate excessive steric hindrance on the substrate [58, 59].

Consider a typical RCM of hepta-1,6-diene shown as follows:



Ring-closing metathesis has been made for macrocarboxylation and macrolactonization reactions



SCHEME 7: Olefin categorization into type I, type II, type III, and type IV and their reactivity.

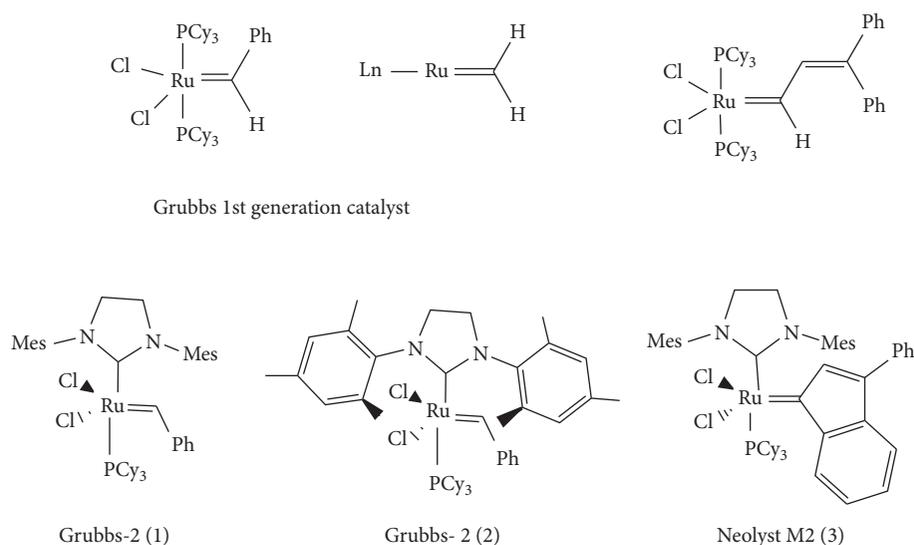


FIGURE 2: Structures of Ru-based catalysts used for olefin metathesis.

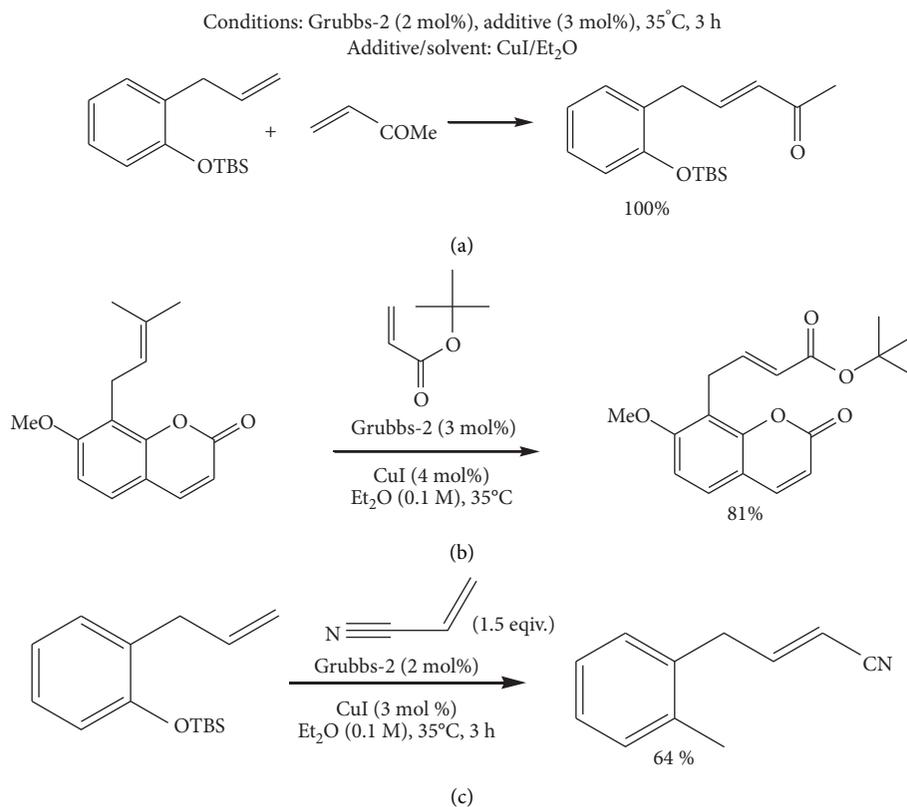
(formation of large ring cyclic esters) which had been difficult to take place now as a routine exercise in organic synthesis. Pharmaceutically active compounds having complex rings can be also produced via RCM reactions (Scheme 11) using Grubbs first generation catalyst [57].

RCM combined with CM has also been used in the total synthesis of bioactive natural products and producing functionalized oligomers, commonly known as telechelic materials. These materials are normally difficult to prepare in high yield and are finding growing application in the production of multiblock polymers such as styrene-butadiene-styrene and thermoplastic polyurethanes [40, 57].

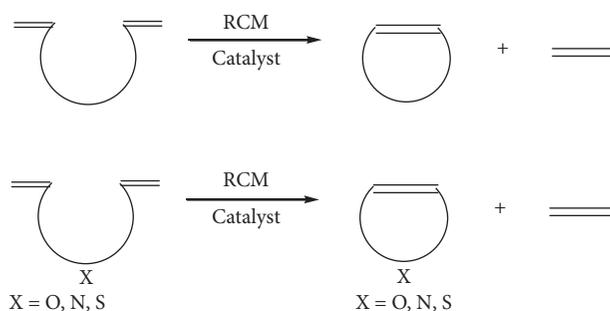
## 5. Effect of Substituents on Ring-Closing Metathesis Reactions

Electron-rich olefins make the ring-closing metathesis reaction fast (Figure 3(a)), whereas olefin precursors having electron-withdrawing groups retard the reaction. Indeed, if the heteroatom is present in the olefin precursor, it competes with the olefinic double bond to coordinate and react with the catalyst so as to be problematic to get the target product (Figure 3(b)) [61–63].

The success of RCM depends on to what extent the competing acyclic diene metathesis polymerization



SCHEME 8: (a) Full conversion of the substrate into product with the effect of CuI. (b) Copper-assisted cross metathesis on osthole. (c) Effect of CuI on cross metathesis with acrylonitrile.



SCHEME 9: General reaction of RCM for the synthesis of carbocyclic and heterocyclic molecules.

(ADMET) can be overcome. Decreasing the concentration of the substrate helps to reduce ADMET to some extent but this affects negatively the performance of the catalyst. In general, the ring-closure olefin metathesis reaction is influenced to a great extent by a number of factors. These include (1) the efficiency of the catalyst, (2) the nature of the resulting rings, (3) the size of the rings to be formed, and (4) the functional groups/substituents present in the substrate [59].

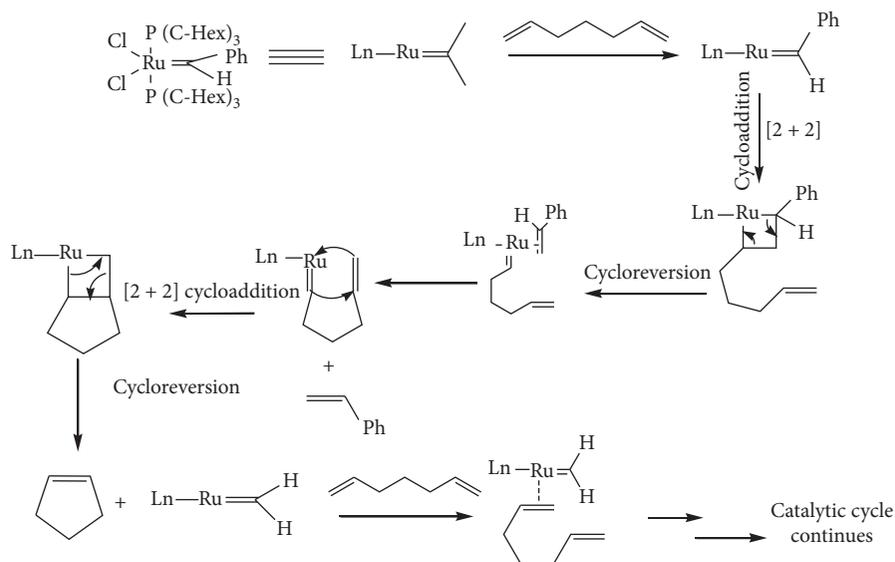
## 6. Ring-Opening Metathesis Polymerization

Ring-opening metathesis polymerization is a process of one or more cyclic olefins transformation to polymer catalyzed by metal-carbene compounds. Indeed, the number of double bonds both in polymer and in monomer is equal [59, 64].

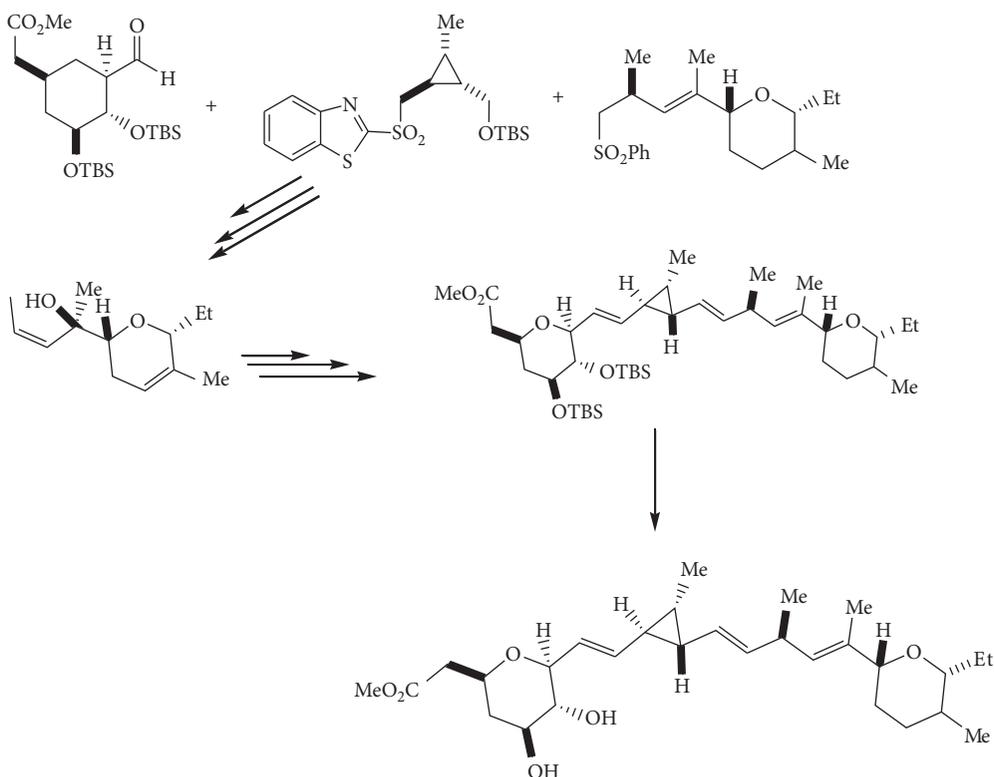
The driving force behind the ROMP reaction (Scheme 12) of cyclic olefins is reliant on the release of ring strain energy, which compensates for the loss in entropy upon polymerization. Typically, ROMP is a thermodynamically favored process for cyclic olefins that have lower ring strain energy by which equilibrium will be formed between the monomers and polymers [65, 66].

To overcome this problem, the position of the equilibrium can be shifted to the ring-opened polymer via two approaches;

One involves lowering the temperature and the second involves increasing the monomer concentration. During ROMP (Scheme 13), the initiation step involves the coordination of a cyclic olefin to a metal alkylidene complex. Subsequent [2+2] cycloaddition produces a



SCHEME 10: A plausible reaction mechanism for this RCM is given [10].



SCHEME 11: Synthesis of (+)-ambruticin S via RCM reactions [60].

metallacyclobutane intermediate to form a growing polymer chain. This intermediate undergoes cycloreversion to afford a new metal alkylidene. Analogous steps are repeated during the propagation stage until polymerization ceases; that is, the monomer is completely consumed, and the reaction reaches equilibrium or the reaction is terminated [17, 67, 68].

ROMP is commonly quenched by the addition of ethyl vinyl ether, which reacts with the metal-carbene species of a growing polymer chain end and removes the metal from the polymer. Omitting this procedure leads to degradation of the polymer product and causes metal residue contamination in the isolated material [17].

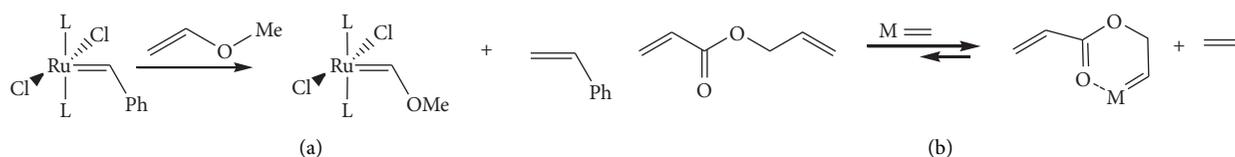
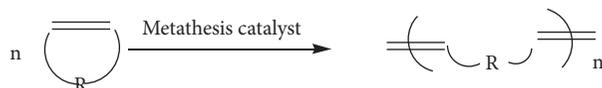
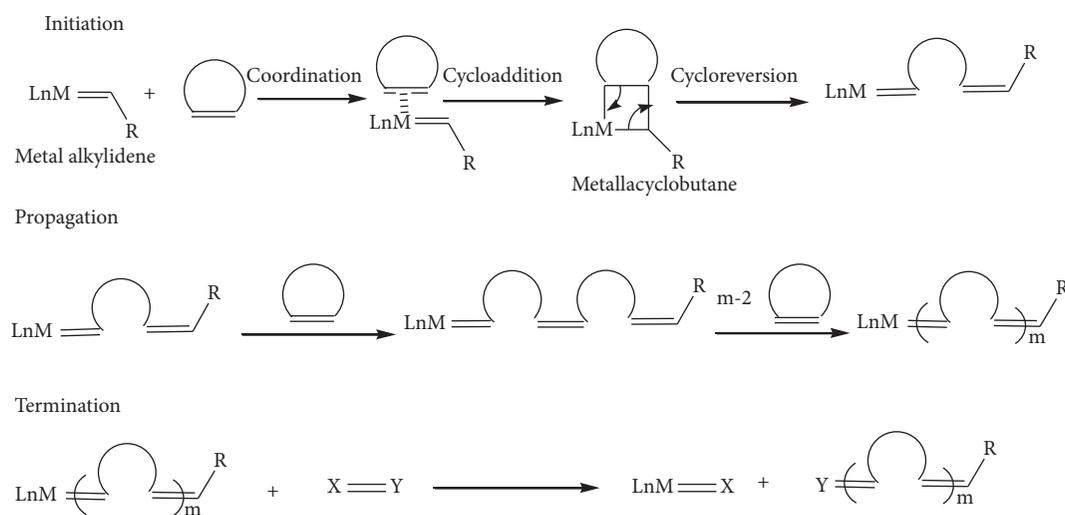


FIGURE 3: (a) Reaction between a general metathesis catalyst and an electron-rich olefin. (b) Possible deactivation of the catalyst via intramolecular heteroatom chelation.



SCHEME 12: ROMP general reaction.



SCHEME 13: ROMP reaction mechanism.

ROMP is commonly accompanied by intermolecular and intramolecular chain-transfer reactions as illustrated in Scheme 14.

In the intermolecular chain transfer, a polymer chain having an active metal alkylidene on its terminus reacts with a double bond in another polymer chain. The individual polymer chains increase or decrease in molecular weight accordingly, keeping the total number of polymer chains unchanged. In the intramolecular chain-transfer reaction (backbiting), the carbene terminus of a polymer chain reacts with itself to form a polymer chain with reduced molecular weight and release a cyclic oligomer. Intermolecular and intramolecular chain transfers both increase the polydispersity of the polymer product.

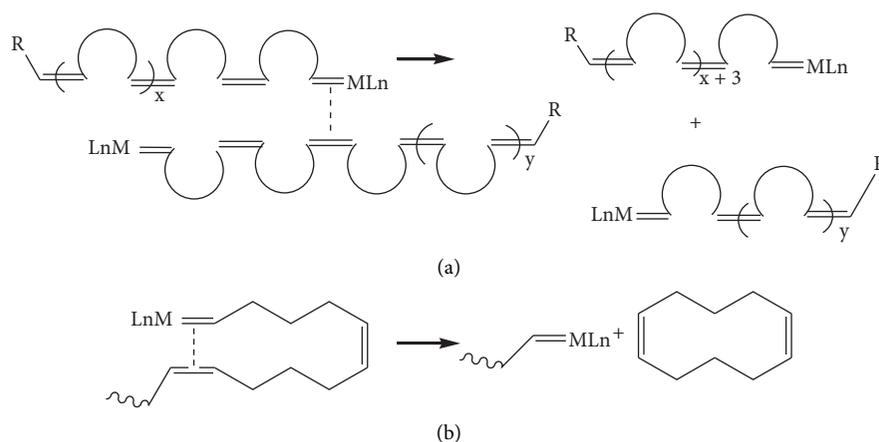
Strained cyclic olefins having no bulky groups around the double bonds are used as ROMP monomers (Figure 4).

Over the past several decades, ring-opening metathesis polymerization (ROMP) has become an effective method for the preparation of a wide range of linear polymers due to the development of well-defined ruthenium alkylidene metathesis complexes developed by Grubbs and coworkers having high functional group tolerance and robustness. The

most commonly studied monomers in ROMP are highly strained, bicyclic olefins such as norbornene and its derivatives. In contrast, monocyclic olefins with five-, six-, and seven-membered rings have a lower ring strain energy, where bond angles are significantly less strained. Because of this, it is very difficult to undergo ring-opening metathesis polymerization reaction with these olefins [66, 69–74]. But currently, researchers proved that the ring strain of a molecule can be manipulated if the ring structure is made up of a molecular photoswitch. Among various photoswitch molecules, 1-(1-indanylidene)indan commonly known as stiff-stilbene is the one [75].

Krishnan et al. reported that photoinduced strain assisted ROMP synthesis of main-chain stiff-stilbene polymers by activating macrocyclic  $\pi$  bond connected to stiff-stilbene photoswitch through photoisomerization [76] (Scheme 15).

ROMP is also used in manufacturing industries for the production of different polymers and copolymers. It has also been widely used for synthesizing molecular bottlebrushes which are applicable as nanowires, elastomers, lubrication, antifouling, and other purposes [67, 77].



SCHEME 14: Chain-transfer reactions accompanied in ROMP. (a) Intermolecular chain transfer. (b) Intramolecular chain transfer.

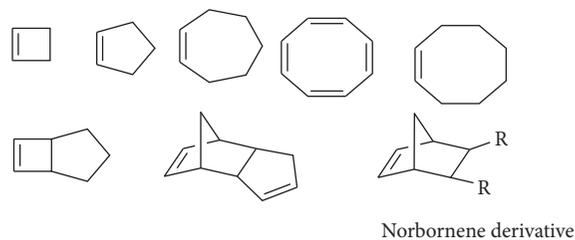
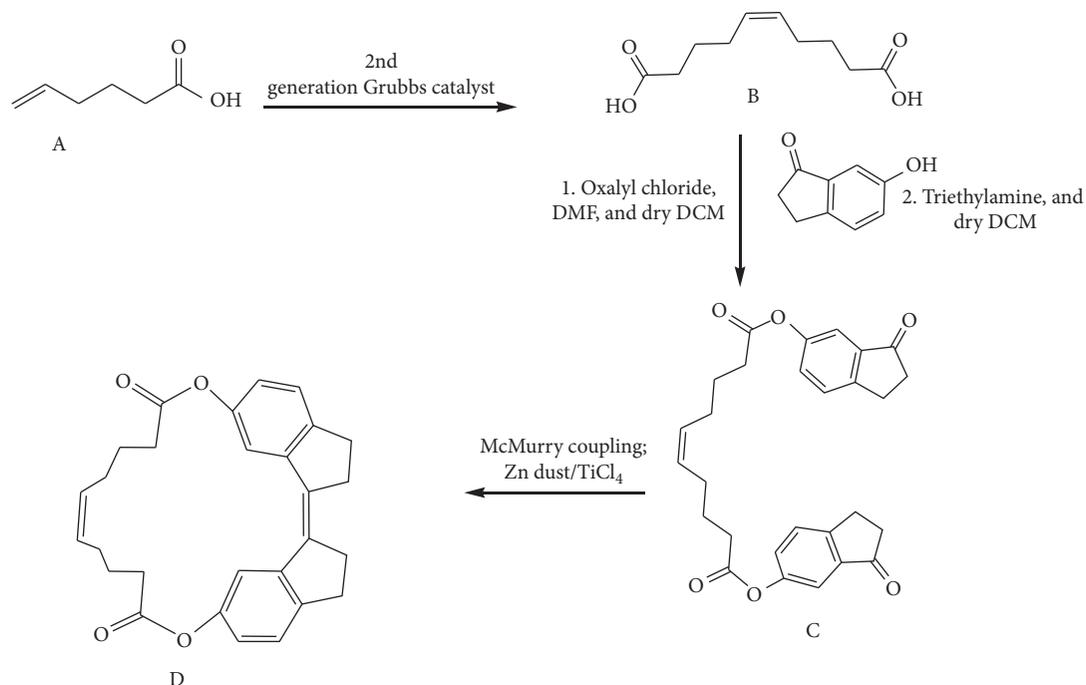


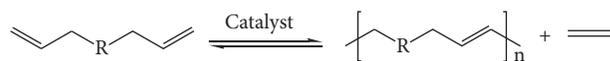
FIGURE 4: Representative ROMP monomers.



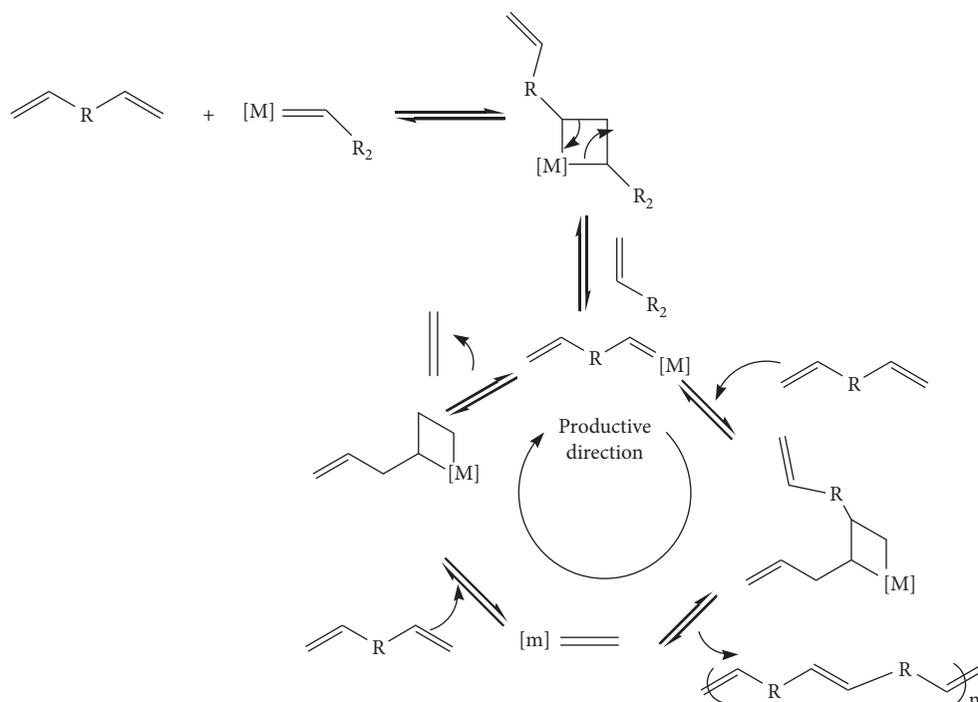
SCHEME 15: Synthesis of macrocycle D using the main-chain stiff-stilbene via ROMP and other reaction sequences.

*Acyclic Diene Metathesis Polymerization, ADMET.* The ADMET polymerization is a step condensation polymerization reaction of diene monomers driven by the removal of

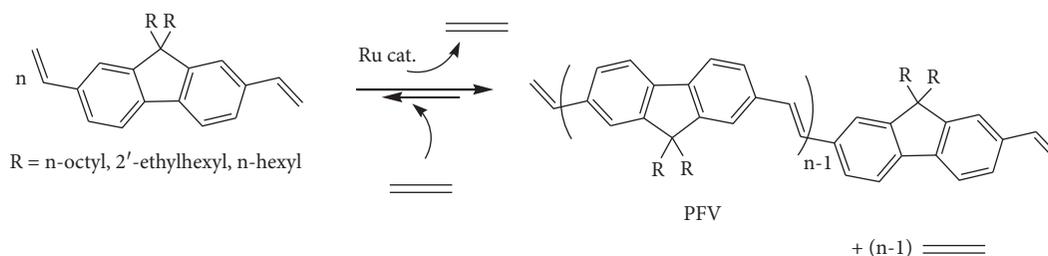
the condensate, typically ethylene, to obtain high polymer and since the polymerization involves an equilibrium process, the polymerization is reversible [5, 78–80].



SCHEME 16: ADMET polymerization: general reaction.



SCHEME 17: Reaction mechanism of ADMET polymerization.



SCHEME 18: Synthesis of trans-poly(9,9-di-n-octyl-fluorene-2,7-divinylene) (PFV) from 2,7-divinyl-9,9-di-n-octyl-fluorene using Schrock type molybdenum alkylidene [86].

The ADMET and ROMP mechanisms both proceed through the equilibrium polymerization of olefins via metathesis. However, ADMET differs by involving the polymerization of acyclic dienes, with its equilibrium shifted to the polymer by the removal of a small alkene (entropically) (Scheme 16). ROMP is typically shifted to high polymers via a favorable enthalpy change via ring strain release. The major mechanistic difference is that ROMP follows a chain-growth process where the active alkylidene acts as a catalytic initiator. In contrast, ADMET follows a step condensation mechanism and the alkylidene behaves as a true catalyst [81, 82].

The ADMET polymerization proceeds via a metal-carbene mechanism (Scheme 17), in which the metal methylidene is the true catalyst formed during the

polymerization cycle (the following scheme). This is the same metal-carbene mechanism operating in cross metathesis. Coordination of the metallic center of the catalyst with a terminal olefin from either the monomer or polymer is followed by a reversible cycloaddition to produce a metallacyclobutane intermediate. This undergoes further reversion leading to either a productive or a nonproductive pathway. Chain growth is promoted by the productive metathesis pathway resulting from cycloreversion, which will not restore the coordinating olefin and free catalyst. This pathway is characterized by the production of the condensate, commonly ethylene, which should be removed from the reaction mixture in order to drive the equilibrium towards chain growth [83, 84].

ADMET polymerization has been used in synthesizing even noble conjugated organic molecules which are semi-conductors applicable as different electronic devices. This reaction is preferred from the other conventional methods like Heck coupling and Horner–Wittig Emmons reactions because of structural regularity and molecular purity (free from halogens, phosphorus, etc.) of synthesized polymers. ADMET polymerization reaction is effective to produce structurally defect-free conjugated polymers (Scheme 18) [85].

ADMET polymerization is achieved when the following three main variables are kept i.e., monomer purity, catalyst stability, and the melting point of the final polymers [64, 82].

A functional group with catalyst poisoning potential must be separated from the metal center by two or more methylene spacers for the reaction to proceed cleanly to polymer. This monomer structure phenomenon has been reported elsewhere and has been termed the “negative neighboring group effect” [64].

## 7. Conclusion

Olefin metathesis reactions have been developed in many synthetic routes such as polymer industries, petrochemicals, pharmaceutical industries, and other manufacturing industries for the formation of C-C bonds due to the facile reaction sequences and environmentally benign conditions. A variety of olefin metathesis reactions have emerged in different focusing areas. These olefin metathesis reactions are facilitated and applicable in large due to the development and modification of reaction catalysts as well as optimization of reaction conditions. Nowadays, even the impossible olefinic metathesis reactions are successful as a result of sophisticated research efforts by discovering different reactive and many functional group tolerance and compatible catalysts which can perform stereoselective reactions so that they are able to build targeted materials. Currently, this synthetic route is interconnected with the other reaction processes to yield valuable products.

## Data Availability

All data are incorporated in the body of the manuscript, and since it is a review, the data are available from referenced sources.

## Conflicts of Interest

The author declares no conflicts of interest.

## References

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